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FULL PAPER

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Study of Anti-Apoptotic mechanism of Ruthenium (II) Polypyridyl Complexes via RT-PCR and DNA binding

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A set of novel mononuclear polypyridyl complexes of Ru (II) with N – N donar ligands 1, 10 phenanthroline (phen), 2, 2′ bipyridine (bpy), 4, 4′-dimethyl 2, 2′ bipyridine (dmb) and an intercalating ligand (bnpip = 2-(4-butoxy-3-nitrophenyl)-1*H*-imidazo [4,5-f] [1,10] phenanthroline) have been synthesized and characterized by various spectral methods. The RT - PCR assays suggest that ruthenium (II) complexes inhibit MCF-7, breast cancer cell line by inducing apoptosis via inhibition of cell cycle check points cyclin D, cyclin E and also upregulation of caspase 8 (protein involved in late Apoptosis). Further the binding potency of Ru (II) complexes were investigated using various spectroscopic techniques like UV–visible, fluorescence and viscosity studies. The complex binds to DNA in an intercalative mode as confirmed by viscosity data with differential binding strength. All complexes show cleavage of the pBR322 DNA through a singlet oxygen production. Theoretical evidence via docking of the complex with DNA reveals the significant residues of binding as guanine.

KEYWORDS

DNA binding, molecular docking, morphology, Photocleavage, RT-PCR

1 | INTRODUCTION

Although cancer growth existed throughout the previous couple of decades, it is as yet one of the real reasons for death around the world. Till today, the most dependable remedy for disease is to expel or to obstruct the expansion of dangerous tissues. The revelation of cisplatin inhibition of DNA replication and cell division has shown that metal complexes can expect a unique function in the treatment of malignant growth, opening permeability for anticancer research dependent on metallopharmaceuticals.[1,2] Many metal complexes, for example, cisplatin, carboplatin and oxaliplatin were researched for their anti-tumor properties against a wide scope of tumors.[3] In the journey of anticancer drugs containing metals other than platinum, ruthenium compounds exhibiting most promising ones.[4] Because of its ligand exchange kinetics of metal complexes in aqueous solution, which are similar for Pt (II) complexes.[5] Ruthenium with its variable oxidation states, low poisonous quality, high selectivity for malignant growth cells due to its capacity to mimic iron to biomolecules.[6,7] In fact, the cellular uptake of ruthenium (III) gives off an impression of being mediated by transferrin.[8] Iron prerequisite is more prominent for quickly isolating cells (cancer cells), this outcome in up-regulation of the number of transferrin receptors on the cell surface. An expansion in the ruthenium fixation in malignancy cells when compared

with healthy cells has been confirmed in-vivo.[9] In the meantime, as the medication is focused to disease cells, its harmfulness is decreased in light of the fact that less of it achieves the sound cells.

Ruthenium complexes are straight away analyzed for their utility as DNA structural tests, DNA foot printing, sequence specific cleavage operators and potential anticancer medication. The Interaction of small molecules with DNA has been concentrated widely, as it is material of legacy, controls the structure and capacities.[10] Ruthenium (II) complexes of dipyridophenazine (dppz) ligand were studied widely due perhaps to their potent DNA binding and high cytotoxicity.[11–13] Ruthenium complexes containing imidazole and indazole are potent against various tumors.[14,15] After broad preclinical tests, the compounds [indH][transRu(N-ind)$_2$Cl$_4$] (KP1019) and [imiH][trans-Ru(N-imi)(S-dmso)Cl$_4$] (NAMI-An) entered the clinical preliminaries.[4] The clinical studies revealed that NAMI-A causes skin blisters and results in intense pain,[16] and with KP1019 the low solubility, makes it challenging to set dosage in clinical trials.[17] Our research group reported few ruthenium (II) polypyridyl derivatives and their DNA binding investigations with several intercalating ligands.[18–21] Yun-Jun Liu et al., also published ruthenium (II) polypyridyl complexes with different ligands, DNA binding behaviour and their anticancer properties.[22–27] In the present article, we report the synthesis, characterization, binding capacities and mode of binding of three new ruthenium (II) complexes. In order to understand mode of action and the mechanism of apoptosis of the [Ru (phen)$_2$(bnpip)]$^{2+}$, [Ru (bpy)$_2$(bnpip)]$^{2+}$ and [Ru (dmb)$_2$(bnpip)]$^{2+}$, we performed cell death assays, MTT assay and Annexin V staining and RT PCR to evaluate the up-regulation of pro-apoptotic genes and down regulation of anti-apoptotic genes.

2 | EXPERIMENTAL SECTION

2.1 | Materials

RuCl$_3$.xH$_2$O, 1,10-Phenanthroline, 2,2′-bipyridine, 4,4-dimethyl 2,2′-bipyridine, and 4-butoxy-3-nitrobenzaldehyde were purchased from Sigma Aldrich. The super coiled (CsCl purified) pBR322 DNA (Bangalore, Genie, India) was used as received. All other chemicals and solvents were acquired from neighbourhood sources. Every solvent was sanitized before use according to standard systems.[28] The spectroscopic titration was done in the Tris-buffer (5 mM Tris–HCl, 50 mM NaCl, pH 7.2) at room temperature. DNA was dissolved in Tris–HCl buffer (pH = 7.2).

2.2 | Analytical measurements

The UV–visible absorption studies were carried out on Shimadzu UV-2600 spectrophotometer for the determination of K_b values. IR data is recorded as KBr disks on a Perkin-Elmer FT-IR-1605 spectrometer. For NMR, Bruker 400 MHz NMR spectrometer with high resolution probe Z was used for NMR studies, sample was dissolved in DMSO-d_6 and referencing is relative to TMS (^{1}H and ^{13}C). Compound purity was confirmed by elemental analysis with Perkin-Elmer 240 elemental analyzer for Micro analysis (C, H and N). Luminescence measurements were carried out on Cary Eclipse spectrofluorometer using a 1 cm path length. Viscosity studies are carried out utilizing Ostwald viscometer.

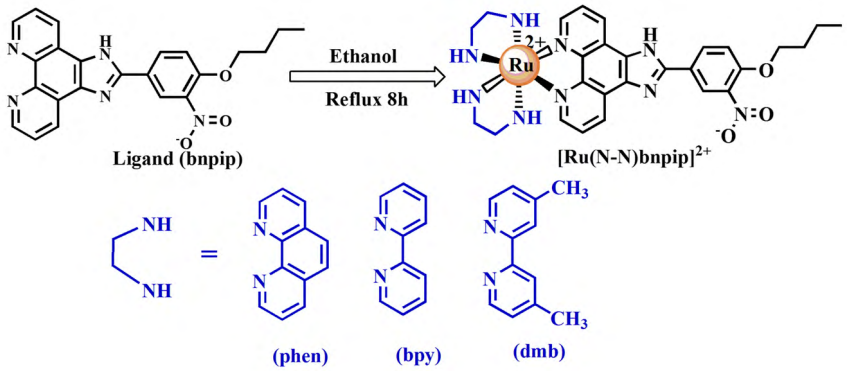
2.3 | Synthesis

The starting materials 1,10-phenanthroline-5,6-dione (phendione), cis-[Ru(N –N)$_2$Cl$_2$], Where N – N = phen, bpy and dmb were synthesized according to literature.[29,30] Schematic drawing of ruthenium (II) complexes were shown in Scheme 1.

2.3.1 | Synthesis of ligand (bnpip)

The ligand was prepared according to the methodology in the literature.[31] A mixture of phendione(0.53 g, 2.50 mM), 4-butoxy-3-nitrobenzaldehyde(0.6527 g, 3.50 mM), ammonium acetate (3.88 g, 50.0 mM) and glacial acetic acid (15 ml) was refluxed together for 4 hr. The above solution was cooled to room temperature and diluted with distilled water, drop wise addition of concentrated NH_3 to the solution leads to formation of yellow precipitate, which was gathered, washed with H_2O and dried. The crude product recrystallized with $C_5H_5N.H_2O$ and dried (yield: 93.45%). Anal. data for $C_{23}H_{18}N_5O_3$: calc. C, 66.98; H, 4.40; N, 16.98; found: C, 66.51; H, 4.45; N, 16.62. ES$^+$- MS Calc: 413.15; found: 414.30 [M + H]$^+$(S10). ^{1}H NMR (DMSO-d_6, 400 MHz):δ 8.96(d, 2H), 8.74(d, 2H), 8.61(s, 1H), 8.34(d, 1H), 7.72(t, 2H), 7.41(d, 1H), 4.15(t, 2H), 1.72(q, 2H), 1.47(m, 2H), 0.95(t, 3H) (S4). ^{13}C[^{1}H] NMR (100 MHz, DMSO-d_6, d, ppm): 152.17 (2C), 148.19 (1C), 147.57 (1C), 143.42 (2C), 139.07 (2C), 134.75 (1C), 131.72 (1C), 129.38 (1C), 126.31 (2C), 123.24 (1C), 122.99 (2C), 122.33 (2C), 115.46 (1C), 69.15 (1C), 30.38(1C), 18.50 (1C), 13.53 (1C)(S7). IR (KBr, cm^{-1}): 3093 (ν, N-H), 2956(ν, C-H), 1531 (ν, N-O), 1450 (ν, N-O), 1070 (ν, R-O-C)(S1).

SCHEME 1 Synthetic route the preparation and structures of ruthenium (II) complexes(**1–3**)



2.3.2 | Synthesis of complexes

[Ru (phen)$_2$(bnpip)](ClO$_4$)$_2$.2H$_2$O (1)

Cis-[Ru (phen)$_2$Cl$_2$].2H$_2$O (0.284 g, 0.5 mM), bnpip (0.206 g, 0.5 mM) and ethanol (15 ml) were refluxed at 120 °C under N_2 atmosphere for 8 hr. A light purple colour solution was obtained, it was cooled to room temperature and few drops of saturated aqueous $NaClO_4$ solution was added for neutralization with vigorous stirring. The Brick red solid was collected and rinsed with small amount of water, ethanol and diethyl ether, then dried under vacuum (yield: 94.91%). Anal. data for $RuC_{47}H_{38}Cl_2N_9O_{13}$: cal. C, 50.91; H, 3.45; N, 11.37; found: C, 50.12; H, 3.48; N, 11.15. ES$^+$-MS cal: 875.19; found: 874.47(S11). ^1H NMR (DMSO-d_6), 400 MHz δ 8.77 (d, 6H), 8.40(s, 1H), 8.16(d, 6H), 8.09(d, 1H), 8.03(d, 4H), 7.78(t, 6H), 7.62(d, 1H), 4.23(t, 2H), 1.70(q, 2H), 1.45(m, 2H), 0.92(t, 3H)(S5). $^{13}C[^1H]$ NMR (100 MHz, DMSO-d_6, d, ppm): 152.80 (1C), 152.60 (1C), 150.45 (1C), 147.20 (6C), 145.47 (2C), 139.33 (4C), 136.80 (6C), 132.25 (1C), 131.47 (1C), 130.41 (4C), 128.60 (1C), 128.03 (4C), 126.25 (2C), 122.85 (2C), 121.59 (6C), 116.04 (1C), 69.38 (1C), 30.29 (1C), 18.47 (1C), 13.53 (1C) (S9). IR (KBr, cm^{-1}): 3414 (ν, N-H), 2956(ν, C-H), 1529 (ν, N-O), 1427 (ν, N-O), 1083 (ν, R-O-C), 628 (ν, Ru-N)(S2).

[Ru (bpy)$_2$(bnpip)](ClO$_4$)$_2$. 2H$_2$O (2)

This was synthesized adopting the procedure as explained for complex 1 above by taking cis-[Ru (bpy)$_2$Cl$_2$].2H$_2$O (0.260 g, 0.5 mM) and bnpip (0.206 g, 0.5 mM) (yield: 81.34%). Anal. data for $RuC_{43}H_{38}Cl_2N_9O_{13}$: calc. C, 48.69; H, 3.61; N, 11.88; found: C, 48.18; H, 3.39; N, 11.63. ES$^+$-MS calc: 827.19; found: 826.36(S12).^1H NMR (DMSO-d_6, 400 MHz):δ 9.13(d, 2H), 8.81(d, 4H), 8.64(s, 1H), 8.43(d, 4H), 8.16(t, 4H), 8.08(d, 2H), 7.85(d, 1H), 7.73 (t, 2H), 7.68(d, 1H), 7.53(t, 4H), 4.26(t, 2H), 1.77(q, 2H), 1.51(m, 2H), 0.97(t, 3H)(S6).$^{13}C[^1H]$ NMR (100 MHz, DMSO-d_6, d, ppm): 166.90 (4C), 156.47 (1C), 152.79 (1C), 151.15 (6C), 145.26 (2C), 139.15 (1C), 137.86 (4C), 134.98 (1C), 132.13 (2C), 131.47 (2C), 128.60 (6C), 127.83 (2C), 126.90 (1C), 125.44 (1C), 124.40 (4C), 115.93 (1C), 69.38 (1C), 30.37 (1C), 18.53 (1C), 13.82 (1C).IR (KBr, cm^{-1}): 3415 (ν, N-H), 2956(ν, C-H), 1531 (ν, N-O), 1463 (ν, N-O), 1085 (ν, R-O-C), 626 (ν, Ru-N)(S3).

[Ru (dmb)$_2$(bnpip)](ClO$_4$)$_2$. 2H$_2$O (3)

This was synthesized adopting the procedure as explained for complex 1 above by taking cis-[Ru (dmb)$_2$Cl$_2$].2H$_2$O (0.288 g, 0.5 mM), bnpip (0.206 g, 0.5 mM) (yield: 81.34%). Anal. data for $RuC_{47}H_{46}Cl_2N_9O_{13}$: calc. C, 50.54; H, 4.15; N, 11.29; found: C, 50.01; H, 4.05; N, 11.13. ES$^+$-MS calc: 883.25; found: 882.25 (S13).^1H NMR (DMSO-d_6, 400 MHz):δ 8.98 (d, 2H), 8.91(d, 4H), 8.70(s, 4H), 8.52(q, 2H), 8.08(d, 2H), 7.90(d, 1H), 7.71(s, 1H), 7.66(d, 4H), 7.43(d, 1H), 4.26(t, 2H), 2.53(s, 12H), 1.76(q, 2H), 1.48(m, 2H), 0.95(t, 3H).$^{13}C[^1H]$ NMR (100 MHz, DMSO-d_6, d, ppm): 156.25 (4C), 152.80 (1C), 152.38 (1C), 150.35 (4C), 149.43 (2C), 147.94 (4C), 139.34 (2C), 137.43 (1C), 133.95 (1C), 131.46 (2C), 129.95 (2C), 128.60 (8C), 124.97 (2C), 123.65 (1C), 122.86 (1C), 121.59 (2C), 116.03 (1C), 69.38 (1C), 30.32 (1C), 20.71 (4C), 18.49 (1C), 13.55 (1C).IR (KBr, cm^{-1}): 3414 (ν, N-H), 2956(ν, C-H), 1531 (ν, N-O), 1450 (ν, N-O), 1085 (ν, R-O-C), 628 (ν, Ru-N).

2.4 | Biological assays

The human breast cancer cells, MDA-MB-231 were cultured in Dulbecco's modified Eagle's medium (DMEM) supplemented with 10% fetal bovine serum, 100 µg/ml streptomycin and 100 U/ml penicillin. The cells were maintained at 37 °C and 5% CO_2. Stock solutions of complexes were prepared in DMSO and stored at 4 °C and subsequently, these stock solutions were further diluted to required concentration prior to treatment of cells.

2.4.1 | Cytotoxicity assay

The cytotoxicity exerted by the Ruthenium complexes was assessed using MTT assay.[32] The assay is based on

the principle of only live cells which are actively metabolizing can reduce yellow MTT to blue formazan. Cells were seeded in 96-well culture plates (10^4 cells per well) and incubated overnight at 37° C in CO_2 incubator. Cisplatin and ruthenium complexes to be tested were then added to the wells to achieve final concentrations ranging from 2×10^{-7} to 2×10^{-4} M. Control wells were prepared by addition of culture medium (100 μL) and DMSO was used as solvent control. The plates were then incubated at 37 ° C in a 5% CO_2 incubator for 48 hr. After completion of the incubation, stock MTT dye solution (20 μL of 10 mg/ml MTT) was added to each well. After 3 hr of incubation, 120 μL DMSO was added to solubilise the formazan crystals. The optical density of each well was then measured on Biorad ELISA spectrophotometer at a wavelength of 570–590 nm. The IC_{50} values were determined by plotting the percentage viability vs concentration on a logarithmic graph and the concentration at which 50% of cells remained viable relative to the control was calculated. Each experiment was repeated at least three times to obtain mean values.

2.4.2 | Cellular uptake and morphology of cells

MCF-7 cells were seeded in 35 mm culture plates and incubated overnight at 37 °C in a 5% CO_2 incubator. Different concentrations of ruthenium (II) complexes to be tested were added to each well while replacing with fresh medium. The plates were incubated at 37 °C in a 5% CO_2 incubator for 24 hr and 48 hr, the cells were imaged in phase contrast microscope with 10X objective.

2.4.3 | Nuclear morphology and cell apoptosis assay

Cells undergoing apoptosis were assessed using PE-annexin-V apoptosis detection kit (Dead Cell Apoptosis Kit with Annexin V Alexa Fluor® 488 and PI kit) according to the manufacturer's instructions (Life Technologies Inc). Briefly, cells were plated in 6-well plates at a density of 1×10^5 cells/well and were treated for 48 hr with different concentrations of ruthenium complexes. Post treatment, cells were recovered, washed with binding buffer (BB) and centrifuged. Annexin-V FITC (10 μL) was added to the pellet and incubated in the dark for 15 min at room temperature. Subsequently, cells were washed and re-suspended in BB, and PI solution (20 μg/ml) was added and incubated in dark for 10 mins. The cells were then centrifuged and mounted in PBS with 90% glycerol containing 1 mg/ml anti-fade (paraphenylenediamine) and 0.5 mg/ml, 4, 6-diamidino-2-phenylindole (DAPI). The cells were imaged using Olympus BX51 fluorescent microscope at 40X magnification.

2.4.4 | Real-time RT-PCR

An RT-PCR analysis was done to study the expression of specific genes related to apoptosis as described.[33] Several studies have shown that cyclin D and cyclin E are regulated during apoptosis. Hence we studied their expression at mRNA level. We also monitored the expression of caspase 8 as it an apoptotic marker. The primers to amplify the specific genes were designed by using the Primer Express (TM) software (Applied Biosystems) or obtained from published literature or Primer Bank (http//pga.mgh.harvard.edu/primerbank/). The primers used include cyclin D; forward:5′-ATGTTCGTGGCC TCTAAGATGA-3′, reverse: 5′-CAGGTTCCACTTGAGCT TGTTC-3′. Cyclin E; forward:5'-TTTCAGGGTAT CAGTGGTG-3′ reverse:5′-TGTGGGTCTGTATGTTGTG-3′ and caspase 8;forward: 5'-AAGTTCCTGAGCCTGG ACTACAT-3′, reverse:5'-ATTTGAGCCCTGCCTGGTG TCT-3′. All primer pairs were tested for specificity and amplification efficiency under the same conditions. (denaturation at 95 °C for 30 s, amplification with 40 cycles of:- {95 °C for 20 s, 60 °C for 20 s, 72 °C for 30 s}, and 72 °C for 5 min). GAPDH was included in the gene set as internal control gene for normalization. After treatments, total RNA was prepared using Trizol method from MCF-7 cells either treated with ruthenium (II) complexes (**1**–**3**) or left untreated for 24 hr. cDNA was generated from total RNA using the Verso cDNA synthesis kit (thermo scientific make) cDNA synthesis kit. 1 micro gram cDNA was used in each RT-PCR reaction; subsequently, real-time quantitative PCR was carried out in an ABI PRISM 7900 (Applied Biosystems) sequence detection system with the cDNA as template using gene-specific primer sets and the dynamo kit containing SYBR green dye (Finnzymes). At the time of use, diluted cDNA was mixed with the appropriate amount of SYBR green PCR master mix (DyNAmo Color Flash SYBR Green qPCR kit) and added to each of the wells and PCR was carried out as described above. All measurements were made in duplicate. The expression of genes was analysed by Delta Delta CT (ΔΔCT) method.

2.4.5 | Antimicrobial studies

Standard disk diffusion technique has been employed to test the Antimicrobial activity of the complexes against E.

coli, Bacillus subtilis and S. aureus. Two unique concentrations 1,000 μM, and 500 μM in DMSO were utilized for testing spore germination of every microbes. Filter paper disks of 5 mm size were prepared utilizing whatman filter paper no.1 (cleaned in an autoclave) immersed with 10 μL of complexes and was set in the petri dishes containing LB (Luria Bertini) agar media immunized with E. coli, Bacillus subtlis and S. aureus independently. The petri dishes were incubated at 25 ± 0.2 °C and the zone of inhibition were noted after 24 hr. The plates were then observed and the distances across of the inhibition zones (in mm) were estimated and compared with known standard antibacterial medication ampicillin at a similar concentration.

2.5 | DNA binding

The abilities of complexes **1**–**3** bind to DNA were examined according to known procedures. Stock solutions of complexes were prepared in DMSO and further dissolving in Tris buffer (5 mM Tris HCl, 50 mM NaCl, pH 7.1) to required concentrations for the usage in emission and absorption spectroscopy. Maintaining the complex concentration constant and varying the DNA concentration, spectra were recorded and calculated the binding constant by using UV–visible and fluorescence methods. An Ostwald viscometer is used with BPE buffer (6 mM Na_2HPO_4, 2 mM NaH_2PO_4, 1 mM Na_2EDTA, pH = 7.0) recorded and compared with proven ethidium bromide.

2.6 | Molecular dynamic simulations & molecular docking studies

The present examination centres around MD simulations and docking of ruthenium (II) complexes with DNA as discussed in our earlier protocols.[34,35] The created 3D ruthenium (II) complexes were docked to ds DNA (PDB ID: 423D) utilizing Patch Dock server.[36,37] Patch Dock results were obtained as a lot of scoring capacities dependent on the shape complementarity and the nuclear desolvation energy of the changed complex.

2.7 | Photocleavage experiments

Photocleavage experiments carried out using super coiled pBR322 DNA. Super coiled pBR322 DNA was treated with different concentrations (20–80 μM range) of ruthenium (II) complexes with in TAE buffer (Tris–HCl, 18 mM NaCl buffer pH = 7.2).

3 | RESULT AND DISCUSSION

3.1 | Synthesis and characterization

All the synthesized complexes were thoroughly characterized by their elemental (C, H, and N) analysis, mass, proton (^1H) NMR, ^{13}C-NMR, FT-IR spectroscopic measurements. From FT-IR spectra, the bnpip ligand vibrations of ν_{NH} at 3093 cm^{-1}, ν_{NO} at 1531, 1450 cm^{-1} are shifted to ν_{NH} at ≈ 3414 cm^{-1}, ν_{NO} at ≈ 1529, 1427 cm^{-1} after complex development. Appearance of a new band at ≈ 628 cm^{-1}, an indication of formation metal – Nitrogen bond which has been assigned to $\nu_{RuN.}$[38] This indicates all six Ru-N bonds are equal bond length.

From ^1H NMR spectra, the ligand having aliphatic protons gives peak at δ 4.15 to 0.95 ppm, after complex formation these protons were shifted to around δ ~ 4.26 to 0.92 ppm. In each of the edifices, the N– H protons on the imidazole ring were not seen; because the protons are extremely dynamic and quick proton transfer between two imidazole N's, along these lines no peak was seen for the N-H group of imidazole ring.[39,40] From ^{13}C [^1H] Spectra of all the complexes show a characteristic peak at an aliphatic region, but compare to ligand the values were shifted, confirming the complex formation.

From absorption spectroscopy, all three complexes (**1**–**3**) were exhibiting metal to ligand charge transfer bond peak at ≈ 460, 455 and 470 nm respectively. But ligand does not have this peak as shown in Figure 1. It confirms the complex formation.

3.2 | Biological studies

Over the past few decades, ruthenium (II) complexes have successfully been used in clinical research, yet the mechanisms followed by these compounds to eliminate cancer are to be explored. In the present study, the potential anti-proliferative effects of **1**, **2** and **3** complexes on the viability of MCF-7 breast cancer cell lines were assessed by Annexin V staining, MTT reduction, fluorescent microscopy and RT-PCR analysis.

3.2.1 | MTT assay

All the three complexes were evaluate the concentration, where the cells were 50% viable by performing MTT assay. After treatment of MCF-7 cells for 48 hr with **1**, **2** and **3** complexes in a range of concentrations (2.5–0.4 μM) as shown in Table 1, the percentage inhibition of growth of the cancer cells was determined. The cell viabilities (%) of concentrations were obtained by

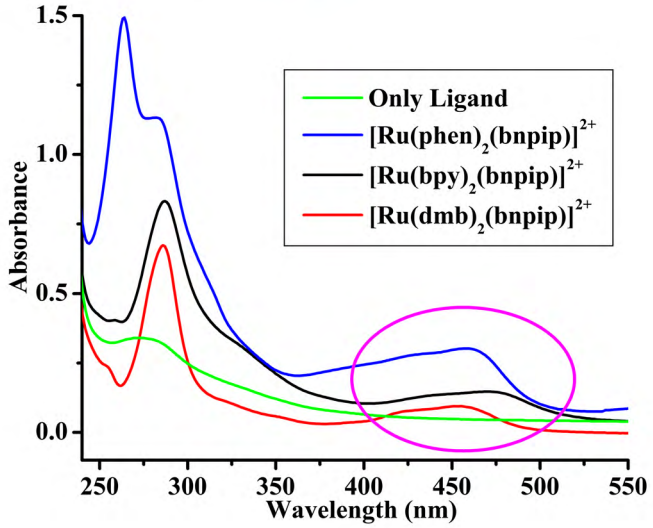


FIGURE 1 The absorption spectrum of only ligand (bnpip) and complexes [Ru (phen)2(bnpip)]2+, [Ru (bpy)2(bnpip)]2+ and [Ru (dmb)2(bnpip)]2 +

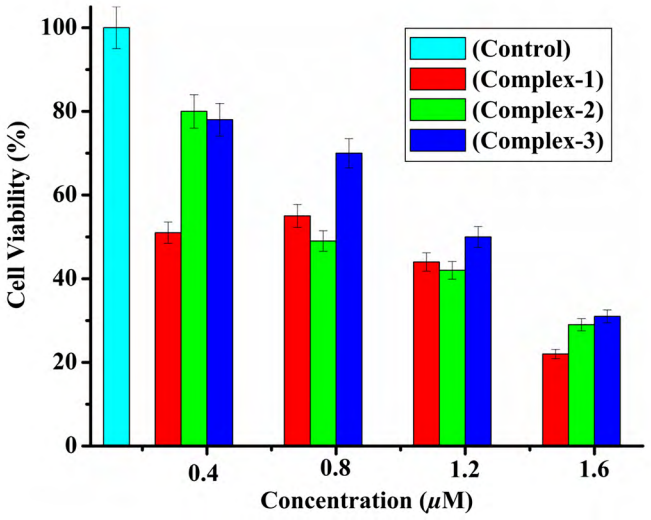


FIGURE 2 Cell viability of MCF-7 cell line in vitro treatment with complexes [Ru (phen)2(bnpip)]2+ (1), [Ru (bpy)2(bnpip)]2+ (2) and [Ru (dmb)2(bnpip)]2+ (3). Each data point is the mean ± standard error obtained from at least three independent experiments

plotting absorbance measured at different concentrations as shown in Figure 2.

3.2.2 | Cellular uptake and morphology of cells

MCF-7 cells exhibited morphological changes such as membrane blebbing, which are characteristics of apoptosis. These changes increased with time i.e. from 24 hr to 48 hr, more number of cells were dead and found floating in the medium. Figure 3 shows the nuclear fragmentation, cells in early and late apoptotic stages. Cells show shrinkage, vacuoles indicating various apoptotic stages.

3.2.3 | Nuclear morphology and cell apoptosis assay

Further, to confirm nuclear degradation and apoptosis, we used annexin V, PI and DAPI staining to treated and untreated cells. An early event of apoptosis is translocation of membrane phosphatidyl serine (PS) from the inner side of the plasma membrane to outer side. Annexin V conjugated to FITC binds to phosphotidyl serine which can be detected in fluorescent microscope. Propidium iodide is non permeable DNA binding dye which can enter only dead cells whose membranes are ruptured. DAPI is permeable DNA binding dye and therefore can enter live as well as dead cells. We used these stain to identify and confirm apoptosis after treatment. Control cells did not show annexin - V and PI staining but in MCF-7 cells treated with Ruthenium complexes, annexin V is found bound to the cells. Propidium Iodide staining was also observed in some of the treated cells confirming cell death (Figure 4).

TABLE 1 The IC50 values for complexes **1–3** against MCF-7 cell lines

S.No.	Complex	IC 50(μM)
1.	**Complex-1**	0.41(±0.014)
2.	**Complex-2**	2.3(±0.021)
3.	**Complex-3**	1.5(±0.019)
4.	**Cisplatin**	11.3(±0.011)

The cytotoxic activity and DNA binding affinities are found to be associated with the size of ancillary ligand. The mechanism supporting the cytotoxic activity of the metal based drugs is poorly implied. However, several studies indicated that apoptosis of cells is an important mechanism of cytotoxic action of such compounds.[41] Apoptosis is defined as highly complex and sophisticated programmed cell death, involving an energy-dependent cascade of molecular events leading to distinct morphological and biochemical changes.[42] The vivid pathways (Extrinsic and intrinsic) require activation of different apoptotic and anti-apoptotic genes playing an important roles in induction of apoptosis.[43,44] Caspase 8, an initiator caspase of extrinsic pathway has been found associated with breast cancer and it's expression has been found altered in several breast cancer cell lines.[45] In

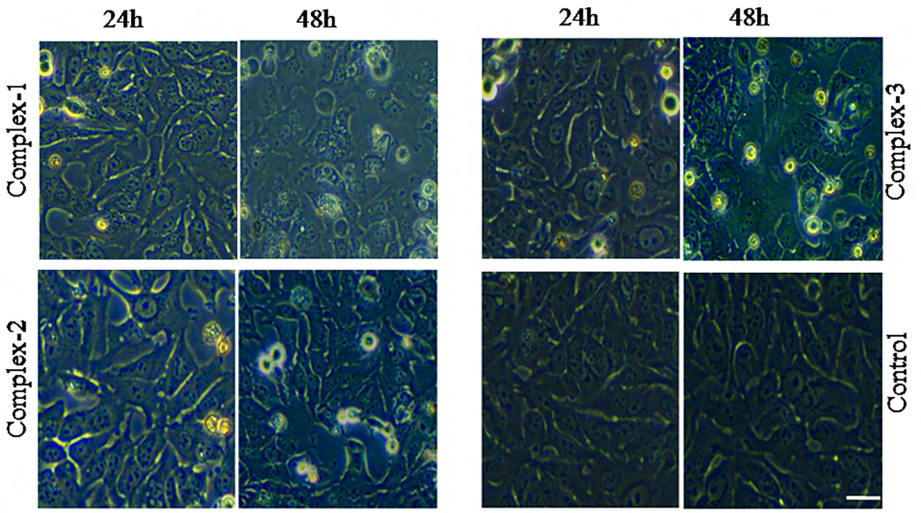


FIGURE 3 MCF-7 cells were exposed to IC50 concentration of complexes [Ru (phen)2(bnpip)]2+ (1), [Ru (bpy)2(bnpip)]2+ (2), [Ru (dmb)2 (bnpip)]2+ (3). Images were taken at 24 h and 48 hr time point using phase contrast microscope (Olympus)at 10X objective. Scale 10 μm

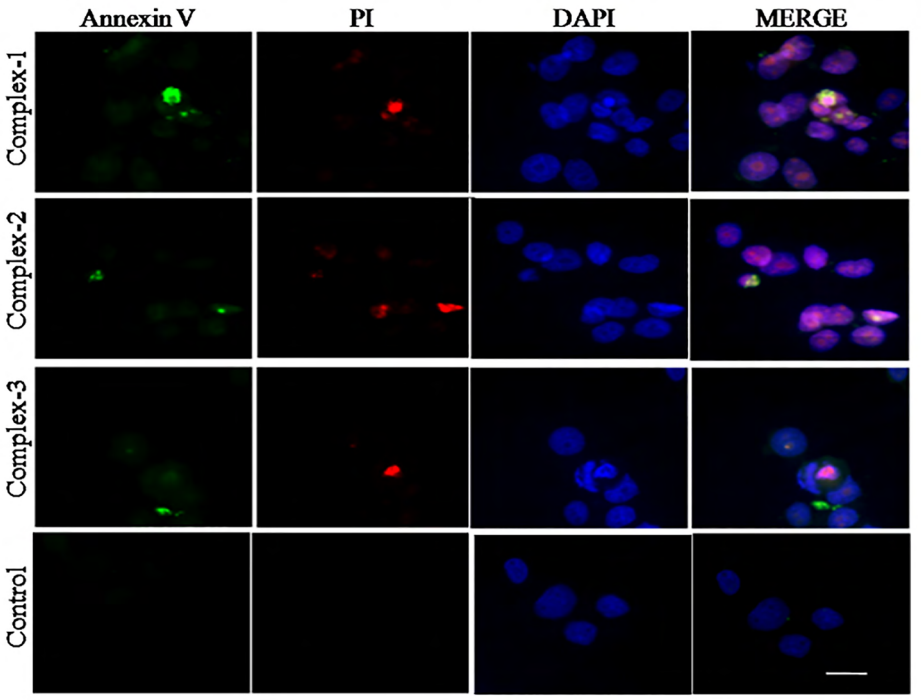


FIGURE 4 Apoptotic morphology was investigated by staining treated and untreated MCF-7 cells with Annexin V, Propidium Iodide and DAPI. Annexin V is observed in Green, propidium Iodide is shown in Red colour. DAPI stained nuclei are seen in blue colour respectively. Scale bar -20 μm

many tumours regulation of cyclin D1 was demonstrated to be required for tumour maintenance and it's reduction in different types of human cancer cells (breast cancer, mantle cell lymphoma, squamous cell carcinoma, and colorectal cancer) was shown to enhance their sensitivity to radiation (i.e. chemotherapy).[46] The abundance of the cyclin E transcript protein is found in carcinomas of the lung, gastrointestinal tract and breast in addition to lymphomas and leukemias.[47] Cyclin E has been used as a prognostic marker as 18% to 22% of breast cancers patients have shown higher levels of expression. In our study, MCF - 7 cells treated with ruthenium compounds were exhibiting specific apoptotic features which were confirmed by annexin V, propidium Iodide and DAPI staining.

3.2.4 | Real-time -PCR

Further, we studied gene expression by RT-PCR to understand the effect of ruthenium complexes on the regulation of caspase 8 (Figure 5), cyclin D (Figure 6) and cyclin E (Figure 7) during treatments. Caspase 8 was found upregulated by many fold compared to control cells. Cyclin D and cyclin E which are cell cycle check points and are found in abundance in cancer cells were

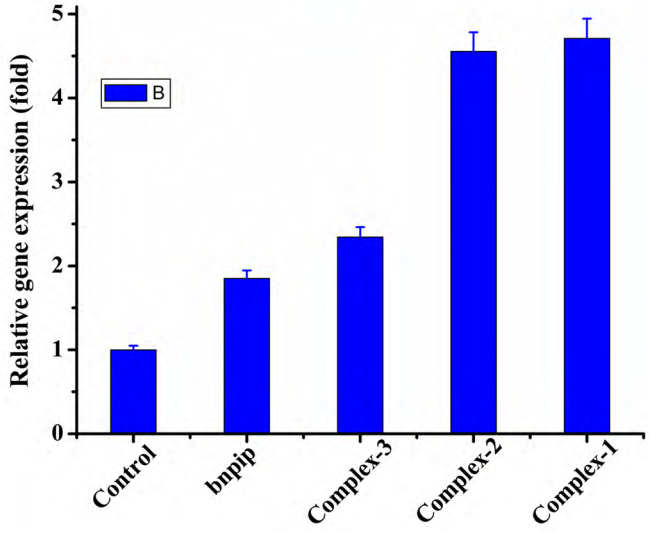


FIGURE 5 RT-PCR analysis showing changes in relative expression of Caspase 8 during treatment of MCF-7cells with complexes. After treatments, total RNA was prepared, cDNA was synthesized and using gene specific primers RT-qPCR analysis was done. Fold increase in gene expression was calculated by ΔΔCT method. The lanes are as follows; Control, bnpip ligand, [Ru (phen) 2(bnpip)]2+ (1), [Ru (bpy)2(bnpip)]2+ (2) and [Ru (dmb)2(bnpip)]2 + (3)

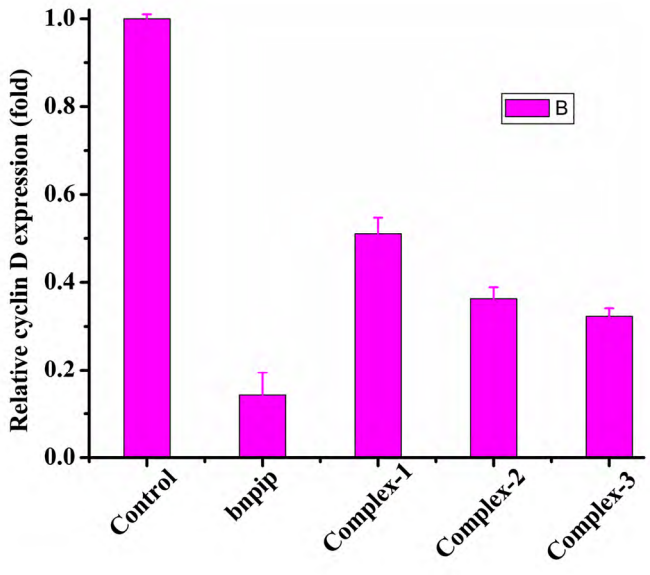


FIGURE 6 RT-PCR analysis showing changes in relative expression of Cyclin D during treatment of MCF-7cells with complexes. After treatments, total RNA was prepared, cDNA was synthesized and using gene specific primers RT-qPCR analysis was done. Fold increase in gene expression was calculated by ΔΔCT method. The lanes are as follows; Control, bnpip ligand, [Ru (phen) 2(bnpip)]2+ (1), [Ru (bpy)2(bnpip)]2+ (2) and [Ru (dmb)2(bnpip)]2 + (3)

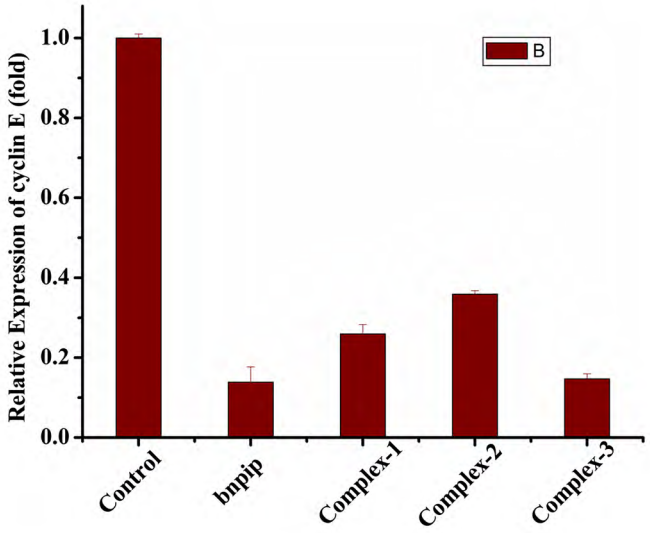


FIGURE 7 RT-PCR analysis showing changes in relative expression of Cyclin E during treatment of MCF-7cells with complexes. After treatments, total RNA was prepared, cDNA was synthesized and using gene specific primers RT-qPCR analysis was done. Fold increase in gene expression was calculated by ΔΔCT method. The lanes are as follows; Control, bnpip ligand, [Ru (phen) 2(bnpip)]2+ (1), [Ru (bpy)2(bnpip)]2+ (2) and [Ru (dmb)2(bnpip)]2 + (3)

found down regulated after treatment with **1**, **2**, and **3** complexes.

3.2.5 | Antimicrobial studies

Antimicrobial action for the complexes **1–3** was tried utilizing paper disc method against the microscopic organisms E. coli, S. aureus and Bacillus subtilis at 1000 μM and 500 μM fixation in DMSO arrangement. DMSO demonstrated insignificant action as compared with ruthenium (II) complexes. $[Ru\ (phen)_2(bnpip)]^{2+}$ showed marginally more active than $[Ru\ (bpy)_2(bnpip)]^{2+}$ and $[Ru\ (dmb)_2(bnpip)]^{2+}$. The outcomes were communicated as zone hindrance measurement (in mm) (Table 2). The antimicrobial activity is reliant on the concentration of the complex.[48] These outcomes can be related to the activity of the drug ampicillin at a similar concentration.

3.3 | DNA binding studies

3.3.1 | Electronic absorption spectra

The Electronic spectra of the synthesized complexes show characteristic intense π-π* ligand and MLCT (metal-to-ligand charge transfer) transition in UV region and visible region respectively. For metallointercalators,

TABLE 2 The antimicrobial activity of the ligand (bnpip) and ruthenium (II) complexes (**1–3**) with different concentrations

	Escherichia coli(E.coli)		*Staphylococcus aureus(S.A)*		*Bacillus subtilis(B.S)*	
Complex	**500 μL**	**1000 μL**	**500 μL**	**1000 μL**	**500 μL**	**1000 μL**
Bnpip	6	7	7	8	6	7
Complex-1	9	12	8	10	10	12
Complex-2	8	10	9	10	8	12
Complex-3	8	10	8	10	10	11
Ampicillin	27	32	18	20	28	30

DNA binding is characterized by hypochromism and a red shift in the MLCT and ligand bands.[49] The absorption spectra of complexes **1–3** in the absence and presence of CT-DNA at a fixed complex concentration, with increasing the DNA concentration were shown in Figure 8. As the DNA concentration increased, the MLCT band of $[Ru(phen)_2(bnpip)]^{2+}$ at 460 nm showed hypochromism of about 10% with a red shift of 6 nm, for $[Ru(bpy)_2(bnpip)]^{2+}$, MLCT band at 455 nm showed hypochromism of 14% with a red shift of 2 nm and $[Ru(dmb)_2(bnpip)]^{2+}$ MLCT band at 470 nm showed hypochromism of 11% with a red shift of 6 nm. Similar hypochromic behaviour was reported for the complex $[Ru(phen)_2dppz]^{2+}$, where dppz ligand plays major role for the intercalation binding with DNA.[50]

In order to measure the binding strength of complexes **1**, **2** and **3**, the intrinsic binding constant K_b of ruthenium (II) complex to DNA was determined by measuring the absorbance at MLCT for the three complexes (shown in Figure 8) using Equation.[1] The intrinsic binding constants K_b for complexes **1**, **2** and **3** were 1.40 (±0.02)x10^6 M^{-1}, 1.00(±0.02)x10^6 M^{-1} and 0.80(±0.01) x10^6 M^{-1} respectively shown in table 3. The K_b values varies even the same intercalating ligand in all three

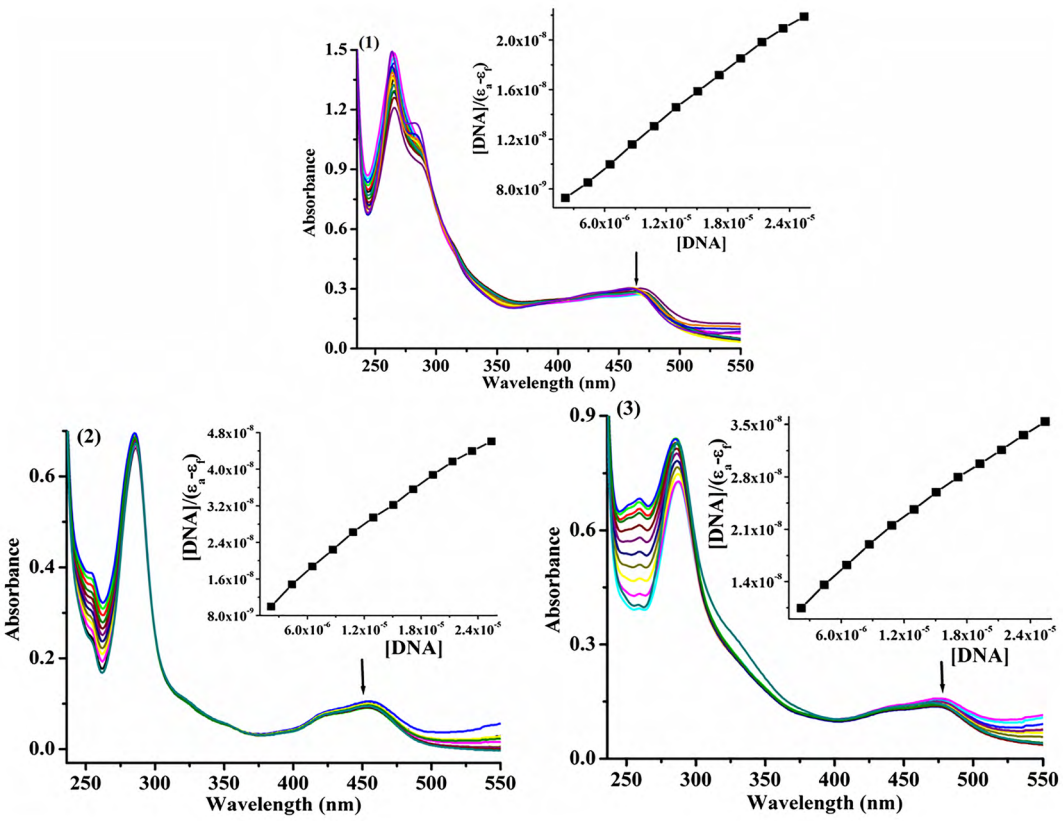


FIGURE 8 Absorption spectra of complexes 1–3 in Tris–HCl buffer upon addition of CT-DNA. Arrow shows hypochromic and bathochromic shifts upon increase of DNA concentration. Inserted plot, [DNA]/(εb-εf) versus [DNA] for the titration of DNA with ruthenium (II) complex, which gives intrinsic binding constant (Kb)

TABLE 3 Absorption, Emission and quenching binding constants of ruthenium (II) complexes (**1–3**) with CT-DNA

S.No.	Complex	K_b for Absorption(M^{-1})	K_b for Emission(M^{-1})	K_{sv}
1.	**Complex-1**	$1.4(\pm0.021) \times 10^6$	$6.0(\pm0.021) \times 10^6$	3971
2.	**Complex-2**	$1.0(\pm0.015) \times 10^6$	$5.3(\pm0.015) \times 10^6$	3032
3.	**Complex-3**	$0.8(\pm0.018) \times 10^6$	$4.4(\pm0.018) \times 10^6$	2134

complexes is due to planarity and size of the anthracene ligand. The K_b values are comparable with the known DNA intercalators Δ-[Ru (phen)$_2$(dppz)]$^{2+}$ ($3.2x10^5$ M^{-1}), Λ-[Ru (phen)$_2$(dppz)]$^{2+}$ ($1.7x10^5$ M^{-1}),[51] EB ($1.4x10^6$ M^{-1}),[52] suggesting more stacking interaction of the aromatic chromophore of the three complexes with the base pairs of the DNA. The complex **1** exhibits a slightly stronger DNA binding affinity than **2** and **3**, which is recognized to an intense electrostatic interaction between DNA and complex **1**. The binding constant of complexes from dmb, bpy, to phen the surface area and hydrophobicity increases, which leads to a strong DNA-binding affinity for complex **1**. Complex-**3** ([Ru (dmb)$_2$(bnpip)]$^{2+}$) exhibits less binding strength compared to complex-**2** with DNA. It may be due to ancillary ligand having methyl groups at 4 and 4′ positions that causes steric hindrance and donate electrons to ruthenium (II) and enhances the electron density, thereby decreasing the binding constant from complex- **2**.

3.3.2 | Luminescence spectra

The binding of complexes **1**, **2** and **3** with DNA was further examined by luminescence titration measurements. All three complexes exhibit strong emission bands at 597 nm, 605 nm and 620 nm, respectively at room temperature, when excited between 460 nm, 455 nm and 470 nm. Changes in emission spectra of the ruthenium (II) complexes **1–3** with an increasing DNA concentrations are shown in Figure 9. As DNA concentration increases, the emission intensities of the complexes gradually increases until emission intensity becomes stable. The three complexes intensities in the presence of DNA

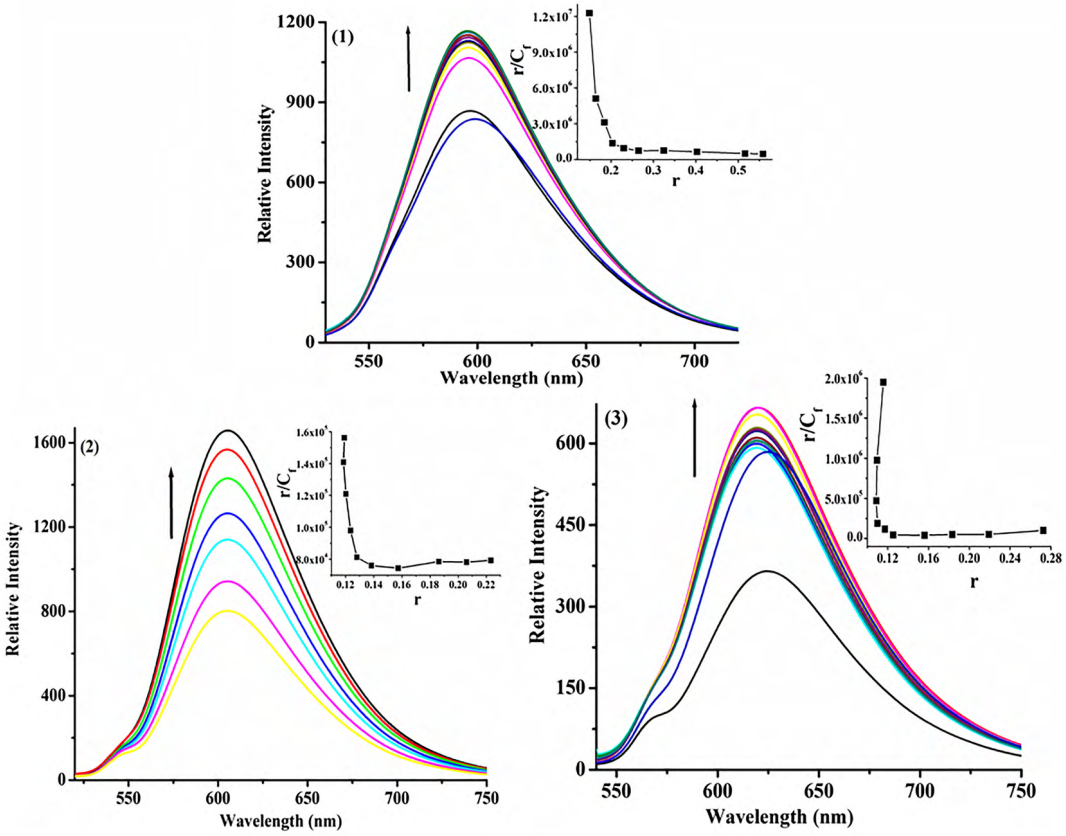


FIGURE 9 Emission spectra of complexes 1–3 in Tris–HCl buffer upon addition of CT-DNA. The arrow shows the intensity change upon the increase of DNA concentration. Inset: Scatchard plot of above complex, which gives binding constant (Kb)

were increased to 1.34, 1.00 and 1.62 times as compared to those of the DNA-free complexes, respectively. The intrinsic binding constant was obtained from the fluorescence data using a modified form of the Scatchard equation[53] with a plot of r/C_f versus r, where r is the binding ratio C_b/[DNA] and C_f is the free ligand concentration. Scatchard plots for complexes **1–3** have been obtained from luminescence spectra and binding constants (K_b) were 6.0 x 10^6, 5.3 x 10^6 and 4.4 x 10^6 M^{-1}. The K_b values of complexes **1–3** obtained from above two titration measurements (absorption and luminescence titration) are in agreement with each other.

In addition to comparing the DNA binding with ruthenium (II) complexes, the fluorescence quenching experiment was carried out. A negatively charged quencher $[Fe(CN)_6]^{4-}$ was used to be repelled by the negative phosphate backbone of the DNA, a extra deeply DNA-bound cationic ruthenium (II) complex have to be greater protected from quenching than freely bound complex. In the absence of DNA, complexes **1–3** had been successfully quenched by using $[Fe(CN)_6]^{4-}$, while in the presence of DNA quenching decreases. As DNA concentration increases the proportion of quenching is decreases. The Stern-Volmer plots for free complex and in presence of increasing amounts of DNA shown in Figure 10. The slope measures the binding affinity. The quenching constant (K_{sv}) of three complexes were tabulated in Table 3. Emission quenching data indicates that all complexes bind to DNA more effectively.

3.3.3 | Light switch on and off studies

In light-switch experiment, the emission intensity quenching and restoration were observed by the addition of Co^{2+} and EDTA solutions respectively. The $[Ru(bpy)_2(bnpip)]^{2+}$ complex intercalates into the base pairs of DNA, hence the interaction between DNA and $[Ru(bpy)_2(bnpip)]^{2+}$ complex is strong. This may be observed by the enhancement in the emission intensity of the complex bound DNA (light switch on). When Co^{2+} is added to the DNA-$[Ru(bpy)_2(bnpip)]^{2+}$ species it may binds to the nitrogen's of imidazole present in the intercalating ligand, forming a heterometallic complex (Co^{2+}-$[Ru(bpy)_2(bnpip)]^{2+}$). It results the decrease in the emission intensity of complex bound DNA (light switch off).[54] Further addition of polyanionic EDTA attracts the Co^{2+} ions forming a Co^{2+}- EDTA complex, thus restoring the DNA-$[Ru(bpy)_2(bnpip)]^{2+}$ species, hence the emission intensity is recovered (light switch on) as shown in Figure 11. A similar examination was observed for other two complexes. The adjustment of luminescence intensity in the DNA-bound complex in the presence of Co^{2+} and EDTA explains its utilization in the modulation of drug therapy.

3.3.4 | Viscosity measurements

Three synthesized ruthenium (II) complexes mode of binding with CT DNA was further investigated by viscosity measurements. The binding mode is interpreted by the changes in the viscosity of the CT DNA upon addition of metal complex. The intercalation mode of binding causes the DNA base pairs to move away from each other in order to accommodate metal complexes hence the length of DNA increases.[55,56] As DNA length increases, the flow time of viscosity also increases. The impact of the ruthenium (II) complexes on the viscosity of DNA is shown in Figure 12 it can be seen that, the viscosity of DNA increased marginally with increasing quantities of the complexes, demonstrating the binding mode of complexes may be through intercalation. The viscosity increasing order follows EB >**1** > **2** > **3** (EB = Ethidium Bromide). This is in consistent with UV–vis and luminescence spectroscopy results.

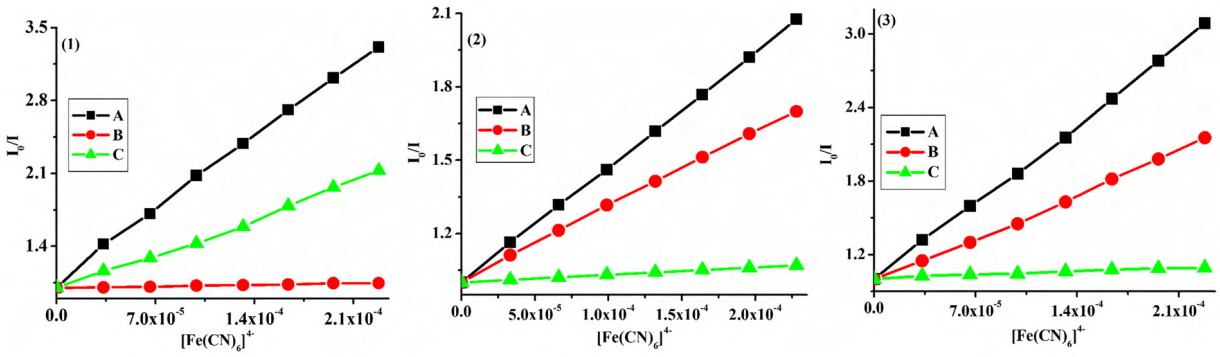


FIGURE 10 Emission quenching of complexes 1–3 with [Fe (CN)6]4- in the absence of DNA (A), presence of DNA 1:20 (B) and 1:200 (C). ([DNA] = 3.0 x 105 M), pH = 7.1, at room temperature

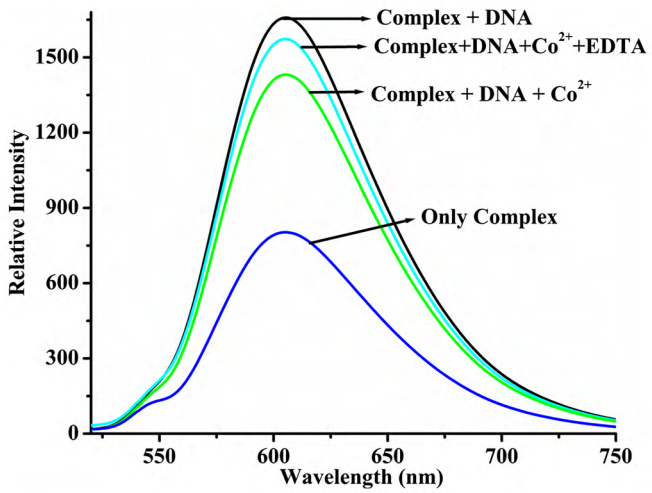


FIGURE 11 DNA light switch on and off experiment showing the luminescence changes upon addition of Co2+, EDTA and DNA to complex 2

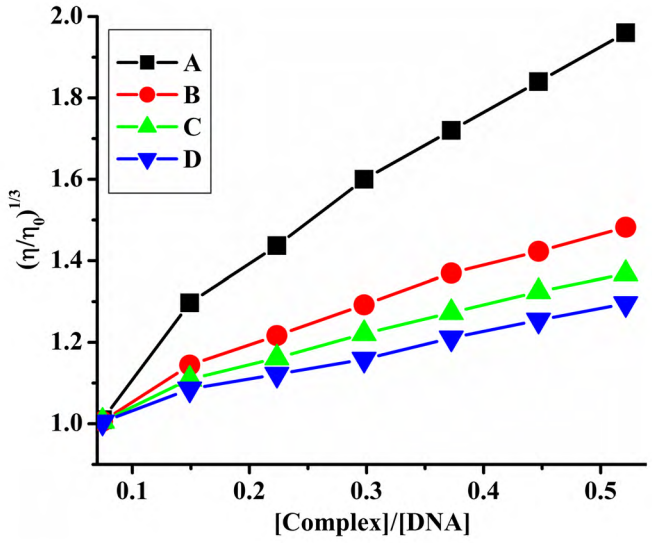


FIGURE 12 Effect of increasing amounts of Ethidium bromide (EtBr), [Ru (phen)2(bnpip)]2+ (1), [Ru (bpy)2(bnpip)] 2 + (2) and Ru (dmb)2(bnpip)]2+ (3) on the relative viscosity of calf thymus DNA at 30(±0.1)0C. ([DNA] = 3.0 x 105 M), pH = 7.0, at room temperature

3.4 | Molecular docking studies

Table 4 shows the Ru – N and Ru – Intercalating ligand bond lengths (Figure 13), which has an effect on its DNA binding. The ligand is 15.5434 Å long and has a lengthening effect upon binding to metal. The intercalator ligand and metal complexes exhibit specificity in binding to guanine, the order of DNA binding is I > II > III, which can be understood with Atomic contact Energies (ACE) as given in Table 5. The intercalator has weak binding as compared to corresponding metal complex, which can be attributed to stronger interaction via hydrogen and vanderwaals forces of attraction in the metal complex. The strength of interaction of metal complex might be due to the rigidity of the intercalator, which is due perhaps owing to ancillary ligand. The nature of the ancillary ligand and length of intercalator has an influence on the DNA binding and is independent of the cytotoxicity.

3.5 | Photocleavage experiment

The cleaving efficacy of three ruthenium (II) complexes has been estimated by their capability to cleave supercoiled pBR322 DNA from different forms by gel electrophoresis experiment as shown in Figure 14. DNA alone is used as control (lane 1), it does not show any notable cleavage of pBR322 DNA. But in the presence of metal complexes pBR322 DNA was cleaved into two different forms. The complexes **1–3** at three different concentrations (10, 20 and 40 μM), were utilized for these cleaving, significant decline in the capabilities of the bands for the metal-bound DNA when compared with untreated control DNA was seen, which recommends the cleavage of DNA by metal complexes.[57] The results show that the amount of cleavage improved with increasing concentration of complexes, show their potential chemical nuclease activity.

For the photo activated cleavage of the plasmid DNA, reactive species are responsible for cleavage of pBR322 DNA in different forms. The reactive species are O_2, H_2O_2 and OH^- (Type I) and $^1O_2$ and $^3O_2$ (Type II). We

TABLE 4 Bond lengths of the 3D conformers of metal polypyridyl complexes(**1–3**), the bond lengths were calculated using HYPERCHEM 7.5 program

Complex	Ru-N_1[a]	Ru-N_2[a]	Ru-N_3[a]	Ru-N_4[a]	Ru-N_5[b]	Ru-N_6[b]	Total Energy	Ru-Int
Complex-1	1.94482	1.94481	1.95618	1.94867	1.94871	1.95	267.93	17.5963
Complex-2	1.99577	1.92494	1.99183	1.92133	1.92197	1.99041	303.6	17.5784
Complex-3	1.94699	1.94709	1.95079	1.94284	1.94284	1.94689	271.98	17.5724

[a]N_1, N_2, N_3 and N_4 are polypyridyl (phen/bpy) nitrogen bonded to metal
[b]N_5 and N_6, N of bnpip ligand bonded to metal

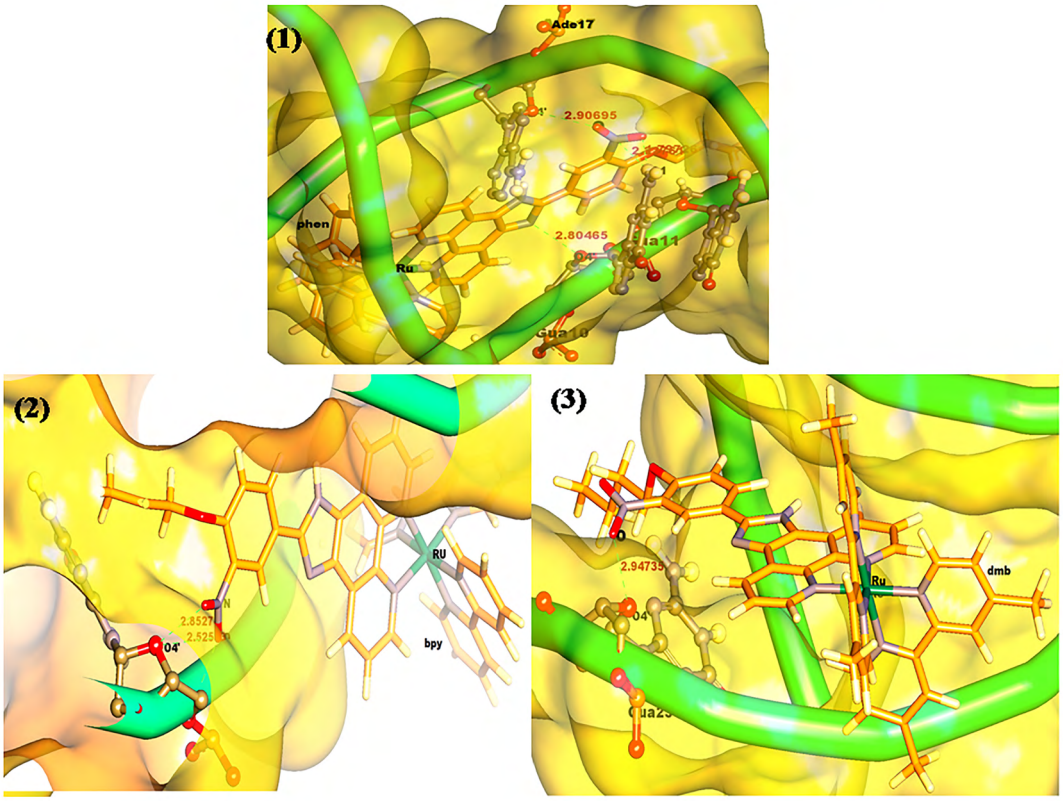


FIGURE 13 3D Model of the three ruthenium (II) polypyridyl complexes [Ru (phen)2bnpip]2+ (1) [Ru (bpy)2bnpip]2 + (2) and [Ru (dmb)2bnpip]2 + (3) with bonding modes. Docked complex of DNA with Ruthenium complex showing the interactions. 1. [Ru (phen)2 (bnpip)] + 2 – DNA complex, 2. [Ru (bpy)2(bnpip)] + 2 – DNA complex, 3. [Ru (dmb)2(bnpip)] + 2 – DNA complex binding interactions in the docked complex are represented as green dashed lines, DNA as ribbon model (green) with surface and in metal complex-carbon (Orange), metal ion (blue),Oxygen (Red), nitrogen (Purple) and hydrogen (grey)

investigated the DNA cleavage of synthesized complexes by gel electrophoresis in the presence of various radical scavengers such as Histidine ($^1O_2$), sodium azide (NaN_3) ($^1O_2$), Mannitol (hydroxyl radical scavenger), Hydrogen peroxide (H_2O_2) (hydroxyl radical scavenger) and DMSO (hydroxyl radical scavenger).[58,59] In the presence of

TABLE 5 Binding interactions involving the docked poses of DNA with metal complexes. Desolvation energy

S. No	Metal Complex	Patch Dock score	Binding interactions (donor group–acceptor group)	Bond length (A°)	ACEa (kcal/mol)
1.	**bnpip(L)**	4462	N11 – BT20 O5’	3.1546	−395.3
			N16 – BG19 O4’	2.5180	
2.	**Complex-1**	5620	AG10 – N43	2.2376	−633.04
			AG10 – O50	1.7972	
			N41 – AG10 O4′	2.8046	
			O44 – BA17 O4′	2.9069	
			O45– BG11 O4′	2.9195	
3.	**Complex-2**	5808	N43 - AG10 O4′	2.8581	−471.21
			O44 – AG10 O4′	2.9299	
			O44– AG10 O5′	2.5253	
			O45- AG10 O4′	2.8527	
4.	**Complex-3**	5624	O44 – AG23 O4′	2.9473	−434.99
			N43 – BG23 O4′	3.1599	

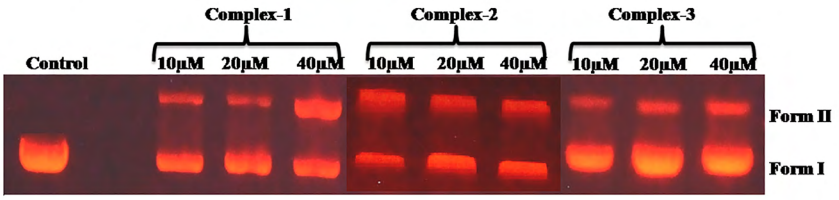


FIGURE 14 Agarose gel electrophoresis of pBR322 DNA in the presence of different concentrations (10, 20, and 40 μL) of complexes (1–3) after irradiation at 365 nm for 30 min

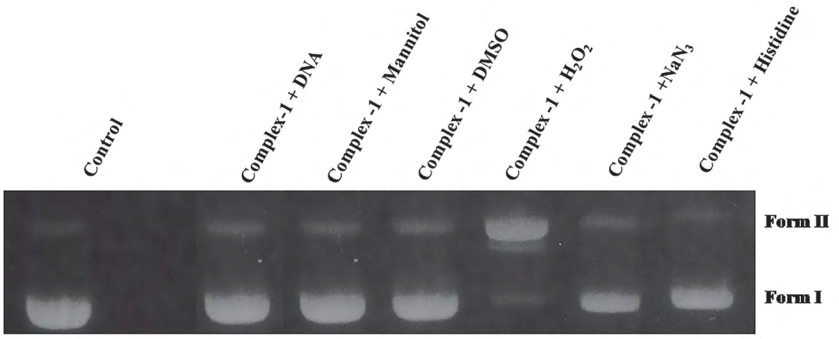


FIGURE 15 Photocleavage of pBR322 DNA experiments in the presence of Complex-1 ([Ru (phen)2(bnpip)]2+) (20 μM) and different reactive oxygen species inhibitors (Scavangers)

histidine (20 μM) and NaN_3(20 μM), cleavage was not seen (form II is not seen) or very much diminished compared to what was seen for the complexes with DNA (absence of histidine and NaN_3). In presence of mannitol, H_2O_2 and DMSO form II is formed, similar to complexes with DNA. Mannitol, H_2O_2 and DMSO are an $^{\cdot}OH$ radical inhibitors so there is no change in the cleavage pattern, which indicates that the $^{\cdot}OH$ radical is not responsible for cleavage (Figure 15). These results indicate that $^1O_2$ plays significant role in the photocleavage mechanism.

4 | CONCLUSIONS

In summary, the *in vitro*cytotoxicity of ruthenium (II) polypyridyl complexes (**1–3**) with new intercalator ligand (bnpip) has been estimated. The ancillary ligand on the metal complex plays an important role in modulating the activity. We discovered ruthenium complexes containing the 1, 10 phenanthroline ligand to be powerful inhibitors of malignancy cells. We additionally demonstrate that inhibition of malignant growth cell after treatment with the ruthenium complexes includes both cell cycle arrest (cyclin D1 and cyclin E) and apoptosis induction (Caspase 8). Interestingly, all the complexes manage a similar arrangement of qualities which is suggestive of the way that these complexes may use a common mechanism of apoptosis induction. The selection of ligands is basic for cytotoxicity and in the arrangement analyzed, the best ligand is 1, 10 phenanthroline. The cytotoxicity of the intercalating ligand improves upon complexation with ruthenium. For this the experimental studies like DNA binding studies also supporting the same order. In photocleavage, $^1O_2$ is responsible for DNA cleavage.

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SUPPORTING INFORMATION

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Evaluation of DNA Binding Antimicrobial and Cell Viability Activity of Furan-Based Cobalt (III) Polypyridyl Complexes

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Abstract

This article describes the DNA binding properties of three new Cobalt (III) Polypyridyl complexes $[Co(phen)_2CMIP]^{3+}$ (1), $[Co(bpy)_2CMIP]^{3+}$ (2) and $[Co(dmb)_2CMIP]^{3+}$ (3) where CMIP=2-(2-Chloro-8-methylquinolin-3-yl)w-1H-Imidazo[4,5-f][1,10]phenanthroline, phen = 1,10-phenanthroline, bpy = 2, 2′ bipyridine and dmb = 4, 4 - dimethyl-2, 2′- bipyridine. They have been synthesized and characterized by IR, ^1H &^{13}C NMR and Mass spectra. The DNA – binding constant (K_b) of the complexes was determined to be in the order of 10^6 with an intercalative mode of binding. Photoactivated cleavage and antimicrobial studies of three complexes were shown better results, Cytotoxicity (MTT assay) showed growth inhibition in dose dependent manner. Among three complexes, complex 1 was more active than other two complexes.

Keywords

Co(III) polypyridyl complexes, Antimicrobial activity, Intercalation, Photoactivated cleavage, *HeLa* cells, MTT assay.

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INTRODUCTION

The clinical drawbacks of cisplatin are apparent, including the limited applicability, the acquired resistance, and the serious side effects, such as neurotoxicity and nephrotoxicity[1,2]. These limitations of cisplatin have motivated extensive investigations into alternative metal-based cancer drugs. Over the years, complexes of Ru, Ir, Cu, Ni, Zn, Co, etc., have been reported to posses much better anticancer property than *cis*-platin[3-6]. Cobalt is an essential trace element present in the human body. It is involved in important biological functions such as fatty acid and amino acid metabolism, haematopoiesis, and in the form of vitamin B_{12} it is indirectly involved in synthesis of DNA. Interestingly, one cobalt complex containing Schiff base ligand (Doxovir) has recently passed phase II clinical trial for anti-viral treatment[7]. Several *in vitro* studies suggest that cobalt complexes possess promising anti-cancer activity[8].

Cobalt is widely distributed in the biological systems such as cells and body, and thus the interaction of DNA with cobalt compound has attracted much attention[9]. The binding properties of cobalt with calf

thymus DNA were studied by several methods, and the experimental results showed that the size and shape of the intercalated ligand had an important effect on the binding affinity of the compounds with DNA[10]. Hisaeda and co-workers discovered a new water-soluble dicobalt compound having two cobalt-carbon bonds and reported that this dicobalt compound showed higher ability for DNA cleavage in comparison with the corresponding monocobalt compound[11]. The interaction of DNA with cobalt (II) tridentate compound, and the photocleavage studies showed that the cobalt (II) compound increased to nicking of DNA in the presence of plasmid DNA[12]. Our previous works have shown that Ru (II) polypyridyl complexes containing *N*, *N*-chelating ligands were DNA intercalative and antiproliferative agents[13-20]**.**

This paper discussing about synthesis and various biological activities of newly synthesized furan derivatives of Co (III) polypyridyl complexes (**1-3**). Interactions of these compounds with CT-DNA were investigated by UV, visible spectroscopy, fluorescence spectroscopy and viscosity measurement.

MATERIALS AND METHODS

Materials

$CoCl_2$. $6H_2O$, 1, 10-Phenanthroline, 2, 2' bipyridine, 4, 4' dimethyl 2, 2' bipyridine and 2-Chloro-8-methylquinoline-3-carbaxaldehydewere purchased from sigma. All the solvents were purified before use, as per standard procedures[21]. CT (Calf Thymus) DNA was purchased from Aldrich, its solution gives a ratio of UV absorbance at 260 and 280 nm of 1.8–1.9, indicating that the DNA was sufficiently free of protein[22], Supercoiled pBR 322 plasmid DNA (stored at -20 °C) was obtained from Fermentas life sciences, agarose (Genei) from Sigma. Double distilled water was used for preparing various buffers. Ampicillin for antimicrobial studies was purchased from local pharmaceuticals.

Physical measurements

UV–Visible spectra recorded with an Elico BL 198 spectrophotometer. Fluorescence measurements performed on an Elico SL 174 spectrofluorometer. IR spectra recorded on KBr disks on a Perkin–Elmer FT-IR-1605 spectrometer. ^1H NMR spectra recorded on a Bruker 400 MHz spectrometer with DMSO-d_6 as solvent at RT and tetramethyl silane (TMS) as the internal standard. Microanalysis (C, H, and N) carried out with a Perkin-Elmer 240 elemental analyzers.

Synthesis and characterization

Compounds 1, 10-phenanthroline-5, 6-dione[23], cis-$[Co(phen)_2Cl_2]$. $2H_2O$, cis- $Co(bpy)_2Cl_2]$. $2H_2O$ and cis-$[Co(dmb)_2Cl_2]$.$2H_2O$[24] were synthesized according to methods in the literature. Synthetic scheme of Co(III) complexes shown in Fig. 1.

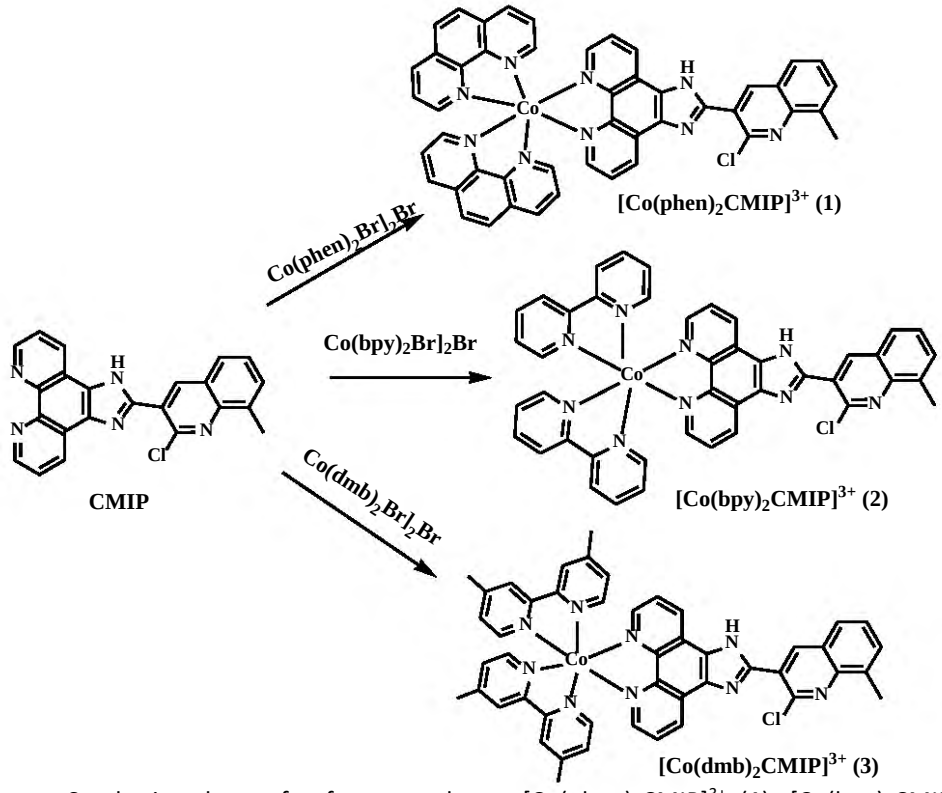

Fig. 1: Scheme; Synthetic scheme for four complexes, $[Co(phen)_2CMIP]^{3+}$ (**1**), $[Co(bpy)_2CMIP]^{3+}$ (**2**) and $[Co(dmb)_2CMIP]^{3+}$ (**3**).

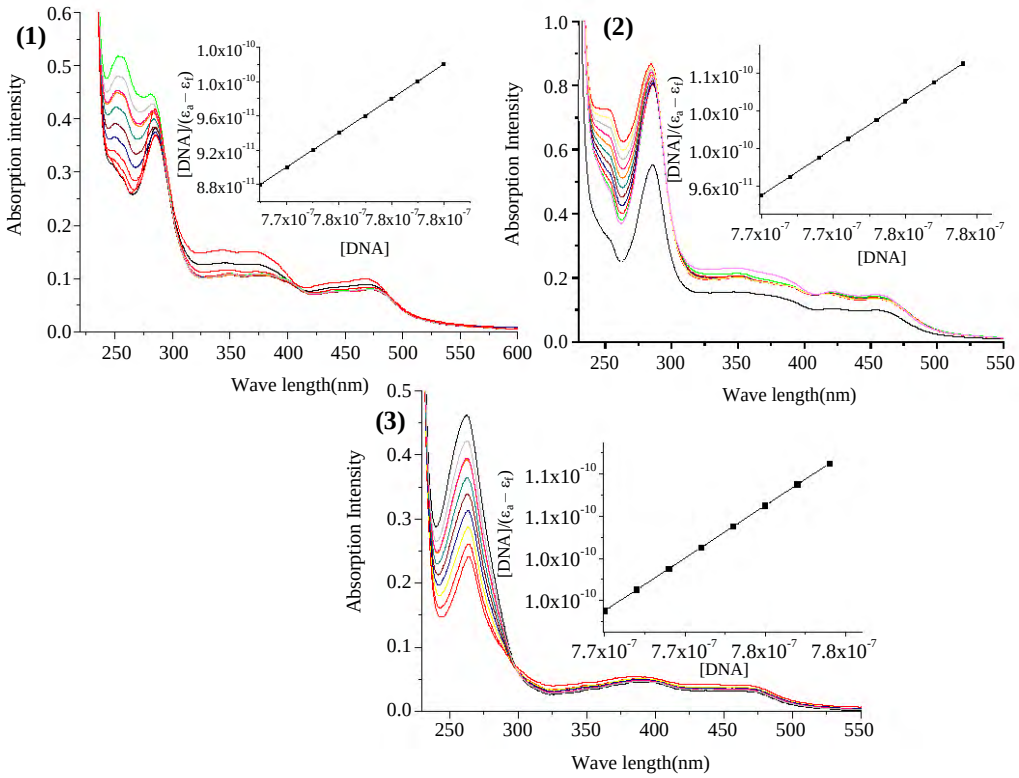

Fig. 2: Absorption spectra of four complexes 1, 2 and 3 in the absence (top red peak in each spectra) and in the presence of increasing concentration of CT-DNA. A plot of [DNA]/ (ε_a - ε_f) vs [DNA] is shown in the inset. [DNA] = 2.5X10^{-4} M, [Complex] = 10^{-3}M.

Preparation of CMIP ligand

CMIP=2-(2-Chloro-8-methylquinolin-3-yl)-1H-Imidazo[4,5-f][1,10]phenanthroline was prepared by the addition of 1, 10-phenanthroline-5, 6-dione (0.53 g, 2.50 mM), 2-Chloro-8-methylquinoline-3-carbaxaldehyde (0.7196 g, 3.5 mM), Ammonium acetate (3.88g, 50 mM) and glacial acetic acid (10 mL) were refluxed together for 4 h as per Steck and Day[25], and then cooled to room temperature and diluted with water. Drop wise addition of ammonia gave a yellow precipitate which was collected, washed with water, dried, and purified by recrystallization from pyridine-H_2O (9:1, v/v);Yield: 0.51 g (73%),Analytical data: Elemental Analysis for $C_{21}H_{12}ClN_5$: Calc. (%): C: 68.20; H: 3.27; N: 18.94; Found: C: 68.18; H: 3.30; N: 18.97; ESI-MS (m/z): Calcd: 369, found: 370 $[M+H]^+$.^{1}H NMR (DMSO-d_6, 400 MHz): δ: 8.9 (H-C=N), 7.2-8.2,m (H-C=C), 2.3 (CH_3), ^{13}C[^{1}H]-NMR (DMSO-d6, 100 MHz): 150 (-C=N), 122 (-C*=C), 148 (-C(Cl)=N), 136(C-C*(C)=C), 153 (N-C=C), 155 (N-C=C), 21 (1^0 C).

Synthesis of [Co(phen)$_2$(CMIP)] (ClO$_4$)$_3$. 2H$_2$O (1)

This complex was prepared by mixing Cis-[Co(phen)$_2$Br$_2$] Br. 2H_2O (0.143 g, 0.25 mM) and CMIP (0.5565, 1.5 mM) in 20.0 mL of ethanol and was refluxed for 6 hrs. After filtration it was then cooled to room temperature and added saturated aq.solution of $NaClO_4$. The obtained light yellowish solid was cooled and washed with small amount of water and then dried under vaccum. Yield: 0.45 g (71%). Elemental Analysis for $C_{45}H_{32}Cl_4N_9O_{14}Co$, Calc. C: 48.11; H: 2.87; N: 11.22, Found: C: 48.13; H: 2.89; N: 11.25 %). ESI-MS (m/z): Calcd: 263, found: 264 for {[Co(phen)$_2$(CMIP)]$^{3+}$ - (ClO_4)$_3$. 2H_2O}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ: 9.1 (H-C=N), 6.3-8.2,m (H-C=C), 4.8 (H-C-N), 2.3 (CH_3), ^{13}C[^{1}H]-NMR (DMSO-d$_6$, 100 MHz): 153 (-C=N), 122 (-C*=C), 118 (-C*=C-Cl), 127 (3^0 C=), 123(=C-N), 138 (=C(H)-C=), 135 (=C(Cl)-C=), 21 (1^0 C).

Synthesis of [Co(bpy)$_2$(CMIP)] (ClO$_4$)$_3$. 2H$_2$O (2)

This complex was synthesized with similar procedure of the above complex (1), with cis-[Co(bpy)$_2$Br$_2$] Br.2H_2O (0.578 g, 1 mM) in place of cis-[Co(phen)$_2$Br$_2$] Br. 2H_2O Yield: 0.44 g (72%). Elemental Analysis for $C_{41}H_{32}Cl_4N_9O_{14}Co$, Calc. C: 45.79; H: 3.00; N: 11.72. Found: C: 45.80; H: 3.03; N: 11.74 %.). ESI-MS (m/z): Calcd: 246, found: 248 for {[Co(bpy)$_2$(CMIP)]$^{3+}$-(ClO_4)$_3$. 2H_2O}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ: 9.1 (H-C=N), 6.3-8.5,m (H-C=C), 4.8 (H-C-N), 5.4 (H-C=C-Cl), 2.3 (CH_3), ^{13}C[^{1}H]-NMR (DMSO-d$_6$, 100 MHz): 153 (-C=N), 122 (-C*=C), 118 (-C*=C-Cl), 127 (3^0 C=), 123(=C-N), 138 (=C(H)-C=), 135 (=C(Cl)-C=), 21 (1^0 C).

Synthesis of $[Co(dmb)_2(CMIP)](ClO_4)_3.\ 2H_2O$ (3)

This complex was synthesized with similar procedure of the above complex (1), with cis-$[Co(dmb)_2Br_2]$ Br. $2H_2O$ (0.721 g, 1 mM) in place of cis-$[Co(phen)_2Br_2]$ Br. $2H_2O$. Yield: 0.39 g (69%). Elemental Analysis for $C_{45}H_{40}Cl_4N_9O_{14}Co$, Calc. C: 47.76; H: 3.56; N: 11.14. Found: C: 47.77; H: 3.58; N: 11.17 %.). ESI-MS (m/z): Calcd: 265, found: 266 for $\{[Co(dmb)_2(CMIP)]^{3+}$ - $(ClO_4)_3.\ 2H_2O\}$. ^1H NMR (DMSO-d_6, 400 MHz): δ: 9.1 (H-C=N), 6.3-8.4,m (H-C=C), 4.8 (H-C-N), 5.4 (H-C=C-Cl), 2.3 ($-CH_3$), $^{13}C[^1H]$-NMR (DMSO-d_6, 100 MHz): 153 (-C=N), 122 (-C*=C), 118 (-C*=C-Cl), 127 (3^0 C=), 123(=C-N), 138 (=C(H)-C=), 135 (=C(Cl)-C=), 36 (3^0 C), 21 (1^0 C), 24($-CH_3$).

DNA binding and Photo activated Cleavage studies

The DNA-binding and photo activated cleavage experiments were performed at room temperature. Buffer A [5 mM tris(hydroxymethyl)aminomethane (Tris) hydrochloride, 50 mM NaCl, pH 7.0] was used for absorption titration, luminescence titration and viscosity measurements. Buffer B (50 mM Tris-HCl, 18 mM NaCl, pH 7.2) was used for DNA photocleavage experiments. Solutions of calf thymus DNA (CT DNA) in buffer A gave a ratio of UV-Vis absorbance of 1.8–1.9:1 at 260 and 280 nm, indicating that the DNA was sufficiently free of protein[26]. The concentration of DNA was determined spectrophotometrically (ε_{260} = 6600 M^{-1} cm^{-1}).

The absorption titrations in the buffer were performed using a fixed concentration (20 µM) complex to which increments of the DNA stock solution were added. The intrinsic binding constant K, based on the absorption titration, was measured by monitoring the changes in absorption at the MLCT band with increasing concentration of DNA using the following equation[27].

$$[DNA] / (\varepsilon_a - \varepsilon_f) = [DNA] / (\varepsilon_b - \varepsilon_f) + 1 / [K_b (\varepsilon_b - \varepsilon_f)]$$

where [DNA] is the concentration of DNA in base pairs, ε_a, ε_b and ε_f correspond to the apparent absorption coefficient A_{obsd} /[Co], the extinction coefficient for the free Cobalt complex and the extinction coefficient for the ruthenium complex in the fully bound form, respectively. In plots of [DNA] / ($\varepsilon_a - \varepsilon_f$) versus [DNA], K_b is given by the ratio of slope to the intercept.

In the emission studies fixed metal complex concentration (20 µM) was taken and to this DNA with varying concentrations was added. The excitation wavelength was fixed, and the emission range was adjusted before measurements. The fraction of the ligand bound was calculated from the relation $C_b = C_t$ [(F - F_0) / F_{max} - F_0)], where C_t is the total complex concentration, F is the observed fluorescence emission intensity at a given DNA concentration, F_0 is the intensity in the absence of DNA and F_{max} is when the complex is fully bound to DNA. Binding constant (K_b) was obtained from a modified Scatchard equation[28]. From a Scatchard plot of r/C_f vs r, where r is the C_b / [DNA] and C_f is the concentration of free complex.

Viscosity measurements were carried out on Ostwald Viscometer maintained at a constant temperature at 25.0 (± 0.1) °C in a thermostatic bath. DNA samples approximately 200 base pairs in average length were prepared by sonication to minimize the complexities arising from DNA flexibility[29]. Flow time was measured with a digital stopwatch, and each sample was measured three times, and an average flow time was calculated. Relative viscosities for DNA in the presence and absence of complex were calculated from the relation $\eta = (t - t_0)/t_0$, where t is the observed flow time of the DNA-containing solution and t_0 is the flow time of buffer alone[30, 31]. Data were presented as $(\eta/\eta_0)^{1/3}$ versus binding ratio[32] where ηis the viscosity of DNA in the presence of complexes and η_0 is the viscosity of DNA alone.

For the gel electrophoresis experiment, supercoiled pBR 322DNA (0.1 µg) was treated with the Co (III) complex in buffer B, and the solution was then irradiated at room temperature with a UV lamp (365 nm, 10 W). The samples were analyzed by electrophoresis for 1.5 h at 80 V on a 0.8% agarose gel in TBE (89 mM Tris-borate acid, 2 mM EDTA, pH = 8.3). The gel was stained with 1 µg/ml ethidium bromide and photographed on the Gel documentation system, UVDI - 312.

Antimicrobial Studies

The antibacterial activity of the complexes was studied against Escherichia coli and Staphylococcus aureus. Each of the Cobalt (III) complex was dissolved in DMSO at different concentrations of 500 µM and 1000 µM. Paper disks of Whatman filter paper no. 1 were sterilized in an autoclave. The paper disks saturated with 10 µL of the Cobalt (III) complex were placed aseptically in Petri dishes containing agar medium inoculated separately with E. coli and S. aureus. The Petri dishes were incubated at 37 °C and the inhibition zones were recorded after 24 h of incubation. The results were also compared with the results for the standard antibacterial drug ampicillin as a positive reference and DMSO as a negative reference at the same concentrations.

Cell viability studies by MTT assay

The cell viability was evaluated by MTT assayand performed as per standard protocol. *HeLa* cells, (human cervical carcinoma cell line) were seeded 5,000/well in 96 well plates and after overnight incubation; cells were treated with complexes 1, 2

and 3 in varying concentrations for 48h. After incubation, MTT reagent was added (5 mg/ml) and incubated further for 4h at 37°C in dark. After then, media was aspirated and to dissolve the crystals DMSO was added to each well. The optical density was measured at 570 nm. Untreated cells were taken as controls. Experiment was repeated with three independent times, each time with triplicates. Data represented here as mean± SEM.

RESULTS AND DISCUSSION

DNA Binding studies

It has been reported that DNA damaging agents can activate the intrinsic pathway of apoptosis involving the release of cytochrome c and other mitochondrial apoptogenic factors[33] and trigger autophagy simultaneously as a self-defence mechanism[34,35]. DNA binding studies have been performed to determine whether Co(III)-induced apoptosis and autophagy are correlated with their abilities to cause DNA damage.

Absorption spectroscopic studies

The MLCT bands (≈ 450 nm) changes were monitored in the presence of increasing concentration of CT-DNA. The subsequent increase in the concentration of the DNA led to a hypochromic shift in the intensity of the MLCT peak and it reached a saturation point for all three complexes as shown in the fig. 2. This decrease in intensity of the CT band was accompanied by considerable red shift in the spectral band. These observations clearly show that three complexes showed dual mode of DNA binding. It is possible that initially because of the π – π stacking within the metal complexes, bind DNA electrostatically and at higher concentration of DNA the complexes get destacked and get intercalated between DNA bases. Such dual mode of DNA binding by a Co (III) complex has previously been reported[36]. The DNA binding constant (K_b) values of 1, 2 and 3 complexes were in the order of 10^5 as shown in the table 1. The difference in K_b values was due to their different ancillary ligands. Complex 3 shows the less binding strength to double-helical DNA. Due to the presence of methyl groups on the 4 and 4′ positions of the ancillary ligand, dmb causes steric hindrance when the complex intercalates into the DNA base pairs. Electron deficient rings interact more strongly with polyanion (DNA) than electron rich rings, so methyl group present on dmb ring may enhance the electron density on complex moiety and make electron rich, hence the binding constant for complex 3 is less than other two complexes.

Table 1: K_b values of three complexes

Complex	K_b for absorption studies (M^{-1})	K_b for Emission studies (M^{-1})
$[Co(phen)_2CMIP]^{3+}$(1)	3.15 (± 0.01) $X10^5$	3.11 (± 0.02) $X\ 10^5$
$[Co(bpy)_2CMIP]^{3+}$ (2)	2.73 (± 0.01) $X10^5$	2.75 (± 0.01) $X\ 10^5$
$[Co(dmb)_2CMIP]^{3+}$(3)	2.50 (±0.02) $X10^5$	2.32 (± 0.01) $X\ 10^5$

Emission spectroscopic studies

Emission intensity (≈ 600 nm) of complexes from the MLCT excited states upon excitation at 460 nm is found to depend on DNA concentration. As shown in Fig. 3, upon the addition of DNA, the emission intensities increased from initial. The enhancement of emission intensity is indicative of binding of the complex to the hydrophobic pocket of DNA and is protected by DNA efficiently and the complexes mobility is restricted at the binding site, which leads to decrease in the vibrational modes of relaxation. The intrinsic binding constant from fluorescence data was obtained from a modified Scatchard equation[37] for all the complexes, and binding constants (K_b) were in the order of 10^5 as shown in table 1. K_b values for both absorption and luminescence studies are almost comparable with small differences in numerical[38].

Viscosity experiment

Viscosity experiments are sensitive to length changes to DNA and least ambiguous for binding mode in solution in the absence of crystallographic structural data[39]. The effects of the complex and ethidium bromide (EB) on the viscosities of CT-DNA are shown in Fig. 4. EB, being as a classical DNA intercalator, can strongly raise the relative viscosity by lengthening the DNA double helix through intercalation. As revealed in Fig. 4, upon increasing the amounts of the three complexes, the relative viscosity of DNA increases similar to the behaviour of EB. This observation suggests that the principal mode of DNA binding by the complex involves base-pair intercalation, in which, relative increased of viscosity is in agreement order with the results obtained by electronic absorption, fluorescence spectroscopy.

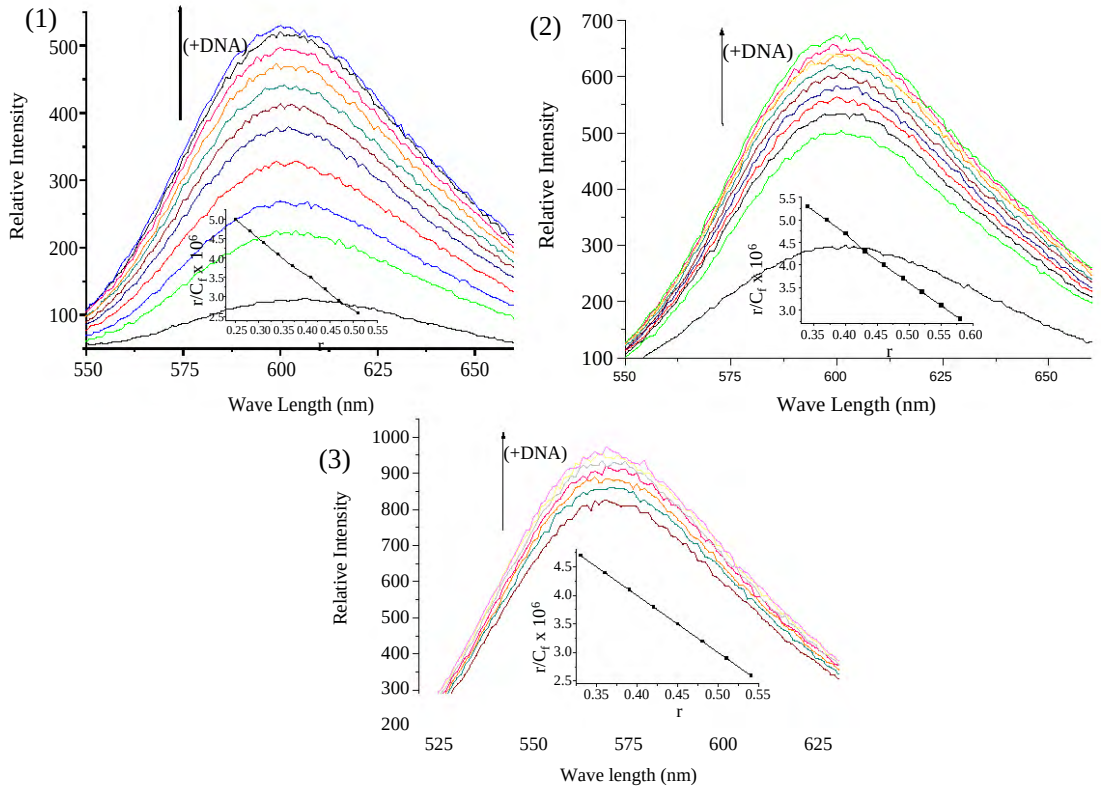

Fig. 3: Emission spectra of four complexes 1, 2 and 3 in the absence and in the presence of increasing concentration of CT-DNA. Inset: Scatchard plot of r/C_f above complexes, which gives binding constant (K_b). [DNA] = 2.5X10^{-4} M, [Complex] = 10^{-3}M.

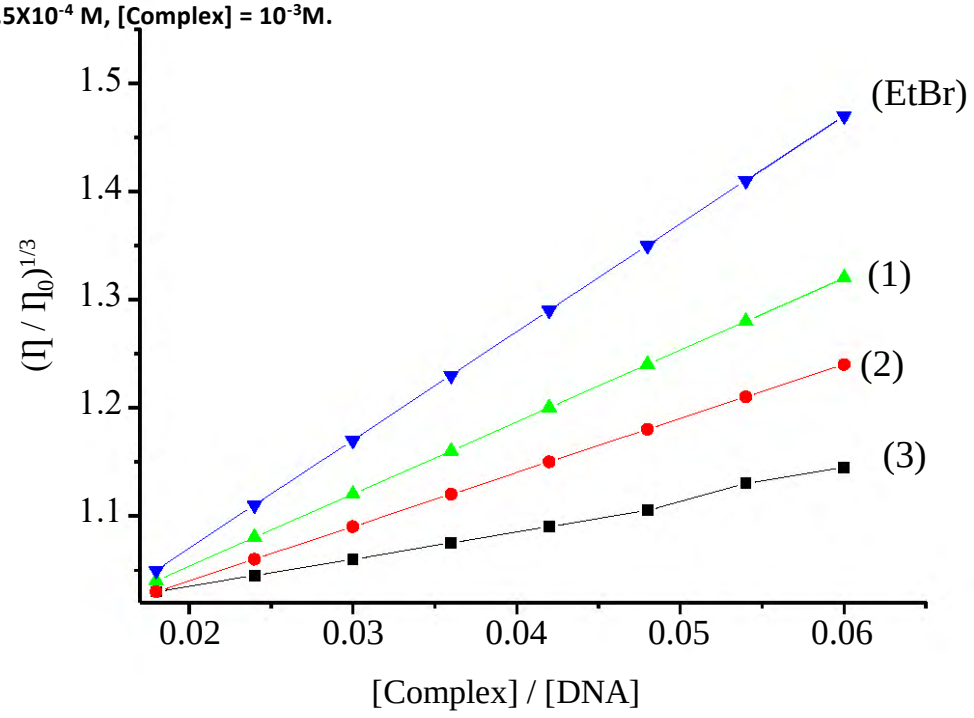

Fig. 4: Effect of increasing amounts of EtBr, complexes [Co(phen)$_2$CMIP]$^{3+}$ (1), [Co(bpy)$_2$CMIP]$^{3+}$ (2) and [Co(dmb)$_2$CMIP]$^{3+}$ (3) on the relative viscosity of CT-DNA at 25 (±0.1)^0 C. [DNA] = 2.5X10^{-4} M.

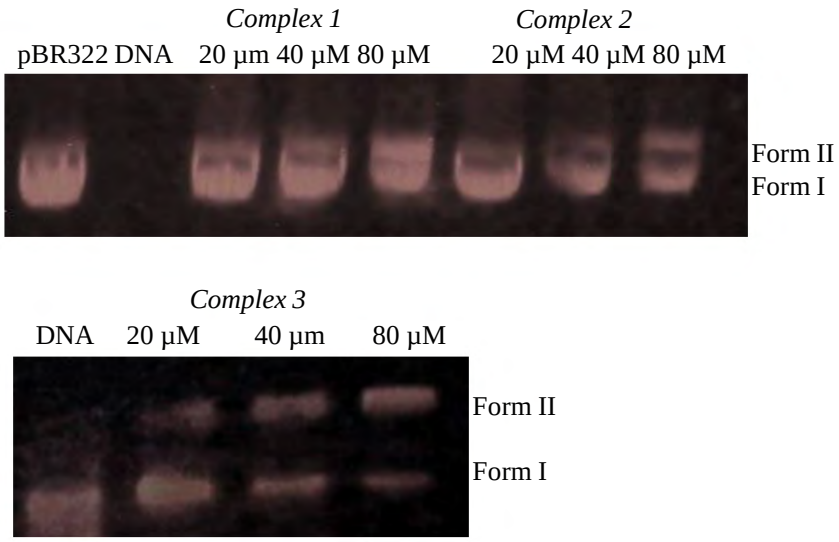

Fig. 5. Photo activated cleavage studies of $[Co(phen)_2CMIP]^{3+}$ (1), $[Co(bpy)_2CMIP]^{3+}$ (2) and $[Co(dmb)_2CMIP]^{3+}$ (3) with the concentration range of 20 to 80 µM.

Photo activated cleavage of pBR 322DNA

Nuclear activity of 1-3 Cobalt (III) complexes were performed on pBR322 DNA and monitored by agarose gel electrophoresis. When plasmid DNA is subjected to electrophoresis, relatively fast migration is observed in the intact supercoiled form (form I). If scission occurs on one strand (nicking), the supercoiled form will relax to generate a slower-moving open circular form (form II). If both strands are cleaved, a linear form (form III) that migrates between form I and form II will be generated[40]. Plasmid DNA incubated with four complexes with different concentrations (20 µM, 40 µM and 80 µM) pBR322DNA and irradiated at 365 nm for 60 min. We observed no DNA cleavage was in the control, in which the metal complex was absent (lane 1). When the concentration of 1-3 Cobalt (III) complexes was increased from 20 µM to 80 µM, the amount of form I gradually decreased, whereas the amount of form II increased as shown in fig. 5.

Antimicrobial activity

Three Cobalt (III) complexes were screened invitro for their antimicrobial activity against E. coli and S. Aureus with Ampicillin as positive control and DMSO as negative control. We observed variation in the inhibition zone (radius in mm) with two different concentrations (0.5 mg/ml and 1 mg/ml) 1-3 complexes. The antimicrobial activity increased as the concentration of the compounds increased. The antibacterial activity data for the complexes at various concentrations (Table 2) indicate that the complexes exhibited appreciable activity against E. coli and S. aureus. The complexes were more effective against S. aureus than against E. Coli but were less effective than the standard drug ampicillin. As an increase in the lipophilic character of the complex favours its permeation through the lipid layer of the bacterial membrane, it shows more activity [41].

Table 2: Antimicrobial studies of Complexes 1-3

Complex	Bactirial Inhibition zone (mm)			
	Conc. (1000 µM)		Conc. (500 µM)	
	B.S	E.Coli	B.S	E.Coli
DMSO	--	--	--	--
$[Co(phen)_2CMIP]^{3+}$(1)	12.0	10.2	6.9	6.6
$[Co(bpy)_2CMIP]^{3+}$ (2)	10.1	9.7	6.0	5.5
$[Co(dmb)_2CMIP]^{3+}$(3)	9.5	9.5	5.7	4.9
Ampicilin	16.2	14.3	10.0	9.9

Cell viability studies by MTT assay

All three complexes were tested against HeLa cells to assess the viability by using MTT assay. These three compounds show significant cell death in dose dependent manner. Viability of the cells decreased upon increasing the concentration of the compound as shown in fig. 6. The IC50 for complex **1** is 14.1μM for 48h whereas for complex **2** ansd complex **3** were 36.2 μM and 52μM.

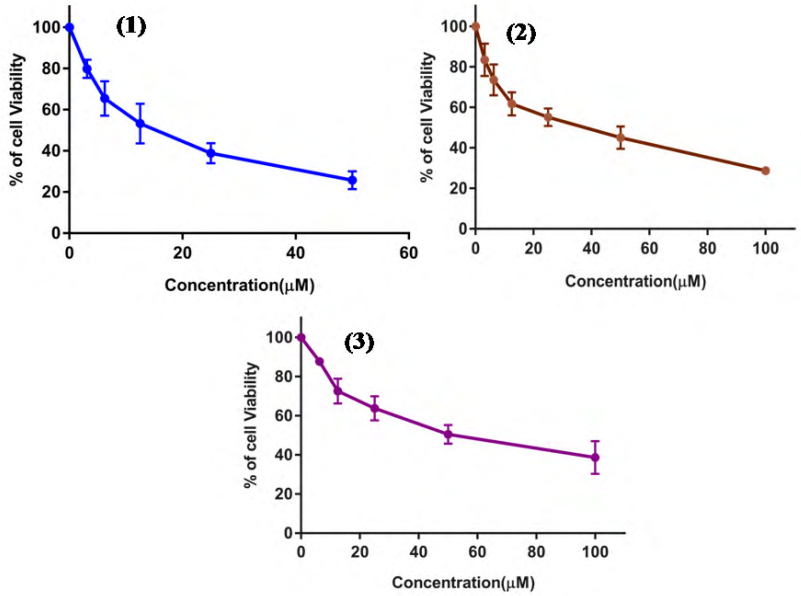

Fig. 6. HeLa cells were treated with complexes 1, 2 and 3 with different concentrations for 48h and the untreated cells were used as a control and then cell viability was evaluated by the MTT assay.

CONCLUSION

Three new Cobalt (III) polypyridyl complexes $[Co(phen)_2CMIP]^{3+}$ (**1**), $[Co(bpy)_2CMIP]^{3+}$ (**2**) and $[Co(dmb)_2CMIP]^{3+}$ (**3**) were synthesized and characterized. The DNA-binding behavior shows that the three Co (III) complexes were interacting with CT DNA through intercalative mode. Upon irradiation, these complexes can effectively cleave pBR322 DNA into three separate forms. The cytotoxicity assay indicates that complexes **1, 2** and **3** can suppress the tumor cell proliferation in dose dependent manner. In DNA binding studies, complex**1** showed the greatest intrinsic binding constant due to π-π stacking with DNA base pairs may exert some additional interactions such as hydrogen bonding with functional groups present on the edge of the DNA.

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We are grateful to CFRD Osmania University for recording NMR and also grateful to Dr. Mohan Rao, (CCMB) Hyderabad for invitro studies.

Abbreviations

CT-DNACa:lf thymus DNA
HEPES: [4-(2-hydroxyethyl)-1 piperazineethanesulfonic acid]
DMSO: Dimethyl sulfoxide
TMS: Tetramethylsilane
UV-Vis: Ultra Violet – Visible Spectroscopy
NMR: ^{1}H &^{13}C – Nuclear Magnetic Resonance Spectroscopy
IR: Infra-Red Spectroscopy
ESI–MS: Electrospray ionization mass spectrometry
MLCT: Metal-to-ligand charge transfer
MTT:3-(4,5-Dimethylthiazol-2-Yl)-2,5-Diphenyltetrazolium Bromide
Tris: Tris(hydroxymethyl)aminomethane
CMIP:2-(2-Chloro-8-methylquinolin-3-yl) w-1H-Imidazo[4,5-f] [1,10] phenanthroline
Phen: 1, 10- Phenanthroline
Bpy: 2, 2' – bipyridine
Dmb: 4, 4' – Methyl, 2, 2' - bipyridine
Ppt: Precipitation

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A SURVEY ON DEEP LEARNING BASED RECOMMENDER SYSTEM ON APPLICATION DOMAIN CLASSIFICATION

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Abstract: Recommender system is major hardware for setting up an astounding correspondence among buyers and retailers in electronic business. Sensible and stunning correspondence to locate the fit thing is considered to have an epic outcomes to increase of offers accomplishment. Recommender framework set up in within 90s. In light of specific procedure, there are four of recommender structure model to be express system orchestrated separating, Contents Based, Knowledge Based and Demographic disengaging. Supportive separating is viewed as more pervasive than another tree frameworks. It offers clearly focal centers like good karma, eccentricity and accuracy. Regardless of the manner in which that it has two or three inclinations in recommendation result, with an extreme goal to improve the deficiency of the recommender structure, many including AI, AI with shallow layers was dominating in the 90's for example neural system, SVM. This paper gives a review of suggestion structures, which spotlights on critical learning approaches and the arrangement of occupations. The point by point portrayal of each suggestion framework is clarified, and the related datasets are promptly presented.

Keywords: *Recommender system, deep learning, neural network, Ecommerce.*

I. INTRODUCTION

The rule electronic business recommender structure was make and present in within 90s, The target foundation is the route by which web business clients could finding the reasonable thing suitably [1]. We can envision, the progression of Internet clients has broadened by and large. These parts were impact number of clients and number of things correspondingly developing essentially. By then online business affiliation must give a significant number of things to a monstrous number of clients at whatever point and any spots. Picking among a ton of thing is hard to be finished by clients. For instance, what thing needs to purchase, what news ought to be investigated, what film ought to be watched, what music to tune in, what hoisting ought to be looked, and so forth. Recommender structure is in like way especially steady for online business affiliation is to collect the measure of offers. In online business, there is enormous instrument how to give better data among buyer and maker that explicitly recommender structure. This instrument intends to make earth shattering correspondence for both. A wide degree of relationship, for example, Amazon.com, Netflix.com, eBay.com, Half.com, CDNOW, J.C. Penney, and Procter and Gamble have suitably passed on suggestion advancements to develop web and stock game plans and improve client responsibility [2]. Web business has changed the course in different affiliations coordinate. To them, online business is never again a decision at any rate a target. Different affiliations are battling with the most basic issue: what is the best framework for structure up and coordinating in the automated economy? A few affiliations are moving their affiliations absolutely to the Web (e.g.egghead.com). Some are stirring up fortifications, by then turning them off as independent online business substances (for example barnesandnoble.com) [3]. The Internet has basically influenced the direct of business. Markets, adventures, and affiliations are being changed. The new economy requests the abuse of new models and rules. Data advancement (IT) straightforwardly drives affiliations and markets.

A recommender structure can envision whether an individual would buy a thing or not built up on the patient's inclinations. This structure can be executed dependent on a patient's profile or a thing's profile. This paper clarifies the thing based total separating based flourishing recommender

structure which gives beneficial data to patients subject to the thing's profile. These days there are different web journals and social discoursed open on the web where individuals can give assessments, surveys, online journals and trade points of view concerning things. Resulting to social event examinations for anything by patients, the recommender framework picks choices about patients who don't give any evaluations. Diverse e-business goals are working with the help of a recommender structure to broaden their compensation in the intense market [6]. Endless patients purchase their things through online electronic business goals. In the wake of purchasing things, they give their suppositions or any remarks about that thing in an individual web gathering. Thusly, making pay is the basic target everything being identical. Utilizing this recommender structure process, we can expand our business advantage in the market. While the propensities made by clients can be delineated as being generally shielded, decisions made in different segments may have progressively remarkable repercussions for the end quiet. Specifically, in the bit of human organizations, decisions can be hazardous as they are worried over the life and thriving of patients. The recommender framework ought not just help key specialist and divert threats or thwarted expectations, yet it ought to comparably screen patients and regulate treatment as huge, screen indispensable signs and present constantly by techniques for a concentrated server as for human organizations. These cutoff points address the reasonableness of Record structure.

II. RELATED WORK

In recommender systems, two fundamental segments anticipate squeezing businesses, to be unequivocal patients and things. Patients give their propensities about express things and these inclinations must be found of the collected information. The gathered information are tended to as an utility framework which gives the estimation of every patient-thing pair that tends to the level of inclinations of that patient for unequivocal things. Accordingly, the recommender motors are depicted into patient-based and thing based recommender motors. In a patient-based recommender structure, patients give their decisions and evaluations of things [11]. We can support that thing to the patient, which isn't surveyed by that patient with the assistance of a patient-based recommender motor, considering the likeness among the patients. In a thing based recommender structure, we utilize the similitude between things (not patients) to make wants from patients. Information gathering for recommender structures is the rule work for want [12].

2.1. Times of Recommender System

(1) Information Collection Phase: This stage aggregates basic data about patients and readies a patient profile subject to the patient's attributes, practices or assets gotten to by the patient. Without structure up a well-depicted patient profile, a recommender motor can't work reasonably. A recommender framework heaps of information which are amassed in various ways, for example, unequivocal examination, certain data and mixture data. Express investigation takes data given by patients as exhibited by their vitality on a thing while grasped data takes tolerant inclinations in an aberrant way through watching decided lead [1].

(2) Learning Phase: This stage considers an assessment accumulated in the past stage as data and approach this investigation by utilizing a getting the hang of figuring to manhandle the patient's highlights as yield [1,2,13].

(3) Prediction/Recommender Phase: Preferable things are embraced for patients in this stage. By isolating examination gathered in data accumulation arrange, a craving can be made through the model, memory-based or watched exercises of patients by the structure [1,2].

The seasons of recommender structure are tended to in Figure 1.

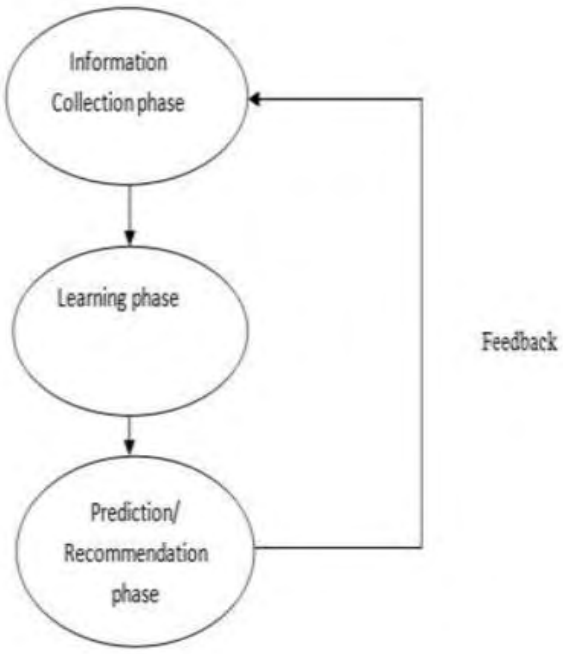

Figure 1. Phases of the recommender system.

2.2. Different Types of Filtering Based Recommender System

There are three types of filtering based recommender system available, which is shown in Figure 2.

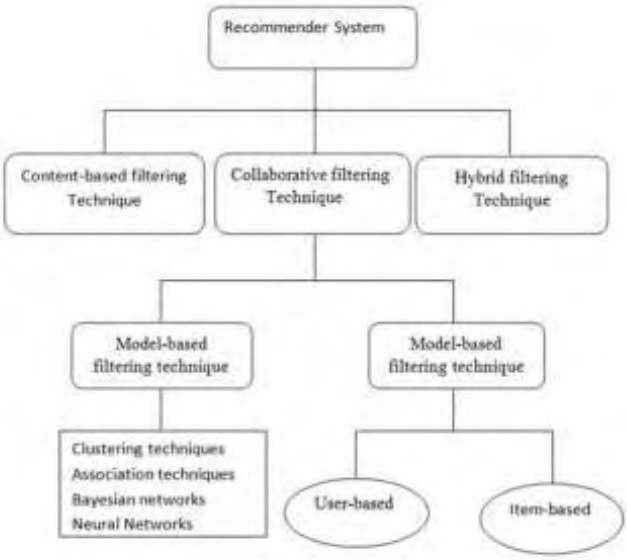

Figure 2. Hierarchy of Recommender System based on filtering.

(1) Content based Filtering Recommender System: The content-based filtering technique focuses as for the appraisal of features and attributes of things to make conjectures. Content-based filtering is conventionally used in case of chronicle recommenders. In this system, a recommendation is made reliant on patient profiles, which deal with the different attributes of things close by patient's past acquiring history. Patients give their tendencies as evaluations which are sure, negative or objective in nature. In this framework, positive assessed things are endorsed to the patient.

(2) Collaborative based Filtering Recommender System: Collaborative filtering predicts obscure outcomes by making a patient-thing arrangement of decisions or inclinations for things by patients. Equivalent characteristics between patients' profiles are assessed by sorting out the patient-thing framework with patients' inclinations and interests. The region is made among social events of patients. The patient who has not evaluated to unequivocal things heretofore, that patient gets recommenders to those things by considering positive examinations given by patients in his neighborhood. The CF in the recommender structure can be utilized either for the gauge or recommender. Gauge is a rating respect Ri,j of thing j for patient I. This communitarian sifting framework is commonly masterminded in two unique ways: memory based and model based synergistic disengaging. Figure 3 clarifies the entire procedure of the system sifting methodology.

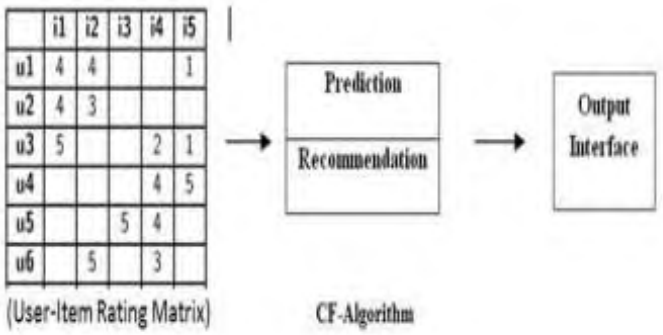

Figure 3. Collaborative Filtering Technique.

(3) Hybrid Filtering Recommender System: This methodology includes the more than two methodologies in order to fabricate the precision and execution of a recommender system. The cross breed filtering technique is performed by any of the going with ways: amassing a united recommender structure that combines both of the more than two procedures; applying some helpful isolating in a substance based philosophy, and utilizing some substance based isolating in the synergistic system. This strategy uses particular creamer methodologies, for instance, the course cross breed, weighted blend, mixed hybrid and changing cream as demonstrated by their exercises.

III. DEEP LEARNING FOR RECOMMENDER SYSTEM

Given the phenomenal achievement of the significant learning seemed various applications fields, it has starting late been proposed for updating the recommender structures quality. In this portion, we explore the particular significant learning structures used in the field of recommender system where we see that the coordination of significant learning is performed with the synergistic filtering model similarly as the substance based model where different plans can be taken an interest in a comparative structure.

The significant learning is a class of AI estimations. It relies upon the advances of the neural frameworks which are rebranded in the continuous years as significant learning. The significant learning shows his display in treating various application fields like talk affirmation, object area and trademark language taking care of exhibited by the trust offered by the most requesting undertaking on earth, for instance, Google, Facebook and Microsoft. The model of significant learning is addressed as a course of nonlinear layers

which structure a consultation of data. The significant learning is used for coordinated and unsupervised learning endeavors. In the composition, the nearness of significant learning is related to PC vision region including article and talk affirmation. The building of a neural framework is on a very basic level made from three layers: input layer, covered layer and yield layer. The refinement between the different sorts of frameworks is related to the kind of covered layer and the amount of covered layers choose the significance of the neural framework. The least troublesome phony neural framework is feedforward neural framework where the information moves from the data center points forward yield center points through the disguised center points a comparable path and without making circles or cycles in the framework. The advancement between layer is controlled with an activation work which can be immediate or nonlinear, for instance, tanh, sigmoid and Rectified Linear Unit (ReLU). The activation limits manage the looking at information sources loads wij. The designing of neural framework is depicted in Fig. 1. The red concealing presents the exercises associated on the clear feedforward neural framework to make an irregular neural framework where neurons in the covered layer are related drearily to neurons in the data layer.

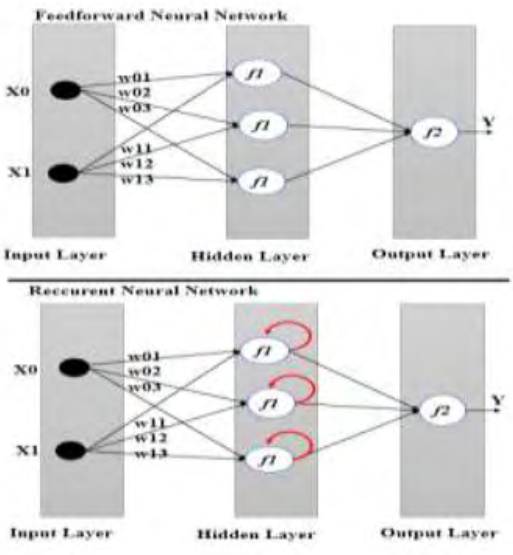

Fig. 1. Feed forward vs. recurrent neural network architecture

There are several categories of deep learning models. Among these models we cite the following which differ in term of complexity and application fields [21]-[24]:

• Multilayer Perceptron it is a variety of Feedforward Neural Network which is the most clear significant learning approach. MLP have diverse disguised layers which are interconnected in a feed-forward way. The mapping between the data and the yield layers is driven by an abstract activation work.

• Unsupervised Learning Networks: This social affair covers three express structures which are Autoencoders, Deep Belief Networks (DBNs) and Generative Adversarial Networks (GANs).

The Autoencoder resembles MLP building with the unequivocality that the yield layer has undefined number of center points from the data layer to repeat the wellsprings of information yet in which the standard of dimensionality reduction is associated. The Deep Belief Network (DBNs) is produced using two deals with of layers Restricted Boltzmann Machines (RBMs) used for pre-planning stage and feed-forward framework used for finetuning stage.

The particularity of the Restricted Boltzmann Machines layer is the reliance between the two utilized layers where no intra-correspondence between them is permitted thus the assignment limited. The Generative Adversarial Network is made out of two neural systems. The principal system is utilized for applicants' age named as generator and the second for the competitors' assessment named as discriminator.

Convolutional Neural Network: It is a subclass of feedforward neural framework with the expressness of pooling errands and convolution layers. The convolution is a powerful thought that associates in structure continuously vivacious part space reliant on a sign. It is successfully associated in the PC vision and picture getting ready regions especially object affirmation and picture gathering.

• Recurrent Neural Network: It is a variety of feedforward neural frameworks. It is depicted by its ability to send information after some time steps. using of the inside memory of the framework and the circles errands which structure the genuine diverge from other feedforward neural framework It is comprehensively used in normal language getting ready, talk affirmation and computerized control applications. LSTM (Long Short-Term Memory) is a variety of Recurrent Neural Network model.

• Recursive Neural Network: Its plan empowers the recursive framework to get the hang of fluctuating progressions of parts of an image or words using a typical weight cross section and a matched tree structure. The complexity between a Recursive Neural Network and Recurrent Neural Network is

that the recursive one can be considered as a dynamic framework where there is no time factor to the information course of action and information sources are arranged continuously as shown by a tree structure. This structure is fit not solely to recognize challenges in an image, yet notwithstanding degage the association between all things in a scene. It is profitable as a scene or sentence parser.

IV. POSSIBLE RESEARCH DIRECTIONS

Deep learning-based recommendation methods can feasibly use multi-source heterogeneous data to moderate the data sparsity and cold start issues. In the past three years, the investigation on significant learning-based recommender systems has pulled in progressively more thought from the academic world and industry. This fragment discusses the possible research course of significant learning-based recommender structure.

A. CROSS-DOMAIN RECOMMENDER SYSTEM BASED ON DEEP LEARNING

A couple of existing works demonstrate the ampleness of significant learning in getting the hypotheses and differentiations transversely over different spaces and making better recommendations on cross-zone stages. At this moment, using significant learning frameworks, various sorts of data as a bound together commitment by introducing depictions, building significant level desire models for proposal by organizing various types of cross-arrange heterogeneous data. Cross zone recommendation can help target space proposition with the data picked up from source zones, gives a charming response for these issues. Single space proposal just spotlights on one zone while ignores the customer interests on various regions, which moreover strengthens data sparsity and cold start issues. Significant learning is fitting to move learning as it learns highlevel thoughts that unwind the assortment of different regions. A champion among the most extensively considered subjects in cross space recommendation is move acknowledging which expects to improve learning assignments in a solitary region by using data moved from various territories. Henceforth, it is a possible research course of significant learning based recommender system.

B. SCALABILITY OF DEEP LEARNING BASED RECOMMENDER SYSTEM

Versatility is fundamental to the handiness of proposal models in genuine systems as extending data volumes in the tremendous data. Significant learning has displayed to be fruitful and promising in enormous data examination. We can change of the model multifaceted nature and flexibility with the exponential advancement of parameters. At present, the size of the framework is beginning to push toward progressively significant anyway less parameters. Another possible research course is high-dimensional data can be pressed to littler embedding to decrease the space and estimation time during model learning. The future research is to pack the overabundance parameters with the objective that the framework may have better exactness anyway have less parameters.

C.EXPLAINABILITY OF DEEP LEARNING BASED RECOMMENDER SYSTEM

Deep learning-based recommender systems use the significant learning model to clearly envision the customer tendencies by using multi-source heterogeneous data [106]. The eventual outcome of the model getting ready is to get the heaps between the neurons of significant neural framework. It is difficult to give a reasonable explanation direct to the recommendation results. Hence, making sensible proposals give off an impression of being unfathomable. One way is to make legitimate desires to customers, empowering them to understand the parts behind the framework's recommendations, demonstrate an appropriate proposition inspiration to disclose to the customer why the structure considers such a proposition to be reasonable. The other course is to focus on unveil ability to the master, testing burdens and establishments to see continuously about the model. Thusly, it can't avoid being it is moreover another possible research heading of significant learning-based recommender system, and consequent stage would to be to design better significant learningbased recommender models to give conversational or generative explanations.

D. ATTENTION MECHANISM BASED RECOMMENDER SYSTEM

Attentional framework has practically encouraged the non-interpretable stresses of significant learning models. Thought framework has provoked progressively unmistakable degrees of interpretability since the thought burdens not simply give encounters about the internal activities of the model and yet can give sensible results to customers. Attentional framework isn't only prepared for updating execution yet acknowledges increasingly critical explain limit. Applying the thought segment to recommender systems can help recommender structures to understand the most educational features of the thing, endorse the most operator thing, and

improve the interpretability of the model [107-113]. At the present time, thought part has been associated with significant learning models. For example, Attention part gives a better course of action and causes RNN than all the more promptly recall inputs. Thought based CNNs can perceive the most instructive bit of the issue from the information. Given that models are starting at now fit for finding the most illuminating parts of the wellsprings of information, we acknowledge that is another possible research heading.

E. DEEP COMPOSITE MODELS BASED RECOMMENDER SYSTEM

In current recommender systems, different portions should be outlined, including the effect of mixed affiliations, client thing correspondences, the dynamic progress of client inclinations, and so on. More fragments be shown can improve the presentation of recommender structures. Huge composite model joining assorted huge neural structures connects with a much increasingly essential asset for showing the heterogeneous qualities of the picking segments in recommender framework. There beginning at now have been a couple of examinations which organize grouped critical learning techniques together for improving shows. In any case, the endeavors are obliged veered from the potential developments, in light of the way that the model ought to be sorted out in a reasonable manner rather than discretionarily and uniquely fitted for accommodating necessities. Along these lines, the examination of huge composite models-based recommender structure is also one of things to come headings. Essentially, critical learning has wound up being prominent in recommender structures sort out both in the scholarly system and industry. By then, this zone of research is vivacious, there is much opportunity to improve in the as of late referenced research direction, in any case we in like way recognize that noteworthy learning will adjust recommender structures on a very basic level and get progressively open doors rethinking the client encounters for best customer devotion sooner rather over later.

V. CONCLUSION

The thrilling augmentation in the proportion of data being made by electronic and motorized devices requires the prerequisite for adroit techniques and applications that can properly and astutely store, method, get to and research information for most outrageous points of interest to customers. Significant learning-based recommender systems(DLRS) are of such driving responses for these challenges, which are legitimate instruments to quickly help the strategy of information pursuing. Significant learning-based recommender structures can pick up capability with the lethargic depictions of customers and things from immense data, and a while later build up a recommendation model, finally make an amazing proposition list for the customer. The essential endeavors of the significant learning-based recommender systems are the best approach to deal with the immense multi-source heterogeneous data, manufacture progressively proper customer models according to customer tendencies necessities, and improve the introduction and customer satisfaction. Differentiated and customary recommender structures, significant learning-based recommender systems can use significant learning technique to normally get acquainted with the inert features of customer and thing by joining various sorts of multi-source heterogeneous data, model the gathering instances of customer lead, even more reasonably reflect the customer's different tendencies and improve the precision of proposition. It is believed that this overview will support tenderfoot and new experts to understand the improvement of DLRS. Moreover, ace examiners can use this overview as a benchmark to make DLRS and as a sort of point of view to the requirements of DLRS.

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Applications of Artificial Intelligence in Machine Learning: Review and Prospect

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ABSTRACT

Artificial intelligence(AI) is a combination of computer science, physiology, philosophy with mathematics and several other disciplines. AI and its applications is a very important aspect of computer and science revolution. As the world is fast globalizing, the hope for AI machines to take up human mental and physical capacity is rising, as it is believed will relieve menial works and duties that pose risk to life. In this paper, a brief review and future prospect of the vast applications of artificial intelligence in machine learning has been made.

KEYWORDS

Artificial Intelligence, Machine Learning, Supervised Learning, Unsupervised Learning, Reinforcement learning algorithms.

1. INTRODUCTION

The ultimate goal of AI is to develop human like intelligence in machines. However, such a dream can be accomplished through learning algorithms which try to mimic how the human brain learns. Machine learning, which is a field that has grown out of the field of Artificial Intelligence, is of utmost importance as it enables the machines to gain human like intelligence without explicit programming. However, AI programs do the more interesting things such as web search or photo tagging or email anti-spam.

So, machine learning was developed as a new capability for computers and today it touches many segments of industry and basic science.

In the area of machine learning research, more emphasis is given to choosing or developing an algorithm and conducting experiments on the basis of algorithms. Such highly biased view reduces the impact on real world applications.

In this paper the various applications under the appropriate category of machine learning has been highlighted. This paper makes an effort to bring all the major areas of applications under one umbrella and present a more general and realistic view of the real world applications.

Apart from this, two application suggestions have been presented forward. The field of machine learning is so vast and ever growing that it provides to be useful in automating every facet of life.

2. MACHINE LEARNING

Machine learning is an application of artificial intelligence that provides systems the ability to automatically learn and improve from experience without being explicitly programmed. Machine learning focuses on the development of computer programs that can access data and use it to learn for themselves.

According to Arthur Samuel, machine learning is defined as the field of study that gives computers the ability to learn without being explicitly programmed. Arthur Samuel was famous for his checkers playing program. Initially when he developed the checkers playing program, Arthur was better than the program. But over time, the checkers playing program learnt what the good and bad board positions were, by playing many games against itself.

A more formal definition was given by Tom Mitchell as, “A computer program is said to learn from Experience(E) with respect to some Task(T) and some performance measure(P), if it’s performance on Tas measured by P improves with experience (E), then the program is called a machine learning program.”

In the checkers playing example, the experience E, was the experience of having the program playing games against itself. The task T was the task of playing checkers and the performance measure P was the probability that it won the next game of checkers against some new opponent. In all fields of engineering, there are larger and larger datasets that are being understood using learning algorithms.

3. Types of Machine Learning Methods

3.1 Supervised Machine Learning Algorithms

They can apply what has been learnt in the past, to new data using labeled examples to predict future events. Starting from the analysis of a known training data set, the learning algorithm produces an inferred function to make predictions about the output values. The system is able to provide targets for any new input after sufficient training. The learning algorithm can also compare it's output with the correct, intended output and find errors in order to modify the model accordingly.

3.2 Unsupervised Machine Learning Algorithms

They are used when the information used to train is neither classified nor labeled. Unsupervised learning studies how systems can infer a function to describe a hidden structure from unlabelled data. The system doesn't figure out the right output, but it explores the data and can draw inferences from the data sets to describe hidden structure from unlabelled data.

3.3 Semi Supervised Machine Learning Algorithms

They fall somewhere in between supervised and unsupervised learning since they use both labeled and unlabelled data for training – typically a small amount of labeled data and a large amount of unlabelled data. The systems that use this method are able to considerably improve learning accuracy. Usually, semi supervised is chosen when the acquired labeled data requires skilled and relevant resources in order to train it/ learn from it. Otherwise, acquiring unlabelled data generally doesn't require additional resources.

3.4 Reinforcement Machine Learning Algorithms

This is a learning method that interacts with its environment by producing actions and discovers errors or rewards. This method allows machines and software agents to automatically determine the ideal behavior within a specific context in order to maximize its performance. Simple reward feedback is required for the agent to learn which action is best; this is known as the reinforcement signal.

4. INTEGRATION OF ARTIFICIAL INTELLIGENCE AND MACHINE LEARNING

Machine learning enables analysis of massive quantities of data. While it generally delivers faster, more accurate results in order to identify profitable opportunities or dangerous risks, it may also require additional time and resources to train it properly. Combining Machine Learning with Artificial Intelligence and Cognitive Technologies can make it even more efficient in processing large volumes of information.

5. APPLICATIONS

5.1 Unsupervised Learning

In Machine Learning, the problem of unsupervised learning is that of trying to find hidden structure in unlabelled data. Since the examples given to the learner are unlabelled, there is no error or reward signal to evaluate a potential solution.

5.1.1 Analysis of gene expression data: Cancer diagnosis

Cancer can be defined as a class of diseases that is characterized without control of self growth. There are about 900 different types of cancer claiming the lives of innumerable people across the world. Thus, identifying the type of cancer is a crucial step in its treatment. It is done through classification of patient samples.

The classification process and results may be improved by analyzing the gene expression of the patient which may provide additional information to the doctors. The merger of medical science and technology has already led to a lot of life saving break-throughs in the field of medicine[1].

5.1.2 Social Network Analysis

Unsupervised Machine Learning Algorithms can automatically identify the friends within a user circle in Facebook or Google or it can identify the maximum number of mails sent to a particular person and categorize into collective groups. It also identifies which are groups of people that all know each other[7].

5.1.3 Market Segmentation

Many companies have huge databases of customer information. So, unsupervised machine learning algorithms can look at this customer data set and automatically discover market segments and automatically group customers into different market segments so that the company can automatically and more efficiently sell or market the different market segments together. Again, this is unsupervised learning because it is known in advance what the market segments are, or which customer belongs to which segment[7].

5.1.4 Cocktail Party Problems

Consider a cocktail party with two people, where both are talking at the same time. Two microphones are placed in the room at two different distances from the speakers; each microphone records a different combination of these two speaker voices. These two microphone recorders are given to an unsupervised learning algorithm called the Cocktail Party Algorithm. The cocktail party Algorithm separates out these two audio sources that were being added or being summed together[9].

5.1.5 Medical Records

With the advent of automation, electronic medical records have become prevalent. So if medical records are turned into medical knowledge, diseases could be understood in a better way.

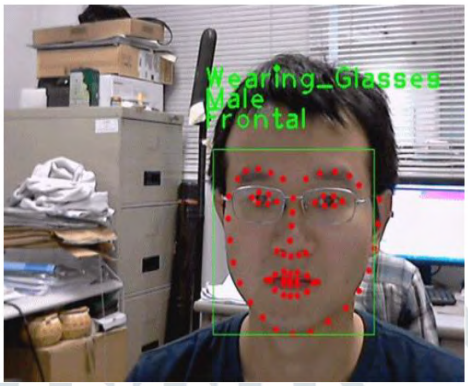
5.2 Supervised Learning

5.2.1 Pattern Recognition

It is the process of recognizing patterns by using machine learning algorithm. Pattern Recognition can be defined as the classification of data based on knowledge already gained or on statistical information extracted from patterns and/or their representation. One of the important aspects of pattern recognition is its application potential. In typical pattern recognition application, the raw data is processed and converted into a form that is amenable for a machine to use. Pattern recognition involves classification and clustering of patterns.

Problem Domain	Application	Input Pattern	Pattern Class
Bioinformatics	Sequence Analysis	DNA/Protein sequence	Known type of genes/patterns
Data mining	Searching for meaningful patterns	Points in multi dimension space	Compact and well separated clusters
Document classification	Internet search	Text document	Semantic categories
Document image analysis	Reading machine for the blind	Document image	Alphanumeric characters / words
Industrial automation	Printed circuit board inspection	Intensity or range image	Defective / non defective nature of product
Multimedia database retrieval	Internet search	Video clip	Video genres e.g. action, dialogue etc
Biometric recognition	Personal identification	Face, iris & finger print	Authorized user for access control
Remote sensing	Forecasting crop yield	Multispectral image	Land use categories, growth pattern of crops
Speech recognition	Telephone directory enquiry with operator	Speech waveform	Spoken words

(a)Pattern Recognition



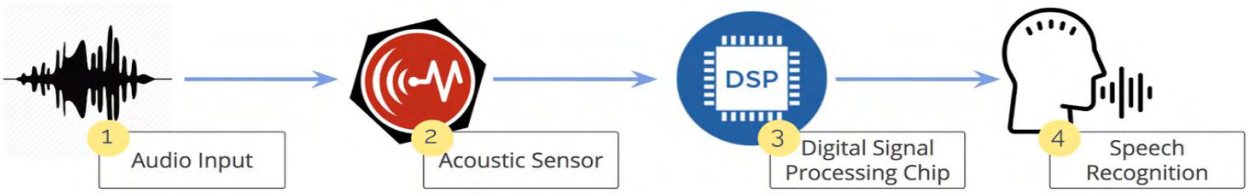
(b) Facial Recognition

5.2.2 Facial Recognition

Facial recognition is one of the common uses of machine learning. There are many situations for using facial recognition. As an example, high quality cameras in mobile devices have made facial recognition a viable option for authentication as well as identification. Apple's iPhone X is one of its examples. Facial recognition application works in the software identifies 80 nodal points on a human face. Nodal points are end points used to measure variables of a person's face, such as the length or width of the nose, the depth of the eye sockets and the shape of cheek bones [5].

5.2.3 Voice Recognition

Voice recognition or Speech recognition converts voice/speech into text. It is also known as Automatic Speech Recognition (ASR). Some examples are Google Assistant, Siri, Cortana and Alexa. Voice Recognition is one of the categories in Deep Learning.



The system analyses the human specific voice and uses it to fine-tune the recognition of that person's speech, resulting in increased accuracy. Simple voice commands convert to decode and may be used to initiate phone calls, select radio stations or play music from a compatible smart phone, mp3 player or music loaded flash drive. Voice recognition software measures the unique biological factors, which form the users voice, from the sounds that a user makes while speaking[4].

5.2.4 Financial Services

Machine learning has a lot of potential in the finance and banking sectors. For example, Taaffeite Capital Management trades in a fully systematic and automated fashion using proprietary machine learning systems. In the finance world, stock trading is one of the most important activities. Stock market prediction is an act of trying to determine the future value of a stock other financial instrument traded on a financial exchange.

A Machine learning approach is trained from the available stocks data and gains intelligence. It then uses the acquired knowledge for an accurate prediction [2][3].

5.2.5 Health Care

The increasingly growing number of applications of machine learning in healthcare allows us to glimpse at a future where data, analysis, and innovation work hand in hand to help countless patients. One of the chief ML applications in healthcare is the identification and diagnosis of diseases and ailments which are otherwise considered hard to diagnose. Machine learning and deep learning are both responsible for the breakthrough technology called Computer Vision. Another sought after application of machine learning in healthcare is in the field of radiology.

5.2.6 Spam Filtering

It is mainly used to filter unsolicited bulk Email (UBE), junk mail, or unsolicited commercial email (UCE) from the emails. The spam filter saves the user from having to wade through tons of spam email, that's also a learning algorithm. The spam filter can also be learned by watching which emails you do or do not flag as spam. So in an email client if spam button is clicked to report some email as spam, but not other emails and based on which emails are marked as spam, the email program learns better how to filter spam email[6].

5.2.7 Information retrieval

Information retrieval(IR)is finding material of an unstructured nature that satisfies an information need from within large collections. The user provides an outline of their requirements- perhaps a list of keywords relating to the topic in question, or even an example document. The system searches the database for documents that are related to the user's query, and presents those that are more relevant. The IR process can be divided into four distinct phases: indexing, querying, comparison and feedback [8].

6. CONCLUSION

Humans have always sought to build a comfortable life, the proof of this lies in the fact that we have always depended on machines to get our work done more easily, in a faster more efficient manner. In the past machines have been used to reduce the manual labour required to the get a job done, but at present, with the advent of machine learning humans seek to build machines which are not only strong but also intelligent and hence machine learning has emerged to become an area of study that is ever in the bloom.

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SENTIMENT ANALYSIS BASED INTELLIGENT PRODUCT RECOMMENDER SYSTEM

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Abstract:- Evaluation appraisal is one of the dreary model examine centers in the field of substance mining. Mining feeling from customary language is a scraping undertaking. Supposition assessment gives tremendous data to basic ace in different spaces. Explicit tendency ID philosophy are open in any case may not render most clear outcomes in all point of view. In this paper, tendency of clients concerning the affiliations given by E-shopping regions is considered. The inclination or appraisal of the individuals is initiated by reviews, assessments and emojis. The things which have positive assessment

from the past clients are proposed for the present clients. For this stochastic learning estimation which investigates various information sources identified with the affiliations is utilized. The end is alloted negative, positive and impartial. Appraisal happens dependent on procedure. The proposed structure will discover counterfeit systems about a thing with the assistance of MAC address near survey posting plans. Client will login to the structure by giving the username and riddle key and will see different things and can give learn about the thing. To discover the survey is a phony or valid, the MAC region of the structure which is astounding is checked by the proposed framework. Thusly phony audits are not seen.

Keywords:-Text Mining, Sentiment Analysis, Ratings, Reviews, Emoticons, Recommend, Fake reviews

I. INTRODUCTION

As we watch out for all grip, it's Associate in Nursing time of information sway, during which we will all in all consistently get tremendous extents of learning. Along these lines, it's in pounding may need of selecting the satisfying and intriguing information rapidly. in order to choose this huge issue, proposition structure ascends at the fundamental minute. Among the present suggestion tallies, the thing based satisfying segregating proposal recipe is that the most in general utilized one. Its standard depends upon the client's evaluation of things. the truth is to watch out the closeness among clients, and supporter things to the objective client regarding the records of the for all intents and purposes indistinguishable clients. In any case, the proportion of customers and thing continues stretching out at a high rate, that will fabricate the cost to sweep out the bearing rundown for each client. The intensity of one typical pc won't fulfill the need and besides the super pc can regard a foolish extent of. in order to choose the issue, we tend to expected to utilize Map slice back way to deal with oversee total the heading structure. In addition, we will by and large pass on the work to some pc packs and additionally the PC record of the present pc bundle just relies on the past one or the beginning data. thusly the pipeline improvement are gotten the chance to help the power more. The assessment demonstrates that the structure will blend the intensity of some standard workstation to strategy tremendous scale data in an extraordinarily short time span [1]. The undertaking survey information acknowledge a basic action inside the suggestion of study masters. during this paper, we will when all is said in done expect to work out survey pro's evaluating by maltreatment the certified rating records furthermore the legitimate choice outcomes on the past comes, and by recommends that of explicit guidelines, we will all in all structure a rating system for comes and pros. For the data exiguity burden of the rating framework and in addition the "cool beginning" downside of most recent talented suggestion, we will when all is said in done recognize that those undertakings/experts with comparative centers have close to segment vectors and propose an audit skilled steady proposition condition fortified subject relationship. Promptly, we will all in all get themes of tasks/specialists kept up idle Dirichlet task (LDA) model, and assembling the subject relationship course of action of activities/stars. By at that point, through the subject relationship between undertakings/specialists, we find a neighbor game-plan that offers the best closeness with objective assignment/ace, and orchestrate the social gathering into the pleasing separating suggestion condition kept up framework goals. At long last, by learning the rating system to begin include vectors of the comes and experts, {we can|we are capable to} envision the assessments that an objective task will offer contender study pros, and in this way make several bucks the audit capable

suggestion. Appraisals on veritable instructive gathering demonstrate that the engineered procedure may predict the audit talented rating a great deal of appropriately, and improve the direction effect of survey experts [2]. Recommender frameworks apply information revelation procedures to the matter of making changed recommendations for data, thing or associations all through a live correspondence. These frameworks, especially the k-closest neighbor pleasing confining predominantly based ones, space unit picking up in all cases ground on the net. The titanic progression inside the proportion of possible information and besides the gathering of occasion producers to web areas beginning late addresses some key difficulties for recommender structures. These are: making top quality recommendation, acting a few proposition for reliably for two or three clients and things and accomplishing high thought inside the substance of data sad quality. In obsolete strong segregating structures the proportion of work will reach out with the degree of people inside the structure. New recommender structure improvements area unit required that may rapidly make top quality recommendations, notwithstanding for unpleasantly gigantic scale issues. To deal with these issues we have evaluated thing based satisfying separating structures. Thing based procedure starting study the client thing structure to spot association between very surprising things, therefore utilize these relationship with in a contorted way process suggestions for clients [3]. Exponential improvement of information made by on-line social affiliations requests viable and versatile recommender structures to direct obliging outcomes. outdated frameworks become unfit because of they expel affiliation information; existing social proposition structures consider social partnership structure, at any rate social talk data has not been completely thought of [6]. it's major and hard to breaker social talk factors that zone unit got from clients' inspiration of social practices into social proposal. During this paper, we will when all is said in done research the social proposition burden on the clarification of mental science and humanism thinks about that show 2 indispensable segments: unequivocal affinity and social impact. We watch out for at an opportune time blessing the certified criticalness of those 2 factors in on-line lead measure. By then we will with everything considered propose a wonderful probabilistic structure objectives system to go along with them out of contraption house. We will when all is said in done constantly offer an adaptable recipe which may steadily system the gigantic scale data. We will when all is said in done direct assessments on each Face book vogue bifacial and Twitter vogue simplex social association educational records. The cautious outcomes and appraisal on these 2 epic educational records exhibit that our system in a general sense beats the present approachs [4].. Generally, we have seen a flourishing of zone - based obliging systems. A semantic depiction of area information is required to oblige the need of zone seeing, analyzing, course and tending to. During this paper, we will manage in uncertainty expect to audit the recorded foundation of heading of social affair (POI) by obliterating the flooding heterogeneous client made substance (UGC) from absolutely remarkable pleasing systems. We will obviously get some information about the substance depictions, photographs, client appearance models, and setting for a domain semantics comparability progress. We will all around battle that the scene recorded foundation expect a colossal improvement in client appearance lead. Supported this contention, a bound together dish proposal condition is orchestrated by joining scene valid foundation as a regularize. Notwithstanding etymologizing client inclination fortified client setting appearance data, we will control in uncertainty put dumbfounding load on a zone phonetics comparability. At long last, we will when all is said in done direct a concentrated presentation assessment of region phonetics similarity and strategy recommendation over a confirmed world dataset amassed from Foursquare and Instagram. Starter results show that the UGC data will well outline the setting phonetics that aching to help the intrigue execution.

II. RELATED WORK

Existing structure Sentiment evaluation is energized on 3 totally abrupt levels: audit level, sentence-level, and verbalization level. Survey level assessment and sentence-level assessment consider to design the assumption of a whole assessment to in any event one of the predefined thought polarities, identically as positive, negative and regularly reasonable. notwithstanding the way wherein that state level assessment consider to evacuate the inclination most remote scopes of each part that a client passes on his/her point of view to the positive piece of a specific product.Zhanget al. propose a freely guided and lexiconbased evaluation plan way to deal with oversee control see thought most removed inspiration driving a survey that contains each issue words and emojis. similarly, that they use end for proposition. Lee et al. propose a recommender structure abuse the acceptability of experts to watch out every novel and applicable recommendations[8]. By separating the client assessments, they will propose basic managers to an objective client kept up the client masses. the present work fundamentally bases on referencing clients into joined assessment (for example positive or negative), and that they don't go more in mining client's supposition. The present procedures on an astoundingly principal level effect thing class data or name information to survey the social impact. These structures square measure all bound on the oversaw data, that isn't constantly reachable on unequivocal areas. Everything considered, USer blueprints will give us bits of information in mining social chose

thought and client propensities. we will when all is said in done propose an estimation based rating measure structure inside the structure of framework considering. In our work, we will when all is said in done utilize social clients' supposition to interpret examinations. Regardless, we will everything considered oust thing choices from client examines. By at that point, we find the supposition words, that square measure balanced portray the thing decisions. In addition, we will oversee in uncertainty use feeling word references to figure estimation of a specific client on Associate in Nursing thing/thing. The focal responsibilities of our point of view square measure as looks for after: we will when all is said in done propose a client nostalgic mensuration approach, that is predicated on the mined thought words and supposition degree words from client considers. We will when all is said in done utilize estimation for rating infer. Client slant proportionality bases on the client intrigue propensities. Client end impact reflects at any rate the supposition spreads among the unequivocal clients. Thing name closeness shows the potential giganticness of things. We will all around weave the 3 sections: client end vague quality, social examining influence, Associate in Nursingd thing name closeness into a probabilistic cross district understanding structure to hold a right proposal. The exploratory outcomes and talked display that client's social estimation that we tend to mined could be a key consider up rating check shows up. In our paper, we watch out for not just mine social client's appraisal, at any rate conjointly audit social energetic impact and thing's name. At last, we will with everything considered bring every one of them into the recommender structure. the motivation driving our point of view is to watch out sensible signs from audits and anticipate social clients' evaluations. we will in general cementing client doubt comparability, lay individual idea impact, and thing name closeness into a bound together structure considering bundling work to accomplish the rating figure task.

III. PROPOSED METHOD

We propose an end based rating need strategy inside the course of action of cross area enlisting. In our work, we will when all is said in done utilize social clients' tendency to translate evaluations. Regardless, we will when all is said in done oust thing choices from client reviews. By at that point, we find the supposition words, that square measure balanced delineate the thing choices. Similarly, we will administer in uncertainty use end word references to discover supposition of a specific client on Associate in Nursing thing/thing. The basic responsibilities of our strategy square measure as scans for after:

a)We propose a client nostalgic mensuration approach, that is predicated on the mined end words and tendency degree words from client investigates. b. We use supposition for rating need. Client supposition closeness pivots the client intrigue inclinations. Client supposition impact reflects at any rate the end spreads among the conspicuous clients. Thing name indistinct quality exhibits the potential criticalness of things. c. We join the 3 segments: client end comparability, social sharp impact, Associate in Nursingd thing name resemblance into a probabilistic framework understanding structure to hold a right suggestion. The exploratory outcomes and talks show that client's social supposition that we tend to mined could be a key consider up rating need shows up. d. The extra strategy proposed as intersection point framework is utilized for perceiving social end sway among client and accomplices. the extra fragment like poor, odious, phenomenal is other than else inside which it's essentially to foresee the pivotal thing.

IV. ALGORITHM

As explained before the structure watches out for two issues. Regardless, building recommendation system for Algerian customers subject to evaluations appraisal. Second, dealing with the four vernaculars, of Algerian customers, including: Arabic, Algerian tongue, French and English. Fig. 1 amasses the different events of proposed strategy.

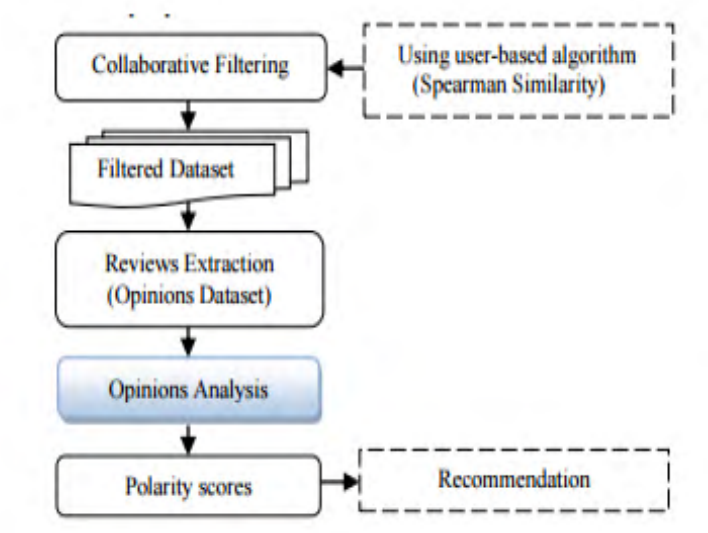


Fig: The proposed process for recommendation system based on opinions analysis.

1. Run of the mill disconnecting Breese et al. [21] pulled back communitarian isolating counts into two classes: memory-based figurings [22-26] and model-based

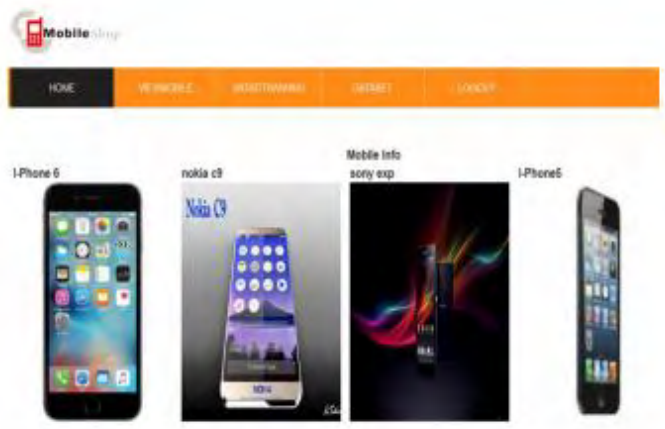
estimations [27-39]. Memory-based checks register a measure by joining examinations of picked customers or things that are picked a choice to be genuine. Model-based figurings use each and every open rating to end up being progressively acquainted with a model, which would then have the choice to be used to envision the rating of some sporadic thing by some theoretical customer. Memory-based CF incorporates can be in like manner limited into userbased CF figurings and thing based CF estimations. In this work, we used the customer based CF figurings [23, 25], where a ton of k nearest neighbors of the target customer is seen first by learning the affiliations or similarities between the customers' evaluations. We likely found that spearman closeness was the best similarity measure for the proposed structure. Spearman similitude contains finding a relationship coefficient, not between the qualities taken by the two segments, regardless between the spots of these properties. It is portrayed by:

$$r_s = \frac{\sum_{i=1}^{n}((rang(x_i - \overline{rang(x)})(rang(y_i - \overline{rang(y)}))}{\sqrt{\sum_{i=1}^{n}((rang(x_i - \overline{rang(x)})^2 \sum_{i=1}^{n}(rang(y_i) - \overline{rang(y)})^2}}$$

Where, (xi) and (yi) are the declaration's conditions in the model. The for all intents and purposes indistinguishable attributes between the customers expel up from - 1 to 1. We picked the value 0 as a point of restriction to see the closest neighbors of a customer. The amazing isolating with spearman closeness picks the things picked by in each practical sense foggy customer's profiles. These last post concentrates identified with their tendency things

V. EXPERIMENTAL RESULTS

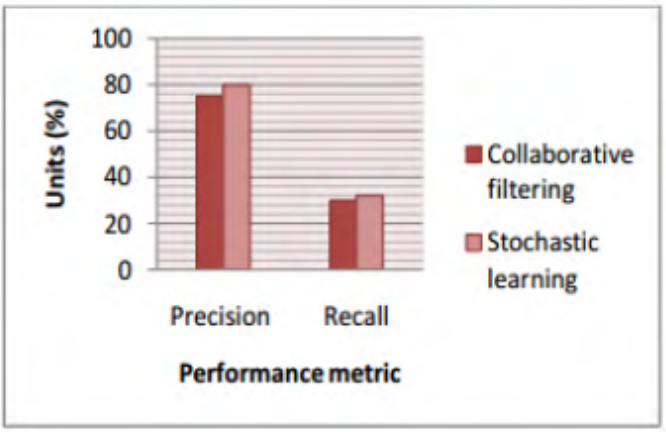
A site for booking phones is made using C#.NET framework as front end plan and SQL SERVER as back end.



$$\text{Precision} = \frac{\text{Number of Relevant Products extracted}}{\text{Total Number of Products extracted}}$$

$$\text{Recall} = \frac{\text{Number of Relevant products extracted}}{\text{Total Number of Products in}}$$

Database To look at the proposal structure, various types of suggestion incorporates are used.Some things in online business were taken reliant on appraisals. By then normal on exactness and standard on survey is made due with every evaluation. Result shows that proposed framework gave the better result in examination of structure.



V.CONCLUSIONS

In this proposed work, a novel execution of a thing suggestion structure dependent on mix recommendation check is appeared. The fundamental unprecedented condition of this method is the visual relationship of the information dependent on the disguised structure, and a basic reducing in the size of the intrigue space per result yield. Likewise the client can without a colossal measure of a stretch deals the things any place at whatever point. Evaluations, audits and emojis are examined and appointed positive and negative examinations. The things can be looked with the assistance of concentrate based segregating. Macintosh based disengaging technique can be utilized to keep up an essential decent ways from phony plans. This strategy was studied against determined client information amassed through an online webpage page, by utilizing a subset of the things loved by every client as commitment to the framework. The present outcomes are amazingly superior to unusual technique. In the long run, it is felt that with an otherworldly dataset and various updates this system may accomplish better outcomes. Mix Recommendation is one of the standard modules of the framework which demolitions the disadvantages of the standard Collaborative and Content Based Recommendations. Thusly encouraging outcomes are gotten utilizing this model.

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SUSTAINABLE DEVELOPMENT: WELLBEING ECONOMICS APPROACH

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A B S T R A C T

India is an example of co-existence of 'the embarrassingly rich and the desperately poor'. Each sector, industry, community or group is in pursuit of its survival, identity and growth. Pursuit of self-interest is supposed to inherently ensure progress of society, according to received theories and imposed practices, but apparently failed to do so.

This paper takes a multi-pronged approach and inquires into the inter- and intra- sectored interactions on wellbeing and measures to make it non-exclusive and equitable. The current real-time instances chiefly from the banking sector are a part of the study to prove the serious repercussions caused by ignoring the complexity of interactions and integrations and treating each factor or variable independently with de-unified knowledge. Consultative participatory institution is presented as an institution that enables interactions of every other variable and factor each reinforcing the other thus avoiding extremities in decision-making and producing unified knowledge in the process. Development and growth with a wellbeing perspective, endogeneity of ethics and non-exclusivity with consultative participatory standpoint is the sine qua non. A criterion for measuring the inclusivity in terms of consultative participation is taken as an indicator of measuring unity of knowledge.

Keywords: *Wellbeing, Consultative Participatory Institution, Unified knowledge, Endogeneity of ethics.*

1 Introduction

Today a vast majority of Indians are facing issues such as poverty, malnutrition, lack of basic amenities of water & sanitation, unemployability, price-rise, absence of sound health care system, affordable housing, good education, erosion of ethics, environmental degradation and credit crunch. The vertical growth of a small percentage and the horizontal increase in debasement of a large percentage necessitates us to revisit the epistemic reference, if any, for this lop-sided unsustainable 'growth'.

GDP was originally conceived as a metric to monitor cyclical fluctuations of the market, hence not designed or expected to gauge societal well-being. Budgets and plans are laid-out in terms of sectoral growth targets and not in terms of rates of poverty-reduction, employment-generation, health, education, environment and ethics and living standards of the people. Such plans are sectored growth plans and not broad-based nation-building plans. The crucial issues effecting the masses is attempted to be resolved as an outcome of pursuing growth-centric policies. The Economic Advisory Committee and mainstream economics justify and are convinced that the surplus revenue generated out of more growth could be and would be directed towards the lower strata of the society. However, revenue generation that does not involve all the sectors and communities cannot in turn allow percolation of wealth downward. The received or accepted thought-process that considers 8% growth rate as a goal-post for Indians and a bench-mark to read India's progress needs to be revisited.

This paper discusses the political economy of wellbeing premising on unity of knowledge. The epistemic concept of unity of knowledge entails dynamic interactions, thus, participation of societal, political, economical, environmental, ethical , technological and diversely unified institutional and non-institutional variables in a consultative participatory institutional milieu. This is a perspective for sustainable world systems.

Thus, the outcome of a consultative participatory institution would be knowledge guided by unified world view generated out of pervasive complementarities, participatory development, causationary inter- and intra- sectoral linkages and evolutionary learning between the variables conducted through mutual discourses, participants of which are conscious of the episteme of unity of knowledge. Thus we render the episteme of unity of knowledge and unified world view into integrated wellbeing. The aim is to ensure broad-based development as opposed to pocketed development through wide consultative participation. Thus, a new approach of sustainability by a change in the structure of development into a wellbeing perspective is discussed.

2 Objective:

This paper presents an alternative thought process in order to premise on an episteme that can generate unified knowledge. Unified knowledge is knowledge that arises organically out of discursions of complex and dynamic inter- and intra- sectoral interactions recognized as natural to the world systems. Consequently, wellbeing of universe is a natural outcome, caused through endogeneity of all factors including ethics, environment, polity, society, economy and technology.

3 Background:

Economy is being built up on the edifice of growth. Democracy is about inclusive growth as non-inclusive growth could undermine democracy. The economic growth so far has been far from inclusive. We have had Nobel laureates and leaders speak out against this socio-economic injustice but political needs and expediencies have been overriding economic compulsions and resolves. Socio-economic movements such as Occupy Wall Street and Jan Lok Pal Bill, brought to fore the failures of market and political system, viz., capitalist democracy. It was a joint failure of the political system of democracy and the economic system of mainstream neo-classicism.

What we need is consultative participatory discourses that shape fresh thought processes evolving policies that lead to equitable and sustainable growth. The political economy of inclusive growth decisively leads us to understand the failures of corporate governance, where the political processes colluded with the financial institutions to shape the markets in favour of the agenda of the colluders under the garb of liberalism and deregulation.

4 Scholarly opinion on current issues of the non-inclusive neo-classical economic regime:

Citing shortcomings of the present market system, in a lecture at Indian Statistical Institute, Kolkata, Nobel Laureate Joseph Stiglitz said that, market forces were not efficient in producing and distributing information and knowledge. He pointed out that gap of knowledge is wider than gap of resources between developed and developing countries. He advocated a balanced role between markets, government and civil society. He criticized the developing countries attitude of borrowing and adapting technologies from north. He rightly pointed out that much of technological or other invention in developed nations has been targeted towards saving labour. Whereas in developing countries labour is in abundance and unemployment is the burning problem. Labor saving inventions only aggravate the social issue. He stressed that real scarcity is that of natural resources hence inventions should be towards saving resources and environment. There is serious dearth of research centers in developing world to focus on scarcities. He pointed out the failures in development thinking. Intellectual Patent Rights often restricted the use of knowledge and contributed to creating monopolies. He said that democratic ideals create knowledge economy and said non-inclusive growth could destabilize democracy.

Nobel laureate and Harvard professor Amartya Sen has always been a critic of the Indian academic-political-industrial obsession with the Gross Domestic Product(GDP) or growth rate targets over the more substantial goals such as universal guarantees such as basic health care, education, food and empowerment

through livelihood entitlements. This approach is of serious concern to the agricultural sector as more than 50% of Indian population are involved in agriculture sector activities and majority of this sector are poor.

Prof Mehbubul Huq, a Pakistani economist who was the founder of Human Development Report recommended lesser military expenditure for the sub-continent and use of funds on education and poverty reduction. He said political will and commitment is vital for all strategies to take shape. In his book 'Poverty Curtain' he specified that that growth is thought to bring about employment. Unemployment is treated as step-child of planning and growth.

5 Neo-classical theory and goals pursuing non-inclusive growth:

The usual arguments put forth by the neoclassical proponents of free-trade, free-markets, capital flow liberalization and economic growth are the market-driven competitive forces for efficient allocation of resources. Yet the missing element in capitalist globalization argument vis-à-vis market competition is a recognition of the short and long run social and private costs that globalization brings about through its approach based on market-driven competition. Neoclassical economics views long term survival in terms of market competition and efficient allocation of resources. All policies, institutions and programs remain exogenous to this fundamental condition.

6 Unity of Knowledge:

An inclusive growth entails the set up of an inclusive world system or unified world view. Unified world system is by its very nature the idea of that of causational linkages, consultative participation, complementarities and evolutionary learning. The objective of this framework is wellbeing. Inclusive growth is hence a natural offshoot of this framework.

The episteme of unity of knowledge necessitates the representatives of various entities to acknowledge and pay heed to the circular causational complementarities amongst the variables of the analyzed system and their entities. The natural systems are essentially unified, characterized within, as diverse dynamic complementary interactions, integrations and evolutions, and the natural laws are as defined and upheld by the principle of unity of knowledge and unified world-systems.

The institution of Consultative participation treats the diverse system representations as sub-systems that do not compete; rather they complement with each other. Thus the entities and representatives of the variables are recursively interrelated under a reinforcing mechanism generated out of the characteristics of broad

participation, wide representation, resulting into transparency, judicious responsibility and accountability leading to socio-economic efficiency and equitable development.

The knowledge deduced and the simulated levels of common wellbeing of the participating entities and the corresponding variables in this regard would go through a circular causation knowledge-gaining process. The interactive and evolutionary form of learning in unity of knowledge in Consultative Participatory institutional model is all-inclusive and integrated.

7 Conclusions:

Intellect cannot cast away what is discernibly good and true. There has to be an intellectual exchange between received and alternative ideas. This paper has discussed new grounds on the theme of socio-economic reconstruction at global and national levels by presenting concept and application underlying the science, society and economy embedding. The theme of consultative participatory political economy as a new idea of political economy in this socio-economic sense has been discussed. Such a definition recognizes the traditional one on conflict and power in the ownership, distribution and production of resources. But it extends to the moral and ethical foundation of unity of knowledge and its epistemic influence on the construction of politico-economic issues under study. Such a path towards moral and ethical reconstruction of the socio-economic question was considered as the way towards new socio-politico-economic contracts as human and wellbeing centric. The concept of unity of knowledge and its discursively driven organic participation has been discussed for political and institutional consideration.

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INNOVATIONS IN BANKING SECTOR - E-BANKING PRODUCTS

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INTRODUCTON

The term Innovation means to make something new. Banks no longer restrict themselves to traditional banking activities, but they have explored newer avenues of increasing their business and capturing new markets. Today we have a fairly well developed banking system with different classes of banks. Some of them have engaged in the areas of consumer credit, credit cards, merchant banking, Internet and phone-banking, leasing, mutual funds etc.

Banking in India

- In India, "The General Bank of India "was the first bank started in 1786.
- The qualitative and quantitative changes in the banking sector took place when, "The Bank of Bengal" was started in 1806.
- The Reserve Bank of India started in 1935 became the central banking authority.
- The Banking Company Act was passed in 1955.
- 14 Major Banks were nationalized in the year 1969 and 7 more banks in 1980 were nationalized.
- IN 1990's greater emphasis was being placed on Technology and Innovation
- Opening up of the economy and implementation of the recommendations made by Narasimham Committee influenced the Indian Banking sector to a greater extent.
- New concepts like personal banking, retail banking, total branch automation etc.were introduced.

Concept of E-Banking

Liberalization and de-regulation process which started in 1991-92 made drastic changes in the Indian Banking System. From a totally regulated environment, the banks in India gradually moved into a market driven competitive system. E-Banking or electronic banking is a major innovation in the field of banking. Information revolution led to the evolution of Internet which led to the e-commerce continued by the evolution of E-banking. In the present Era, we cannot think about the success of any service or industry including the banking industry without Information Technology. The Information Technology has increased contribution of banking industry in the economy. Financial transactions can now be processed quickly and easily in fraction of seconds. Banks are able to generate more and more business opportunities resulting in greater profitability. The Information Technology Revolution in banking sector has not only provided improved services to the customers but also reduced operational costs of the banks.

History of E-Banking

The history of E-Banking dates back to 1980's.The term online banking became popular in the late 90's and referred to the use of a terminal, keyboard and monitor to access the banking system using a phone line. The first online banking service was introduced in 1994 in the United States of America. This service was developed by Stanford Federal Credit Union which is a financial institution and provided the first online internet banking services to all of its members in 1994.Later on the idea was snapped by various other banks.

E- Banking in India

In India e-banking is of recent origin. The traditional model for banking has been through branch banking. Only in the early 1990s there has been start of non-branch banking services.

Opening up of the economy in 1991 marked the entry of foreign banks in India .These banks brought new technology with them. The concept of internet banking has been simultaneously evolving with the development of the World Wide Web. The online shopping promoted the use of credit cards through internet. Banking products became more and more competitive and the need for diverse products and services was felt.

The credit of launching internet banking in India goes to ICICI Bank. Citibank and HDFC Bank followed with internet banking services in 1999.The ICICI bank firstly introduced online banking in India in 1996 under the brand name "Infinity". Currently 78 percent of its customers are registered for online banking. 1996 to 1998 marked the adoption phase while usage increased only in 1999 owing to online charges, increased PC penetration and technology friendly atmosphere.

Several initiatives have been taken by the Government of India as well as the Reserve Bank to facilitate the development of e-banking in India. The Government of India enacted the IT Act, 2000 with effect from October 17, 2000 which provided legal recognition to electronic transactions and other means of electronic commerce. The Reserve Bank monitors and reviews the legal and other requirements of e-banking on a continuous basis to ensure that e-banking would develop on sound lines and e-banking related challenges would not pose a threat to financial stability. A high level Committee under chairmanship of Dr. K.C. Chakrabarty and members from IIT, IIM, IDRBT, Banks and the Reserve Bank prepared the „IT Vision Document- 2011-17", for the Reserve Bank and banks which provides an indicative road map for enhanced usage of IT in the banking sector.

Modern banking is virtual banking which means the customer cannot see the bank but with the help of technology all the banking activities can be conducted from anywhere in the world. The Reserve Bank of India constituted a working group on Internet banking. The group divided Internet banking products in India into three types based on levels of access granted. They are,

1) Information only System
2) Electronic Information Transfer System
3) Fully Electronic Transactional System

Components of E-Banking

- Internet
- Wire Application Protocol based mobile (WAP is a technology started for accessing information over a mobile wireless network)
- Automated telephone
- ATM network
- SMS and FAX messaging components
- Multipurpose Information Kiosks

Using the above components financial transactions can be conducted from anywhere and allow non-stop working time.

The three broad facilities that e-banking offers are

- **Convenience** - Complete your banking at your convenience in the comfort of your home.
- **No more Q's** - There is no queue at an online bank.
- **24x7 Service** - Bank online services are provided 24 hours a day, 7 days a week and 52 weeks a year.

E-banking simply refers to the use of electronic channels like phone, mobile, internet etc for delivery of their services to their valuable customers The use of e-banking technology includes using ATM's, Smart cards, ATM, Telephone banking, Internet banking and Mobile banking.etc. for doing day to day banking services.

E-banking products and services in India

- Internet Banking
- ATM
- Mobile Banking
- RTGS
- NEFT
- Debit and Credit Cards
- Smart Cards
- POS

Internet Banking: It is a system of banking in which customers can view their account details, pay bills and can transfer money by means of the internet. This includes the delivery of new and traditional banking products and services through electronic delivery channels. This system allows conducting the banking transactions online. It is the use of electronic means to transfer funds directly from one account to another rather than by cheque or cash.

Automated Teller Machine: ATM's are widely used as electronic channels in banking. It is operated by a plastic card with special features. It is a computer controlled device through which the customer can make withdrawals, check the balance in account.etc.

Mobile Banking: This refers to the use of a smart phone or other cellular device to perform online banking tasks while away from home computer. The activities such as monitoring account balances, transferring funds between accounts, payment of bills, locating an ATM etc.

RTGS: It stands for Real Time Gross Settlement**.** It is a fund transfer mechanism where transfer of money takes place from one bank to another. It is primarily for large volume transactions .The time taken for effecting funds transfer from one account to another is normally two hours.

NEFT: It stands for National Electronic Fund Transfer. It facilitates transfer of funds to other bank accounts in over 36000 bank branches across the country. It is simple, secure, safe, faster way to transfer funds.

Debit Card: It is a plastic card which provides an alternative payment method to cash for purchases. Functionally it can be called an electronic check as the funds are withdrawn directly either from the bank account or from the remaining balance on the card. It is used instead of credit card to pay bills such as utilities, insurance, etc.

Credit Card: It is a part of a system of payments named after the small plastic card issued to users of the system. It is a card entitling its holder to buy goods and services based on the holders promise to pay for the same. The issuer of the card grants credit to the user or customer from whom the user can borrow money for payment to a merchant or as a cash advance to the user.

Smart Card: It is a micro chip based card used for making purchases without need of any PIN. It is a powerful card which carries out functions of ATM card, Debit card and Credit card.

POS: Point of Sale is the time and place where a retail transaction completes. It is the point at which a customer makes a payment to the merchant in exchange for goods or after provision of service.POS terminals are the electronic devices deployed at merchant outlets to accept the debit and credit cards.

Benefits of E-banking

E-banking helps the customers as well as banks by overcoming the drawbacks of manual system as computers are capable of storing, analyzing, consolidating, searching and presenting the data as per the requirement of customers and banks with a lot of speed and accuracy. It increases the efficiency in the area of effective payment by enhancing the delivery of banking services in quick time. E-banking has helped banks to retain the current customers, increase customer satisfaction, acquire further share in the markets and reduce the costs of delivering service to the customers. Delivery of services has gained increasing popularity through electronic platform. It provides alternative way for delivery of services in a faster way to the customers. Various services are being offered by banks through electronic banking.

Advantages to the Banking institutions

- E-banking helps in reducing the cost of delivering the services to the customers.
- It provides banks with competitive advantage among their peers.
- It reduces the use of paper money that helps the central bank in printing less paper notes.
- Through websites, banks can earn revenue by promotional activities.
- Customers can avail e-banking facility from anytime, anyplace, therefore there is a need to invest more and more on relevant infrastructure.

Advantages to the customers

- E-banking delivers 24x7 services to customer.
- Easy access to account information in quick time.
- Payment can be made online for the purchase of goods and services.
- With e-banking, customers can check account balance, can get statement of their account, apply for loans, check the progress of their investments and collect other relevant information.

Challenges of E-banking

The latest developments in information technology have also brought many challenges in successful delivery of e-banking services to the customers. Speedy changes in technology, complex, high costs, security and data privacy issues, new rules and regulations, lack of trained manpower are some of the challenges faced by the commercial banks in India.

Customers need to have skill to deal with computers and browsers. The people who are not comfortable with computer and internet often find it difficult to make use of the e-banking facilities. In many instances, a simple pressing wrong key may create a big problem.

Security Risk

Increasing number of fraudulent bank websites will mislead the customers. For example a suspicious bank website www.sbionline.com will create confusion with the original bank website www.onlinesbi.com.

Fake e-mails are sent to the customers from fraudulent banks.

Personal Information verification e-mails are also sent to customers from fraudulent banks.

Fake calls and messages to the customers insisting them to disclose ATM numbers and their passwords.

Guides the customers to enter fraudulent links on the web site.

CONCLUSION

The banking sector in India has become stronger in terms of capital and number of customers. It has become globally competitive and diverse aiming at higher productivity and efficiency. Exposure to worldwide competition and deregulation in Indian financial sector has led to the emergence of better quality products and services. Reforms have changed the face of Indian banking and finance. The banking sector has improved in terms of technology, products and services, information systems etc. With new opportunities unfolding in banking sector India is sure to emerge as a global power in banking services in the days to come.

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EMERGING TRENDS IN BANKING - IMPACT OF INFORMATION TECHNOLOGY IN BANKING INDUSTRY

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Abstract:

This paper explains that most of the banks have begun to take an innovative approach towards banking with the objective of creating more values for customers and consequently the banks. E-Banking enables the people to carry out most of their banking transactions using a safe website which is operated by respective banks. Various Innovations in Banking and Financial Sectors are ECS, RTGS, NEFT, EFT, ATM, Retail Banking, Debit and Credit cards and many more. With the emergence of Privatization, Globalization and Liberalization in India, banks are focusing on Research and Development and applying various innovative ideas and technology. There is a close relationship between the development of banking sector and the new innovations in technology and Electronic data processing. The present article focuses on the benefits and challenges of changing Banking trends and to study the performance of existing technology based products and services being offered by Banks in India and their future prospects as well as the advancement of banking sector by information technology.

KEY WORDS: *Banking Innovation, Information Technology, Payment and Settlement System in Banks, E-Banking.*

1. INTRODUCTION:

Banking environment has become highly competitive today. To be able to survive and grow in the changing market environment, banks are going for the latest technologies, which is being perceived as an enabling resource that can help in developing more flexible structure that can respond quickly to the dynamics of a fast changing market scenario. It is also viewed as an instrument of cost reduction and effective communication with people and institutions associated with the banking business.

The Banking sector is undergoing the process of radical transformation due to excessive competition of foreign and private players and changes in tastes, preference and habits as well as expectations of customers for newer products. The traditional view of business which was the right product must be available in the right place at the right time is replaced now by a more dynamic and flexible concept that any product should be available at anytime and anywhere.

Since the nationalization of banks in 1969, the public sector banks or the nationalized banks have acquired a place of prominence and since then have been instrumental in ascertaining tremendous progress. The need to become highly customer focused has forced the slow moving public sector banks to adopt a fast track approach. The Indian Banking has finally worked up to the competitive dynamics of new Indian market and its relevant issues concerning the various challenges of Globalization. Banks that employ IT solutions are perceived to be futuristic and proactive players capable of meeting the multifarious requirements of large customer base. Indian Banking industry is going through a phase of metamorphosis and has witnessed changing strategies by different banks to adapt to the evolving competitive environment. This shift from traditional social banking to profit banking, implementation of prudential norms pertaining to Capital Adequacy norms, income recognition, asset classification, exposure norms etc. have given rise to increased competition and thrown greater challenges in banking sector. With these variations in the level of IT in Indian Banks, it is useful to take account of the trends in IT and also to see the comparative position with Indian Banks.

The relevance of the status of Indian Banks with the perception when they get into IT up gradation is the main objective which strongly supports the inclusive growth in the Banking sector. IT has helped the Banking industry to deal with the challenges the new economy poses. Technology has opened up new markets, new products, new services and efficient delivery channels for the banking industry. Few examples are such as Online Banking, Mobile Banking and Internet Banking. The progress of technology and development of worldwide have significantly reduced the cost of global fund transfer. The IT revolution has set the stage for unprecedented increase in financial activity across the globe. It is IT which enables the banks in meeting such high expectations of the customers who are more demanding and also tech-savy compared to their counterparts of the yesteryears.

2. OBJECTIVE OF THE STUDY:

The main Objective of this research paper is to review the implementation of IT in Banking Industry. Technological innovations have enabled the industry to open up new delivery channels, seeking the help of IT to deal with the challenges that a new economy poses. The Objectives of the present study are:

1) To study the rapid advancement occurring in the banking sector.

2) To analyse the performance of existing technology based products offered by the banks in India and its future prospects.

3. METHODOLOGY:

The present review paper is based on the Secondary data. It analyses the available literature on Banking technology and various existing and upcoming innovative products offered by banks in India. The Secondary data pertaining to the study was obtained from the various journals, books, newspapers and websites of the concerned Banks.

4. REVIEW OF LITERATURE:

Banking sector plays a very important and crucial role in the development of Indian economy with the use of technology; there had been an increase in penetration, productivity and efficiency of banking practices. It has not only increased the cost effectiveness but also has helped in making small value transactions feasible. Bhosle and Sawant in research paper, "Technological Developments in Indian Banking sector" discussed the role and concept of banking sector in the development of Indian economy. The paper highlights that the technology allows taking place faster and offering unparallel convenience through various delivery channels like MICR, CTS, RTGS, and NEFT etc. Many researchers have given their views on the innovation in the services.

- Avasthi and Sharma (2000) in their study have analyzed that advances in technology are set to change the face of banking business. Technology has transformed the delivery channels by banks in retail banking. The study has also explored the challenges that banking industry and its regulator faces.
- Arora (2003) in his study highlighted the significance of bank transformation. Technology has a definite role in facilitating transactions in the banking sector and the impact of technology implementation has resulted in the introduction of new products and services by various banks in India. Mangnale, Chavan and Randive, in their research paper "E-CRM in Indian Banking Sector, Golden Research Thoughts" analyzed in their study that technology, people and customer are the three elements on which depends the whole success of banking in the fast changing economic environment. This paper analyzes the concept of e-CRM in Indian banks from its various dimensions covering specifically the needs, process, present status and future prospects.

- KPMG, "Technology enabled transformation in Banking", The Economic Times Banking Technology, Conclave 2011,this article has concluded that banking will be transformed by new technology by 2015.customer friendly products, delivery channel, easy and accessible services and competitive pricing would be driving forces-and technology shall pay a dominant role in all these. Models using mobile devices and efficient payment systems will make banking services widely available 24 x 7 The various technological platforms provided by the banks to its customers bring greater flexibility and operational convenience by providing computerized banking environment, speedier transactions, accurate statements, ATMs offering 24

hours banking, Mobile banking, Internet banking; anywhere and at anytime. Customer terminals are proved to be a milestone in the development and growth of banks.

5. TECHNOLOGY AND INNOVATIONS IN BANKING:

Banking environment has become highly competitive today .Developments in the field inclusive of information technology strongly supports the growth and inclusiveness of the banking sector by facilitating inclusive economic growth. IT improves the front end operations with back end operations and helps in bringing down the transaction costs for the customers. Major events in the field of IT in banking sector in India are:

- Introduction of ATMs in 1987.
- Card based system in late 1980's and 90's.
- Electronic Clearing Services (ECS) in early 1995
- Electronic Funds Transfer (EFT) in early 2000.
- Introduction of RTGS in 2004.
- National Electronic Fund Transfer (NEFT) in 2005 by replacing EFT.
- CTS in the year 2008.
- The Payment and Settlement Systems Act passed in December 2007.

➢ AUTOMATED TELLER MACHINES:

ATMs were introduced to the Indian Banking industry during 1987 by HSBC Bank in Mumbai. With the advent of ATMs, banks are able to serve the customers outside the banking halls. Now the ATMs are equipped with modern technologies and facilitate various features for its customers who include Bill payments, ticket booking, Mobile recharges, Ubiquitous multifunction, ATMs biometric, Multilingual ATMs and ATM network switches. The number of ATMs in India is growing at a brisk pace. ATM segment witnessed a growth of 24% for the period from 2012-2015. According to available data the number of ATMs which were 92,455 in 2012 is increased to 1, 74, 988 in year 2015, which is a good sign for whole industry.

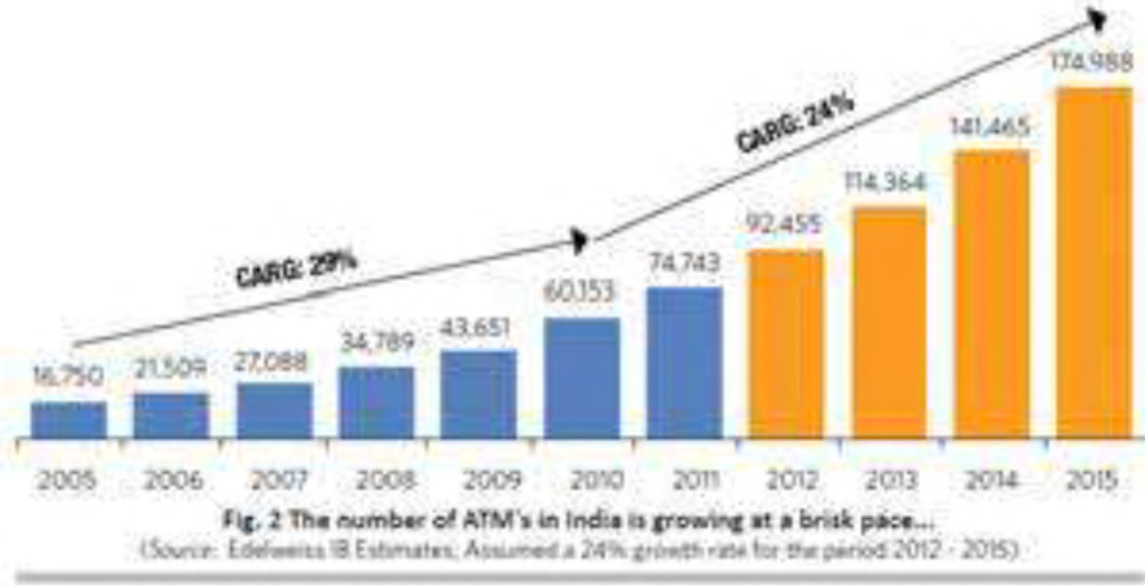


Fig. 2 The number of ATM's in India is growing at a brisk pace...
(Source: Edelweiss IB Estimates; Assumed a 24% growth rate for the period 2012 - 2015)

Source: Edelweiss IB Estimates

➢ CARD BASED SYSTEM:

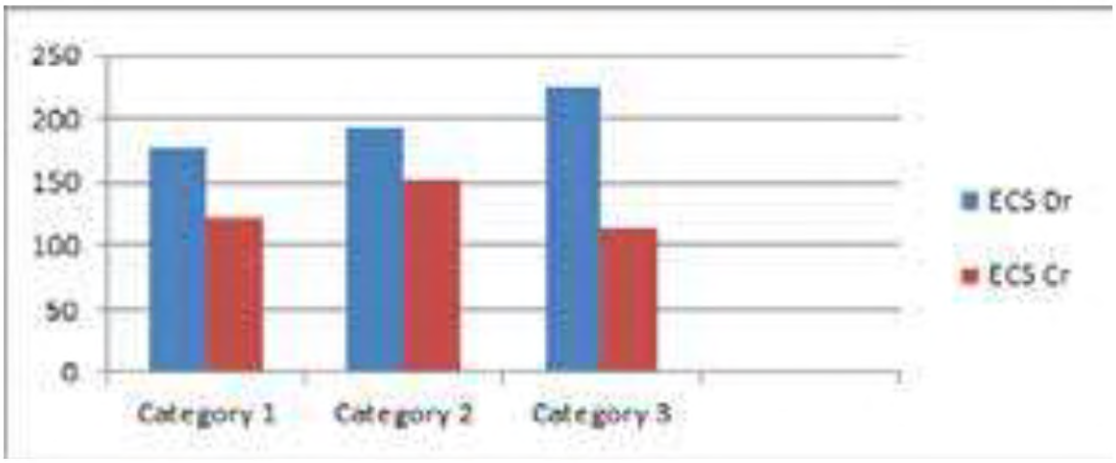
Among the Card based delivery mechanisms for various banking services, are Debit Cards and Credit Cards. The amount of Debit Card transactions increased rapidly which was Rs.469.1 million in year 2012-2013 and Rs.808.1 million in year 2014-2015, whereas the amount of Credit Card transactions was Rs.396.6 million in year 2012-2013 and Rs. 615.1 million in the year 2014-2015.

ITEMS	2012-2013	2013-2014	2014-2015
DEBIT CARDS	469.1	619.1	808.1
CREDIT CARDS	396.6	509.1	615.1

➢ ELECTRONIC CLEARING SERVICES (ECS):

ECS introduced by RBI in 1995, akin to Automated Clearing house system. ECS has two variants i.e. ECS Debit clearing services and Credit clearing services.ECS Debit operates on the principles of single credit multiple debits and is used by utility service providers for collection of electricity bills, telephone bills and other charges and also by banks for collection of principal and interest repayments.ECS Credit handles bulk and repetitive payment requirements of corporate and other institutions and is used for transactions like payment of salary, dividend, pension,

interest etc.ECS Debit amount is increased from Rs. 176.5 million to Rs. 226 million from 2012-2013 to 2014-2015 and ECS Credit amount is decreased from Rs. 122.2 million to Rs. 115.3 from 2012-2013 to 2014-2015.



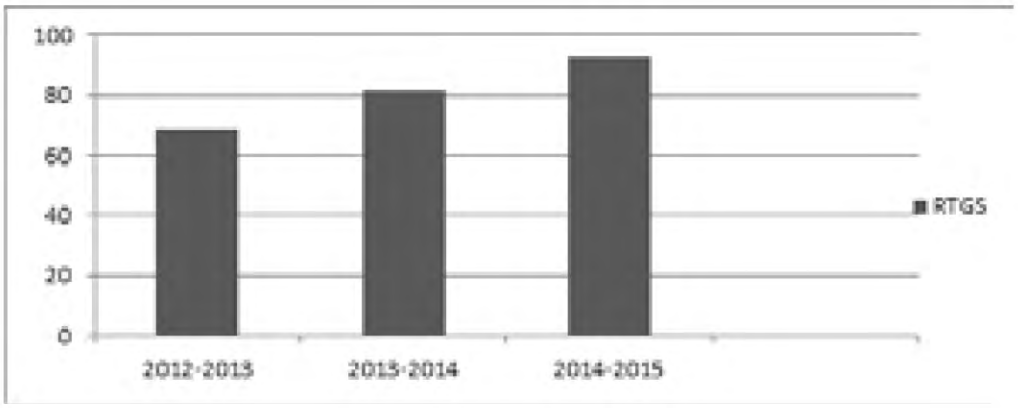
Source: rbi.org.in

➢ ELECTRONIC FUND TRANSFER:

The EFT system enables an account holder of a bank to electronically transfer funds to another account holder with any other bank..The most widely used EFT programs is Direct deposits, in which payroll is deposited straight into an employee bank account, although it transfer the funds through an electronic terminal including Credit card, ATM and Point of Sales (POS) transactions.

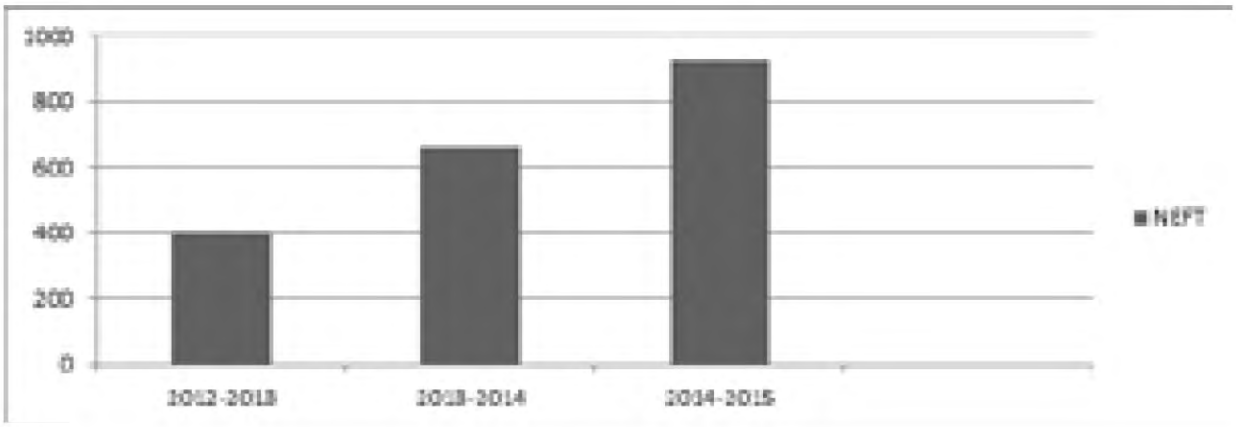
➢ REAL TIME GROSS SETTLEMENTS (RTGS):

The introduction of RTGS in 2004 was instrumental in the development of infrastructure for Systematically Important Payment System (SIPS) and it settles all interbank payments and customer transactions above 2 Lakhs. RTGS was launched by RBI, which enabled a real time settlement on a gross basis. To ensure that RTGS system is used only for large value transactions and retail transactions take an alternate channel of EFT. The reach and utilization of RTGS has witnessed a sustainable increase since its introduction. In the year 2012-2013 to 2014-2015 transactions related to customer remittances have raised from Rs.68.5 million to Rs.92.8 million. This shows the increasing popularity of RTGS in Indian banking industry.



➢ NATIONAL ELECTRONIC FUND TRANSFER (NEFT):

New and improved variant of EFT was implemented in November 2005 to facilitate one to one fund transfer requirement of individuals as well as corporate. It uses the Structured Financial Messaging Solution (SFMS) for EFT message creation and transmission from the branch to the banks gateway and to the NEFT centre, so it can transfer the funds with more security. With the SFMS facility, branches can participate in both RTGS and NEFT System. Using the NEFT infrastructure, a one –way remittance facility from India to Nepal has also been implemented by the RBI since 15th May, 2008. Overall EFT and NEFT based clearing increased from Rs.394.1 million to Rs.927.6 million in year 2012-2013 to 2014-2015.



6. INNOVATIVE PRODUCTS AND POLICIES OF BANKS:

• "My Saving Rewards", the program allow customers to accumulate reward points on a host of savings account transactions such as bill pay, online shopping, EMI payment etc.

• 24x7 fully electronic branches are opened to undertake real time transactions by the customer.

• "E-Locker", an online service for storing important documents for privilege banking customers.

• UID authentication for Aadhaar based payments and enabling corporate to pay taxes online.

• Cash Deposit Machines (CDMs) are installed for cash deposits by customers at these machines by using their ATM cum Debit card.

• E-trade SBI, a web based portal launched in March 2011 to access trade finance services with speed and efficiency.

• To facilitate the Electronic Benefit Transfer (EBT) scheme for routing MGNREGA where all scheduled commercial banks were instructed to open Aadhaar enabled bank accounts of all the beneficiaries.

• Expansion of branches in remote locations either through a bank branch or Business Correspondence (BC) or other modes so that every eligible person should have a bank account.

• Know Your Customer (KYC) norms simplified to facilitate financial inclusion and customer services.

• The RBI is replacing the existing RTGS with a new NGRTGS system which includes which includes few extra features like advanced liquidity management facility; Extensible Markup Language (XML) based messaging system etc.

• Recently launched scheme of government "Jan Dhan Yojana" with the motive that every family must have a bank account

• Today, the banks installed Solar ATMs, windmills to fulfill their own energy needs, paperless banking etc. SBI is the largest deployed of Solar ATMs.

7. CONCLUSION:

Today, Information Technology is used in two different avenues in banking- Communication and Business Process Re-engineering (BPR). It is reported that about 250 million internet users are there in India, which is among the top three in the world and this number is set to grow to 350 million by end of 2015.The E-banking, Mobile banking, Net banking and ATMs facility has gained the success among the customers. Today's generation is showing a keen interest in adopting all such technology enabled banking facility. Payment settlement systems like RTGS, NEFT, EFT, ECS, and CTS have proved to be successful among the customers using these facilities. Therefore, the IT revolution has set the stage for overcoming the challenges the new economy poses keeping in view the unprecedented increase in financial activity across the world.

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Economic Security through Micro Insurance - Problems and Prospects

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Abstract

Micro Insurance, commonly called as the insurance for the poor, is characterized by low value products and low premium. In India, it is a step to promote insurance coverage among economically vulnerable section of the society. IRDA'S Micro Insurance Regulation 2005, has strengthened the growth of regulated micro insurance in India and paved path for expanding the outreach to insurance to rural and underserved section of society. This paper throwing light on concept of micro insurance, its growth during post privatisation, significance of Micro Insurance in creating economic security. In this paper the problems and prospects of Micro Insurance in India were also highlighted.

Keywords: *Micro insurance, IRDA, Economic Security, Financial Inclusion etc*

INTRODUCTION:

Insurance occupies an important place in the complex modern world risk, which can be insured, has increased enormously in every walk of life. This has led to growth in the insurance business and evolution of various types of insurance covers. The insurance sector acts as a mobiliser of savings and a financial intermediary and is also a promoter of investment activities. It can play a significant role in the economic development of a country, while economic development itself can facilitate the growth of the insurance sector.

Insurance is a form of risk management which is used primarily to hedge against the risk of a contingent, uncertain loss. Insurance is defined as the equitable transfer of the risk of loss, from one entity to another, in exchange for payment. Insurance is essentially an arrangement where the losses experienced by a few are extended among many who are exposed to similar risks. It is a protection against financial loss or loss of life of a person that may occur due to an unexpected event. The insured receives a contract called an insurance policy which details the conditions and circumstances under which the insured will be compensated.

OBJECTIVES OF THE PAPER:

- To understand the concept of insurance and its growth in India, post privatisation of insurance sector,
- To analyse the role and significance of Micro Insurance in creating economic security
- To understand the problems and prospects of Micro Insurance in India.

SOURCES OF DATA:

The main sources of data used for the paper are Secondary one. IRDA Annual reports, KPMG report on Indian insurance sector and other related literature are used for the paper.

Insurance can be broadly classified into : (a) life insurance, and (b) general or non-life insurance.

(a) Life insurance or life assurance is a contract between the policy owner and the insurer, where the insurer agrees to pay the designated beneficiary a sum of money upon the occurrence of the insured individual's death or other event, such as terminal or critical illness. In return, the policy owner agrees to pay a stipulated amount at regular intervals or in lump sums. Life-based contracts tend to fall into two major categories:

- **Protection policies:** These are designed to provide a benefit in case of a specified event, typically against lump sum payment. A common form of this policy is term insurance.
- **Investment policies:** The main objective is to facilitate the growth of capital by single or regular premiums. The common forms in this category include whole life, universal life and variable life policies.

(b) General insurance or non-life insurance policies, including automobile and homeowners' policies, provide payments depending on the loss from a particular financial event. General insurance typically comprises any insurance cover that is not deemed to be life insurance. Some categories of general insurance policies are: vehicle, home, health, property, accident, sickness and unemployment, casualty, liability, and credit. The terms of insurance generally depend on the company providing the cover.

Status of Life Insurance Sector in India - An Overview:

Since the opening of the sector in 2001, Indian life insurance industry has gone through two cycles-- the first one being characterised by a period of high growth with a CAGR of approx. 31 percent in new business premium between 2010-17 and a flat period showing a CAGR of around 2 percent in new business premium between 2010-19. During this period, there has been increase in penetration from 2.3 percent in FY01 to 3.4 percent in FY12, increased coverage of lives, substantive growth through multiple channels viz. agency, banc- assurance, broking, direct, corporate agency and increased competitiveness of the market due to growth of private players from four in FY01 to 24 private players in FY13.

Insurance Density and Penetration in India:

Two important indicators of the level of development of the insurance sector in any country are:

(i) Level of insurance penetration which is measured as the percentage of insurance premium in gross domestic product (GDP); and

(ii) Insurance density ratio (wherein insurance density is defined as the per capita expenditure on insurance premium and is directly correlated with per capita GDP).

Both insurance penetration and density have increased significantly over the years, especially with the opening up of the insurance industry to the private sector (as shown in Table 1). However, the increase has been marginal as far as the non-life insurance sector is concerned. While the density of life insurance in India grew from USD 15.7 in 2004 to USD 42.7 in 2018, the density in the non-life insurance industry for the same period grew from USD 4 to USD 10.50. Similarly, penetration in the life insurance sector increased from 2.53 per cent in 2015 to 3.17 per cent in 2018 and very marginally in the non-life insurance sector from 0.64 per cent in 2019 to 0.78 per cent in 2017. Thus, penetration in the non-life insurance sector has remained virtually constant over the years. India's insurance penetration is lower than the world average which in 2017 was 7.0 per cent,

while for India it was 5.2 per cent. Although, the penetration of Indian insurance is higher than that of some South Asian countries like Pakistan (0.7%), Bangladesh (0.9%) and Sri Lanka (1.4%), it lags behind other Asian countries like Japan (9.9%), South Korea (10.4%) and Singapore (6.8%).

However, in the life insurance sector, India's performance in terms of percentage of penetration at 4.6 per cent in 2018 is comparable with some developed countries and is above the world average of 4.0 per cent. In the non-life insurance sector, India with 0.6 per cent lags behind the world penetration average of 3.0 per cent in the year 2019.

Several factors are responsible for the low levels of insurance penetration in the country. These include low consumer preference, untapped rural markets and constrained distribution channels. In urban areas, life insurance penetration is approximately 65 per cent, and is considerably lesser in the low-income unbanked segment. In rural areas, life insurance penetration in the banked segment is estimated to be approximately 40 per cent, and at best is marginal in the unbanked segment. Before opening the sector to private insurers, it was felt that low levels of insurance penetration were due to ineffective market strategies adopted by Life Insurance Corporation (LIC) of India. Being a monopoly, the company had no strategic market plan. Advertising initiatives were limited to the print and electronic media, which mainly promoted LIC's products as being tax saving tools for salaried individuals. Although the level of penetration has increased after the entry of other players, it is still low compared to other countries. As per the surveys conducted on low levels of density and penetration, the problem has been exacerbated due to:

- agents' inability to clearly explain the features of the products;
- lengthy documents that are not user friendly; and
- the perception that agents are only concerned with their commissions.

Micro Insurance - Insurance for the Masses:

Micro insurance refers to insurance products which are designed to provide risk cover for low- income people. Generally, these products are focused towards providing adequate coverage to the customer segment with flexible payment schedules for the lower premiums. Although there are various benchmarks to distinguish micro insurance from insurance, product design (size of premium and risk cover) and access are key differentiators for micro insurance products. Simple products which are easily accessible through an efficient distribution process to keep the overall cost of products low are qualified under micro insurance.

Unlike in case of the urban regions, penetration of the insurance industry in rural regions has been relatively lower. Rural population has relatively lower access to information and lacks awareness of insurance products, mostly rendering them to be the 'un-insured' class of population. However, in order to make them aware of the insurance products and more importantly the need for insurance, it is necessary to educate them in person thus requiring a high touch service model to be followed. This requires identifying the 'centres of influence' to create awareness of insurance products, educating them on the need to be insured and finally converting them in a cost effective manner to tap this 'un- insured' and 'under-insured' market. They potential opinion leaders in the rural markets can be Headmasters of local government schools, Sarpanch of the gram panchayats, Non-Governmental Organizations (NGOs) and Self Help Groups (SHGs) that work in certain rural districts or even be the banking agent or business correspondent.

The large untapped rural 'un-insured' population represents a significant growth opportunity and those who take the approach of identifying influencers might have a distinct advantage in the future. Certain facts and figures of potential points of presence in the rural regions:

- As per the 2018 census, there were 589 District Panchayats, 6,321 Intermediate Panchayats and 238,957 Village Panchayats across India
- As at 31 May 2019, there were 713 Multi-State Co-operative Societies in India
- As at 31 March 2019, there were 9,743 branches of Microfinance Institutions (MFIs) across India
- As at 31 March 2019, there were 10,78,407 government schools covering 644 districts across India
- As at date there are 48,125 voluntary organisations/state organisations registered under the NGO-partnership system with the Government of India.

The micro insurance business took its roots in India with a few schemes launched by non government organizations (NGOs), micro finance institutions (MFIs), trade unions, hospitals and cooperatives to create an insurance fund against a specific peril. These schemes were outside the ambit of the regulations and operated more on good faith of these institutions.

Life:

While many individual and group life Microinsurance products are offered by insurers in the form of term and endowment, credit life cover (protection against outstanding principal and interest of loan if the borrower dies) has been a starting point for many insurance companies in India, driven mostly by push-based sales by MFIs. However, credit life tends to offer little value to clients, with coverage limited to the duration of the loan.

a. Janashree Bima Yojana - A social security scheme of LIC (state owned largest life insurance company) launched in 2000, provides benefit to the weaker sections of society (covers 45 vocational and occupational groups such as workers in foodstuff, textiles, wood, paper, leather products, brick kiln workers, carpenters, fishermen, handicraft artisan, handloom amongst others). The premium for the scheme is INR 200 per member;

50 percent premium under the scheme is met out of the Social Security Fund. The balance premium is borne by the member and/ or Nodal Agency. The members get a cover of INR 30,000 (~USD 600) in the event of death, INR 75,000 (~USD 1500) in the event of death/total permanent disability and INR 37,500 (~USD 750) in the event of permanent partial disability. As on 31 March 2018, about 30 million people had been covered under this scheme.

b. BASIX - A leading MFI offers group life Microinsurance in collaboration with Aviva Life Insurance Company India Ltd. In FY2011, it had over 2 million customers paying an average annual premium of < INR 100 (~USD 2). However, post Andhra Pradesh crisis in 2017, when the state government brought in legislation to curb coercive loan recovery practices and banned MFIs from approaching the doorstep of their customers, the MFI business in the state has fallen, resulting in the coverage almost halving to a little under 1 million customers.

Health/Personal accident:

In India, health-care is funded mostly through out of pocket expenditure comprising ~60 percent of healthcare spending in 2018. Health is unarguably a product most demanded by low income groups. A number of schemes exist; donor-funded, subsidised, insurer and government schemes being the main formats.

a) Rashtriya Swasthya Bima Yojana (RSBY)

RSBY has been launched by Ministry of Labour and Employment, Government of India in 2008 to provide health insurance coverage for Below Poverty Line (BPL) families. Over 33 million BPL families (> 100 mn members) have been enrolled across 472 districts across the country; 12,531 hospitals empanelled to provide benefits under the programme.

Key features of the scheme:

- Hospitalisation coverage up to INR 30,000 (~USD 550) for most of the diseases that require hospitalisation; cashless benefit through smart card
- Fixed package rates for hospitals
- Pre-existing conditions are covered from day one and there is no age limit
- Coverage extends to five members of the family which includes the head of household, spouse and up to three dependents
- Beneficiaries need to pay only INR 30 (< USD

1) as registration fee while Central and State Government pays the premium to non-life insurers (maximum INR 750/ ~USD 14) selected by the State Government for each district on the basis of competitive bidding.

Challenges for the success of Micro Insurance in the Rural India:

The challenges from the perspective of key stakeholders can be broadly classified into three categories viz. Un-insured target customer, Distribution intermediary and Insurance Company.

The Un-insured target customer: Given the lack of social security in India, in the event of disability, meager financial savings and reliance on borrowings from unorganised lenders are the only options available to a majority of the poor. While the developed countries provide social security network to their citizens, India's large population and low per capita income implies that provision for any sort of social security system is bound to be a significant drain on the country's limited resources.

Most customers in the target segment have low financial literacy and are unable to view insurance as a risk mitigation tool. Low awareness levels and lack of understanding of underlying benefits creates a barrier to purchase of intangible assets like insurance .

Further, the insurance companies have been focussing on reducing losses and improving profitability rather than increasing cost effective distribution reach to the lower strata. Poorly designed policies, lack of education, mis-selling through inadequately trained agents and rejections during claims settlement has led to lack of trust with this customer segment.

Distribution Intermediary: It is imperative to use an effective distribution channel mix to reach out to the target customer segment. Poor households live for the present rather than the future. Given their fatalistic attitude, the concept of insurance is linked to expenditure, rather than risk cover. Lack of adequate training to the distribution intermediary coupled with lack of motivation, makes it difficult to explain the products to largely uneducated customers. The feasibility of various products is also dependent on the availability of infrastructure, which is often lacking or low in quality. Limited incentive on a low premium product makes it difficult to cover operational costs of reaching out to the customers.

Further, delays in claim settlement and complicated formalities by the insurance companies also pose as a road block. It is important for the intermediaries to be able to build personal credibility with the client.

Insurance Company: Insurance companies are faced with challenges like high cost of customer acquisition given the high operating and administrative cost involved in reaching remote areas vs. value of premiums and unpredictable payment capacity of the segment. Moreover, given some of the operating models of the insurance companies the cost of customer service is also high. Regulatory compliance in terms of statutory requirements for customer acquisition, documentation also forces a cost build up for the companies. The companies do not have enough data on various sub-segments and associated risks for analysis and pricing. As a result, the claims ratio in the micro insurance segment is unpredictable.

CONCLUSION:

For India to reach its rightful place as a developed nation, it must financially empower its entire population. A key element of this empowerment is a base risk cover that covers elements of life, disability and health. Th is empowerment can only be achieved through the collaborative efforts of the government, regulators and private enterprises, who must be able to build commercially viable and scalable models for financial inclusion.

The key issues and challenges impending growth of micro insurance in India from the perspective of the key stakeholders - the un-insured customer, the distribution intermediary and the insurance company, can be addressed by way of structural regulatory and policy changes coupled with extensive leverage of emerging technologies. Regulatory and structural chan ges should encourage further capital deployment and enable operational flexibility resulting in reduction in customer acquisition and policy management costs. The suggested measures will aid in increasing the micro insurance penetration in our country which can be achieved through focussed efforts and suitable partnerships across the industry and government bodies.

For micro insurance to succeed, demand has to be generated through building awareness, creating specific and simple products, and above all, by simplifying the processes of underwriting and claims management.

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Applications of Machine Learning Algorithms

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Abstract: *— The goal of various machine learning algorithms is to device learning algorithms that learns automatically without any human intervention or assistance. The emphasis of machine learning is on automatic methods. Supervised Learning, unsupervised learning and reinforcement learning are discussed in this paper. Machine learning is the core area of Artificial Intelligence. Although a subarea of AI, machine learning also intersects broadly with other fields, especially statistics, but also mathematics, physics, theoretical computer science and more. Machine learning algorithms and its purpose is to learn and perform specific tasks. Humans are always interested in making intelligent computers that will help them to do predictions and perform tasks without supervision. Machine learning comes into action and produces algorithms that learn from past experiences and make decisions to do better in the future*

Keywords:- *Classification, Clustering, Super vised Learning,UnSuper vised learning, Reinforcement learning.*

I. INTRODUCTION

Machine learning is a subject that is based on computer algorithms, and its purpose is to learn and perform specific tasks. Humans are always interested in making intelligent computers that will help them to do predictions and perform tasks without supervision. Machine learning comes into action and produces algorithms that learn from past experiences and make decisions to do better in the future. Arthur Samuel, way back in 1959, said: “Machine Learning is the field of study that gives computers the ability to learn without being explicitly programmed". Thus it is what precisely machine learning is. Here, past experiences are called data. We can say that machine learning is actually a field that gives computers the capability to learn without being programmed. For example, a telecom company is very much interested in knowing which customers are going to terminate their service. If they are aware or can predict those customers, they can offer them special deals to retain them. A machine learning program always learns from past data and improves with time. In simpler words, if a computer program improves on a certain task based on a past experience, then we can say that it has learned. Machine learning is a field that discovers structures of algorithms that enable learning from data. These algorithms build a model that accepts inputs, and based on these inputs, they make predictions or results. We cannot provide all the preconditions in the program; the algorithm is designed in such a way that it learns itself. Sometimes the words, machine learning and Artificial Intelligence (AI), are used interchangeably. However, machine learning and AI are two distinctive areas of computing. Machine learning is solely focused on writing software that can learn from past experiences. Applications of machine learning include sentiment analysis, email spam detection, targeted advertisements (Google AdSense), recommendation engines used by e-commerce sites, and pattern mining for market basket analysis. Some real-life examples of machine learning are covered in the next section. Speech conversion from one language to another This Skype feature helps break the language barrier during voice/video calling. It translates a conversation into another language in real time, allowing both sides of speakers to effectively share their views in their native languages.

Suspicious activity detection from CCTVs

This is a wonderful example of how an application of machine learning can make society a safer place. The idea have a machine learning algorithm capture and analyse CCTV footage all the time and learn from it the normal activities of people, such as walking, running, and so on. If any suspicious activity occurs, say robbery, it alerts the authorities in real time about the incident.

Medical diagnostics for detecting diseases

Doctors and hospitals are now increasingly being assisted in detecting diseases such as skin cancer faster and more accurately. A system designed by IBM picked cancerous lesions (damage) in some images with 95 percent accuracy, whereas a doctor's accuracy is usually between 75—84 percent using manual methods. So, the computing approach can help doctors make more informed decisions by increasing the efficiency of recognizing melanoma and spotting cases where it is difficult for a doctor to identify it. Machine learning can be divided into three categories:

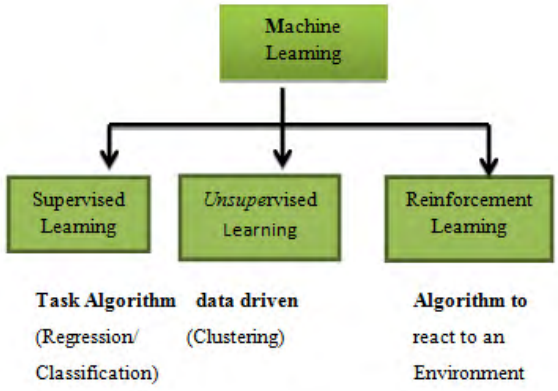

Figure 1.1 types of Machine learning

SUPERVISED LEARNING:-

Supervised learning is a type of machine learning where we have input and output Variables and we use an algorithm to learn the mapping from the input variable to the output variable. Y = f(X) The goal here is to understand the mapping very well, and that enables us to transform the input into the output. When our program receives the input data, it runs the mapping function to generate output data. Why is this called supervised learning? Actually, the algorithm that is used to learn from the training dataset is similar to a teacher supervising the process. For each run, the algorithm makes predictions on the training dataset and the teacher is doing the correction. Once we get an acceptable level of correct predictions, the learning will stop and the algorithm will move on to the production environment. In supervised learning, there are dependent and independent variables. We need to understand the effect of each variable used in the mapping and see the effect on the output variable. We can further group supervised learning into classification and regression problems: Classification: A classification problem is when we need to predict a category. For example, we have a patient's history record in a hospital and we want to predict how many people have high chances of a heart attack. Here, the output variable will be yes or no. Regression: A regression problem is when we need to predict a number or value. For example, when predicting a stock value, it always results in a real number. There are further divisions of classification and regression problems that include time series predictions or recommendations and so on. Some famous examples of supervised learning algorithms are as follows: Random forest (classification or regression problems) Linear regression (regression problems) Support Vector Machines (SVM) (classification problems) Now we will learn supervised learning from a real-life example. Let's say we are in a garden and we have a bag full of different types of fruits. Now we need to remove all the fruits from the bag and put the same types of fruits together. That's an easy task because we're already aware of the physical characteristics of each fruit. For example, we know which one is a mango and which is an apple. So, it's very easy to arrange them in groups. Here, our previous memory is working like training data. We've already learned the fruit names from the training data; here, the fruit names are actually output or decision variables.

Table 1.1 fruit characteristics:

Sno	Colour	Size	Shape	Fruit Name
1	Green	Small	Round	Grape
2	Green	Big	Half Moon	Banana
3	Red	Small	Heart	Cherry
4	Red	Big	Round	Apple

Table 1.1: Characteristics of fruits Let's say we take out a new fruit from the bag and now we need to place it into the correct group. We will check the color, size, and shape of the new fruit and take a decision based on the results to put it into the correct group. For example, if the fruit size is big, the color is red, and the shape is round with slight curves, then we can easily say it's an apple and place it in an apple group. This is called supervised learning because we've already learned something from training data and then we apply that knowledge to the new data (test data). The technique used for this type of problem is called classification. Why? It is a classification problem because we are predicting a category; here, the category is fruit name.

Unsupervised learning

Unsupervised learning is a type of machine learning in which we have only input variables and no output variables. We need to find some relationship or structure in these input variables. Here, the data is unlabelled; that is, there is no specific meaning for any column. It is called unsupervised learning because there is no training and no supervision. The algorithm will learn based on the grouping or structure in the data, for example, an algorithm to identify that a picture contains an animal, tree, or chair. The algorithm doesn't have any prior knowledge or training data. It just converts it into pixels and groups them based on the data provided. In unsupervised learning, we group the parts of data based on similarities within each other. The data in unsupervised learning is unlabelled, meaning there are no column names. This is not important because we don't have any specific knowledge/training of the data. Unsupervised learning problems can be further grouped as clustering and association problems:
Clustering: A clustering problem is for discovering a pattern or understanding the way of grouping from the given data. An example is a grouping of customers by region, or a grouping based on age.

Association: Association is a rule-based learning problem where you discover a pattern that describes a major/big portion of the given data. For example, in an online book shop, the recommendation engine suggests that people who buy book A also buy certain other books. Some popular examples of unsupervised learning algorithms are:
Apriori algorithm (association problems) K-means (clustering problems) Now take up the same fruit grouping example again from the earlier section. Suppose we have a bag full of fruits and our task is to arrange the fruits grouped in one place. In this instance, we have no prior knowledge of the fruits; that is, we have never seen these fruits before and it's the first time we will be seeing these fruits. Now, how do we perform this task? What are the steps we will do to complete this task? The first step is to take a fruit from the bag and see its physical characteristics, say the color of this particular fruit. Then arrange the fruits based on color.

Table 1.2 Grouping Based on Color

Colour	Fruit name
Red Group	Cherries and Apples
Green Group	Grapes and bananas

Table 1.2: Grouping based on color Now we will group them based on size and color. See the result in Table 1.3:

Table 1.3 Grouping based on Size and Color

Size and Colour	Fruit name
Big and Red	Apple
Small and Red	Cherry
Big and Green	Banana
Small and Green	Grapes

Table 1.3: Grouping based on size and color It's done now! We've successfully grouped them. This is called unsupervised learning and the approach is called clustering. Note that in unsupervised learning, we don't have any training data or past example to learn from. In the preceding example, we didn't have any prior knowledge of the fruits.

Reinforcement learning

We use Machine Learning to constantly improve the performance of machines or programs over time. The simplified way of implementing a process that improves machine performance with time is using Reinforcement Learning (RL). Reinforcement Learning is an approach through which intelligent programs, known as agents, work in a known or unknown environment to constantly adapt and learn based on giving points. The feedback might be positive, also known as rewards, or negative, also called punishments. Considering the agents and the environment interaction, we then determine which action to take. In a nutshell, Reinforcement Learning is based on rewards and punishments. Some important points about Reinforcement Learning:
It differs from normal Machine Learning, as we do not look at training datasets.

- Interaction happens not with data but with environments, through which we depict real-world scenario.
- As Reinforcement Learning is based on environments, many parameters come in to play. It takes lots of information to learn and act accordingly.
- Environments in Reinforcement Learning are real-world scenarios that might be 2D or 3D simulated worlds or game based scenarios.
- Reinforcement Learning is broader in a sense because the environments can be large in scale and there might be a lot of factors associated with them.
- The objective of Reinforcement Learning is to reach a goal.
- Rewards in Reinforcement Learning are obtained from the environment.

The idea that we learn by interacting with our environment is probably the first to occur to us when we think about the nature of learning. When an infant plays, waves its arms, or looks about, it has no explicit teacher, but it does have a direct sensorimotor connection to its environment. Exercising this connection produces a wealth of information about cause and effect, about the consequences of actions, and about what to do in order to achieve goals. Throughout our lives, such interactions are undoubtedly a major source of knowledge about our environment and ourselves. Whether we are learning to drive a car or to hold a conversation, we are acutely aware of how our environment responds to what we do, and we seek to influence what happens through our behavior. Learning from interaction is a foundational idea underlying nearly all theories of learning and intelligence.

The Reinforcement learning is a type of machine learning that enables the use of artificial intelligence in complex applications from video games to robotics, self-driving cars, and more.

Reinforcement learning is learning what to do—how to map situations to actions—so as to maximize a numerical reward signal. The learner is not told which actions to take, but instead must discover which actions yield the most reward by trying them. In the most interesting and challenging cases, actions may affect not only the immediate reward but also the next situation and, through that,

all subsequent rewards. These two characteristics—**trial-and-error** search and delayed reward are the two most important distinguishing features of reinforcement learning.

Reinforcement learning (RL) formalizes the problem of learning an optimal behavior policy from the experience directly collected from an unknown environment. Such general model already provides powerful tools that can be used to learn from data in a very diverse range of applications (e.g., see successful Correct behavior, reinforcement learning is trying to maximize a reward signal instead of trying to find hidden structure.

- It Differs from normal machine Learning as we done the training data sets
- Interface between the environment through the real world scenarios
- As reinforcement learning is based on many parameter come to play and to learn about and act accordingly
- The reinforcement learning to use the to reach the goal
- Reward in reinforcement learning obtained the environments

To demonstrate some key ideas, we start with a simplified learning algorithm that is suitable for a deterministic model, namely:

st+1 = f(st, at)
rt = r(st, at)
We consider the discounted return criterion:
V π (s) = ϒt r(st , at), given s0 = s, at = π(st)
V ∗ (s) = max π V π (s)
Recall our definition of the Q-function (or state-action value function), specialized to the present deterministic setting:

Q(s, a) = r(s, a) + ϒV ∗(f(s, a))

The optimality equation is then

V∗(s) = maxaQ(s, a)

applications of RL to computer games, energy management, logistics, and autonomous robotics). Nonetheless, practical limitations of current algorithms encouraged research in developing efficient ways to integrate expert prior knowledge into the learning process. Although this improves the performance of RL algorithms, it dramatically reduces their autonomy, since it requires a constant supervision by a domain expert. A solution to this problem is provided by transfer learning, which is directly motivated by the observation that one of the key features that allows humans to accomplish complicated tasks is their ability of building general knowledge from past experience and transfer it in learning new tasks. Thus, we believe that bringing the capability of transfer of learning to existing machine learning algorithms will enable them to solve series of tasks in complex and unknown environments.

Reinforcement learning is different from supervised learning, the kind of learning studied in most current research in the field of machine learning. Supervised learning is learning from a training set of labeled examples provided by a knowledgeable external supervisor. Each example is a description of a situation together with a specification—the label—of the correct action the system should take to that situation, which is often to identify a category to which the situation belongs.

Reinforcement learning is also different from what machine learning researchers call unsupervised learning, which is typically about finding structure hidden in collections of unlabeled data. The terms supervised learning and unsupervised learning would seem to exhaustively classify machine learning paradigms, but they do not. Although one might be tempted to think of reinforcement learning as a kind of unsupervised learning because it does not rely on examples of or, in terms of Q only:

Q(s, a) = r(s, a) + ϒ maxa'Q(f(s, a), a')

Our learning algorithm runs as follows:

• Initialize: Set Q^(s, a) = Q0(s, a),
for all s, a. • At each stage n = 0, 1, . .
. : – Observe sn, an, rn, sn+1.
– Update Q^(sn, an): Q^(sn, an) := rn + ϒ maxa' Q^(sn+1, a')

THE DIFFERENCE BETWEEN MACHINE LEARNING

The similarities of the above algorithms are:

- A machine learning algorithm learns from past experiences and produces an output based on the experiences.
- The algorithms have strong relations to mathematical optimization.
- The algorithms are related to statistical computation.

Supervised learning	**Unsupervised Learning**	**Reinforcement learning**
The output is based on the training data set. classification is used here	The output is based on the clustering of data.	The output is based on the agent's interaction with the environment. It used deterministic or nondeterministic way of learning.

Priori is necessary	Priori is not necessary.	Priori is required.
It will always produce same output for a specific input.	It will produce different outputs on each run for a specific input.	The output changes if the environment does not remain same for a specific input.

CONCLUSION

Machine Learning Research spans almost four decades. Much of the research has been to define various types of learning, establish the relationships among them, and elaborate the algorithms that characterize them [9]. But, much less effort has been devoted to bring machine learning to bear on real world applications. But recently researchers have found broader applications of machine learning to real world problems. Some of these are:

- Bioinformatics
- Brain-machine interfaces
- Classifying DNA sequences
- Computational finance
- Computer vision, including object recognition

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Human Resource in Digital Era: A Paradigm towards Progress

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Abstract

This topic is a general overview of the digital transformation and its implications on management, digital transformation is no longer a niche subject as it jumps into the boardrooms of leaders in the tech sector and industries, regions and geographies. The Digital India program is a flagship program of the Government of India, with a vision to transform India into a digitally empowered society and knowledge economy. The current digital age is but a stepping-stone in the development of a world enabled by the exponential use of technology in the workplace. The digital age is advancing at such a rapid pace that it is fundamentally changing the way organizations operate, whether in the private or public sector, and they need to develop new ways of thinking about service delivery. Which affect the operating model has been made. We therefore discuss the impact on the functions of human resources (HR) and all other management areas in an organization and their role in identifying new approaches to managing people and the entire organization.

Digitization is of critical importance for data processing, storage, and transmission, as it "allows all types of information to be carried across all formats with the same efficiency as well as interlaying". Digitalization is often seen as an essential factor in the 4th Industrial Revolution and being such a factor, it is powerful enough to have implications on current and future management practices. The need to connect with others and the critical thinking of social intelligence, soft skills, empathy, passion, open mind, creativity, innovation and human resource management.

Keywords- Digitalization, Human resources management practices, future challenges, digital transformation, digitalization management effects.

Introduction

Companies that embed digital transformation into their strategic framework are leveraging digital technologies to change their business models, their operations, and their interactions with stakeholders. In all industries, HR (HR) is one of the areas most affected by digitization - whether through big data analytics, social networks or mobile solutions. Digitization offers many new challenges, HR departments, which offers an exceptional opportunity to be strategic in their organizations and to strengthen their roles in the re-design of e, addressed the needs of HR professionals in the field is necessary for digitization, which are targeted to the needs of HR activities clearly defined strategic and operative In addition to the inclusion of the corporate culture and the development of digitalization. Digital natives and the older generation are no different from what they are looking for in owners. Employer attraction, safety, leadership and workplace position are very important for both groups.

The world has undergone cultural, social and economic changes based on the growing dominance of digital technology. In sum, these changes have led to the present era being classified as a "digital age". In line with these changes, digital technologies play a significant role in the lives of employees and in human resource management (HRM), which seem to be affecting in many ways. This special issue focuses on the impact of these changes on HRM, changes in the workforce, the use of technology in delivering HRM activities in general, and more specifically to HRM.

Why Digitization?

It is known for the big data it contains. To manually calculate this data, it takes several days and workers in this field can verify it. Much of the information in the manual system is generalized and mediated and because of this; The company is suffering from a lack of accurate data. We cannot afford to close our eyes to the most common technology. All we can do is get up and come up with the technology to work for you. We are so accustomed to completing everything manually that the software works on our behalf. This is why technology is invented, to completely eliminate the work that we manually do and in return help us accomplish more than we could ever accomplish on our own. Technology is here to stay and the best we can do is get on board and learn from it now before it grows too much and we are not able to catch up with it. Fear of failure and making mistakes, especially in business can keep you enslaved for the longest time. Establishing a new easier way to manage this data is a sign of relief for many individuals and companies. This can only happen through digitalization of the Human Resource Department. Digitalization of this sector will help the HR workers to ascertain specific details that help them improve in their decision making over the management of people. This in return will feed the company with accurate information that will help in achieving the set objectives.

Where to Start in Digitalization of the HR Department?

There is always a starting point for everything in this good earth. You only need two things - determination and expertise. With so much knowledge freely shared on technology platforms, we cannot say that we are short-changed. Before we start today, it's too late.

Today, there are a large number of well-learned followers who know the world of technology behind their hands. Such technology specialists are within or without our companies, but not far from our reach. There are people you bring on board to start and share ideas with them to help them begin their long journey to freedom. Before that, make sure that your HR department has a team of people who are flexible, enthusiastic and ready to learn and of course, literate. Such people will take seriously what is placed in their hands. Simply selling the idea to experts and then cracking the idea to them, defining it in terms of technology, developing tools to use and so on. At this point, we want to clarify that it is easier than what was done. Do not assume that what is suggested will automatically work, 90% of it fails. Do not try to take whatever has been suggested and take it down the throat of HR personnel, it will not work. Take time with this group of experts and allow them to try it out with your HR group. This is the only way you will be able to tell what works and what does not. It is also important to talk to other companies that have successfully digitized their HR department ahead of you. It equips you with smart ideas to handle matters in a more creative way. Realizing your weaknesses as a business is not a weakness; Rather, it is a strength because learning to do the right thing will make you better. Okay, it can cost the business some money and maybe move downstream but in the long run, the learned truth has benefited from it. There are simple easy steps that you can take to help you strategize by adopting how you will digitalize your HR field and all areas of your business.

What Does Digitalization Require?

Digital HR will require the creation and flow of mobile applications, design thinking, behavioral economics, and the use of fixed analytics. We have to realize that this is not just about building apps and all, but also developing platforms that have a wide range of apps built with analytical and cloud technology.

Creating such platforms allows you to use hundreds of applications on it, such as recruitment, collaboration, goal setting, employee attendance, employee welfare and many more. Designing such a platform allows you to integrate all data in one place, which is used to make recommendations throughout the day to users.

Digitalization challenges

- **Digital workforce:** How can organizations drive new management practices (what we call "digital DNA"), a culture of innovation and sharing, and a set of talent practices that facilitate a new network-based institution?
- **Digital workplace:** how organizations can create a working environment that enables productivity; Uses modern communication tools (such as the workplace by Facebook, Microsoft Teams, and many others); And promotes engagement, well-being and a sense of purpose?

- **Digital HR**: How can organizations change the HR function itself to operate in a digital way, use digital tools and apps to deliver solutions, and continuously experiment and innovate?

This shift is occurring rapidly, as HR leaders are being inspired to take on a larger role to help the organization "go digital", not just "do it digital." In the last five years, HR discipline has grown rapidly. Three years ago, we wrote about HR's "race to the cloud", as companies raced to replace legacy talent systems with legacy HR platforms. Two years ago, we characterized HR as a "need for makeover" as a function, as companies focused on reorganizing HR professionals, integrating the organization, and implementing analytics. This year, as digital management practices and agile organization design become central to business thinking, HR is changing again, focusing on people, work, and platforms. We refer to the resulting set of HR practices as "digital HR". Today, the focus of HR has shifted towards building the organization of the future. Companies are hiring young, digitally savvy workers who are comfortable working on their own and sharing information in a transparent way. They want an integrated, digital experience at work - which is built around teams, productivity and empowerment - and HR hopes to deliver it.

New equipment and expanded transport facility Digital HR

To empower employees to have more control over their career management, IBM developed a proprietary career management system, which helps people find new jobs and recommend new assignments by looking at their peers' patterns. Within HR, IBM leveraged the company's AI investments in Watson to use CIP (Cognitive Human Interface Personality), a cognitive assistant that can handle a wide range of HR-related questions. CHIP is an intelligent platform (available via computer, text message and soon voice) that identifies the 200 most frequently asked employee questions (such as "Tell me about the benefits of my leave" or " Find me an expert in digital marketing ") and become smarter all the time. The system has already reduced call center time and is proving popular with employees. IBM, a global company with more than 400,000 people, is leading the transition to digital HR, using a variety of experiments to drive a new digital HR solution. Following an employee hackathon, the company strengthened its performance management process by building a checkpoint, a new feedback process that dramatically increased engagement, alignment, and goal management.

For continuous learning, IBM discontinued its traditional global learning management system and replaced it with a new digital learning platform. The new system enables employees to publish any content they feel is important, curates and recommends training based on role and experience and integrates external learning from the Internet.

Development strategies

• **Redefine your mission:** HR today should define its role as a team that helps management and employees change rapidly and adapt to a digital way of thinking. Familiarize yourself with network organization structures, organizational network analysis and digital leadership models.

• **Upgrading core technology:** Replace legacy systems with integrated cloud platforms for sound digital infrastructure. Upgrade older tools for learning, hiring and performance management, and bring in systems that are easy to use for employees.

• **Develop a multiyear HR technology strategy:** In today's fast-changing HR technology world, it is important to create a multiyear strategy that includes cloud enterprise resource planning (ERP) platforms, apps, analytics and AI, case management, and a range of tools Is included other solutions.

• **Build a digital HR team:** Dedicate teams to explore new vendor solutions and build others, and consider AI solutions to improve service delivery, recruitment and learning. Companies such as RBC and Deutsche Telekom now have digital design teams in HR, who work with IT to design, prototype and roll out digital apps.

• **Organize HR into a network of expertise with strong business partners**: Rethink your HR organization model to focus efforts on the new world of employee experience, analytics, culture, and learning. Make sure these teams communicate well: High-performing HR teams share leading practice and know what other teams are doing.

• **Make innovation a core strategy within HR**: Push yourself to reinforce and innovate in each people's practice. Many organizations are now using new performance management practices that are built around design sessions and hackathons. Investigate new innovations in recruitment, including using data to find high-performing people in the company.

• **Rotate younger people in the HR profession:** Rotate people in and out of HR regularly from business, use innovation teams to reverse-mentor senior leaders, and bring people with analytics skills into the profession by recruiting new MBAs .

• Benchmark: Visit other companies to see what they are doing. HR teams can bring in outside speakers, join research membership programs, and continuously seek out new ideas to promote innovation. Today's leading practices come from innovative ideas developed around an organization's culture and business needs, not from a book.

Conclusion:

Digital technologies can improve manufacturing operations. By automating processes, identifying weaknesses and bottlenecks in the production chain and in the supply chain, testing new ideas before implementing them, your business can save time and money. A digital factory design is a far more flexible workplace. Instead of the traditional, linear approach, where machinery is built based on designers' drawings and development cycles are silenced, digitization makes it possible to plan and develop in tandem. In this way, potential weaknesses can be identified and fixed as you go, rather than as an obstacle. Encouraged by new technologies such as 3D modeling systems and data connectivity, factories can be configured and reconfigured faster than ever for less money. Digitization gives you the opportunity to introduce rigorous quality management and control both for your own products and for your suppliers. Along with providing mental peace, you will also easily meet compliance demands. Customers will be happier, while employees will enjoy their work more. If you have a technologically advanced operation, you will also become more attractive to new employees.

Suggestions:

From the information mentioned, it is easy to tell what digitalization can accomplish but it's not all easy without hitches. Cooperation from all sectors is key in order to enjoy the end-product you want to see. The integration of the Human Resource Department being the hub of every business will fuel it to run smoothly and relationships will be highly improved; not forgetting the data will be precise and accurate.

The Human Resource Digitalization transformation is big and cannot be done in a rush. It has to begin with a change of mind-set within the HR department and every other sector in the business. The business rises from the art of teamwork, and digitalization is one of the key areas that require this kind of teamwork that brings achievements. Everyone in the business has to embrace the forward move right from the beginning to make it smooth sailing. They have to come to the level where they prioritize connectivity, real time operations and automation.

This should be viewed as a revolutionary opportunity all over the company, not just as a one sector responsibility. This is only a small section of digitizing the entire company. This being a very sensitive sector that determines the relationship between the HR and the employees, it must be handled with care. With the right approach that does not threaten the employees; the new technology will be embraced and worked towards with the right attitude.

There is still a long way to go until the HR sector is settled in the technology world and we can toast to that. A journey of a thousand miles starts with one step, its better you start yours today! You have the opportunity to showcase your company's success just like the above example of a successfully digitized company. Remember once you digitize the first sector in your business, all the rest will be easily integrated and brought on board to enjoy a fully digitized company that enjoys life the 21st Century way.

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ONLINE MARKETING: CHALLENGES AND ADVANTAGES

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Abstract:

Online marketing, which is also called internet marketing, involves use of interactive, virtual spaces for the sake of promoting and selling goods and services. In fact, new synchronous, internet-based communication technologies had contributed to the restructuration of major economic sectors including marketing. Being cost-effective, flexible, and fast and enjoying an on unprecedented global reach, internet marketing has brought about different businesses incredible gains. However, this effective, new method also involves its special disadvantages, e.g. lack of personal contact, security and privacy, etc which should be taken account for. The present study, then, concentrates upon the impacts of internet-fostered interactive spaces on marketing practice. The paper starts with defining online marketing and reviewing historical background to utilization of online marketing; different kinds of internet marketing, then, will be shed light upon. The marketing Advantages stem from introduction of this new, virtual space is the next focal point of concentration. The study continues with challenges, such as problems of security, privacy, etc, emerged in the field of marketing from implementation of virtual space produces. Contemplating the solutions to tackle the challenges ahead, we provide the conclusions.

Keywords: Online marketing, offline marketing, Internet, Challenges, Advantages.

Introduction:

Now it is a well-known fact that what we call 'marketing' has undergone substantial changes over the recent years (Petkus, 2010), and the key role in this transformation has been played by internet. Internet "refers to the physical network that links computers across the globe. It consists of the infrastructure of network servers and wide area communication links between them that are used to hold and transport the vast amount of information on the internet"(Chaffey, 2000: 12). Several studies have addressed the way in which introduction of internet have reshaped the structure and performance of different sectors, e.g. hospitality, travel and tourism (Xiang et. al 2008; Beldona 2005; Gretzel, et al. 2006; Kah, et al. 2006; Pan and Fesenmaier 2006; MacKayet al 2005; Weber and Roehl 1999), health and medicine (Rupoert, 2001; Datta, et al., 2008; Gadish, 2007), marketing education (Hollenbeck, et al. 2011; Eastman and Swift, 2001; Kynama and Keesling, 2000, etc. Introduction of internet has changed the rules and marketing practioners have no way but to adhere to it (scott, 2009:8). In fact marketing is just one of numerous fields have been substantially revolutionized by internet-based technological innovations. Halloway maintains that "Information and communication technology, as it is now known, has come to play a key role in all elements of the marketing mix, and the new term recognizes the importance of communication in the interface between a business and its customers" (2004). The most prominent point regarding the advent of Internet to the center stage of commerce and marketing is that Internet is not considered merely a new channel of promotion, a new type among other traditional, pre-Internet types of marketing goods and services. Quite contrary, it has brought about a turning point, a complete shift to a new business model, which results in an inevitable reconceptualization of the very nature of marketing (Deighton 1997; Wind and Rangaswamy 2001). This new understanding is inevitable since new communication technologies have fostered a new dynamic environment in which marketer oriented, top-to-down, unilateral approach gives its place to a customer-oriented, bottom-to-up, reciprocal process.

What is online marketing:

Kotler et al., 2010: 493) Online marketing consists of measures and activities to promote products and services and build relationships with customers over the Internet. Burrett (2008) understands online marketing as ―carefully targeting users and getting them to interact with you while they'reengaged with the most personal, intimate medium ever invented‖ (44). The most comprehensive definition has been articulated by Chaffey (2007), he defines online marketing as ―Applying Digital technologies which form online channels (Web, e-mail, databases, plus mobile/wireless & digital TV) to contribute to marketing activities aimed at achieving profitable acquisition and retention of customers (within a multi-channel buying process and customer lifecycle) through improving our customer knowledge (of their profiles, behaviour, value and loyalty drivers), then delivering integrated targeted communications and online services that match their individual needs". As this relationship concept definitions show online marketing revolve around interaction and building relationship with customers, a point which discriminates it from traditional, offline marketing.

Historic Background:

Internet has its origins in cold war and technological rivalry between USSR and US. In fact "while the World Wide Web was created in 1991, its origin dates back to 1957 when the Soviet Union launched the Sputnik I satellite" (Dickey and Lewis, 2011: 2). US reacted with establishment a department of Defence Advanced Research Project Agency (DARPA) which launched in 1960s ARPANET, an experimental project of computer networks from which what we now know as internet developed. Since then internet contributed to science incredibly and "by the late 1980s the internet was being used by many government and educational institutions" (Ferguson, 2008: 69). So internet was considered an inclusive communicative tool of scientific and research centres for several years and its academic function was its dominant prior to discovering its commercial capabilities which led to its commercialization. As Oksana (2007) puts it: "until the mid-nineties, the research and academic communities accounted for most of the internet population but the commercialization of internet soon gained enormous momentum and the business community quickly became aware of the potential it has to offer"(47). With increasing the number of internet users during the 1990s, entrepreneurs started to appreciate commercial prospects of this new medium. Although there is no complete consensus on when did internet marketing exactly start, but the majority of commentators refer to 1994. So it is widely held that "significant commercial use of the Internet began with the first _banner ads' on web pages in 1994, and the appearance of Internet-based _malls' (the electronic equivalent of a storefront) such as Amazon.com in 1995". Statistics make it clear that this young marketplace, online marketing, has had an astonishing rate of growth. So amazing is the growth rate of this new paradigm of marketing that it is hard to believe how young it is. In fact "in 1994, spending for internet marketing totalled nearly nothing, but increased to over $300 million in 1995. After a decade later, marketing spending and internet marketing business has exploded to nearly $500 billion (according to Forrester Research). Today, it's hard to believe in having an organization which doesn't have some kind of online presence." (Shirvastav and Alam, 2014: 25) This brief historic background is concluded by pointing to the fact that step by step online marketing has became a much more sophisticated practice. So early methods of internet marketing such as online advertising and email marketing has been followed by more younger, developed methods such as search engine optimization or social media marketing.

Different methods of online marketing: Online marketing which is also called internet marketing and e-marketing includes several methods and techniques which are introduced briefly as follows:

Online Advertising: The most known technique of online marketing is online advertising. In this method virtual space is used to put marketing messages on websites to attract internet users. Just similar to methods offline marketing and other types of online marketing, the major objective of online advertising is to increase sales and build brand awareness. Online advertising involves using of internet for displaying promotional

messages on the computer screens (Duguay, 2012) and refers to "deliberate messages placed on third-party websites ... search engines and directories available through Internet access" (Ha, 2008: 31). Online advertising similar to TV ads uses the element of interruption. But it uses it in a much more creative. Contrary to TV advertisement, online advertisement do not force the recipient to pay attention to the promotional peace, but it tries to persuade or attract s/he to do so, because instead of coming in intervals it is placed along or among other non-marketing contents. The now empowered internet recipient still has the power to ignore the advertisement and it is totally up to her/him to click or not. Online advertising, sometimes called display advertising, uses different methods to display a marketing message online. Needless to say that with the progress of technology, new ways of practicing the art of online advertisement is developed. In addition to images, pictures, logos etc, other different methods now used in this field including interstitial banners, pop-ups and pop-unders, map adverts, floating advert, banner advert (stokes, 2009: 30).

Email-marketing: E-mail marketing, using e-mail for sending promotional messages to internet users, has been considered one of the more effective methods of online marketing. Several researchers have shed light upon privileges of conducting online marketing this way (Wreden, 1999; Jackson & DeCormier, 1999; Raad et al., 2010; Nial, 2000). In this regard Peppers and Rodgers (2000) among its benefits point to "high response rates" and "low costs" of email marketing and believe that this advantages "are rapidly turning email marketing into an invaluable tool"(4). Despite these benefits email marketing suffers from deficiencies. One these problems are that online customers can easily ignore the received advertisements and even some email clients would decide to put them in the spam folder. So some measures should be taken to overcome the possibility of ignoring promotional emails on the part of customers. One of the solutions is to not solely rely on email marketing. Marketers should employ different channels and methods of marketing to increase the chance of success. Another measure to transcend problems of email-marketing is permission email marketing. "Permission marketing" has been coined by Godin (1999). In this method recipients are asked for their permission to receive marketing messages from the commercial marketers. So unless the recipients have not expressed their consent, they will not send commercial emails.

Search Engine Optimization (SEP): Nowadays it is hardly possible to imagine a business which has not its own website. But having a well-designed website does not necessary result in an ideal amount of visits. In order for this goal to be accomplished another type of online marketing, called SEM should be adopted. In fact, one of major methods of conducting online marketing is search engine optimization, which is also called search engine marketing. Davis (2006) defines it in this way: "SEO - short for Search Engine Optimization - is the art, craft, and science of driving web traffic to web sites… web traffic is food, drink, and oxygen – in short, life itself – to any web-based business" (2). Parikh and Deshmukh (2013) also offer this definition: " Search engine optimization can be described as a cluster of strategies and techniques used to increase the amount of visitors to a website by obtaining high-ranking placement in the search results page of a search engine (SERP)" (1). The importance of search engine optimization lies in the fact that customers most of the time use engines as a major gate to get around in the internet. So some marketing techniques have been developed to enhance the rank of intended business websites in the search engine results. The purpose of SEO strategies is to place a given website among highly listed entries returned by search engines which in its turn produces more traffic. So, "Web site owners, webmasters and online marketers want search engines to send traffic to their site. Therefore, they need to make sure that their sites are relevant and important in both the eyes of the search engines and the users." (Stokes, 2009:70)

Affiliate marketing: Affiliate marketing is a major component of package of online marketing methods and refers to the process of gaining a commission by promoting products or services of another company. Also in this method two or more website owners can build relationship to increase mutual financial benefits. With respect to its definition, "affiliate marketing is simply defined as : A web-based marketing practice , often using automated systems or specialized software in which a business rewards their affiliate for each visitor, customer, or sale which is brought about as a result of affiliate's marketing efforts. In most cases, the reward

is monetary in the form of a monthly check. Most well-designed affiliate programs are easy to implement, require little or no setup, are free, and can instantly generates a new source of revenue for you"(Brown, 2009:17). Affiliate marketing has been used in a number of businesses for promoting products and services offline. But online environment has extends the prospect of deploying this method dramatically. The reason is that referral or affiliates are very easy to track online. This system of marketing is widely used to promote websites and affiliates are compensated for their effort to attract every single "visitor, subscriber, or customer". These affiliates sometimes are considered to be "an extended sales force" at the service of a website. Because affiliates are rewarded based on their performance, affiliate marketing is also called "performance marketing" (stokes, 2009:46).

Social Media Marketing: Social media has changed every aspect of our life dramatically. In fact it has become "the method of statement in the 21't century, enabling us to express our belief, ideas and manner in an absolute new way ". Beyond changing our way of conducting social life, social media provides world of marketing with unprecedented opportunities and "also have a huge impact on corporation, where they have realize that without a correct plan and social media strategy they have no chance to stand out in the rapidly changing digital freedom" (Saravanakumar and SuganthaLakshmi, 20012: 44). Social Media marketing, thus, has become increasingly a priority without taking which into consideration marketing cannot realize its objectives. Social media especially is promising for small businesses because increases their competitive edge. This new rewarding type of marketing, social media marketing, can be easily defined as" a term used to describe the process of boosting website traffic, or brand awareness, through the use of social media networking sites…most social media marketing programs usually revolve around creating unique content that attracts attention and encourages the viewer to share it with their friends and contacts on social networks. Your business message spreads from one user to another and impacts with the user in a stronger way because it appears to originate from a trusted source, as opposed to the brand, business or company itself" (2014: 2). As is apparent from the above citation the key element of social media marketing is involving user of social networks. If users / readers come across a right and relevant content the likelihood of sharing it with other people in their social networks increases. So if a marketing body succeeds in making social media users share its promotional content with people in their network it that means that it has gained support from a trusted source and possibly will be regarded highly by the recipient. Clearly a promotional content shared by a close friend has much more impact than content directed from the part a marketing party. The impact of contents shared by social network members is high due to the fact they are originally kind of a "word of mouth" circulating on the online environment. With respect to pillars of social media it should be noted that the “social media comes in many forms … [such as] blogs, micro blogs (Twitter), social networks (Face book, Link), media-sharing sites (YouTube, Flickr), social bookmarking and voting sites (Digg, Redit), review sites (Yelp), forums, and virtual worlds (Second Life)" (Zarella, 2010: 3).

Viral Marketing: Another method of conducting online marketing which overlaps remarkably with social media marketing, due to centrality of "word of mouth" to it, is called Viral Marketing. Viral marketing, in fact, is "a form of word of mouth marketing which aims to result in a message spreading exponentially. It takes its name from a virus, because of the similarities that marketers aim to emulate: It is easily passed on. The number of people who have been iinfected grows exponentially"(Stokes, 2009: 150) Viral marketing is a new concept which has been developed with the advent of Internet. Viral marketing spreads through social networks and it is a virtual version of word of mouth. It is a very cheap mode of marketing and if you use it there is no need to spent massive amounts of money on traditional expensive marketing campaigns. Viral marketing works through encouraging people to share, pass along, and forward a marketing message; it is based on a high rate of pas-along form a user to another user. It is clear that harnessing such a powerful instrument, word of mouth, and having others share your products and sell it, guarantees the success, even compared with launching a classical marketing campaign. Among other means of promotion and building brand awareness such as images, jokes, e-carts etc, viral marketing campaigns employ creative digital videos as well. Digital videos are most useful according to Kirby (3006) due to following reasons:

1. They are small enough to be passed from peer to peer via email after downloaded from multiple distribution websites, encouraging greater user-driven spread.
2. They trackable after downloaded, as they are passed form user to user via email, so they are provide brands with greater campaign accountability.
3. There is a less risk of user interference with the agent.
4. Video is familiar, ad-like/film-like format to users, with the added advantage of interactivity (digital video files can include hotspots that enable users to link through the file to a web page).

Advantages of Online Marketing:

Empowering effect: One of advantages of online marketing is related with its enabling effect especially on small businesses since "internet can extent market reach and operational efficiency of small and medium interprises (SMEs)"(Dholekia and Kshetri, 2004: 311). In fact internet creates a kind of democratized environment in which marketing has been restructured in such a way that even small businesses are given a good chance to promote and brand their products on a much more larger scale (Jobber, 2001; Tapp, 2008). It should be, therefore, stressed that "internet has created unprecedented opportunities for small businesses to engage in national and international marketing campaigns which could have been unaffordable due to the huge amount of resources required" (Poon and Jevons, 1997: 29). Email marketing, bogging, launching web-sites, etc are among easily affordable inter-fostered channels than can provide small business with the ability to survive and compete.

Elimination of geographic barriers: One of the key advantages of online marketing is that it removes all geographical limitation from the practice of buying and selling. So internet allows an unlimited global reach (Allen and Fjermestad, 2001; Teo and Tan, 2002; Sigala, 2008) at on outstandingly lower cost. Due to massive cost of traditional media, global reach was once the exclusionary realm of huge multinational corporation, but the advent of cost-effective internet technologies has enabled smaller businesses to enjoy this kind of reach. Overcoming the geographic barriers, marketers are now able to present products and services to different groups of costumers across the universe with the simple condition that they have access to internet (Mohammed, 2010: 2).

24 hours / seven days availability: Internet now can provide customers with timely information due to its availability 24 hours a day, 7 days a week (Lane, 1996). So, due to the establishment of online shops, customers are now able to acquire information and shop online any time of day or night they wish and prefer. So there remain no time limitations in this regard because online businesses have no special closing and opening times. People may visit physical markets after searching internet or the other way round they can surf internet for competitive prices after visiting physical stores. (Sharma, 2011: 203). Besides that there is no doubt that online purchase is more convenient since there is no need to go out of home, visiting different stores and take the burden of comparing different products and prices. The buyers can do their shopping much more effectively from the comfort of their homes. Needless to say a lot of time and energy is saved this way.

Cost-effectivity: It goes without saying that, compared with traditional advertising media channels, which are very resource of gaining a commission by promoting products or services of another company. Also in this method two or more website owners can build relationship to increase mutual financial benefits. With respect to its definition, "affiliate marketing is simply defined as : A web-based marketing practice , often using automated systems or specialized software in which a business rewards their affiliate for each visitor, customer, or sale which is brought about as a result of affiliate's marketing efforts. In most cases, the reward is monetary in the form of a monthly check. Most well-designed affiliate programs are easy to implement, require little or no setup, are free, and can instantly generate a new source of revenue for you"(Brown, 2009:17). Affiliate marketing has been used in a number of businesses for promoting products and services offline. But online environment has extends the prospect of deploying this method dramatically. The reason

is that referral or affiliates are very easy to track online. This system of marketing is widely used to promote websites and affiliates are compensated for their effort to attract every single "visitor, subscriber, or customer". These affiliates sometimes are considered to be "an extended sales force" at the service of a website. Because affiliates are rewarded based on their performance, affiliate marketing is also called "performance marketing" (stokes, 2009:46).

Trackability: Another aspect of the online marketing is its possibility of tracking. In fact "the track-ability of Internet Marketing is one of its greatest assets" (2014). Internet enables measurement of everything taking place on it. So, the number of clicks that a particular promotional piece receives and amount of website traffic is easily measured. In this way the marketer is enabled to track the visitors to her/his website and understand their behaviour. Internet also allows the companies to find out whether their campaigns are working or not, what kind of customers are interested in their products, from where? The ability to track online customers increases dramatically due to the fact that "internet constitutes the most accountable media ever. Web site log software and real-time profiling track the number of users who view each page, location of previously visited pages, date of view, time of view, duration of viewing, links followed, and so on" (Granitz and Greene, 2003: 19).

Personalization: Personalization which comes with customization is another important aspect peculiar to marketing online through internet. So online marketing is a personalized marketing which is also called marketing to the Segment of One or "one-to-one marketing" (Peppers and Rogers,1993). But what is personalization? Personalization refers to tailoring products and services to customers' preferences based on their online, registered purchase history. In fact "since electronic interaction with customers allows the gathering of detailed information on the needs of each individual customer, firms can automatically tailor products and services to those individual needs" (Karavdic and Gregory, 2005:80). This process results in offering customized products to customers. In this way customers are send personalized messages which produces much greater impact compared with impersonalized, generic messages send indiscriminately to mailbox of customers. Personalization results in formation of sustainable relationship with customers; as Riecken (2000) puts it "personalization is about building customer loyalty by building a meaningful one-to-one relationship; by understanding the needs of each individual and helping satisfy a goal that efficiently and knowledgeably addresses each individual‘s need in a given context"(26). Based on metrics internet helps marketer to gather, customer, for instance, can be greeted with targeted offers whenever they visit website. So with the aid of gathered data of customers preferences, the sites can be customizes for the target audience which brings about an increasing interaction and builds up a "sense of intimacy" between marketer and audience. This is especially important due the fact that traditional modes of marketing such as Mass media, TV, and newspapers cannot be shaped by their users' needs, demands, inclinations, and preferences. So personalization and customization is obviously considered a major advantage or opportunity of online marketing via internet (Bhui and Ibrahim, 2013: 223)

Challenges of Online Marketing:

Problem of integrity: Integrated marketing has been a central theme of the profession (Clown and Baak, 2013; Kitchen and Burgman, 2010; Blech and Blech, 2013). On the other hand one of major problems with marketing campaigns is that they employ several offline and online promotions channels such as press, brochure, catalogue, TV, cell phone, e-mail, internet, social media etc, while lack a comprehensive, harmonizing marketing framework. Each item is used in isolation and accomplished as a different task not as a component of an integrated campaign aimed at realization of specified and particular objectives. This deficiency can be compensated for by taking a holistic approach which synchronizes different traditional and internet age modes of marketing communication as moments of an integrated structure. With respect to virtual, online component of an integrated marketing what is "also worth noting (or reminding) is that like offline marketing, all aspects of online marketing are inextricably linked- and in many cases interdependent. Therefore none of the element marketing should stand in isolation. The website will never be visited if there

are no links to it; viral marketing requires email or social media websites to communicate the message and search engines are useless without websites to link to it. So it is that in any internet marketing strategy all components must dovetail together (Charlesworth, 2009:341).

Lack of face-to-face contact: Lack of personal contact is another deficiency of online marketing which has been addressed in online marketing research and literature (Goldsmith and Goldsmith, 2002; Phau and Poon, 2000). Internet transactions involve no embodied, personal interaction and that is why some customers consider electronic modes of providing customer service impersonal and enjoy the experience of shopping in a bricks and mortar, physical store. They prefer to talk to store personnel in a face to face manner, touch the related product with their hands, and socialize with other customers. Virtual marketplace cannot provide for this function of offline shopping and lacks personal interaction. To be more specific "for the types of products that rely heavily on building personal relationship between buyers and sellers such as the selling of life insurance, and the type of products that requires physical examination, Internet marketing maybe less appropriate" (Kiang and Chi, 2001:159). Face to face contacts is not important just in the case of special types of products; here culture is also a relevant variable. For example Rotchanakitumnuai & Speece (2003) can be referred who have highlighted the lack of personal contact in online transactions. Among other things, they refer to Asian cultures in which personal relationships are of a prominent value and that this, together with the transaction context, is often plays a crucial role in ensuring the success of financial deals.

Security and Privacy: Information privacy is among major topics to be taken into consideration in today‘s evolving electronic world. It is clear enough that nowadays customers' data can easily be shared with other companies without asking for their permission. Moreover their more crucial personal data such as usernames and passwords are not immune from hackers (Lantos, 2011: 74). Another related problem is spas and pop-up adds which considered by majority of online customers an instance of intrusion of privacy (Drozdenko & Drake, 2002: 317). These security and privacy issues are among challenges in the way of online marketing. Effective internet marketing, therefore, depends on resolving the related problems in this regard. James W. Peltier et al. (2010) point to the role can be played by marketing curriculum and suggest "that students should be exposed to this topic in varied courses and in varying degrees of coverage" (225). The major dimension with respect to privacy is the choice or consent. This dimension has its roots in this belief that consumers whose data have been collected by the respective company should have control over the ways in which their information is used. Especially they also should be granted the right to have control "over how their personal information is used beyond the purpose for which it was collected" (ibid, 228).

Lack of trust: Closely related with the problem of security and privacy is the issue of lack of trust on the part of customers which has been recognized a great challenge on the way of online marketing growth. And it is the reason why "online trust is growing in importance as a topic of study and its influence on internet marketing strategies is increasing"(Urban et al, 2009: 179). Bart et al (2005) define trust in virtual environment as follows: "online trust includes consumer perceptions of how the site would deliver on expectations, how believable the site's information is, and how much confidence the site commands" (134). Today despite the rapid growth of online transactions several people still mistrust electronic methods of paying and still have doubt whether the purchased items will be delivered or not. On the other hand prevalence of online fraught has made customers hold negative or doubtful attitudes towards online transactions. So much more clearly remains to be done to build up the trust and convince the customers that interactions which take place in the virtual world are as real and honest as those happen in the real, offline world. No doubt, it is an ongoing, long process and needs more time to realize. It should be stressed that unless this trust has not been built, internet marketing cannot be taken advantage from to its fullest potential. So it is imperative for those in charge of online marketing revolutionalize marketing. Marketers and IT managers are challenged with the task of changing the online climate in order to gain retain online consumers. This has generated tremendous interest in learning about online trust and in developing new site designs to respond to the increased power of customers" (Urban, 2008: 39).

Conclusion: Internet has revolutionized every aspect of life including economy and marketing. Introducing major techniques and methods of online marketing, this study has shed light upon opportunities and challenges of Internet. The major advantages internet has are its Empowering effect, Elimination of geographic barriers, 24 hours / seven days availability, Cost-affectivity, Trackability, and Personalization. However, implementation of Internet in the field of marketing involves special disadvantages such as Problem of integrity, Lack of face-to-face contact, Security and Privacy, Lack of trust. Unless these dual characteristic of Internet have not been taken into consideration, it cannot be deployed to its full advantage. An online marketing framework informed by insights from such a consideration would guarantee its financial objectives.

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ROLE OF SHGs FINANCIAL EMPOWERMENT OF SCHEDULED CASTE WOMEN – A STUDY OF SCHEDULED CASTE RESERVED & UNRESERVED CONSTITUENCIES OF ERSTWHILE KARIMNAGAR DISTRICT OF TELANGANA

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Role of SHGs, Financial Empowerment, Caste Women, Unreserved Constituencies

Abstract [English]

The role of microfinance growing because it addresses the financial needs of the low-income population and it is also regarded by the policy-makers as an important instrument for financial inclusion. Microfinance brings credit, loan, savings and other essential financial services 60-90% of the global population who are too poor to be served by regular banks.

The specific objectives of the present study are to examine the patterns of income, expenditure and savings of members before and subsequent to joining of SHGs in select constituencies, to assess the perceptions of the SHG members on women empowerment before and subsequent to joining SHGs in select constituencies and to compare the perceptions of the SHG members on women empowerment of scheduled caste Women in scheduled caste Reserved and Unreserved Constituencies. The primary data was collected by administering a structured questionnaire to the primary members of SHGs sample of

200-member beneficiaries from Manakondur constituency, a reserved constituency for SC and 200 members from Karimnagar constituency an unreserved constituency were selected as respondents for the purpose of this study.

The data collected is processed and analyzed by using statistical test i.e., paired t-test was adopted. The mean score of the decision-making regarding income generation sample respondents in Manakondur stood at 3.60 and in Karimnagar stood at 4.19. This shows that the involvement in decision making regarding income generation has been improved more in Karimanagar constituency when compared to Manakondur constituency. The mean score of the repayment of credit by the sample respondents subsequent to joining SHGs in Manakondur stood at 3.46and in Karimnagar stood at 4.03. This shows that the repayment of credit has been improved more in Karimanagar constituency when compared to Manakondur constituency. Few members of a group should not be allowed to monopolize all loans. Large loans for a single borrower should be avoided. SHGs should enable the poor to decide the purpose of credit, size of the loan and repayment schedule based on viability of activity instead of leader's choice. It should also monitor the end use of credit taken by the members.

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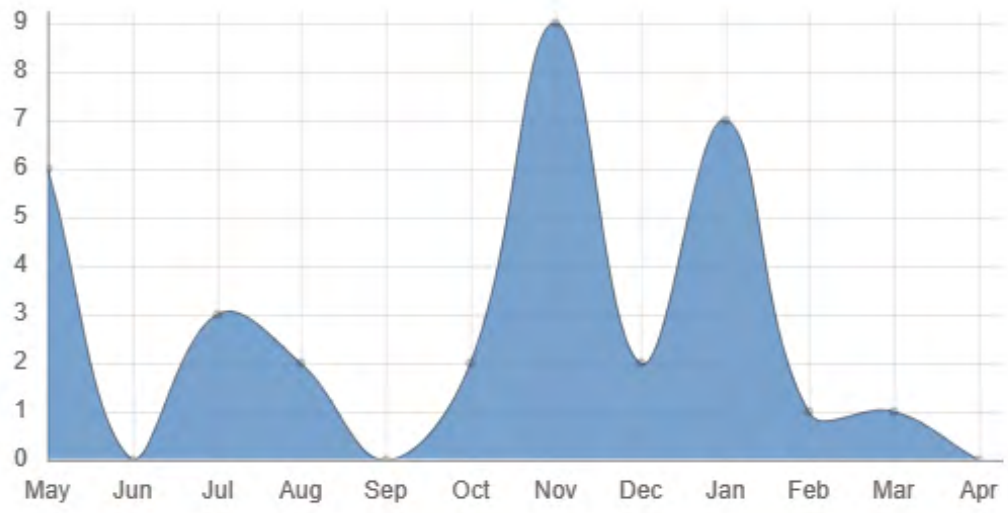

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Study of CO_2 adsorption and separation using modified porous carbon

Madhavi Jonnalagadda[1,2,*], Rumana Anjum[1], Harshitha Burri[1] and Suresh Mutyala[3,4,*]

Abstract

Porous carbon and La_2O_3/porous carbon materials are synthesized for the study of CO_2 adsorption and separation by the volumetric method. The synthesized adsorbents are characterized by X-ray diffraction, N_2 adsorption–desorption isotherms, Raman spectra and scanning electron microscopy with energy-dispersive X-ray analysis. Characterization results confirm the existence of porosity in the synthesized carbon materials and uniform distribution of lanthanum(III) oxide on porous carbon. The CO_2 adsorption capacity for porous carbon and La_2O_3/porous carbon is 21 and 33 $cm^3 g^{-1}$, respectively, at 298 K and 1 bar. High adsorption of CO_2 is obtained for La_2O_3/porous carbon because of the electrostatic interaction between La_2O_3 and CO_2. Moreover, the N_2 adsorption capacity is 2.8 $cm^3 g^{-1}$ for porous carbon and 2.2 $cm^3 g^{-1}$ for La_2O_3/porous carbon at 298 K and 1 bar. The change in N_2 adsorption is due to the decrease in surface area. For La_2O_3/porous carbon, the selectivity of CO_2/N_2 is 33.5 and the heat of CO_2 adsorption is 36.5 kJ mol^{-1} at low adsorption of CO_2. It also shows constant CO_2 adsorption capacity in each adsorption cycle.

Keywords

adsorption cycles, CO_2 capture, heat of adsorption, lanthanum(III) oxide, porous carbon, separation

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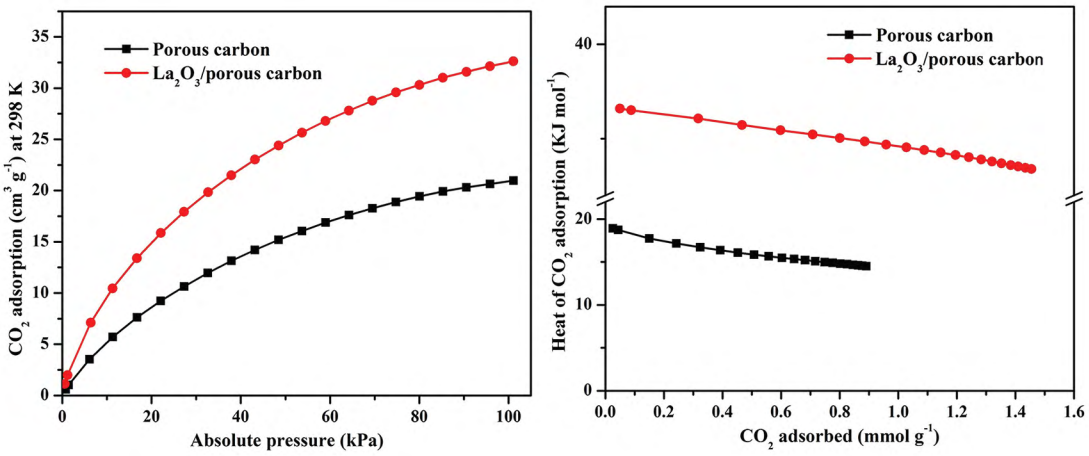

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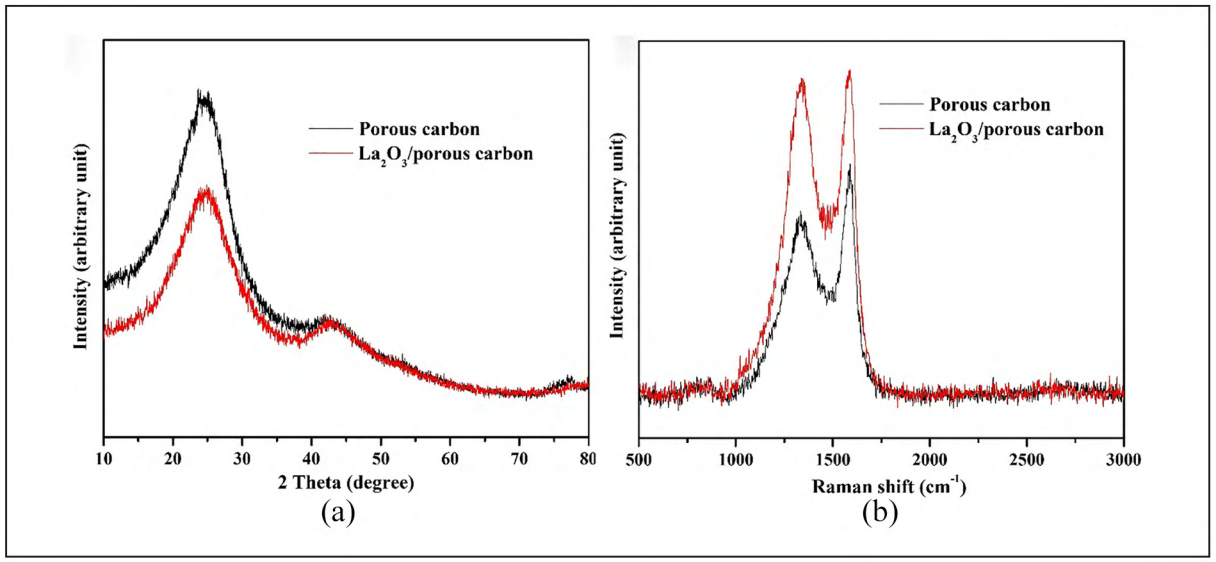

Figure 1. (a) XRD patterns, and (b) Raman spectra of porous carbon and La_2O_3/porous carbon.

Introduction

Global warming is a worldwide environmental issue which is contributed to carbon dioxide. It is liberated by the combustion of fossil fuels coinciding with the high growth of the automobile and petrochemical industries.[1] Day by day, the concentration of CO_2 is increasing and has reached 400 ppm, which is more than pre-industrial levels. Hence, greater effort has to be made to control the CO_2 concentration levels in the atmosphere. Carbon capture and separation (CCS) techniques on solid materials is an important method to lower CO_2 concentration levels, as is the liquid amine solution absorption technique. In power plants, liquid amine solutions are mostly used to capture CO_2. However, high energy is required for regeneration and occurs corrosion of the pipeline system. To overcome these drawbacks, solid materials are used for CCS. So far, materials such as activated carbon,[2] zeolites[3] and mesoporous silica[4] have been used for CO_2 capture and separation.

Activated carbon is a cost-effective adsorbent and has a high surface area. However, the production of activated carbon on a large scale is hindered because of less renewable sources. Porous carbon synthesis from renewable sources is an important aspect. Renewable sources such as sawdust,[5] rice husk,[6] waste tea,[7] biodiesel industry solid residues,[8] cotton stalks,[9] olive and peach stones,[10,11] palm oil ash[12] and coffee grounds[13] have been used to synthesize porous carbon materials. Pongamia pinnata fruit seeds are used for the production of biodiesel. During the production of biodiesel, a large quantity of pongamia pinnata fruit hulls is disposed of without commercial use. From these, porous carbon can also be synthesized by pyrolysis.

The CO_2 adsorption of porous carbon can be enhanced by the incorporation of basic metal oxide and a heteroatom, which generates basic sites on the porous carbon. The Nitrogen-doped porous carbon-derived from Hazelnut-shell has shown CO_2 adsorption capacity of 97 $cm^3 g^{-1}$ at 298 K and 1 bar.[14] Similarly, D-glucose used as a source for N-doped porous carbon synthesis and reported CO_2 adsorption capacity of 88 $cm^3 g^{-1}$ at 298 K and 1 bar, respectively.[15] Porous carbon derived from sustainable biomass stalk showed CO_2 adsorption capacity of 82.5 $cm^3 g^{-1}$ at 298 K and 1 bar.[16] MgO-incorporated mesoporous carbon has shown a CO_2 adsorption capacity of 46.8 $cm^3 g^{-1}$ at 298 K and 1 bar[17] and CeO_2-doped mesoporous carbon demonstrated 39.7 $cm^3 g^{-1}$ of CO_2 adsorption at 303 K and 1 bar.[18] The CO_2 adsorption was higher on Cu_2O and NiO-incorporated porous carbon compared to bare porous carbon.[19,20] Recently, our group reported mesoporous carbon supported MgO for CO_2 capture. This material showed 37.6 $cm^3 g^{-1}$ of CO_2 adsorption on 10 wt% MgO-incorporated mesoporous carbon which was higher than bare mesoporous carbon CO_2 adsorption 20.2 $cm^3 g^{-1}$ at 298 K and 1 bar.[21] For the reported adsorbents, high CO_2 adsorption was obtained for metal oxide incorporated porous carbon due to the electrostatic interaction between the metal oxide and CO_2. In this paper, we have studied the influence of a low content of lanthanum(III) oxide on a porous carbon towards CO_2 adsorption and separation. Moreover, CO_2/N_2 selectivity, heat of CO_2 adsorption and CO_2 adsorption cycles were studied.

Results and discussion

Structural characterization

Figure 1(a) shows the X-ray diffraction (XRD) of porous carbon and lanthanum oxide incorporated porous carbon. Two broad diffraction peaks were observed at $2\theta = 24°$ and 43.5° for the (002) and (100) planes, respectively. These were the main characteristic peaks of porous carbon.[22] Moreover, lanthanum oxide–incorporated porous carbon showed diffraction peaks similar to porous carbon and no peaks related to La_2O_3 appeared. This indicated that La_2O_3 was highly dispersed on porous carbon and/or not detectable by XRD analysis. Chanapattharapol et al.[23] have also reported similar results with iron oxide doped MCM-41 for CO_2 adsorption. The Raman spectra of porous carbon and

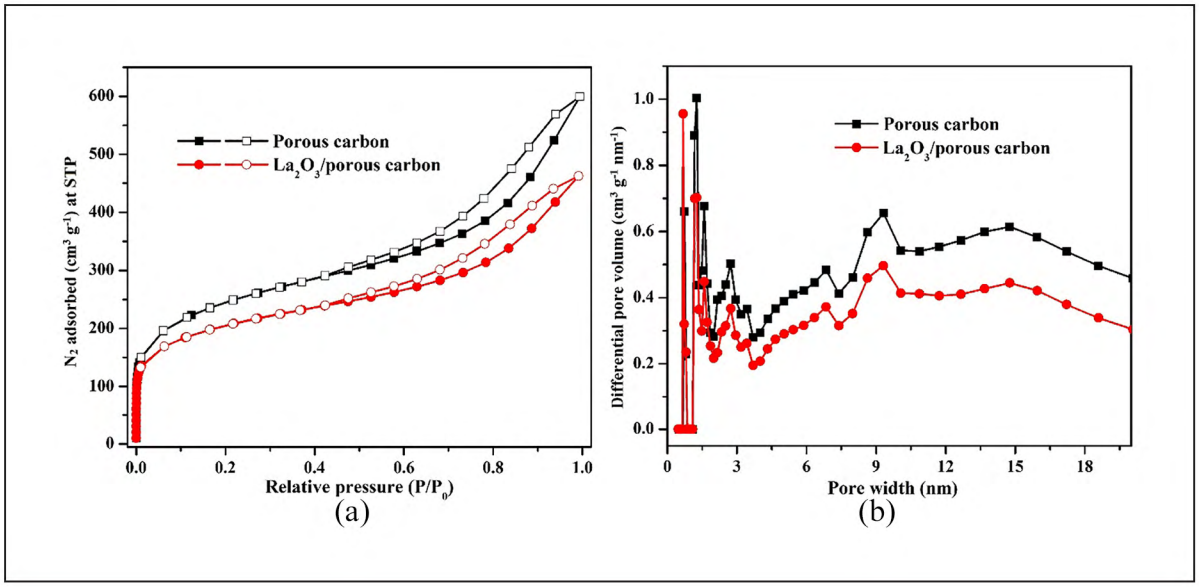

Figure 2. (a) N_2 adsorption–desorption isotherms (closed symbol: adsorption, open symbol: desorption) and (b) pore size distribution of porous carbon and La_2O_3/porous carbon.

Table 1. Textural properties and metal composition of the synthesized samples.

Sample	S_{BET} ($m^2 g^{-1}$)[a]	V_{total} ($cm^3 g^{-1}$)[b]	V_{micro} ($cm^3 g^{-1}$)[c]	V_{meso} ($cm^3 g^{-1}$)[d]	Pore size (nm)[e]	La content (wt%)[f]
Porous carbon	826	0.89	0.12	0.77	4.3	NF
La_2O_3/porous carbon	715	0.76	0.10	0.66	4.2	2.97

[a]BET surface area.
[b]Total pore volume at $P/P_0 = 0.99$.
[c]Micropore volume obtained from the t-plot.
[d]Mesopore volume obtained by subtracting V_{micro} from V_{total}.
[e]Average pore size by BET.
[f]From EDX, NF: not found.

La_2O_3/porous carbon are shown in Figure 1(b). Porous carbon shows Raman bands at 1334 and 1582 cm^{-1}, which are related to the D-band and the G-band, respectively.[24] The D-band corresponds to disordered carbon, whereas the G-band corresponds to graphitic carbon. The ratio of the intensity of D and G-bands (I_D/I_G) was 0.87 for porous carbon and 0.95 for La_2O_3/porous carbon. The high I_D/I_G ratio of La_2O_3/porous carbon indicates a decrease in the graphitic nature of porous carbon by the incorporation of lanthanum oxide.[25]

The porosity of the synthesized adsorbents was determined by measuring the N_2 adsorption–desorption isotherms at 77 K. Figure 2 shows the N_2 isotherms of porous carbon and La_2O_3/porous carbon, and the textural properties are presented in Table 1. Pristine porous carbon showed high adsorption of N_2 below the relative pressure $P/P_0 = 0.1$ and a hysteresis loop between the relative pressure of 0.4 and 1.0. As per the classification of porous materials by IUPAC, the isotherm of the porous carbon material is similar to type I and type IV isotherms.[26] This indicated that the synthesized porous carbon has micropores and mesopores. The specific surface area, pore volume and pore size of porous carbon were 826 $m^2 g^{-1}$, 0.89 $cm^3 g^{-1}$ and 4.3 nm, respectively. Similarly, La_2O_3/porous carbon showed an isotherm curve similar to that of pristine porous carbon. However, the amount of N_2 adsorption was less, which indicated that the pores of pristine porous carbon were occupied with lanthanum oxide. Hence, a change in the textural properties was observed. The specific surface area, pore volume and pore size of La_2O_3/porous carbon were 715 $m^2 g^{-1}$, 0.76 $cm^3 g^{-1}$ and 4.2 nm, respectively. Lou et al.[27] have also observed a change in textural properties by the occupation of ruthenium nanoparticles within the pores of porous carbon material.

Morphological images with chemical composition for porous carbon and La_2O_3/porous carbon are shown in Figure 3. Disordered carbon particles were observed for porous carbon (Figure 3(a)). In La_2O_3/porous carbon, the loaded La_2O_3 covers the surface of the disordered porous carbon (Figure 3(b)). From energy-dispersive X-ray (EDX) results, the amount of lanthanum was 2.97 wt%.

Study of CO_2 and N_2 adsorption

The adsorption of CO_2 and N_2 has been studied by the volumetric method using porous carbon and La_2O_3/porous carbon. The CO_2 and N_2 adsorption isotherms are shown in Figure 4. CO_2 adsorption increased on increasing the pressure, but no equilibrium was attained for both adsorbents. The amount of CO_2 adsorption was 21 $cm^3 g^{-1}$ for porous carbon and 33 $cm^3 g^{-1}$ for La_2O_3/porous carbon at 298 K and 1 bar. The high adsorption of CO_2 with La_2O_3/porous

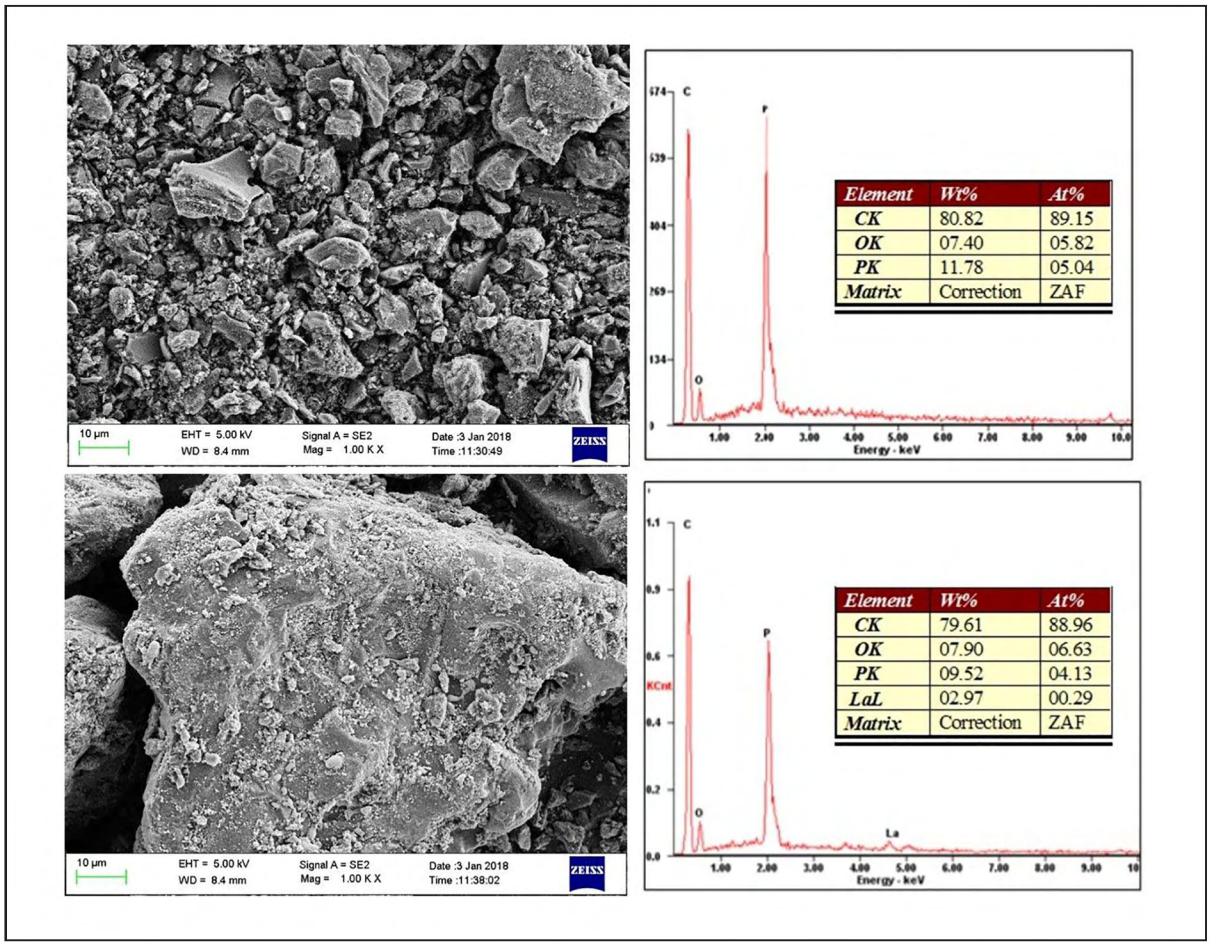

Figure 3. SEM with EDX images of (a) porous carbon and (b) La_2O_3/porous carbon.

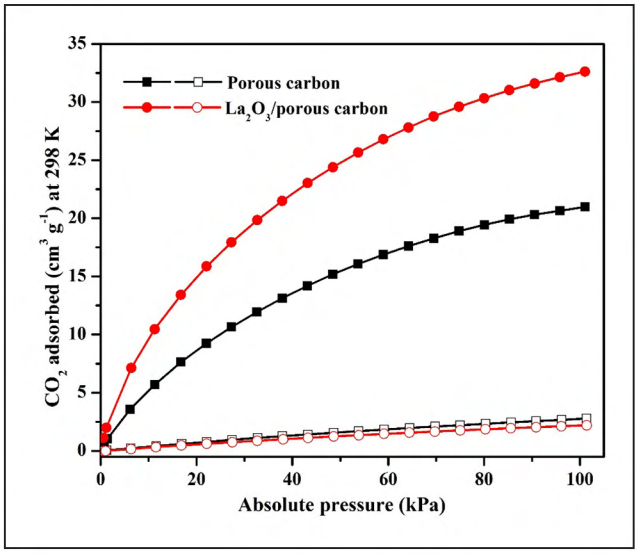

Figure 4. CO_2 and N_2 adsorption of porous carbon and La_2O_3/porous carbon (closed symbol: CO_2 adsorption, open symbol: N_2 adsorption).

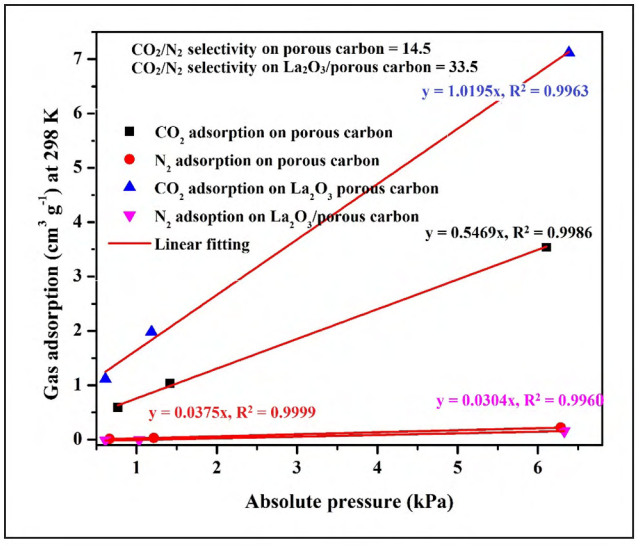

Figure 5. CO_2/N_2 selectivity on porous carbon and La_2O_3/porous carbon.

carbon was due to the electrostatic interaction between lanthanum oxide and CO_2. Along with the CO_2 adsorption study, N_2 adsorption was also studied under similar conditions to those used for the CO_2 adsorption study. The amount of N_2 adsorption was 2.8 $cm^3 g^{-1}$ for porous carbon and 2.2 $cm^3 g^{-1}$ for La_2O_3/porous carbon at 298 K and 1 bar. The decrease in N_2 adsorption was due to a change in the surface area.

In flue gas, carbon dioxide is a major component. So, it is essential to study CO_2/N_2 selectivity. The initial slope method was used to calculate CO_2/N_2 selectivity.[28] Figure 5 shows the CO_2/N_2 selectivity with porous carbon and La_2O_3/porous carbon. For porous carbon, the

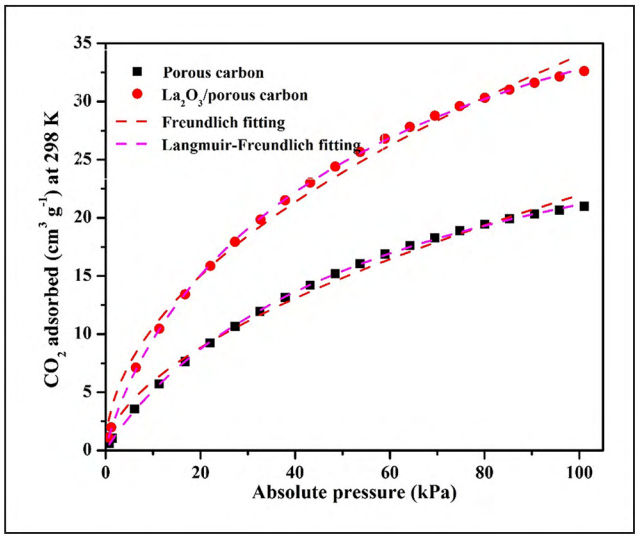

Figure 6. Fitting of isotherm models for CO_2 adsorption on porous carbon and La_2O_3/porous carbon.

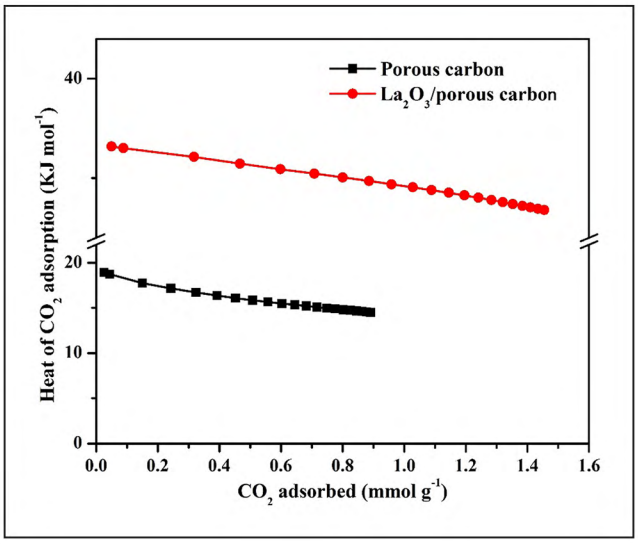

Figure 7. The heat of CO_2 adsorption of porous carbon and La_2O_3/porous carbon.

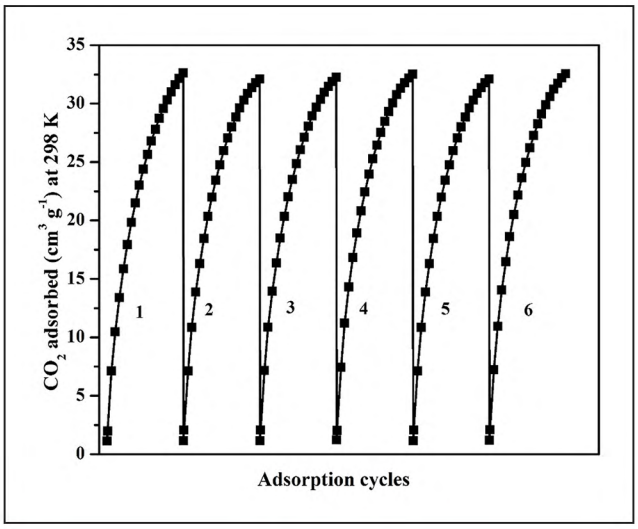

Figure 8. Multiple CO_2 adsorption cycles of La_2O_3/porous carbon.

CO_2/N_2 selectivity was 14.5, whereas for La_2O_3/porous carbon, the selectivity was 33.5. High selectivity was obtained for La_2O_3/porous carbon because of the high adsorption of CO_2 and the selectivity value was higher than those of some reported adsorbents such as HKUST-1 and Mg-MOF-74.[29,30]

The adsorption behaviour of an adsorbent can be calculated by fitting of the experimental CO_2 adsorption with the Freundlich and Langmuir-Freundlich isotherm models.[31] The isotherm models can be written as follows

$$\text{Freundlich isotherm model}: Q = k_F P^{1/n}$$

$$\text{Langmuir} - \text{Freundlich isotherm model}: Q = \frac{Q_{max} K P^{1/n}}{1 + K P^{1/n}}$$

where Q is the adsorption capacity at equilibrium ($cm^3 g^{-1}$); Q_{max} is the maximum adsorption capacity ($cm^3 g^{-1}$); P is the pressure (kPa); k_F and K are the Freundlich and Langmuir–Freundlich constants, respectively; and n is the heterogeneity factor. The experimental CO_2 adsorption of porous carbon and La_2O_3/porous carbon are fitted with the Freundlich and Langmuir–Freundlich isotherm models, as shown in Figure 6. The fitting parameters are presented in Supplemental Table S1. The Langmuir–Freundlich isotherm model was well-fitted with the experimental CO_2 adsorption, regression co-efficient $R^2 > 0.999$. The Q_{max} was higher for La_2O_3/porous carbon because of the strong interaction of CO_2 with lanthanum oxide.

In gas adsorption studies, the heat of adsorption (Q_{st}) is an important parameter. It describes the interaction between the adsorbate and adsorbent. The Q_{st} can be calculated using the virial equation[32]

$$\text{Virial equation}: \ln P = \ln N + \frac{1}{T}\sum_{i=0}^{m} a_i N^i + \sum_{j=0}^{n} b_j N^j$$

$$\text{Heat of adsorption}: Q_{st} = -R\sum_{i=0}^{m} a_i N^i$$

where P is the pressure in Torr, N is the gas uptake in $cm^3 g^{-1}$, T is the temperature in K, R is the universal gas constant ($8.314\ JK^{-1} mol^{-1}$), Q_{st} is the heat of adsorption in $kJ\,mol^{-1}$, ai and bj are the virial coefficients, and m and n are the number of coefficients. To calculate the heat of CO_2 adsorption for porous carbon and La_2O_3/porous carbon, CO_2 adsorption at 303 K was measured for both samples (see Supplemental Figure S1). The amount of CO_2 adsorption was less at 303 K compared with CO_2 adsorption at 298 K because of the increase in the kinetic energy of CO_2. The measured CO_2 adsorption isotherms were fitted with the virial equation (Supplemental Figure S2). From the virial fitting parameters, the heat of CO_2 was calculated. The heat of CO_2 adsorption of porous carbon and La_2O_3/porous carbon is shown in Figure 7. For porous carbon, Q_{st} was 18.9–14.5 $kJ\,mol^{-1}$, whereas for La_2O_3/porous carbon was 36.5–33.4 $kJ\,mol^{-1}$. A high Q_{st} was obtained for La_2O_3/porous carbon because of the strong interaction between CO_2 and lanthanum oxide. At

Table 2. Comparison of the CO_2 adsorption capacity of La_2O_3/porous carbon with reported adsorbents.

Sample	Adsorption method	CO_2 adsorbed ($cm^3 g^{-1}$) at 298 K, 1 bar	Reference
ZIF-98	Volumetric	34	Wang et al.[33]
S-doped microporous carbon	Volumetric	54	Xia et al.[34]
N-doped microporous carbon	Volumetric	53.7	An et al.[35]
Mesoporous N-doped CeO_2	Gravimetric	24 (303 K)	Wang et al.[36]
PEHA-MIL-101	Volumetric	29	Anbia et al.[37]
Zeolite-13X	Volumetric	38	McEwen et al.[38]
La_2O_3/porous carbon	Volumetric	33	Present work

low adsorption of CO_2, a high Q_{st} was obtained. With an increase in CO_2 adsorption, the Q_{st} decreased due to a decrease in the number of active adsorption sites.

Multiple CO_2 adsorption cycles have been studied to determine the adsorption stability of La_2O_3/porous carbon at 298 K (Figure 8). Before studying the CO_2 adsorption cycle, the adsorbent was degasified at 473 K for 2 h under vacuum to remove the adsorbed CO_2. The amount of CO_2 adsorption was constant in each adsorption cycle. The CO_2 adsorption of La_2O_3/porous carbon was compared with the CO_2 adsorption capacity of previously reported adsorbents (Table 2). The synthesized La_2O_3/porous carbon showed 33 $cm^3 g^{-1}$ of CO_2 adsorption at 298 K and 1 bar, which was in-between the CO_2 adsorption capacity of mesoporous N-doped CeO_2 and S-doped microporous carbon.[34,36]

Conclusion

In this work, we have studied CO_2 adsorption and separation by the volumetric method using porous carbon and La_2O_3/porous carbon. The high CO_2 adsorption capacity was obtained on La_2O_3/porous carbon compared to bulk porous carbon at 298 K and 1 bar because of electrostatic interaction of La_2O_3 with CO_2 and CO_2/N_2 selectivity was also higher on La_2O_3/porous carbon. The heat of CO_2 adsorption was 36.5 kJ mol^{-1} at low coverage of CO_2 for La_2O_3/porous carbon and CO_2 adsorption capacity was constant in each adsorption cycle. Therefore, a basic metal oxide can be incorporated on porous carbon to increase the CO_2 adsorption and separation.

Experimental

Lanthanum nitrate hexahydrate [$La(NO_3)_3.6H_2O$, 99.9%] and orthophosphoric acid (H_3PO_4, 85%) were purchased from Sigma-Aldrich, India, and used without purification. Distilled water was used to synthesize the adsorbents. High purity gases (carbon dioxide, nitrogen and helium) were purchased from BOC, India.

Porous carbon was synthesized by using pongamia pinnata fruit hulls which were collected from the forest region of Telangana, India. First, the fruit hulls were washed, dried then made into a powder. The powder was activated using phosphoric acid at room temperature for 24 h followed by drying at 373 K for 12 h. The dried sample was calcined under nitrogen gas with a flow rate of 50 mL/min at 723 K for 4 h, with a heating rate of 5 K/min, and then cooled to room temperature. The sample was washed with distilled water until the pH reached 7, then it was dried at 373 K overnight to afford porous carbon.[39] Porous carbon supported lanthanum oxide was synthesized by the impregnation method.[40] About 0.1 g of lanthanum nitrate hexahydrate was dissolved in 10 mL of distilled water, stirred for 10 min then 1 g of porous carbon was added. The mixture was stirred at room temperature for 1 h and then dried at 373 K overnight. The dried compound was calcined under nitrogen gas at 873 K for 3 h.

XRD patterns were recorded on a Rigaku Ultima-IV X-ray diffractometer using Ni-filtered Cu-K_α radiation operated at a voltage of 40 kV and a current of 30 mA in the scan range of $2\theta = 10°–80°$ with a step size of 0.02°/s. A Micrometric ASAP 2020 porosity analyzer was used to measure N_2 adsorption–desorption isotherms at 77 K. Prior to the adsorption study, about 0.1 g of the sample was degassed at 473 K for 2 h under vacuum. The multi-point Brunauer–Emmett–Teller (BET) surface area was calculated in the relative pressure range of 0.05–0.3, the total pore volume at a relative pressure of 0.99, the micropore volume by the t-plot method and the mesopore volume was calculated by subtracting the micropore volume from the total pore volume. The pore size distribution was plotted using non-local density functional theory. A LabRAM HR800 spectrometer was used to record the Raman spectra. The morphology and elemental composition of each sample were determined from scanning electron microscopy with energy-dispersive X-ray (SEM with EDX) analysis using a ZEISS Sigma 300 scanning electron microscopy analyzer.

The adsorption of CO_2 and N_2 was carried out using a Micromeritics ASAP 2020 gas adsorption analyzer at low pressure and at 298 K. A thermostatic bath connected with water circulating jacket was used to control the sample temperature, and helium gas was used to determine the free space of the sample tube. Before the gas adsorption measurement, 0.1 g of the sample was activated at 473 K for 2 h under vacuum to remove moisture or adsorbed gases and then cooled to the gas adsorption temperature. Ultra-high pure gases were used to measure the adsorption isotherms. The initial slope method was used to calculate the selectivity of CO_2/N_2. The virial method was used to calculate the heat of CO_2 adsorption using adsorption isotherms obtained at 298 and 303 K. The CO_2 adsorption cycles were also studied at 298 K to calculate the adsorption stability of an adsorbent.

Declaration of conflicting interests

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Supplemental material

Supplemental material for this article is available online.

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