Kinetics and equilibrium study of chromium adsorption on zeoliteNaX

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ABSTRACT: This study aims to report Batch adsorption study of hexavalent chromium, Cr (VI) on zeoliteNaX. Kinetics of Cr (VI) adsorption and adsorption isotherms were determined by varying operating parameters such as pH, initial concentration, temperature and contact time. ZeoliteNaX was found to remove Cr (VI) in acidic solutions down to ppm level at pH of about 4. Removal rate of Cr (VI) was found to decrease as pH rises above 4.0. Langmuir, Freundlich, Temkin and Redlich-Peterson models were applied to adsorption equilibrium data to find the best amongst these models. Langmuir model with $R^2 = 0.9711$ best fits the adsorption data. The kinetics of adsorption was found to follow the first order reversible reaction. The separation parameter, R_L values of less than 1.0 i.e., 0.7369, 0.5834 and 0.4828 corresponding to initial concentrations of 10, 20 and 30 mg/L, respectively indicated that adsorption of Cr (VI) on zeoliteNaX is favoured. The estimated values of thermodynamic parameters such as heat of adsorption and standard gibbs free energy confirmed the exothermic nature of adsorption of Cr (VI) on zeoliteNaX.

Keywords: *Diffusion; First order reversible reaction; Isotherm; Mass transfer; Regeneration; Thermodynamics*

INTRODUCTION

Metals and their derivatives are potential pollutants that could be particularly problematic due to their stability and mobility. Hexavalent Chromium, Cr (VI) is reported to be a powerful carcinogen capable of modifying the deoxyribonucleic acid (DNA) transcription process in both animals and humans that may result in important chromosome aberrations. It is, therefore, essential to remove Cr (VI) from wastewaters of electroplating, dye, cement, leather tanning and paint industries which may contain up to hundreds of mg/L of chromium though the tolerance limit of Cr (VI) for discharge into inland surface waters is only 0.1 mg/L and in potable water it is as low as 0.05 mg/L (Kobya, 2004). Several conventional techniques, including adsorption, electro-chemical precipitation, reverse osmosis, etc. are used for treatment of effluents containing metal ions. For one reason or the other, most of these techniques are not suitable for large-scale wastewater treatment, especially in developing countries (Gupta and Babu, 2006). Hexavalent chromium exists mainly as H_2CrO_4, $HCrO_4^-$, $Cr_2O_7^{2-}$ and CrO_4^{2-} in aqueous environment and can not precipitate out by treatment with carbonate or hydroxide (Sun *et*

al., 2007). Adsorption is versatile and effective method for removing chromium particularly when it is combined with appropriate regeneration step. This reduces the problem of sludge disposal and renders the system economically viable, especially when the adsorbents used are also of low cost. Adsorption process is used in a variety of important industrial applications and now it is increasingly used on large scale as an economical and efficient separation technique for metal ion removal from wastewater (Zvinowanda *et al.,* 2009). A number of researchers have studied the removal of heavy metal ions from aqueous solution using different adsorbents like granular activated carbon (Agarwal *et al.*, 1999), soya cake (Daneshvar *et al.*, 2002), rubber tyre and sawdust (Hamadi *et al.*, 2001), activated sludge (Xie and Kang, 2003), fly ash (Meng and Dermatas, 2003), wheat bran (Nameni *et al.,* 2008), natural sorbent materials (Shah *et al.,* 2009) and rice husk based activated carbon (Guo *et al.*, 2003). Easily available activated carbon prepared by pyrolysis of wood / agricultural waste is generally used as an adsorbent in most of the commercial scale treatment units. The activated carbon is used only once and regeneration is not possible when metal ions are removed. In the treatment of industrial effluents containing metal ions,

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chelating agents are also used to enhance the process performance, though at an additional cost of chelating agent. If one has to avoid the use of chelating agents, alternative adsorbents have to be identified. This has prompted many researchers to look for different low cost adsorbents through their experimental studies.

Various kinds of soils and clay materials have been tried by several investigators (Okada *et al.,* 2005). Retention of heavy metal cations in soils is due to their strong adsorption onto the negatively charged soil surfaces, their ability to form complex molecules with organics found in the soil and the formation of oxides, hydroxides and other insoluble minerals in soil (Stewart *et al.,* 2003). Several types of crystalline clay minerals such as zeolites are also suitable due to their easy availability globally (Mark, 1998; Mier *et al.*, 2001; Inglezakis, 2004; Meshko *et al.*, 2006) for the removal of heavy metal cations. The metal adsorption efficiency of such clays is due to their chemical and mechanical stability, high surface area, permanent negative charge and a variety of surface and structural properties (Krishna *et al.,* 2000). Fendorf (1994) concluded from experimental studies that Cr (VI) is appreciably retained in soil colloids having net positive charge due to its anionic nature. Cr (VI) is adsorbed by a variety of soil phases with hydroxyl groups on their surfaces such as those present in kaolinite and montmorillonite (Bradl, 2004). Khan *et al.* (1995) have reported that hydroxylated surfaces of oxides of Al, Ca, Mg, Si, etc. acquire charge when present in aqueous solution through amphoteric dissociation.

Since zeoliteNaX contain oxides of aluminium and silicon, its surface should adsorb Cr (VI) as it may also acquire positive charge in acidic medium. Most of the literature available on adsorption of metal ions by zeolites is for the removal of cations and there is hardly any reference available on the removal of anions like Cr (VI). Hence, study on the application of zeoliteNaX for the removal of Cr (VI) from wastewater as an alternative low cost adsorbent is important. In this study, the possibility of using zeoliteNaX to remove Cr (VI) from aqueous solution is investigated. The effect of various parameters such as contact time, initial pH, temperature and initial concentration of Cr (VI) on the removal efficiency of zeoliteNaX was studied. The adsorption data were analyzed using various equilibrium adsorption models, kinetic models, mass transfer and thermodynamic models. The research work was carried out from January 2008 to April 2009 at University School of Chemical Technology, Guru Gobind Singh Indraprastha University, Delhi 110403, India.

MATERIALS AND METHODS
Chemicals
The stock solution of chromium with concentration of 500 mg/L was prepared by dissolving 1.414g of $K_2Cr_2O_7$ in 1000 mL deionised water in volumetric flask. This solution was then diluted to obtain standard solutions containing 10, 15, 20, 25, 30, 40 and 50 mg/L of Cr (VI). Hydrochloric acid and/or sodium hydroxide solutions were used throughout experiments to adjust pH of the solution.

Adsorbent
Particles of zeoliteNaX represented by chemical formula $Na_{81}(AlO_2)_{81}(SiO_2)_{111}$ having cylindrical shape with size of 1.5 mm and bulk density 600 g/L, purchased from Central Drug House (C.D.H.), India were used as the adsorbent in this study. The adsorbent is contacted with 1M NaCl solution to convert it into a near homoionic state in Na form (Curkovic *et al.*, 1997) followed by washing with deionised water and drying in oven at 373K. The dried adsorbent was stored in desiccator. All the chemicals and the adsorbent used were of LR grade and obtained from C.D.H., India.

Analysis
Chromium concentration in different solutions was determined using atomic absorption spectrophotometer model AAS 4141, ECIL, India at wave length 357.9 nm in flame mode using air-acetylene flame. The pH meter, model PHEP, Hanna instrument, Italy,was used in this study between pH range 4-7.

Equilibrium study
The equilibrium study was carried out by varying parameters such as initial Cr (VI) ion concentration, pH and temperature. 250 mL solution of Cr (VI) was taken in 500 mL conical flask and the initial pH was adjusted using HCl/NaOH. One gram of zeoliteNaX was added and flask was kept in the shaking incubator model DK-S1020, Daiki, Korea at desired temperature for 24 h. Flask was kept sealed in order to minimize losses to atmosphere. After 24 h, the solution was analyzed for Cr (VI) concentration. The amount of Cr (VI) adsorbed on the adsorbent (*Q*) was calculated by material balance of chromium concentration in solution using Eq. (1).

$$Q = \frac{(C_{Ao} - C_A)V}{W} \qquad (1)$$

Where, C_{Ao} and C_A are the Cr (VI) concentration (mg/L) in solution initially and at any time (*t*). *V* is volume taken in flask and W is weight of adsorbent used. At equilibrium state, $C_A = C_{Ae}$ and $Q = Q_e$.

The initial concentration of Cr (VI) was varied from 5 to 50 mg/L. The temperature was varied from 292 K to 308 K and the initial pH was varied from 4.0 to 7.0. Percentage removal was calculated using Eq. 2. Correction for any adsorption of chromium on the conical flask surface was made using the control experiments carried out in the absence of zeoliteNaX. These experiments indicated no detectable adsorption by the conical flask surface.

$$Cr(VI)\,removal(\%) = \frac{100(C_{Ao} - C_A)}{C_{Ao}} \qquad (2)$$

Kinetics study

Kinetics study was conducted by varying initial concentration of Cr (VI). Here, 250 mL solution of Cr (VI) was taken into 500 mL conical flask placed in thermostatically controlled water bath placed on a magnetic stirrer. When pre-determined temperature was attained, 1.0 gm of zeoliteNaX was added to the flask. During the experiment, small samples of the solution were taken out for analysis at predetermined intervals of 2 h because contact time to attain equilibrium with the zeoliteNaX is experimentally found to be about 45-60 min. Concentration of Cr (VI) on the adsorbent was obtained by material balance. The initial concentration of Cr (VI) ion was varied from 5 to 50 mg/L. During the experiment temperature was controlled at 293 ± 1K and

initial pH was adjusted to the optimum value of 4.0. The percentage removal was calculated using Eq. 2.

Regeneration study

One gram of adsorbent used in the equilibrium study was regenerated for 2 h at atmospheric conditions by contacting it with 250 mL of 1 M NaCl solution contained in 500 mL conical flask. This was repeated three times with fresh solution. Finally, the adsorbent was washed with deionised water to remove all the free chloride ions so that the wash water passed the silver nitrate test. This regeneration step was repeated three time to check the effect of regeneration on the uptake capacity of the adsorbent.

RESULTS AND DISCUSSION
Effect of pH

The pH is an important parameter that affects the adsorption behavior of metal ions in aqueous systems. Percentage removal of Cr (VI) vs. pH is shown in Fig. 1 for contact time of 24 h, at 293 ± 1K and two initial concentrations of 10 and 20 mg/L. At initial concentration of 20 mg/L, the removal of Cr (VI) decreases from 48 % to 17 % as pH increases from 4.0 to 7.0. Similar trend for Cr (VI) adsorption on activated carbon is reported by Mohammad *et al.* (1996). The pH determines not only the speciation of metal ions, but also affects the surface charge of the solid adsorbents. Rapid increase in adsorption with decrease in pH is usually because of combined effect of variation in the surface charge and shift in ionic species in the solution (Harter *et al.*, 2001). It can also be explained on the basis of the nature of adsorbent. The metal oxides
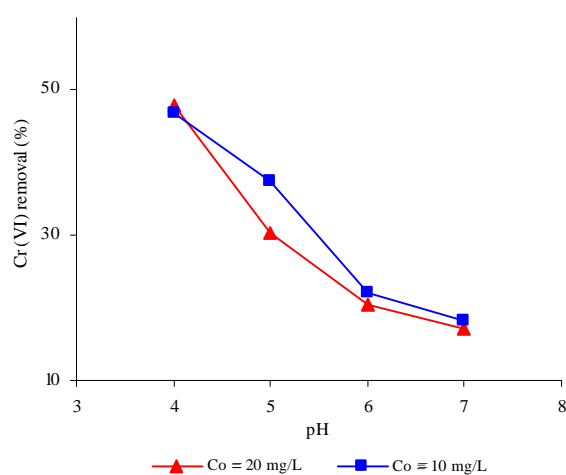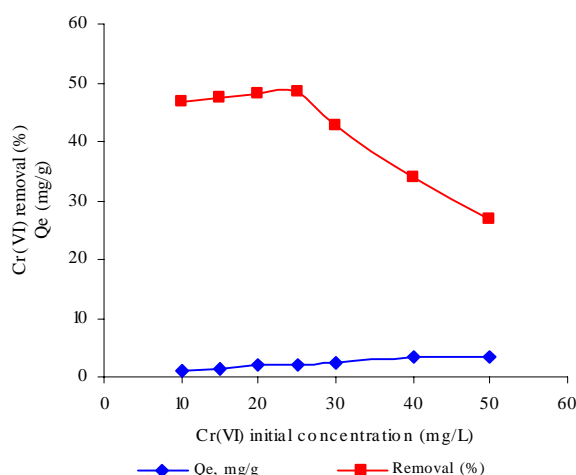

Fig. 1: Effect of pH on Cr (VI) removal

Fig. 2: Effect of initial concentration on Cr (VI) removal

presents in the adsorbent undergo surface hydroxylation in aqueous solution as a result of acid-base dissociation resulting in positive or negative charged surface (Singh *et al.,* 2005). These charges vary depending on the point of zero net charge (PZNC). The PZNC has an important impact on exchange properties of zeoliteNaX. When pH value is less than the PZNC, the variable charge sites develop a net positive charge and conversely, they have a net negative charge when pH value is greater than PZNC. Due to its anionic character, Cr (VI) is favorably adsorbed at lower pH values. There is equilibrium between ions like H_2CrO_4, $HCrO_4^-$, $Cr_2O_7^{2-}$ and CrO_4^{2-} when chromium salt dissociates in aqueous solution. The equilibrium is in favor of H_2CrO_4, $HCrO_4^-$ and $Cr_2O_7^{2-}$ ions at lower pH but it shifts in favor of bivalent CrO_4^{2-} ions as pH increases above 6.0 (Mier *et al.,* 2001). As a result, bivalent CrO_4^{2-} ions become the dominant species. Each of these bivalent ions would neutralize twice the number of sites with univalent charge. The total adsorption capacity for Cr (VI) is, thus, decreased at higher pH.

Effect of initial concentration

Equilibrium percentage removal of Cr (VI) versus initial concentration for contact time of 24 h is shown in Fig. 2. It was found that the percentage removal first increases up to initial concentration of 25 mg/L and then decreases with increase in initial concentration of the adsorbate. But the uptake capacity increases with increase in initial concentration, which may be due to the availability of more number of Cr (VI) ions in solution for adsorption. Moreover, higher initial adsorbate concentration provided higher driving force to overcome various mass transfer resistances of the metal ions from the aqueous to the solid phase resulting in higher probability of collision between Cr (VI) ions and the active sites. This also resulted in higher uptake of Cr (VI) for the given amount of zeoliteNaX.

Effect of contact time

The amount of metal adsorbed also depends on contact time if other parameters like initial concentration, temperature, pH, etc. are kept constant. The effect of contact time on percentage removal of Cr (VI) at optimum pH of 4.0 and temperature of 293 ± 1K is shown in Fig. 3. It shows that Cr (VI) removal increases with increasing contact time at all the initial concentrations and temperatures and approximately 40-50 % of maximum Cr (VI) removed is attained within 10-25 min and the maximum adsorption is attained in about 45 to 60 min. No further

increase in adsorption was noticed up to 24 h. The initial rapid rate of adsorption may be due to the availability of the positively charged surface of the adsorbent for anionic Cr (VI) species present in the solution. The later slow adsorption rate part of the curve may be due to the electrostatic hindrance caused by already adsorbed negatively charged adsorbate species and the slow pore diffusion of the ions (Ghosh and Goswami, 2005).

Effect of temperature

Temperature has an important effect on the process of adsorption. The percentage of Cr (VI) adsorption is studied as a function of temperature. The results obtained are presented in Fig. 3 at temperatures 0f 293 K and 303 K. The decrease in percentage of adsorption with rise in temperature may be due to desorption caused by an increase in the available thermal energy. Higher temperature induces higher mobility of the adsorbate causing desorption.

Equilibrium isotherm

The equilibrium study was carried out for the removal of Cr (VI) by zeoliteNaX. Equilibrium equation, commonly known as sorption isotherm, is basic requirement for the design of a sorption system. The isotherm provides information on the capacity of the sorbent or the amount required for removing a unit mass of pollutant under the operating conditions. Optimizing the design of sorption system to remove Cr (VI) from effluent requires appropriate correlation for the equilibrium data. Four isotherms, namely, Langmuir, Freundlich, Temkin and Redlich-Peterson were tested in the present study. The Langmuir isotherm, one of the first theoretical treatments of non-linear adsorption has been successfully applied to a wide range of data that exhibit limiting or maximum adsorption capacities. It assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate in the plane of the surface. The linear form of the Langmuir isotherm is as follows:

$$\frac{1}{Q_e} = \left(\frac{1}{bQ_o}\right)\frac{1}{C_{Ae}} + \frac{1}{Q_o} \tag{3}$$

Where, Q_e (mg/g) is the adsorbate amount adsorbed on adsorbent at equilibrium and C_{Ae} (mg/L) is equilibrium adsorbate concentration in solution. The parameters Q_o(mg/g) and b (L/mg) are the Langmuir constants that relate the maximum adsorption capacity and energy of adsorption. If the data yield a linear plot $1/Q_e$ versus $1/C_{Ae}$ then it conform to Langmuir isotherm. A further
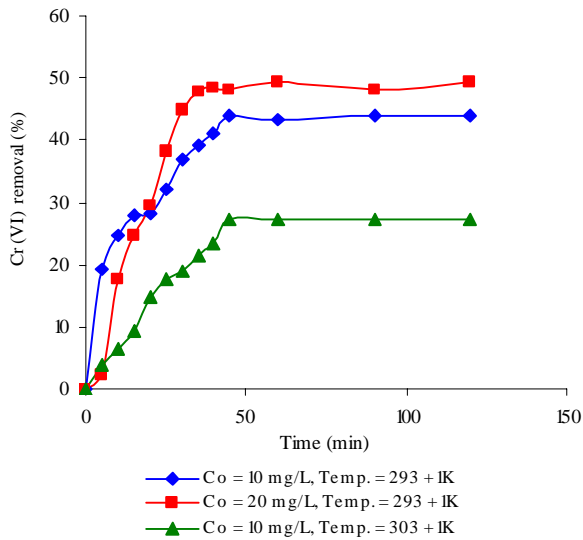
Fig. 3: Effect of contact time and temperature on Cr (VI) removal

analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter R_L (Malik, 2004), known as the separation factor, as given by Eq. 4.

$$R_L = \frac{1}{1 + bC_{Ao}} \tag{4}$$

The value of R_L provides information as to whether the adsorption is irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear favorable ($R_L = 1$) or unfavorable ($R_L > 1$).

Freundlich isotherm represents adsorption equilibrium and is widely used. The empirical equation is capable of describing the adsorption of organic and inorganic compounds on a wide variety of adsorbents. The logarithmic form of the equation is often used to fit batch equilibrium data.

$$\ln Q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_{Ae} \tag{5}$$

Where, K_F (mg/g) and $1/n$ indicate adsorption capacity and adsorption intensity, respectively.

The linear plot of $\ln Q_e$ versus $\ln C_{Ae}$ gives slope of value $1/n$ and an intercept $\ln K_F$. When C_{Ae} equals unity $\ln K_F$ is equal to $\ln Q_e$. In the other case, when $1/n = 1$, the K_F value depends on the units in which Q_e and C_{Ae} are expressed. A favorable adsorption tends to give Freundlich constant n a value between 1 and 10. Larger value of n (smaller value of $1/n$) implies strong interaction between sorbent and metal ions while $1/n$ equal to 1 indicates linear adsorption leading to identical adsorption energies for all the sites. Freundlich

equation fits in nearly all experimental adsorption – desorption data and is especially useful for data from highly heterogeneous sorbent systems (Jonethan, 2009). Temkin isotherm was first proposed to predict adsorption of Hydrogen on platinum electrode in acidic solutions (Jonethan, 2009). Temkin isotherm is based on the assumption that the decline of the heat of adsorption as a function of temperature is linear rather than logarithmic, as implied in the Freundlich equation. A linear form of the Temkin equation can be expressed as:

$$Q_e = A + B \ln C_{Ae} \tag{6}$$

Where, A (mg/g) $= (RT/b_t) \ln(a_t)$ and B (L/mg) $= (RT/b_t)$. If a straight line is obtained when Q_e vs. $\ln C_{Ae}$ is plotted, the intercept on Y-axis gives value of A and the slope can be used to calculate B. Calculated values of A and B are subsequently used for estimating Temkin constants a_t and b_t related to the maximum adsorption capacity and energy of the adsorption. Redlich–Peterson isotherm (Liu and Liu, 2008) is known as three parameter isotherm which represents adsorption equilibrium over a wide concentration range and is represented by the following empirical equation:

$$\ln\left(\frac{C_{Ae}}{Qe} - \frac{1}{k_{rp}}\right) = \ln\frac{\alpha}{k_{rp}} + \beta \ln C_{Ae} \tag{7}$$

Eq. 7 reduces to a linear isotherm at low surface coverage and to the Langmuir isotherm when β is equal to 1. This model fits accurately to the data for several systems, namely bio-adsorption of chromium using suspended and immobilized cells of *Rhizopus arrhizus* (Preetha, 2007), adsorption of cadmium on coconut copra meal (Ho and Ofomaja, 2006), sorption of lead (II) onto peat (Ho, 2006). Redlich and Peterson isotherm incorporates the characteristics of both Langmuir and Freundlich isotherms into a single equation.

Eq. 7 indicates that plot between $\ln\left(\frac{C_{Ae}}{Qe} - \frac{1}{k_{rp}}\right)$ and $\ln C_{Ae}$ will be a straight line with slope b and intercept $\ln(a/k_{rp})$ for constant k_{rp}. Hence, experimental data could be regressed for different value of k_{rp} and optimum value of k_{rp} may be selected for maximum regression coefficient and hence the magnitude of α can be evaluated. The constants evaluated for Langmuir (Eq. (3)), Freundlich (Eq. (5)), Temkin (Eq.
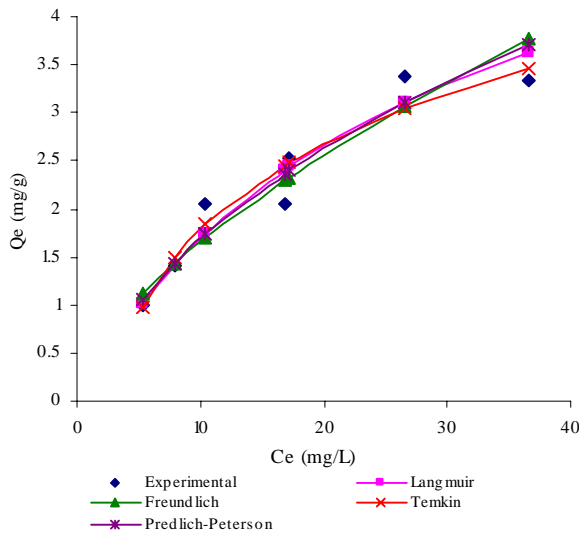
Fig. 4: Asdorption isotherm at Temp. 293+1K, pH 4.0

Fig. 5: Intraparticle diffusion of Cr (VI) on ZeoliteNaX at pH 4.0, Temp. 293 + 1K

Table 1: Estimated isotherm parameters for Cr (VI) adsorption at 293 ± 1K, pH 4.0.

Isotherms	R^2	Estimated isotherms parameters
Langmuir	0.9711	Q_o= 6.414 mg/g , b=0.0357 L/mg
Freundlich	0.9232	K_F=0.3866 , n=1.583
Temkin	0.9281	a_t=0.403, b_t=0.00053
Redlich-Peterson	0.8057	Krp=0.3008, α=0.152, β=0.7121

(6)) and Redlich–Peterson (EQ. (7)) isotherms by regressing the experimental data are presented in Table 1. The experimental and predicted results for zeoliteNaX at 293 ± 1K are shown in Fig. 4. The regression coefficient (R^2) for Langmuir, Freundlich, Temkin and Redlich–Peterson isotherms are found to be 0.9711, 0.9232, 0.9281 and 0.8057, respectively. Thus, the Langmuir adsorption isotherm is the best model for Cr (VI) adsorption on to zeoliteNaX. In the Langmuir equation, Q_o (mg/g) is the measure of adsorption capacity under the experimental condition and the value is 6.414 mg/g and the other constant b is used to evaluate dimensionless constant called separation factor or equilibrium parameter (R_L) using Eq. 3. The calculated values of R_L for the initial Cr (VI) concentration of 10, 20 and 30 mg/L are 0.7369, 0.5834 and 0.4828, respectively. This reflects that in all the cases, R_L values fall between 0 and 1, indicating favorable adsorption of Cr (VI) on zeoliteNaX.

Adsorption kinetics
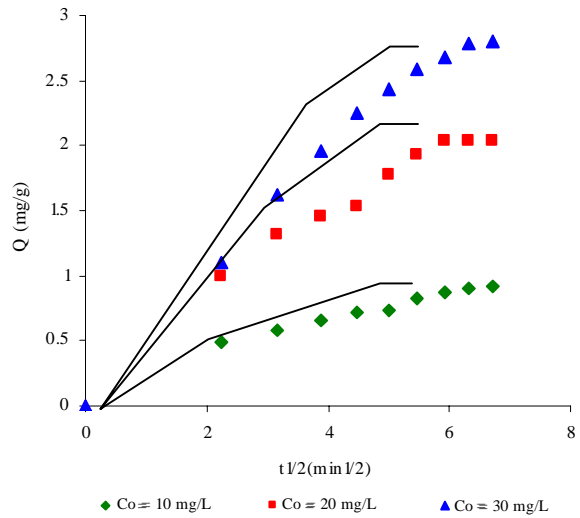   Equilibrium study is important in determining the efficacy of adsorption. It is also necessary to identify the adsorption mechanism for a given system. Kinetic models have been exploited to test the experimental data and to find the mechanism of adsorption and its potential rate-controlling step that include mass transport and chemical reaction. In addition, information on the kinetics of metal uptake is required to select the optimum conditions for full scale batch or continuous metal removal processes. Adsorption kinetics is expressed as the solute removal rate that controls the residence time of the sorbate in the solid–solution interface. Several kinetic models are used to explain the mechanism of adsorption processes. These models include Pseudo-first-order rate model and Pseudo-second-order rate model (Rangaraj, 2003), First-order reversible reaction model (Ghosh and Goswami, 2005), Elovich's model (Ho and Mckey, 1998) and intraparticle diffusion model (Rangaraj, 2003). For the data obtained in the present study, first-order rate model and second-order rate model based on change in adsorbate concentration (C_A) with time are also tested (Levenspiel, 1999).

First order model
The first order rate equation is generally expressed as:

$$-\ln \frac{C_A}{C_{Ao}} = k_1 t \tag{8}$$

Where, k_1 is the rate constant for adsorption. Plot of $-\ln(C_A/C_{Ao})$ Vs t would , therefore, be a straight line passing through origin and the slope will give the rate constant k_1.

Second order model

The second order rate model is also based on change in adsorbate concentration with time and is generally expressed as:

$$\frac{1}{C_A} - \frac{1}{C_{Ao}} = k_1 t \qquad (9)$$

Plot of $(1/C_A)$ vs. t results in a straight line and its slope gives the rate constant k_1.

Pseudo first order model

The Pseudo first order rate model based on adsorption capacity of adsorbent and is generally expressed as:

$$\ln(Q_e - Q) = \ln Q_e - k_1 t \qquad (10)$$

Where, Q_e and Q are the amounts (mg/g) of Cr (VI) adsorbed at equilibrium and at time (t), respectively. Plot of $\ln(Q_e " Q)$ versus t gives a straight line for first order adsorption kinetics which allows computation of the rate constant k_1.

Pseudo-second order model

Pseudo-second order model is derived on the basis of adsorption capacity of the solid phase, expressed as:

$$\frac{t}{Q} = \frac{t}{Q_e} + \frac{1}{k_1 Q_e^2} \qquad (11)$$

The pseudo-second-order rate constant k_1 is determined from experimental data by plotting t/Q vs. t.

Elovich model

Adsorption data can also be analyzed using the Elovich equation at the following linear form:

$$Q = \frac{1}{\sigma}\ln(\theta\sigma) + \frac{1}{\sigma}\ln(t) \qquad (12)$$

Where, θ is the initial adsorption rate constant and the parameter σ is related to the extent of surface coverage and activation energy for chemisorption. Plot

between Q and $\ln(t)$ would be a straight line and slope of the line would give $(1/\sigma)$ and the intercept on Y-axis would provide the value of $\{(1/\sigma)\ln(\theta\sigma)\}$. Thus, parameters θ and σ can be evaluated.

First order reversible reaction model

This model is mostly used for biosorption kinetics (Ghosh and Goswami, 2005). It can, however, describe the adsorption and desorption phenomena simultaneously using rate constant parameters. This model assumes that adsorption of metal (A) on adsorbent (B) follows first-order reversible reaction. The integral form for the model is represented by:

$$-\ln\left(\frac{C_A - C_{Ae}}{C_{Ao} - C_{Ae}}\right) = (k_1 + k_2)t \qquad (13)$$

Where, k_1 and k_2 are rate constants for adsorption and desorption. The plot between $[-\ln\{(C_A - C_{Ae})/(C_{Ao} - C_{Ae})\}]$ vs t would be a straight line with slope $(k_1 + k_2)$. The constants k_1 and k_2 are related to sorbate concentration as:

$$\frac{k_1}{k_2} = \frac{X_{Ae}}{1 - X_{Ae}} = \frac{C_{Ao} - C_{Ae}}{C_{Ae}} \qquad (14)$$

Where, X_{Ae} is fraction adsorption at equilibrium. Hence, k_1 and k_2 can be computed.

Experimental data are regressed to identify the adsorption mechanism for a given system using first-order rate model (Eq. (8)), second-order rate model (Eq. (9)), Pseudo-first-order rate model (Eq. (10)), Pseudo-Second-order rate model (Eq. (11)), Elovich's model (Eq. (12)), first-order reversible reaction model (Eq. (13) and (14)). The results obtained are summarized in Table 2. Kinetics of Cr (VI) adsorption on zeoliteNaX is described well by 2nd order kinetic equation at 10 mg/L ($R^2 = 0.9537$) and 20 mg/L ($R^2 = 0.9573$), Pseudo-first-order rate model at 10 mg/L and 30 mg/L ($R^2 = 0.9571$, 0.9568), Pseudo second order model at 30 mg/L($R^2 = 0.9647$) and Elovich equation at 10 mg/L ($R^2 = 0.9517$) and 20 mg/L ($R^2 = 0.9833$). Only the first order reversible reaction model fits well with all sorbate concentrations having regression coefficient > 0.95. Further, it can be seen from Table 2 that the forward rate constant for the removal of chromium is much higher than the backward rate constant, namely the desorption process. The low value of k_2 (rate constant for desorption process) indicates that the adsorbed chromium is relatively

stable on the adsorbent at temperature and concentration studied.

Intraparticle diffusion model

When mass transfer is the controlling step it is important to identify the diffusion mechanism so Intraparticle-diffusion model is also tested. According to this model, initial rate of the intraparticle-diffusion is given by the following equation (Sengil, 2009).

$$Q = k_{int} t^{1/2} \tag{15}$$

Where, k_{int} (mg/g-min$^{1/2}$) is the intraparticle-diffusion rate constant and Q is the amount of ions adsorbed (mg/g) at time t (min). Plot of q versus $t^{1/2}$ is shown in Fig. 5 for different initial concentrations. All the curves have the same general features. The initial steep portion is followed by gradual linear portion representing the intraparticle diffusion and the plateau represents the equilibrium. Intraparticle diffusion rate constant, k_{int} values are calculated from the slope of gradual linear portion of the curves for C_{Ao} of 10, 20, and 30 are found to be 0.0863($R^2=0.9613$), 0.5397($R^2=0.9787$) and 0.5795 ($R^2 = 0.9697$), respectively. The value for k_{int} is higher at higher concentration.

Thermodynamic parameters

Thermodynamic parameters are required to predict the nature of adsorption of Cr (VI) on zeoliteNaX. Gibbs free energy ("G°"), enthalpy change ("H°") and entropy change ("S°") are some of the important thermodynamic parameters that need to be calculated. The thermodynamic constants; enthalpy change ("H°") and entropy change ("S°") are calculated using the following Eqs. 16 and 17.

$$\ln K = \frac{\Delta H^o}{R} \frac{1}{T} + \frac{\Delta S^o}{R} \tag{16}$$

Plot of lnK vs l/T is used to find the values of "H°" and "S°" from the slope and the intercept. The free energy, "G°" for the specific adsorption is calculated using:

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{17}$$

Where, K is equilibrium constant, R is ideal gas constant (8.314 J/mol K), "G°" and "H° are in J/mol, "S°" is in J/mol K. The calculated thermodynamic parameters are shown in Table 3. The negative value of heat of reaction *"H°"* indicates that sorption of Cr (VI) on zeoliteNaX is exothermic. The value of "G°" for adsorption changes from negative to positive with increasing temperature, that means sorption is less favoured at high temperatures. The decrease in entropy, "S°" shows that the sorbate ions are stable on the solid surface. Association, fixation or immobilization of Cr (VI) ions as a result of adsorption

Table 2: Kinetic models and other statistical parameters at 293 ± 1K and at pH 4.0

Kinetic model	Parameters	Initial Cr (VI) concentration			
		10 mg/L	20 mg/L	30 mg/L	Mean
First-order equation	R^2	0.7669	0.9454	0.8269	
	k_1 (min^{-1})	0.0145	0.0171	0.0149	0.0155
Second-order equation	R^2	0.9537	0.9573	0.9451	
	k_1 (g/mg)/min	0.0015	0.0012	0.0005	0.0010
Pseudo-first-order rate	R^2	0.9571	0.7746	0.9414	
	k_1 (min^{-1})	0.0676	0.1408	0.0926	0.1003
Pseudo-second-order	R^2	0.8641	0.3685	0.7354	
	k_1 (g/mg)/min	0.2245	2.9282	0.3038	1.152
First-order reversible reaction	R^2	0.9601	0.9736	0.9848	
	k_1 (min^{-1})	0.0557	0.0196	0.0594	0.045
	k_2 (min^{-1})	0.0074	0.0014	0.0202	0.0096
Simple Elovich equation	R^2	0.9517	0.9833	0.9358	
	θ	0.3021	0.2147	0.4872	0.3347
	σ	4.5086	1.0734	1.0948	2.2256

Table 3: Calculated k1, k2 and thermodynamic parameters for Cr (VI) adsorption at pH 4.0, Co=10 mg/L

Temperature (^{0}K),	X_{Ae}	k_1 (min^{-1})	k_2 (min^{-1})	ΔG^0 (KJ/mole)	ΔH^0 (KJ/mole)	ΔS^0 (KJ/mole K)
293	0.883	0.0557	0.0074	-4.76045	-148.322	-0.4892
303	0.433	0.0150	0.0196	0.13657		
308	0.297	0.0139	0.0329	2.58509		

Table 4: Equilibrium adsorption capacity at pH 4.0, Temp. 303 ± 1K

Regeneration No.	Initial Cr (VI) Concentration (mg/L)	Equilibrium Cr (VI) removal (%)
I	10	44.40
II	10	42.71
III	10	42.79

is attributed to a decrease in the degree of freedom of adsorbate ions which gives rise to a negative entropy change. Decrease in value of equilibrium constant with temperature rise signifies that the sorption of Cr (VI) onto zeoliteNaX is exothermic in nature. Since adsorption process is exothermic as a rule, the rate constant value of k_1 should decrease with increasing temperature. If the adsorption is exothermic, desorption would be endothermic according to Le Chatelier's principle. Therefore, value of k_2 should increase when temperature rises.

Regeneration study

The Zeolite was regenerated thrice and used to find equilibrium adsorption of Cr (VI) for a contact time of 24 h at initial concentration of 10 mg/L , pH of 4.0 and temperature 303 K. The results of the regeneration study are shown in Table 4. The results show that the adsorption capacity did not decrease appreciably. Hence, zeolitesNaX could be used several times for removal of Cr (VI). Zeolite are being used in pressure swing adsorbers (PSA) for a long time and it is well established that recharge/replacement of zeolites is carried out after thousands of cylcles. The zeolite materials are frequently used as a base for catalysts in several applications (Srivastava, *et al.*, 2005).

CONCLUSION

ZeoliteNaX is identified as an efficient adsorbent for use in the treatment of water contaminated with hexavalent chromium. The results show that zeoliteNaX can efficiently remove chromium from solutions especially at pH close to 4.0 down to ppm level. The Langmuir isotherm gives the best fit for the equilibrium data of Cr (VI) adsoption. Chromium adsorption on zeoliteNaX follows first-order reversible kinetics. The low value of specific rate constant for reverse reaction (desorption process) indicates that the adsorbed chromium is relatively stable on the adsorbent. Therefore, zeoliteNaX can be used for the tertiary level treatment of potable water as well as industrial effluents for the removal of Cr (VI). The kinetics data are useful

for the design and fabrication of wastewater treatment plant. Extensive studies are, however, required to evaluate zeoliteNaX in terms of its competitive adsorption properties and reaction chemistry for situations when other cations and anions are also present in the solution.

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