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Sorption of chromate by HDTMA-Exchanged Zeolites

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ABSTRACT

Sorption of Cr (VI) from aqueous solutions on Erionite, Cowlesite and Willhendersonite modified with hexadecyltrimethyl ammonium bromide (HDTMAB). Experiments were carried out as a function of solution pH, solute concentration and temperature (15°C- 35°C). Modified zeolites were investigated by X-ray diffraction and Fourier transforms infrared analysis. The HDTMA modified zeolites showed significant sorption for chromate ions in aqueous solution. Sorption data for each anion was well described by Langmuir isotherm equation. The thermodynamic parameters (ΔH^o, ΔG^o and ΔS^o) for Cr (VI) sorption on the modified zeolites were also determined from the temperature dependence. FTIR analysis showed that sorbed SMZ forms an ad-micelle surfactant surface coverage, which is responsible for Cr (VI) sorption.

Keyword: HDTMA-exchanged zeolite, chromate, kinetic.

INTRODUCTION

Chromium is a heavy metal that can be very frequently found in a high proportion in waste water discharges from different industries [1]. There are greater concerns about heavy metal contamination [2,3] in the receiving water system and land. High levels of heavy metals can damage soil fertility and may affect productivity [4,5]. Chromium exist in oxidation states +2, +3, +4, +5 and +6, but the most common, stable and abundant forms are Cr (III) and Cr (VI) [6]. The Cr (VI) species is more toxic and carcinogenic than Cr (III), however, it is possible that Cr (III) may be oxidized to Cr (VI) in the appropriate conditions hence the toxicity of Cr (VI) takes place usually, Cr (III) is readily oxidized to hexavalent state at high pH [7]. Leather and chromium planting industries are the major causes for environmental influx of chromium [8,9]. In aqueous solutions, Cr (VI) is very soluble and exists in the form of chromic acid (H_2CrO_4) and in the form of dichromate ($Cr_2O_7{}^{-2}$) while in neutral solutions, Cr (VI) is present in the form of $HCrO^{-4}$ and $CrO_4{}^{-2}$ [10]. Cr (III) is readily oxidized to the hexavalent state at high pH [11]. Cr (VI) has been recognized as a probable agent of lung cancer and it also produces gastrointestinal disorders, dermatitis and ulceration of skin in man [12]. The world health organization (WHO) recommends a maximum level of 50μg/L (PPb) for Cr(VI) in drinking water [13] and the national institute for occupational safety and health (NIOSH) recommends that the levels of chromium should be reduced to 10^{-3} mg/m^3 [14]. There are a number of methods employed [15-19] for removal of hexavalent chromium from industrial waste water such as the use of various types of sorbents. In the last years the sorption of Cr(VI) on several low coast biosorbents has been investigated. Some of the biosorbents tested include Eucalyptus bark, Agave lechugilla biomass, yonimbe bark and grap stalk [20-22]. Recently the ion exchange resin in the cationic form [23], Zeolite [24] betonites [25] and activated carbon [26] have been used to remove Cr. The main industrial activities that cause chromium pollution are mining, metal finishing and leather tanning. In aqueous systems the chromium can be mainly found as Cr(III) can be considered a biotelemetry since it plays an important role in the metabolism of plants and animals. On the other hand, Cr (VI) is very toxic even at very low concentrations, and causes mutagenic effects in plants and animals. The sorption of Cr (VI) on various sorbents has been studied extensively as an alternative process for removing Cr (VI) from water solutions. The activated carbon is the most studied sorbent and his capacity for sorbing Cr (VI) is dependent upon the solution pH. In the last years the sorption of Cr (VI) on several low cost biosorbents has been investigated.

Zeolites are based on an infinitely extending three dimensional network of AlO_4 and SiO_4 tetrahedral linked to each other by sharing all the oxygen ions [27]. The most naturally occurring materials have negative charges on their external surfaces, which will prevent sorption and retention of anions, efforts were made to convert the surface charges from negative to positive by surface modification to increase their anion retention [28] due to strong sorption on negatively charged materials, cationic surfactants were used extensively for modification of clay minerals and zeolites [29,30,31]. The surfactant – modified zeolites were initially intended as sorbents to remove hydrophobic organic compounds from water because of their higher organic carbon contents after modification. Subsequently, researchers found that in the presence of surfactants (i.e. beyond 100% of external cation exchange capacity of zeolites). The sorbed surfactant molecules from an admicelle formation, resulting in strong sorption of anionic contaminants such as arsenate and nitrate [32]. The removal of anionic contaminants from water by SMZ was attributed to surface anion exchange as indicated by the stoichiometry between anion sorbed and counter ions desorbed most of these studies were limited to batch tests, even through a preliminary pilot scale test was performed on using SMZ to remove chromate from water. The purpose of this study was to conduct the sorption of chromate by HDTMA exchanged zeolite at different parameter like kinetics and thermodynamic.

EXPERIMENTAL SECTION

2.1Chemicals & reagents

Sodium nitrate, potassium nitrate, calcium nitrate, aluminium nitrate were purchased from MERCK, surfactant modifier HDTMA, potassium chromate, sulphuric acid were procude from QUALIGENS. A Cr^{+6} complexion reagent solution of 1, 5 diphenylcarbazide (DPC)

[HIMEDIA]. HDTMA was prepared by dissolving 0.25 gm of DPC in 100 ml of acetone, and stored in amber –colored bottle. All reagents were analytical grade and the solution was prepared in DDIW.

2.2 Surfactant modification

The surfactant used is hexadecyltrimethyl ammonium HDTMA, a cationic surfactant and bromide as the balancing counter ion. The synthesize zeolite (HDTMA-E, HDTMA-C, HDTMA-W) 5gm were loaded with cationic surfactant HDTMA 0.25 gm these mixtures were removed. Zeolites were washed with to portions of distilled water and then air-dried.

2.3 Characterization

Powder X-ray diffraction (XRD) was recorded on diffractometer with Cu Kά radiation (Y= 1.54059). FTIR spectra of HDTMA-E, HDTMA- C, and HDTMA- W were recorded on a FTIR - spectrometer (NICOLET-410 spectrometer).

2.4 Batch mode sorption studies

Batch mode sorption studies were carried out by shaking 100 ml conical flasks containing 0.1gm of ECW- HDTMA & 50ml of chromate solution of desired concentration on thermostate water bath shaker at 150 rpm, 25^oC & at an initial pH 1.0. The solution pH was adjusted with 0.1N HCL & 0.1N NaOH solutions. At the end of the sorption period the supernatant was separated by centrifugation 3000 rpm for 30 minute. Then the concentration of the residual chromate ion was determined by UV-visible spectrophotometer. The amount of chromate sorbed was calculated from the concentration in the solution before and after sorption. Effect of pH on sorption of chromate on to HDTMA-ECW was studied for the chromate concentrations. Effect of contact time was studied by withdrawing the sample from the shaker at predetermined time intervals and residual chromate concentration was analyzed as above. Effect of sorbent dose was studied with different sorbate doses (50-250mg 50 ml^{-1}) for the chromate concentration.

RESULTS AND DISCUSSION

3.1 Charecterization of the sorbents

Fig.1 shows the XRD- patterns of HDTMA-E, HDTMA-C & HDTMA-W. The XRD patterns of all zeolites gave a clear diffraction peaks, even though not sharp. X-Ray powder diffraction pattern of these zeoltes have been recorded using Cu Kά radiation in a range $2\theta= 5^o-120^o$ at a scanning speed of 1 step / sec. The FTIR spectra of HDTMA-ECW are shown in Fig. 2 a, b & c. It is found in the range 950-1250 cm^{-1} and 420- 500cm^{-1} strongest vibration at 950-1250cm^{-1} is assigned to T-O stretching and the next strongest band at 420-500cm^{-1} is assigned to T-O bending mode (T= Si or Al). The reason 1800 & 3500cm^{-1} presents to measure sorption bands centered at 3420 cm^{-1} (hydrogen bonded –OH group) & 2921cm^{-1} (C-H stretching of $–CH_2$ group). The intensity of the bond at 2921cm^{-1} increase due to the increase in aliphatic carbon content in HDTMA-ECW which in turn is due to the sorption of HDTMA on to zeolite surface.

3.2 Cr (VI) up take by HDTMA-E, HDTMA-C & HDTMA-W

Chromate exchanged in zeolites (HDTMA- E, C, W) increased by increasing the initial pH value. In the present study, the highest exchange capacity of Cr (VI) was obtained when using solutions with initial pH of 1, which changed to give a final pH value of 9. The results reveal that the sorption percentage is maximum at pH 7. The effect of amount of HDTMA exchanged zeolite on the removal of Cr (VI) is shown in (Fig-3). The results showed that sorption percentage increase as the dose of the sorbent increases. This increasing trend is expected since the number of sorption sites also increase.

3.3 Effect of Cr (VI) concentration on sorption

The sorption of CrO_4^{-2} ion on HDTMA exchanged zeolites were conducted with various initial concentrations (0.01-0.05N) at initial pH 1 (equilibrium pH 7). The results show that the sorption capacities increased with increasing initial concentration (Fig- 4). In order to establish the maximum Cr (VI) sorption capacity, the Langmuir equation of the following form was applied to the sorption equilibria at different concentration:

$$\mathbf{Ce/q_e = 1/\ bqm + Ce/q_m \qquad (1)}$$

Where Ce is the concentration of the metal solution at equilibrium (mmol/L), q_e the amount of Cr (VI) sorbed at equilibrium (mmol/g), q_m the maximum sorption capacity and b is the constant related to binding energy of sorption system. The linearity of the plots (Table.1 & Fig.5) shows that the sorption follows the Langmuir model with maximum capacities for HDTMA-E, HDTMA-C & HDTMA-W respectively. It appears that there is a strong correlation (R^2= 0.9999) between Cr (VI) sorption capacity to exchange capacity of HDTMA in zeolite.

3.4 Thermodynamic parameters

The amount of sorption of Cr(VI) by HDTMA- exchanged zeolite increased as temperature increase from 15°C-35°C. The following relationship has been used to evaluate thermodynamic parameters viz. Gibbs free energy ΔG^o, enthalpy ΔH^o & entropy ΔS^o:

$$\mathbf{\Delta G^o = -RT\ ln\ Kd \qquad (2)}$$

And

$$\mathbf{Log\ Kd = -\ (\Delta H^o / 2.303R)\ 1/\ T + \Delta S^o / 2.303R \qquad (3)}$$

Where Kd is the equilibrium constant calculated as the ratio between sorption capacity and equilibrium concentration. The change in energy (ΔG^o) for Cr(VI) sorption were calculated using eq. 2 for HDTMA-E, HDTMA-C & HDTMA-W respectively at 25°C. The negative values of ΔG^o (Table.2) means that the sorption of Cr (VI) ion on HDTMA–exchanged zeolite is spontaneous. From eq.3 a plot Log Kd vs. 1/T (Fig. 6), positive value of ΔH^o indicate that the endothermic nature of sorption process. A slightly positive entropy change for sorption of Cr (VI) ion on HDTMA- exchanged zeolite is due to fixation of ions on the exchange sites.

3.5 Sorption kinetics of Cr (VI) by HDTMA – exchange zeolites

The kinetics of sorption of Cr (VI) by modified zeolites was studied in batch experiments. The first order rate constants for sorption of Cr (VI) ions determined using Lagergren eqn.

$$\mathbf{Log\ (qe-q) = log\ qe-\ (Kads / 2.303)\ t \qquad (4)}$$

Where q and qe are the amount of metal ions sorbed mgg_{-1} at time t and at equilibrium respectively, Kads is the sorption rate constant.

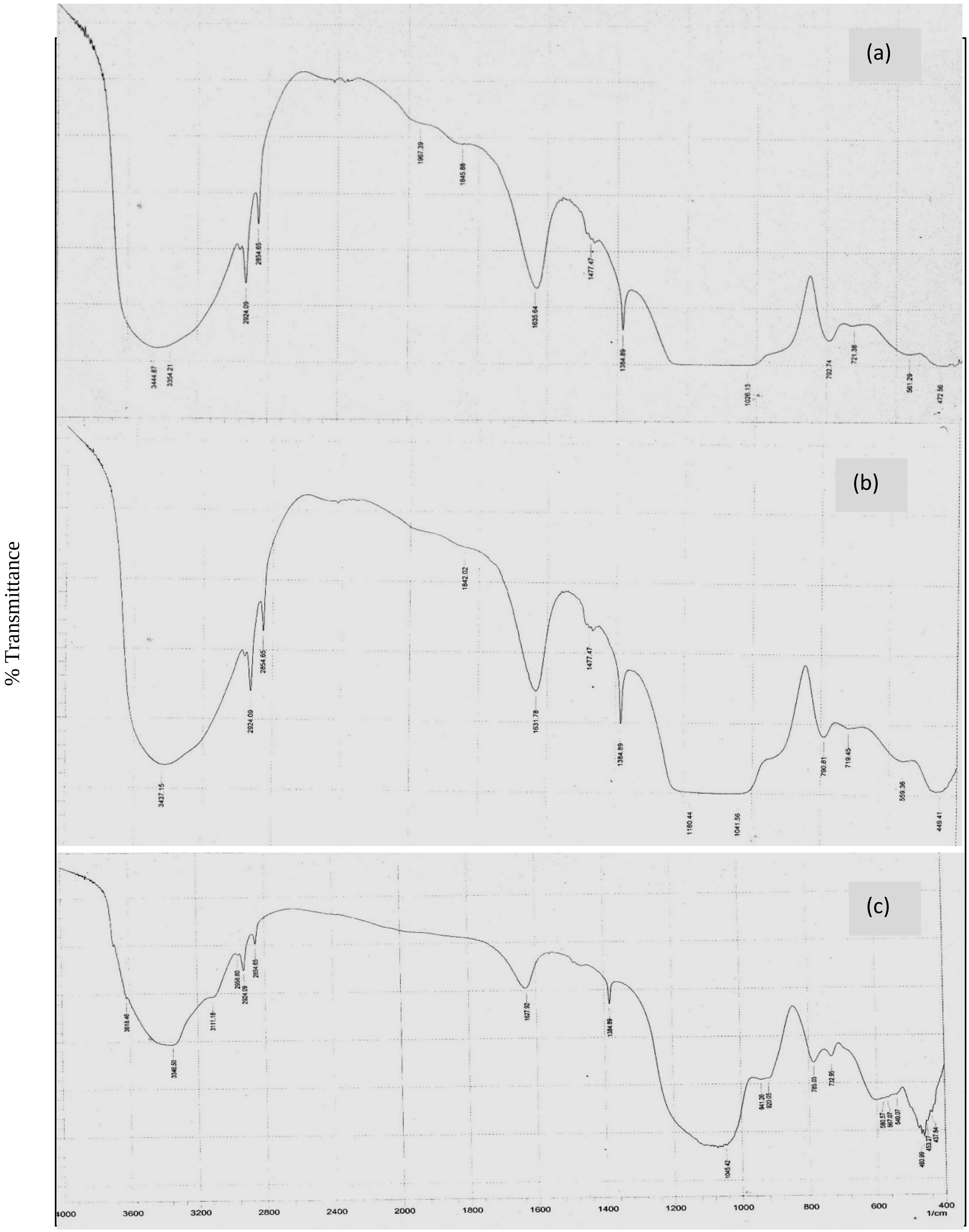
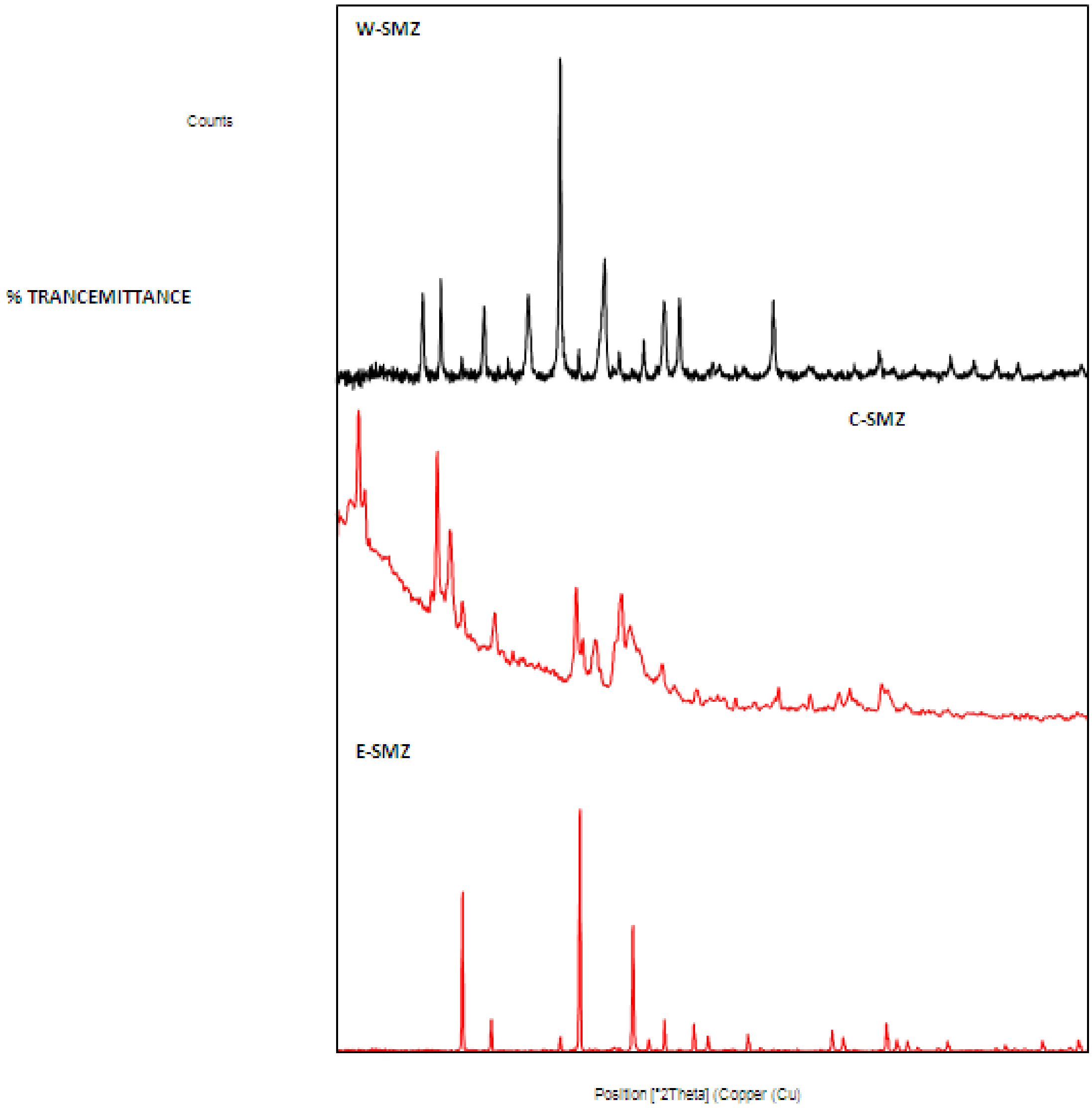


Fig.1(a), (b) & (c) FTIR spectra of hydrothermally synthesize and modified E-SMZ, C-SMZ & W-SMZ



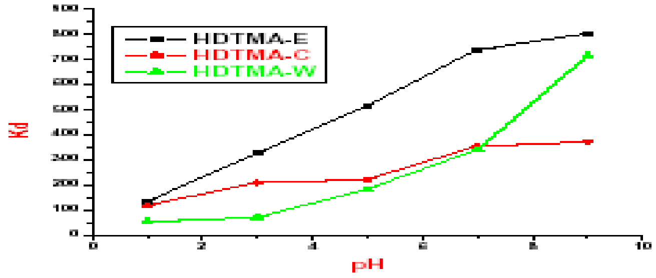


Figure.3. Effect of pH on Sorption of Cr(VI) on HDTMA-Zeolites

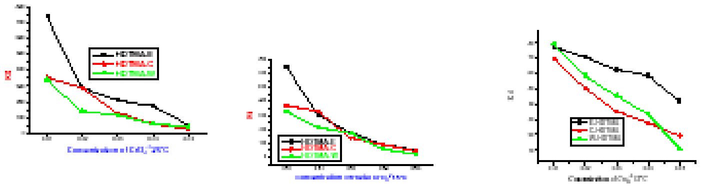


Figure.4. Effect of Cr (VI) concentration on sorption

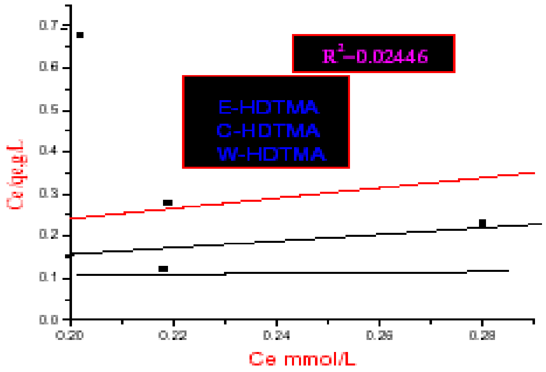


Figure.5. Langmuir isotherm of Cr(VI) sorption by HDTMA- Zeolites

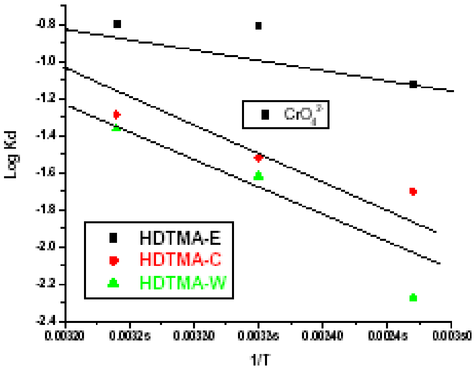


Fig. 6. Plot of Log Kd Vs 1/T for Cr(VI) sorption on HDTMA-Zeolites

Table1: first order Kinetic constants for Cr(VI) onto HDTMA-exchanged zeolites.

Zeolites	First order expression	
	k	R^2
E-HDTMA	-0.01171	0.0626
C-HDTMA	-0.05698	0.6243
W-HDTMA	-0.00811	0.3676

Table2: Langmuir Adsorption isotherm parameters of Cr(VI) on HDTMA-Zeolites

Zeolites	Cr(VI)maximum sorption(qm) mgg^{-1}	Longmuir binding energy constant, (b) Lmg^{-1}
E-HDTMA	-0.3633	-0.1553
C-HDTMA	-1.6345	-0.6271
W-HDTMA	-1.2097	-0.1564

Table3: Thermodynamic Parameters for adsorption of Cr(VI) by HDTMA-Zeolites

Zeolites	Temp(K)	ΔG^0(KJ/mol)	ΔH^0(KJ/mol)	ΔS^0(J/Kmol)
E-HDTMA	288	1.18045	98.694	-24.5244
	298	1.0177		
	308	0.9065		
C-HDTMA	288	-23.2582	69.485	80.9990
	298	-24.0682		
	308	-24.8782		
W-HDTMA	288	-25.7253	98.6946	82.7224
	298	-24.5685		
	308	-25.3798		

A straight line plot of Log (qe-q) V/s t (Table.3 & Fig.7) indicates the applicability of the first order kinetic for Cr (VI) sorption. The Kads values calculated from the slope of the plot for the HDTMAE, HDTMA-C & HDTMA-W.

CONCLUSION

HDTMA–Br was used to modify the surface of zeolites (Erionite, Cowlesite and Willhendersonite). Removal of chromate ion from aqueous solution by surfactant modifier was found to be effective. HDTMA-E, HDTMA-C, HDTMA-W have been characterized using X-ray powder diffraction & FTIR techniques. Optimum pH for chromate removal was found to be pH 7.0. The results also show that the sorption percentage and Kd value increase with increasing initial Cr (VI) concentrations. The sorption followed Langmuir model with maximum Kd value at 25°C for HDTMA-E, HDTMA-C & HDTMA-W respectively. The amount of Cr (VI) by HDTMA-exchanged zeolite increased as temperature increase from 15°C to 35°C indicated that the process was endothermic. The free energy change ΔG° for the sorption at 25°C were -1.01, -24.06 and -24.56 KJ/mol for HDTMA- E, HDTMA-C & HDTMA-W respectively. The negative value of ΔG° shows that the sorption of Cr (VI) ions on HDTMA exchanged zeolite is spontaneous. A slightly entropy change for sorption of Cr (VI) ion on HDTMA exchanged zeolite could be due to fixation of the ions on the HDTMA exchange site that randomly distributed on the sorbents. The kinetic study showed that Cr (VI) sorption followed 1st order kinetic model. The first order rate constant for the sorption of Cr(VI) were 11.7 X 10^{-3}, 56.9X 10^{-3} and 8.11 X $10^{-3}min^{-1}$ for HDTMA- E, HDTMA-C & HDTMA-W respectively.

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REFERENCES

[1] H.B. Bradle, C. Kim, U. Kramar and D. Stuben, introductions of heavy metals. In H.B. Bradle Ed., heavy metals in the environment; origin, Interaction and Remediation. Elsevier Ltd. London, UK, pP. 104-1075.
[2] D.T. Gardiner, R.W. Miller, B.Badamchain, A.S. Azzari, D.R. Sisson, *Agri. Ecosys. Environ*. 55 (**1995**) 1-6.
[3] T.J. Logan, R.L. Chaney. In Proceedings of the workshop on utilization of municipal waste water and sludge on land University of California Riverside (**1983**) 235-326.
[4] A.C. Chang, T.C. Granato, A.L. Page, *J. Environ. Qual*. 27 (**1992**) 521-536 .
[5] P.S. Hooda, B.J. Alloway, *Sci. Total Environ.* 149 (**1994**) 39-57.
[6] S.A. Katz, H. Salem, The biological and environmental chemistry of chromium. (**1994**) New jersey, USA: VCH publisher, Inc.
[7] S.A. Kartz, H. Salem, *J. Appl. Toxicol*. 13 (3) (**1993**) 217-224.
[8] A.J.M. Baker, S.P. Mc Grath, C.M.D. Sidol, R.D. *Res. Cons. Recy*. 11 (**1994**)41-49.
[9] I. Barnhart, *Reg. Toxicol. Pharma*. 26 (**1997**) 53-57.
[10] E. Korngold, N. Belayeb L. Aronov *Separation Purify. Technol* 33 (**2003**) 179-187.
[11] S. A. Katz , H. Salem *J.Appl. Toxical*.13(3) (**1993**) 217-224.
[12] S. Balasubramanian and V. Pugalenthi , *Talanta*, 50 (**1999**) 457- 467.
[13] Zu ed. Reccommendations, guidelines for drinking water quality. Vol 1. Geneva:WHO, (**1993**).
[14] S. Rengaraj, C.K. Kim, J.Yi, *J. Hazard. Mater.*, B87 (**2003**) 273-287.
[15] V.M. Boddu, A. Krishnaiah, L.T. Jonathan, E.D. Smith, *Environ. Sci. Technol*. 37 (**2003**) 4449-4456 .
[16] L. Dupont, E.Guillon, *Environ Sci. Technol*. 37 (**2003**) 4235-4241.
[17] M. Dinesh, P. S. Kunwar, K. S. Vinod, *Ind. Eng. Chem. Res*. 44 (**2005**) 1027-1042.
[18] V.K. Gupta, M. Gupta, S. Sharma, *wat. Res*. 35 (**2001**) 1125-1134.
[19] G. Saumyen, B. Puja, *Wat. Environ. Fed*. 77 (4) (**2005**) 411-417.
[20] V.Sarin, K.K. Pant, *Biosource Technol*., 97(1)15-20 (**2006**) 15-20 .
[21] J. Romero- Gonzalez, J.R. Peralta- Videa, E. Rodriguez, S.L. Ramirez, J.L. Gardea-Torresdey., *J. Chem. Thermodyn*. 37(4) (**2005**) 343-347.
[22] N.Fiol, I. Villaescusa, M. Martinez, N. Miralles, J. Poch, J. Serarols, *Environ. Chem. Lett*., 1(2) (**2003**) 135-139.
[23] S. Rengaraj, C.K. Joo, Y. Kim, J. Yi, *J. Hazard. Mater*. B102 (**2003**) 257-275.
[24] M.A. S.D. Barros, E.A. Silva, P.A. Arroyo, C.R.G. Tavares, R.M. Schneider, M.Suszek, E.F. Aousa-Agewar, *Chem. Eng. Sci.* 59 (**2004**) 5959-5966.
[25] S.M. Bosco, R.S. Jimenez,W.A. Carvalho, *J. Colloidal Interface Sci*. 281 (**2005**) 424-431.
[26] A. Chakir, J. Bessiere, K. Kacemi, B. Ana Marouf, *J. Hazard. Mater*. B95 (**2002**)29-47.2
[27] S. Bhatia, *Zeolite Catalysis* (**1990**).
[28] Li, Z., *Journal of Environmental Quality*, 28 (**1999**) 1457-1463.
[29] S.A. Boyd, M.M. Mortland and C.T. Chiou., *American Journal* , 52 (**1998**) 652- 657.
[30] G.M. Haggerty and R.S. Bowman., *Environmental Science & Technology*, 28 (**1994**) 452-458.
[31] R.S. Bowman, LI. Z., S.J. Roy, T. Burt, T.L. Johnson, R.L. Johnson, S. Burns and J.A.Smith, Kluwer Acadmic Publishers (**2001**) 161-185.

[32] Li. Z., I. Anghel , and R.S. Bowman., *Journal of Dispersion Science and Technology* 19 (**1998**) 843-857.