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REGULAR ARTICLE

Removal of Cr and Mn from aqueous medium using bentonites and their derivatives

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Abstract. Bentonite minerals of Rajmahal Hills and Hazaribagh district along with their derivatives have been used to remove hexavalent chromium and manganese from aqueous medium. Bentonites are smectite group of minerals having swelling power and cation exchange properties. Blue colour with benzidine solution indicates the presence of montmorillonite unit having SiO_2, Al_2O_3, K_2O, Fe_2O_3, FeO and traces of TiO_2 also. The adsorption isotherm and removal performance of hexavalent chromium and manganese have been examined by shaking 100 mL 2 ppm solution with 1 gram of bentonite and their derivatives up to different intervals of time and also with varying amount of bentonite up to fixed time intervals. The percentage removal of chromium (VI) ranges from 12% to 67.7% whereas percentage removal of manganese (VII) varies from 09% to 92.5%. Experimental data showed that the removal of Cr (VI) and Mn (VII) represented both Freundlich and Langmuir adsorption isotherms. Adsorption of Cr (VI) and Mn (VII) on to bentonites and their derivatives follow first-order kinetics. It is concluded that locally available bentonites may be exploited as a low-cost feasible adsorbent for removal of Cr (VI) and Mn (VII) in the laboratory as well as industrial level too.

Keywords. Isotherms; Bentonite; Langmuir; Adsorption; Hexavalent chromium.

1. Introduction

Hexavalent chromium concentration in drinking water has attracted the attention of scientists due to carcinogenic characteristics.[1–4] Chromium (VI) exists in the aquatic medium as $HCrO_4^-$ at pH 4 to 6 or CrO_4^{2-} at pH 8-10 whereas Cr(III) exists as Cr^{+3}, $Cr(OH)_3$ and $Cr(OH)_4^-$.[5,6] Chromium is released into water bodies through metallurgical operations, metal finishing, steel alloy and chrome plating.[7] Various techniques for removal of hexavalent chromium from an aqueous medium such as ion exchange, coagulation, membrane filtration, electrodialysis are available but adsorption is considered the most appropriate method of removal especially by the use of bentonites.[8,9] In addition to this, bacteria may also be used to mitigate heavy toxic elements from aqueous medium. Use of adsorbents e.g., yeast biomass and fungal biomass have been adopted due to its being low cost and abundance in nature. The binding capacity of orange peel powder, rice husk and maize stem powder has already been investigated. Natural herbs and wastes from agricultural operations have the potential to be used as an effective adsorbent of Cr (VI). Many literatures available suggest that active carbon prepared from walnut (Juglans regia L), hazelnut (Corylus avellana) and rice husk have proved to be good adsorbents of toxic heavy metals.[14] Also, fly ash and portland cement have also the potential to remove heavy metals e.g., Cr (VI), Pb (II) and Cd (II). The composition of Portland cement has similarity with clay minerals to some extent as cement has Al_2O_3, Fe_2O_3, SiO_2 and CaO in its composition.[15] Natural zeolites, a crystalline material of linked tetrahedrals have also been recognized as a remover of Cr (VI) due to net structural negative charge in the crystal lattice and surface area.[16] Keeping in view the abundance of bentonite in many states of the country and Rajmahal

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Hills, bentonites have been exploited for removal of heavy metals from solution.[10, 11] Clay minerals of this region are rich in bentonite but contain cristobalite, beidellite, Saponite, Kaolinite along with dirt and stones. Bentonite smectite group of minerals contains chiefly SiO_2, and Al_2O_3 along with K_2O, Fe_2O_3, FeO and traces of TiO_2.[12, 13] Bentonites have large surface areas, layered 2:1 structure, high cation exchange capacity and net structural negative charge as a result of which bentonites have emerged as an excellent adsorbent material as well as ion exchanger.[17–19] The collected samples and their derivatives are powdered separately. They were passed through 300 mesh sieves (0.104 mμ). Further the samples were dried around 110 to 120 °C for about 24 h. The dried powdered samples were packed in well dried small reagent bottles properly Stoppard. They were kept in desiccators and used for all determinations. Bentonite minerals here have been extensively studied to remove hexavalent chromium from aqueous medium. A systematic study has been done e.g. effect of pH change, adsorbent dose and contact time to find out optimum conditions for removal of Cr (VI) and Mn (VII) from aqueous medium.[20]

2. Experimental

U.V. Spectrophotometer is available in the department which has been used for determining hexavalent chromium in the sample.

2.1 *Reagents and solution*

A stock solution of 100 ppm Cr (VI) solution has been prepared from calculated amounts of potassium dichromate by dissolving in 1 litre volumetric flask with deionized water. 2 ppm Cr (VI) solution has been prepared by dilution of the stock solution from formula V1N1= V2N2 where V1 and V2 stand for the initial and final volume, N1 and N2 for initial and final strength respectively. 100 mL 2 ppm Mn (VII) solution has been prepared from 100 ppm stock solution. The reagent has been supplied by Merck Company. Bentonites have been collected from different places of Hazaribagh. Presence of montmorillonite unit gave blue colour with benzidine reagent. S_6 (2540) coding stood for the sample collected from khamba village of Hazaribagh, S_7 (2541) for a sample of Oria village. These samples analyzed by standard qualitative methods showed the presence of SiO_2, Al_2O_3, Fe_2O_3, FeO, MnO, MgO, CaO, Na_2O and K_2O. Sodium derivative of bentonite has been prepared by taking 200 gm sample in a beaker followed by addition of 200 mL 1N NaCl. It was kept in contact for 20 days. After filtration, excess NaCl was removed by repeated washing with deionized water and a solid residue of bentonite was dried for use.

2.2 *Process*

U.V. Spectrophotometer has been used for determining hexavalent Cr and Mn in the sample. The procedure is given below:

When Cr (VI) reacts with diphenyl carbazide in acid medium, a red-violet colour is obtained. Cr (VI) sample is taken in 100 mL volumetric flask and diluted to 100 mL. 2 mL diphenyl carbazide solution is added to the volumetric flask and shaken. After 10 min the absorbance is measured at 540 nm against a reagent blank using the same procedure. The results obtained by this method are in agreement with the result obtained from spectrophotometer pharo 300 at 540 nm. U.V. double beam spectrophotometer pharo 300 did not require preparation of reagents as the reagents have been supplied by Merck Company. So this apparatus has been used to know the residual concentrations of Cr (VI) and Mn (VII) too. 100 mL 2 ppm Cr (VI) solution has been treated with 1 gm bentonite powder up to 1 h, 2 h and 3 h. Again 100 mL 2 ppm Cr (VI) solution has been treated with 1 gm sodium bentonite derivative powder up to 1 h, 2 h and 3 h. Now 1 gm, 2 gm and 3 gm bentonite and sodium derivatives have been treated with 100 mL 2 ppm Cr (VI) solution up to 1 h. Similar experiments have been repeated with for Mn (VII).

3. Results and Discussion

3.1 *Effect of contact time*

The effect of contact time on Cr (VI) removal from aqueous medium has been investigated. On increasing contact time, available sites for adsorption increased and as a result adsorbed amount of Cr (VI) increased with time. Table 1 showed that the residual concentrations of Cr (VI) ion were 1.70 ppm, 1.257 and 1.17 after 1 h, 2 h and 3 h, respectively. Studies revealed that on one hand percentage removal increased from 13% to 41.5% with an increase of contact time from 1 h to 3 h in case of Cr (VI) removal and on the other percentage removal of Mn (VII) increased from 30.5% to 67.25% in 3 h by S_6

Table 1. Concentration of Chromium (VI) ion after treatment with 1 gm of bentonite mineral.

Sl. No	Bentonite Sample No.	Initial conc., of Cr(VI) ion (in ppm)	Residual conc. of Cr(VI) after 1 h (in ppm)	Residual conc. of Cr(VI) after 2 h (in ppm)	Residual conc. Cr(VI) after 3 h (in ppm)
1	S_6 (2540)	2	1.70	1.257	1.17
2	S_7 (2541)	2	1.93	1.34	0.88
3	S_{20}	2	1.76	1.39	0.79
4	Na Derivative of S_6 (2540)	2	1.684	1.521	1.397
5	Na Derivative of S_7 (2541)	2	1.67	1.23	1.19

Table 2. Percentage Chromium (VI) removal after treatment with 1 gram bentonite for 1 h and values of qt, Ct, log qt and log Ct.

Sl. No	Bentonite Sample No.	%Removal	qt	Ct	log qt	log Ct	Ct/ qt
1	S_6 (2540)	13	26	1.70	1.414	0.2304	0.0654
2	S_7 (2541)	3.5	07	1.93	0.845	0.2855	0.2757
3	S_{20}	12	24	1.76	1.38	0.2455	0.0733
4	Na Derivative of S_6 (2540)	15.8	31.6	1.684	1.499	0.2263	0.0533
5	Na Derivative of S_7 (2541)	16.5	33	1.67	1.518	0.2227	0.0506

Table 3. Percentage Chromium (VI) removal after treatment with 1 gram bentonite for 2 h and values of qt, Ct, log qt and log Ct.

Sl. No	Bentonite Sample No.	%Removal	qt	Ct	log qt	log Ct	Ct/ qt
1	S_6 (2540)	37.15	74.3	1.257	1.87	0.0993	0.0169
2	S_7 (2541)	33	66	1.34	1.8195	0.1271	0.0203
3	S_{20}	30.50	61	1.39	1.7853	0.1430	0.0227
4	Na Derivative of S_6 (2540)	23.95	47.90	1.521	1.6803	0.1821	0.0317
5	Na Derivative of S_7 (2541)	38.50	77	1.23	1.8864	0.0899	0.0159

Table 4. Percentage Chromium (VI) removal after treatment with 1 gram bentonite for 3 h and values of qt, Ct, log qt and log Ct.

Sl. No	Bentonite Sample No.	%Removal	qt	Ct	log qt	log Ct	Ct/ qt
1	S_6 (2540)	41.5	83	1.17	1.9190	0.0681	0.0141
2	S_7 (2541)	56	112	0.88	2.049	-0.0555	0.0078
3	S_{20}	60.5	121	0.79	2.0827	-0.1023	0.0065
4	Na Derivative of S_6 (2540)	30.15	60.3	1.397	1.7803	0.1451	0.0231
5	Na Derivative of S_7 (2541)	40.50	81	1.19	1.9084	0.7554	0.0147

(2540) (Tables 2, 3). The maximum percentage removal of Cr (VI) by S_7 (2541) is 56% in 3 h (Figure 1). Maximum percentage removal by sodium derivative of S_6 (2540) and S_7 (2541) are 30.15% and 40.50% in 3 h, respectively shown in Table 4. The maximum percentage removal of Mn (VII) from aqueous solution by S_7 (2541), Sodium derivative of S_6 (2540) and Sodium derivative of S_7 (2541) in 3 h are 35.5%, 31.5% and 49.5%, respectively (Table 8). S_{20} sample is more efficient for removal of Mn (VII)

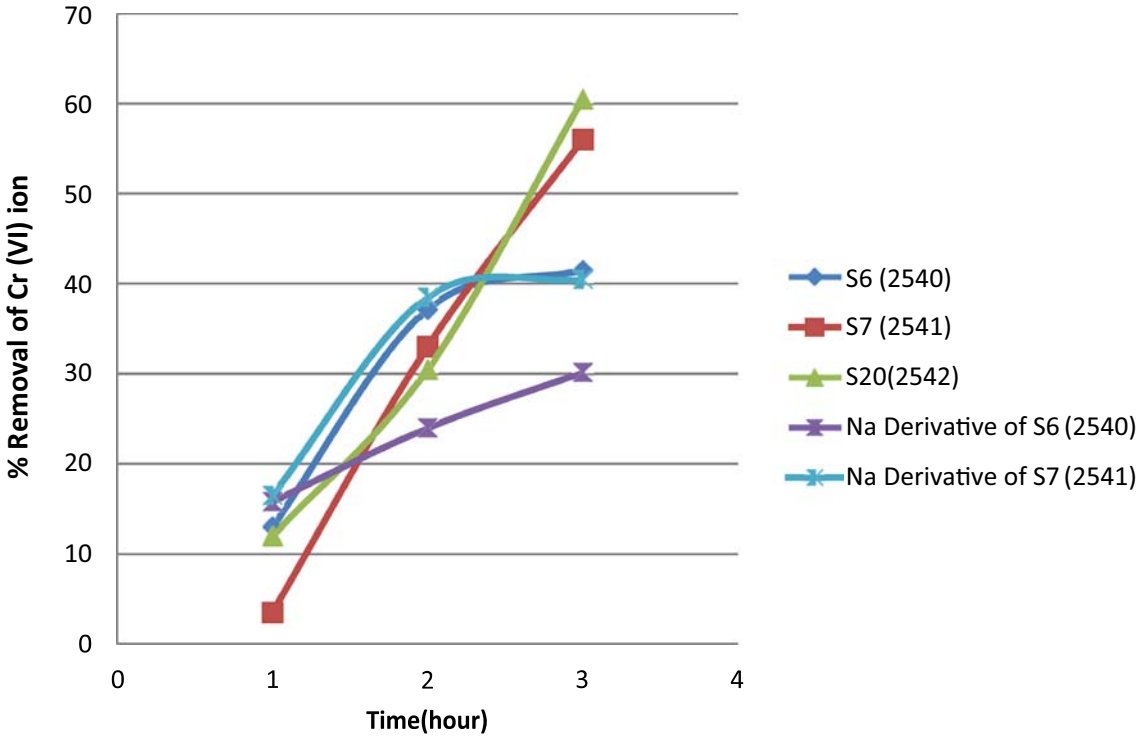

Figure 1. Percentage removal of Chromium (VI) with bentonite and their derivatives up to different time interval.

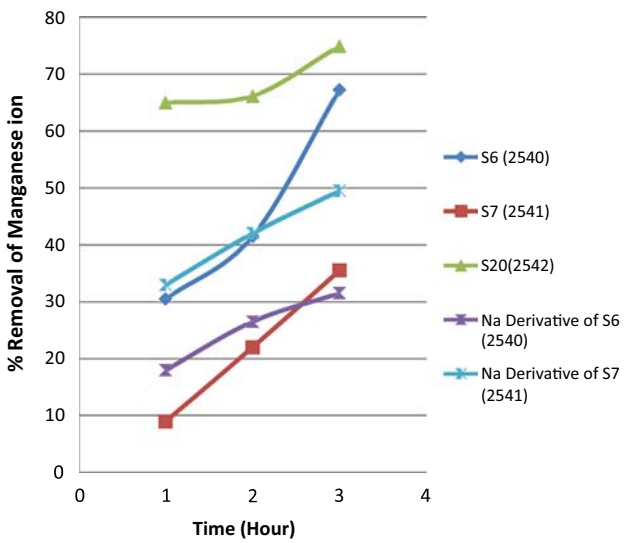

Figure 2. Percentage removal of Manganese (VII) ion with Bentonite and their derivatives up to different time interval.

and maximum percentage removal is 74.9% in 3 h (Figure 2, Table 8). Percentage removal is known from the formula

$$\%\,\text{removal} = [(\text{Ci-Ct})/\text{Ci}] \times 100$$

Where Ci and Ct show initial concentration and concentration at time t, respectively (Figures 1, 2, Tables 5, 6, 7, 8).

3.2 *Effect of adsorbent dose*

When the adsorbent dose was increased, more surface area became available for adsorption. However, complete removal could not be achieved even after increasing the dose of bentonite from 1 g to 3 g. Residual concentrations of Cr (VI) on the treatment of 3 g bentonite with 100 mL 2 ppm Cr (VI) solution could be seen in Table 9. Experimental data showed that maximum removal took place with 3 g sodium derivative of S_6 bentonite sample. Results clearly indicated that percentage removal of Cr (VI) and Mn (VII) both increased with an increased dose of bentonite and derivatives (Tables 10, 11, 12, 13 and 14). Figures 3 and 4 showed an increasing trend of removal percentage. 3 g S_{20} (2542) bentonite sample removed Mn (VII) from aqueous medium up to 92.5% (Table 14) whereas 3 g of this sample removed only 27% Cr (VI) from aqueous medium (Table 12).

3.3 *Isotherm studies*

Experimental data have been analyzed for observing a fit in Freundlich and Langmuir adsorption isotherm. Both of the isotherms are used to know the nature of adsorption. Adsorption isotherms explain the physical or chemical characteristics of bentonite and their

Table 5. Concentration of Manganese (VII) ion after treatment with 1 gm of bentonite mineral.

Sl. No	Bentonite Sample No.	Initial conc. of Mn(VII) ion (in ppm)	Residual conc. of Mn(VII) ion (in ppm) after 1 h	Residual conc. of Mn(VII) ion (in ppm) after 2 h	Residual conc. of Mn(VII) ion (in ppm) after 3 h
1	S_6 (2540)	2	1.39	1.17	0.655
2	S_7 (2541)	2	1.82	1.56	1.29
3	S_{20}	2	0.701	0.677	0.502
4	Na Derivative of S_6 (2540)	2	1.64	1.47	1.37
5	Na Derivative of S_7 (2541)	2	1.34	1.16	1.01

Table 6. Percentage Manganese (VII) removal after treatment with 1 gram bentonite for 1 h and values of qt, Ct, log qt and log Ct.

Sl. No	Bentonite Sample No.	%Removal	qt	Ct	log qt	log Ct	Ct/ qt
1	S_6 (2540)	30.5	61	1.39	1.7853	0.1430	0.0228
2	S_7 (2541)	09	18	1.82	1.2552	0.2600	0.1011
3	S_{20}	64.95	129.9	0.701	2.1136	-0.1542	0.00534
4	Na Derivative of S_6 (2540)	18	36	1.64	1.5563	0.2148	0.0455
5	Na Derivative of S_7 (2541)	33	66	1.34	1.8165	0.1271	0.0203

Table 7. Percentage Manganese (VII) removal after treatment with 1 gram bentonite for 2 h and values of qt, Ct, log qt and log Ct.

Sl. No	Bentonite Sample No.	%Removal	qt	Ct	log qt	log Ct	Ct/ qt
1	S_6 (2540)	41.5	83	1.17	1.919	0.0681	0.0140
2	S_7 (2541)	22	44	1.56	1.643	0.1931	0.0354
3	S_{20}	66.15	132.3	0.677	2.121	-0.1694	0.0051
4	Na Derivative of S_6 (2540)	26.5	53	1.47	1.724	0.1673	0.0277
5	Na Derivative of S_7 (2541)	42	84	1.16	1.924	0.0644	0.0138

Table 8. Percentage Manganese (VII) removal after treatment with 1 gram bentonite for 3 h and values of qt, Ct, log qt and log Ct.

Sl. No	Bentonite Sample No.	%Removal	qt	Ct	log qt	log Ct
1	S_6 (2540)	67.25	134.5	0.655	2.128	-0.1837
2	S_7 (2541)	35.5	1	1.29	1.851	0.1105
3	S_{20}	74.9	149.4	0.502	2.174	-0.2992
4	Na Derivative of S_6 (2540)	31.5	63	1.37	1.799	0.1367
5	Na Derivative of S_7 (2541)	49.5	99	1.01	1.995	0.0043

derivatives.[21, 22] A plot of Log qt vs. Log Ct shows Freundlich isotherm. Linearity of the graph explains that Freundlich isotherm has been followed. qt is calculated as

$$Qt = [(Ci\text{-}Ct)/m] \times V$$

Where m shows the mass of adsorbent in gram and V is the volume in litres. Figures 5 and 6 explain the

Table 9. Concentration of Chromium (VI) ion after treatment with different masses of bentonite mineral.

Sl.No	Bentonite Sample No.	Initial conc. of Cr(VI) ion (in ppm)	Residual conc. of Cr(VI) with 1 gm Bentonite treatment after 1 h (in ppm)	Residual conc. of Cr(VI) with 2 gm Bentonite treatment after 1 h (in ppm)	Residual conc. with 3 gm Bentonite treatment after 1 h (in ppm)
1	S_6 (2540)	2	1.70	1.34	1.22
2	S_7 (2541)	2	1.93	1.698	1.541
3	S_{20}	2	1.76	1.64	1.46
4	Na Derivative of S_6 (2540)	2	1.684	1.21	0.646
5	Na Derivative of S_7 (2541)	2	1.67	1.39	0.677

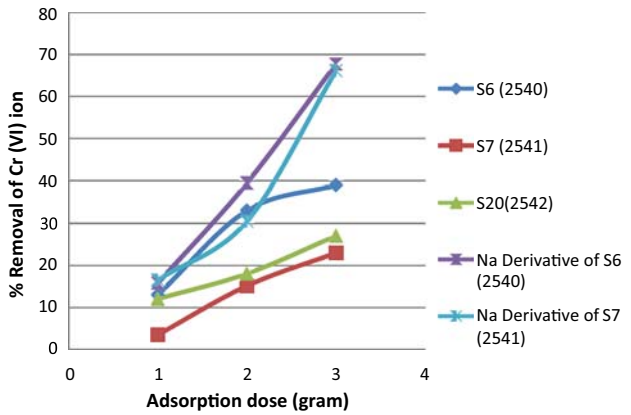

Figure 3. Percentage removal of Chromium (VI) ion with different dosage of bentonite and their derivatives.

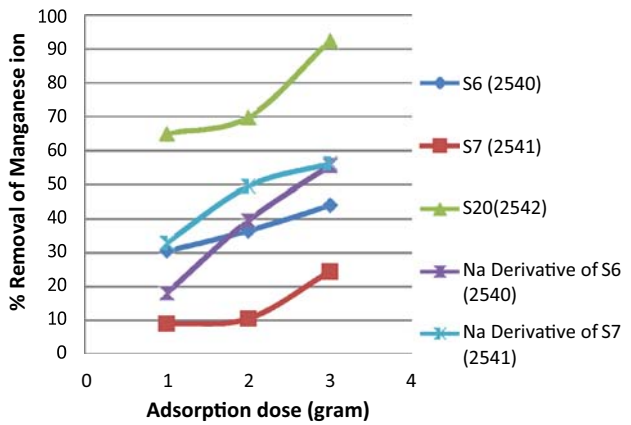

Figure 4. Percentage removal of Manganese (VII) ion Vs different masses of bentonite for (1 h).

Freundlich isotherm for adsorption of Cr (VI) and Mn (VII), respectively by S_6 (2540), S_7 (2541) and S_{20} (2542), sodium derivative of S_6 (2540) and S_7 (2541) sodium derivative. Ct/qt has been plotted against Ct in Figure 7. Linearity of graph shows that monolayer coverage of adsorbate takes place on the surface of bentonite and their derivatives.[23, 24]

3.4 *Kinetic studies*

Amount of adsorbed Cr (VI) and Mn (VII) increased with time shown in Figures 4 and 9. Reaction pathways are explained by chemical kinetics whereas adsorption isotherms give information regarding the mechanism of adsorption.

Linearity is shown in the plot of adsorbed amount Cr (VI) ion by S_7 (2541), S 20 (2542) and Sodium derivative of S_6 (2540) against time and this is also followed for adsorption of Mn linearity in Figure 8 whereas the plot of adsorbed amount of Mn (VII) by sodium derivative of S_7 (2541) against time is shown in Figure 9.

From the experimental data analysis, concerned tables and graphs, the applicability of first-order reaction is established.[25, 26] The bentonite particles have been agitated with solutions of Cr (VI) and Mn (VII) so the possibilities of intraparticle diffusion may not be ruled out. Thus the graphs by bentonite samples and their sodium derivatives attribute to intraparticle diffusion also (Tables 15, 16).[27]

3.5 *Effect of pH*

pH has been assumed to affect the structural stability of adsorbate like Cr (VI) and Mn (VII) along with adsorbent as adsorption is also related to surface charge of bentonites.[28]

Functional groups on the surface of bentonite get ionized and so surface charge becomes pH-dependent.[29] The active functional groups at the bentonite have been recognized as $Si\text{-}O^-$ and $Al\text{-}O^-$ as silica and alumina are present in bentonites.

Adsorption of Cr (VI) on the surface of bentonite has been explained to occur by surface co-ordination process. Cr (VI) at pH >4 exists mainly as $HCrO_4^-$ and CrO_4^{2-} both exist which faces electrostatic attraction with the positively charged bentonite surface

Table 10. Concentration of Manganese (VII) ion after treatment with different masses of bentonite mineral.

Sl.No	Bentonite Sample No.	Initial conc. of Mn(VII) ion (in ppm)	Residual conc. with 1 gm bentonite treatment after 1 h (in ppm)	Residual conc. with 2 gm bentonite treatment after 1 h (in ppm)	Residual conc. with 3 gm bentonite treatment after 1 h (in ppm)
1	S_6 (2540)	2	1.39	1.27	1.12
2	S_7 (2541)	2	1.82	1.79	1.51
3	S_{20}	2	0.701	0.603	0150
4	Na Derivative of S_6 (2540)	2	1.64	1.21	0.89
5	Na Derivative of S_7 (2541)	2	1.34	1.01	0.877

Table 11. Percentage Chromium (VI) removal after treatment with 2 g bentonite for 1 h and values of qt, Ct, log qt and log Ct.

Sl. No	Bentonite Sample No.	%Removal	qt	Ct	log qt	log Ct	Ct/ qt
1	S_6 (2540)	33	33	1.34	1.5185	0.1271	0.0406
2	S_7 (2541)	15.1	15.1	1.698	1.1789	0.2299	0.1124
3	S_{20}	18	18	1.64	1.2552	0.2148	0.0911
4	Na Derivative of S_6 (2540)	39.5	39.5	1.21	1.5965	0.0827	0.0306
5	Na Derivative of S_7 (2541)	30.5	30.5	1.39	1.4842	0.1430	0.0455

Table 12. Percentage Chromium (VI) removal after treatment with 3 g bentonite for 1 h and values of qt, Ct, log qt and log Ct.

Sl. No	Bentonite Sample No.	%Removal	qt	Ct	log qt	log Ct
1	S_6 (2540)	39	26	1.22	1.4149	0.0863
2	S_7 (2541)	22.95	15.3	1.541	1.1846	0.1878
3	S_{20}	27	18	1.46	1.2552	0.1643
4	Na Derivative of S_6 (2540)	67.7	45.13	0.646	1.6544	− 0.1897
5	Na Derivative of S_7 (2541)	66.15	44.1	0.677	1.6444	− 0.1694

Table 13. Percentage Manganese (VII) removal after treatment with 2 g bentonite for 1 h and values of qt, Ct, log qt and log Ct.

Sl. No	Bentonite Sample No.	%Removal	Qt	Ct	log qt	log Ct
1	S_6 (2540)	36.5	36.5	1.27	1.5622	0.1038
2	S_7 (2541)	10.5	10.5	1.79	1.0211	0.2528
3	S_{20}	69.85	69.85	0.603	1.8441	− 0.2196
4	Na Derivative of S_6 (2540)	39.5	39.5	1.21	1.5965	0.0827
5	Na Derivative of S_7 (2541)	49.5	49.5	1.01	1.6946	0.0043

due to ($B\text{-}H_2O^+$). Development of surface sites for hydrated bentonite maybe shown as

$$B\text{-}OH_2^+ = B\text{-}OH + H^+B\text{-}OH = B\text{-}O^- + H^+$$

Where B stands for bentonite surface. $HCrO_4^-$, hydro chromate gets fixed on the positively charged surface of bentonites due to columbic attraction so

Table 14. Percentage Manganese (VII) removal after treatment with 3 g bentonite for 1 h and values of qt, Ct, log qt and log Ct.

Sl. No	Bentonite Sample No.	%Removal	qt	Ct	log qt	log Ct
1	S_6 (2540)	44	29.33	1.12	1.4673	0.0492
2	S_7 (2541)	24.5	16.33	1.51	1.2129	0.1789
3	S_{20}	92.5	61.66	0.15	1.7900	− 0.8239
4	Na Derivative of S_6 (2540)	55.5	37	0.89	1.5682	− 0.0506
5	Na Derivative of S_7 (2541)	56.15	37.43	0.877	1.5732	− 0.0570

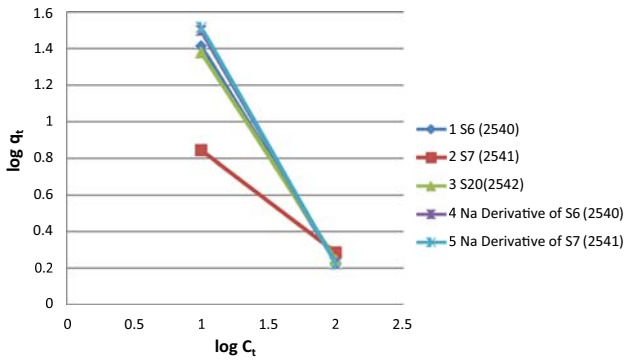

Figure 5. log qt vs. log Ct (Freundlich isotherm Cr (VI) ion-Bentonite system) at 26 °C and pH.

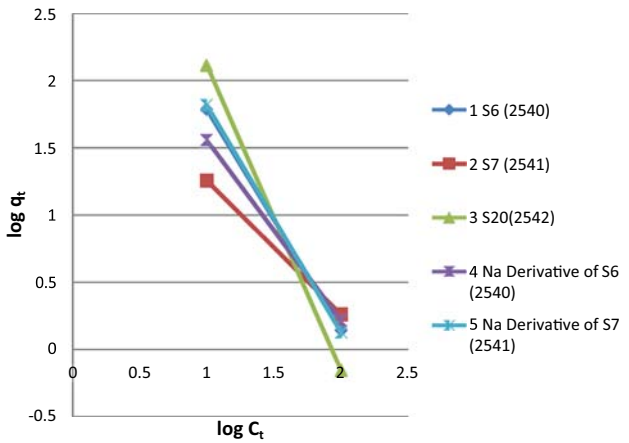

Figure 6. log qt vs. log Ct for Mn (VII) –bentonite system (Freundlich Isotherm) at 26 °C.

maximum adsorption of Cr (VI) takes place within pH range 2-4. On increasing the pH, neutral surface groups predominate which act as active sites for adsorption of both $HCrO_4^-$ and CrO_4^{2-}. Adsorption of Cr (VI) on bentonite surface has been shown by this general reaction.

$$\text{B-OH}_2^+ + \text{HCrO}_{4-} = \text{B-HCrO}_4 + \text{H}_2\text{O} \quad \text{(I)}$$

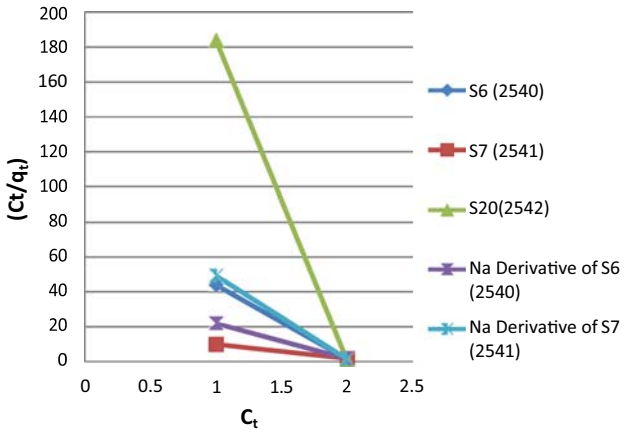

Figure 7. Ct/qt Vs Ct (Langmuir isotherm Mn (VII) – bentonite system) at 26 °C.

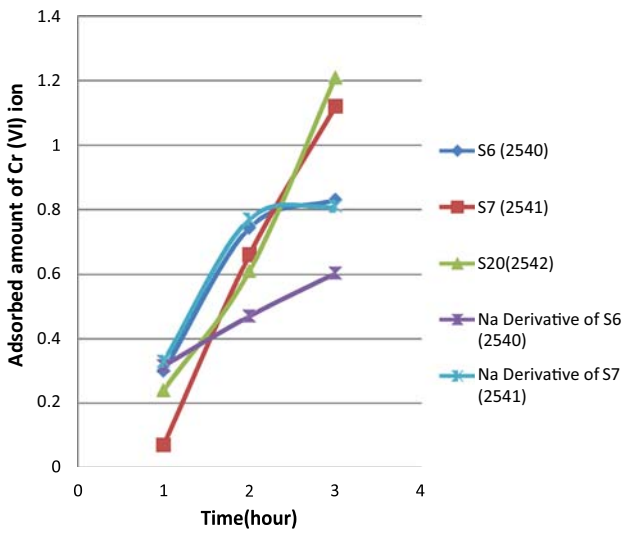

Figure 8. Plot of variation of adsorbed amount of Chromium (VI) ion with time.

$$\text{B-OH} + \text{HCrO}_{4-} = \text{B-HCrO}_4 + \text{OH}^- \quad \text{(II)}$$

$$\text{B-OH} + \text{CrO}_4^{2-} = \text{B-CrO}_{4-} + \text{OH}^- \quad \text{(III)}$$

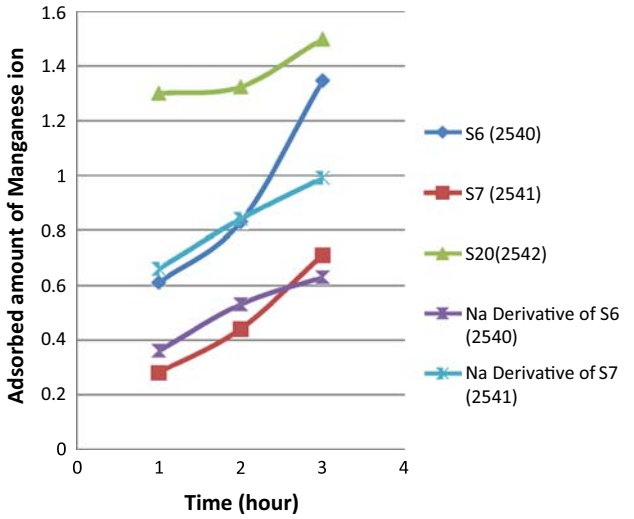

Figure 9. Variation of adsorbed amount of Manganese (VII) ion with time.

Table 15. Variation of adsorbed amount of Chromium (VI) ion with time.

Sample no	Amount adsorbed in 1 h	Amount adsorbed in 2 h	Amount adsorbed in 3 h
S_6 (2540)	0.30	0.743	0.83
S_7 (2541)	0.07	0.66	1.12
S_{20}(2542)	0.24	0.61	1.21
Na Derivative of S_6 (2540)	0.316	0.47	0.603
Na Derivative of S_7 (2541)	0.33	0.77	0.81

Table 16. Variation of adsorbed amount of Manganese (VII) ion with Time.

Sample no	Amount adsorbed in 1 h	Amount adsorbed in 2 h	Amount adsorbed in 3 h
S_6 (2540)	0.61	0.83	1.345
S_7 (2541)	0.28	0.44	0.71
S_{20}(2542)	1.299	1.323	1.498
Na Derivative of S_6 (2540)	0.36	0.53	0.63
Na Derivative of S_7 (2541)	0.66	0.84	0.99

For pH <4, equation (I) and (II) are applicable and for pH >4, equation (III) is applicable. B-HCrO4 is the substrate –adsorbate adducts.

Results of adsorption of Mn (VII) by bentonite also follow the trends of Cr (VI) removal. Maximum removal percentage has been attained in the pH range 2-4. As the pH values increase to 6 adsorbed amount decreases and with a further increase of pH to 10, adsorption decreases abnormally shown in Tables 17 and 18. Thus the best removal takes place at pH 2-4 and optimization of pH for maximum adsorption has been done in the laboratory (Figs. 10, 11, 12, 13).[30]

3.6 *Characterization*

The synthetic bentonite compounds have been characterized by PXRD and FTIR studies. The PXRD studies of the dried sample are done at 2θ position using Cu as anode material (Figures 14 and 15). The diffractometer type used is $D_8$and Cu as anode material. The FTIR is done by the apparatus Perkin Elmer Spectrum version 10.4.1 for the dried sample derivatives (Figures 16, 17).

The montmorillonite can be represented by XRD patterns. Inter planar distance (Å) and corresponding relative intensities in 4.414, 4.3534, 4.396, 4.1984 (Å) having relative intensities 19.63, 90, 17.40, 17.55, respectively. In the OH- stretching region bands around 3620 to 3698 cm^{-1} represent surface OHs and inner OH. Thus the absorption bands at 3446-3698 cm^{-1} represent fundamental stretching vibrations of different OH group e.g. Mg-OH-Al and Fe-OH-Al in the octahedral layer. The bands at 3698.03 and 3621.23 correspond to Al-OH vibration which characterizes montmorillonite. The higher bands are due to surface OHs and band at 3621.23 originates from the inner OH.A band at 3436 cm^{-1} observed indicates the presence of natural disordered Kaolinite in small proportion. 362 cm^{-1} vibration indicates Al-OH-Al. The bands around at 778.2 cm^{-1}, 995.60 cm^{-1}, indicate the presence of MgO and Al_2O_3, respectively. The peak at 1636.10 shows the absorbed water between the layers. The peaks obtained in FTIR analysis characterize the vibration bands of montmorillonite.[35] It may be concluded that peaks are identical to Na-montmorillonite derivative having a trace of impurities e.g.,

Table 17. Chromium (VI) adsorption (removal) of samples at different pH level.

Sl. no	Sample no.	Amount	Time	pH	Initial Conc. (mg/L)	Final Conc.(mg/L)	Percentage removal
1	S_6(2540)	1 gm	1 h	2	2	0.89	55.5%
2	S_6(2540)	1 gm	1 h	4	2	1.06	47%
3	S_6(2540)	1 gm	1 h	6	2	1.08	46%
4	S_6(2540)	1 gm	1 h	8	2	1.22	39%
5	S_6(2540)	1 gm	1 h	10	2	1.36	32%
Sl. no	Sample no	Amount	Time	pH	Initial Conc.(mg/L)	Final Conc. (mg/L)	Percentage removal
1	S_7(2541)	1 gm	1 h	2	2	1.02	49%
2	S_7(2541)	1 gm	1 h	4	2	1.06	47%
3	S_7(2541)	1 gm	1 h	6	2	1.09	45.5%
4	S_7(2541)	1 gm	1 h	8	2	1.17	41.5%
5	S_7(2541)	1 gm	1 h	10	2	1.42	29%

Table 18. Manganese (VII) adsorption (removal) of samples at different pH level.

Sl. no	Sample no.	Amount	Time	pH	Initial Conc. (mg/L)	Final Conc. (mg/L)	Percentage removal
1	S_6(2540)	1 gm	1 h	2	2	1.01	49.5%
2	S_6(2540)	1 gm	1 h	4	2	1.03	48.5%
3	S_6(2540)	1 gm	1 h	6	2	1.23	38.5%
4	S_6(2540)	1 gm	1 h	8	2	1.77	11.5%
5	S_6(2540)	1 gm	1 h	10	2	1.79	10.5%
Sl. no	Sample no	Amount	Time	pH	Initial Conc.(mg/L)	Final Conc.(mg/L)	Percentage removal
1	S_7(2541)	1 gm	1 h	2	2	1.08	46
2	S_7(2541)	1 gm	1 h	4	2	0.82	59
3	S_7(2541)	1 gm	1 h\	6	2	1.22	39
4	S_7(2541)	1 gm	1 h	8	2	1.37	31.5
5	S_7(2541)	1 gm	1 h	10	2	1.41	29.5

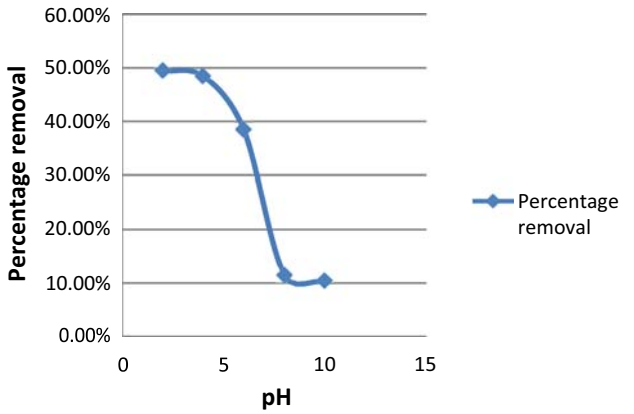

Figure 10. Manganese (VII) adsorption (removal) of samples at different pH level for S_6 (2540).

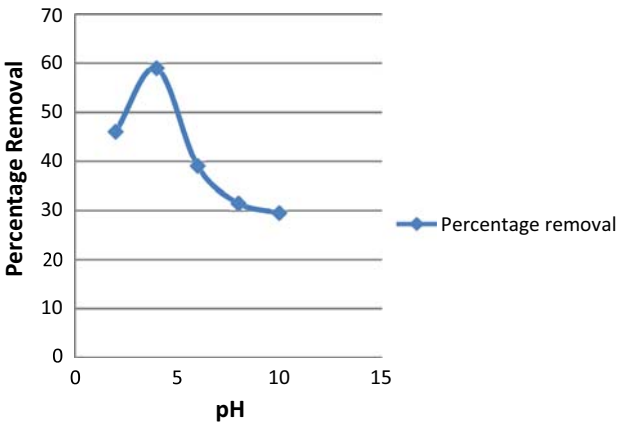

Figure 11. Manganese (VII) adsorption (removal) of samples at different pH level for S_7 (2541).

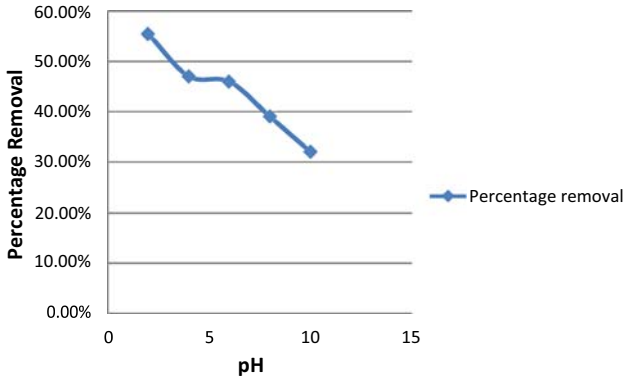

Figure 12. Chromium (VI) adsorption (removal) of samples at different pH level for sample S_6 2540.

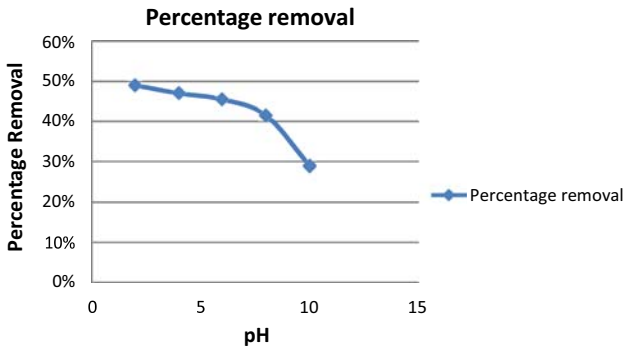

Figure 13. Chromium (VI) adsorption (removal) of samples at different pH level for sample S_7 2541.

Kaolinite. The thermal studies have been done up to a temperature of 1000 °C showing weight loss of 14% and 17% which is due to loss of hygroscopic water and dehydroxylation.

4. Conclusions

Experimental data and observations have established the fact that bentonite and their derivatives are potential adsorbents of Cr (VI) and Mn (VII) from aqueous medium. Furthermore, the adsorption capacity of the bentonite sample increased with decreasing pH value in the range whereas, at higher pH value, the adsorption capacity of bentonite decreases. Thus pH plays an important role in adsorption characteristics. The isothermal studies show that Langmuir is the best fit models for the adsorption of Cr (VI) and Mn (VII). Increased dose of adsorbent enhanced the adsorption capacity. It may be concluded that bentonite minerals have the potential to be employed as an efficient adsorbent of Cr (VI) and Mn (VII) due to its abundance and low cost.

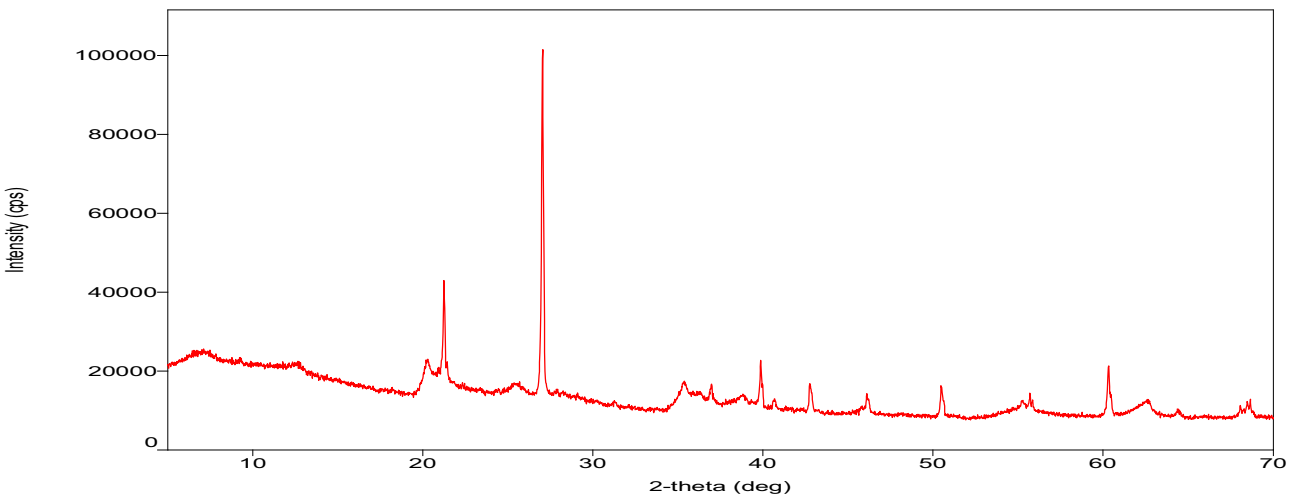

Figure 14. XRD curve for derivative S_7 NaCl (2541).

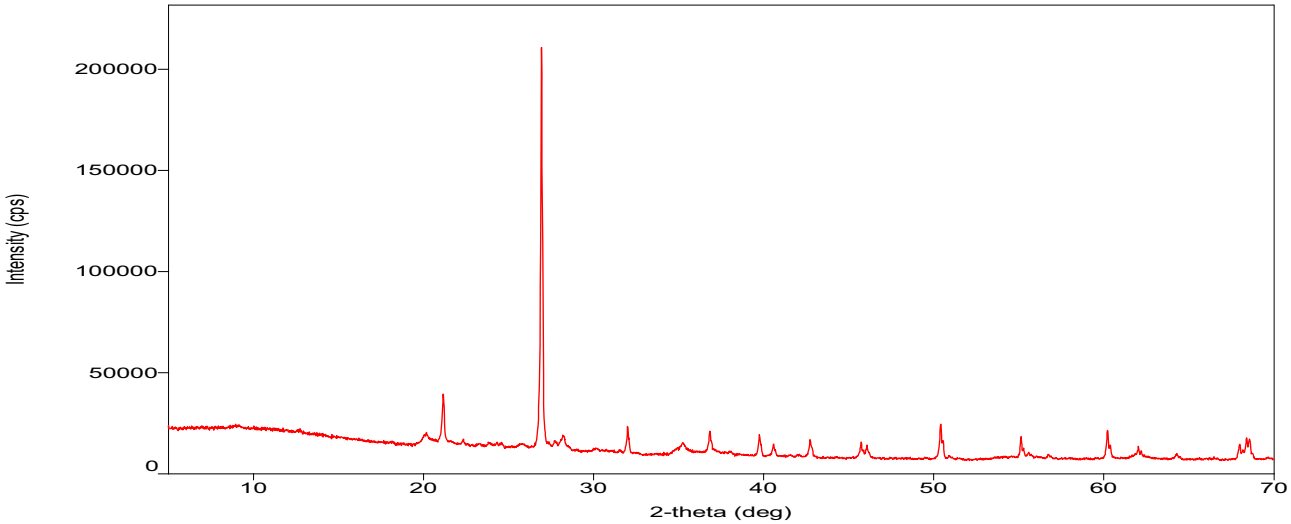

Figure 15. XRD curve for derivative S_6 NaCl (2540).

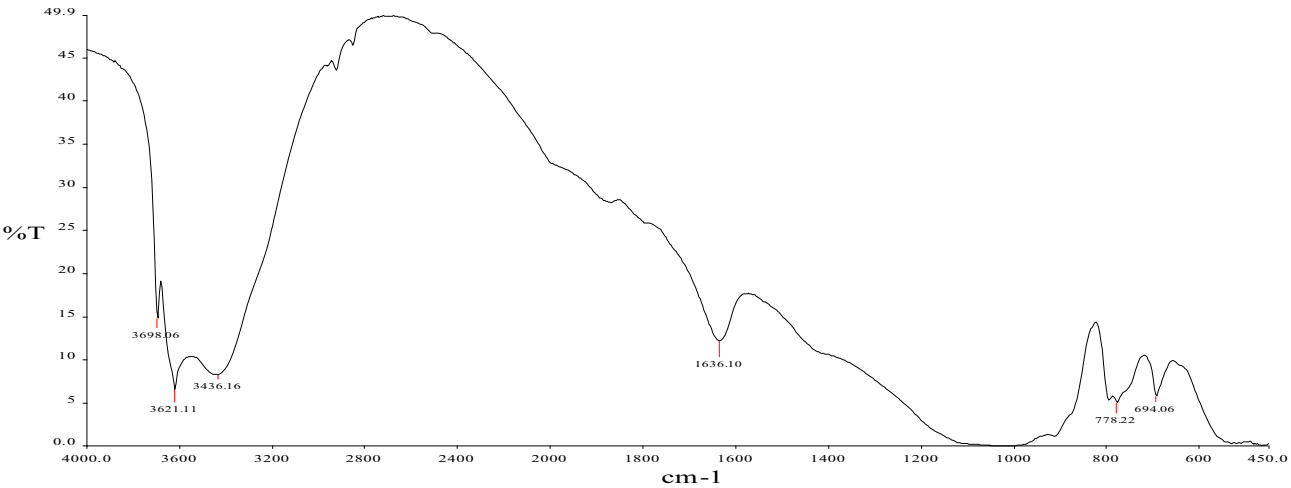

Figure 16. FTIR of derivative S_7Nacl (2541).

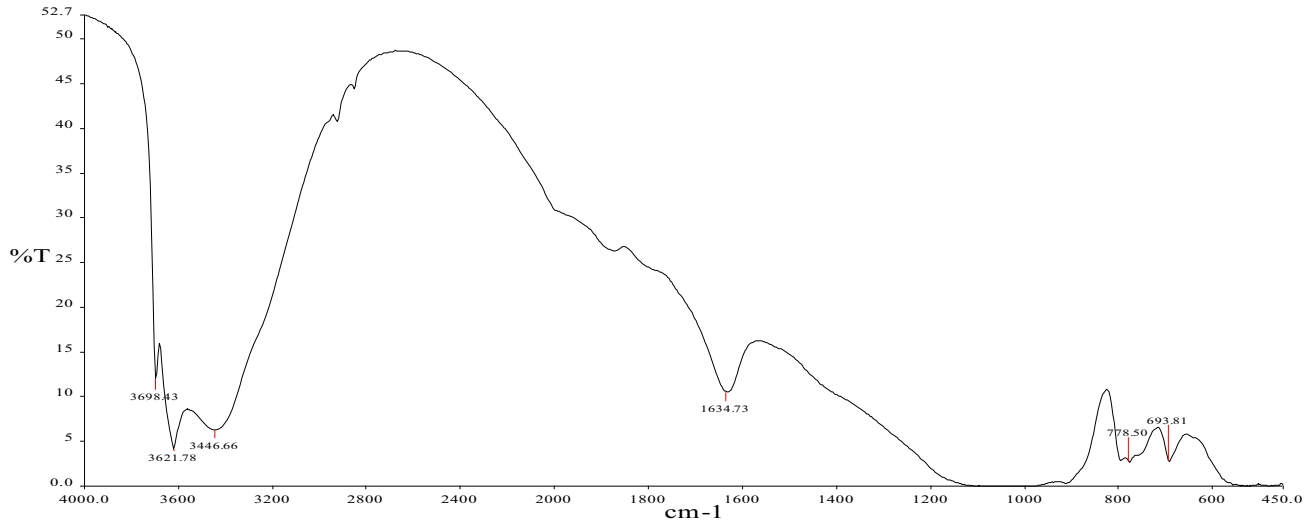

Figure 17. FTIR of derivative S_6 NaCl (2540).

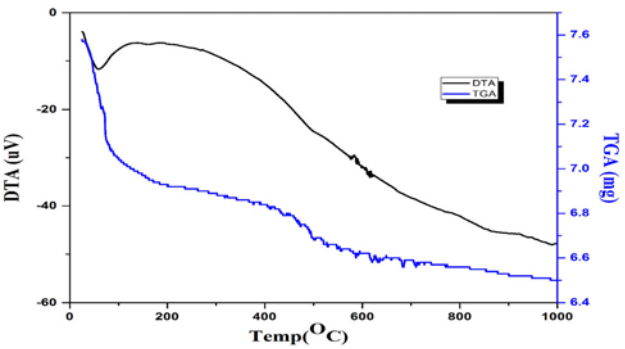

Figure 18. TGA DTA curve for derivative S_7 NaCl (2541).

Supplementary Information (SI)

Tables S1-S5 are available at www.ias.ac.in/chemsci.

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Compliance with ethical standards

Conflict of interest There are no conflicts to declare

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