ORIGINAL PAPER

Adsorption of vanadate(V) on Fe(III)/Cr(III) hydroxide waste

K. Prathap · C. Namasivayam

Abstract Adsorption of vanadate(V) from aqueous solution onto industrial solid 'waste' Fe(III)/Cr(III) hydroxide was investigated. HCl treated Fe(III)/Cr(III) hydroxide was found to be more efficient for the removal of vanadate(V) compared to untreated adsorbent. The adsorption follows second-order kinetics. Langmuir and Freundlich isotherms have been studied. The Langmuir adsorption capacity (Q_0) of the treated and untreated adsorbents was found to be 11.43 and 4.67 mg g^{-1}, respectively. Thermodynamic parameters showed that the adsorption process was spontaneous and endothermic in the temperature range 32–60°C. Maximum adsorption was found at system pH 4.0. The adsorption mechanism was predominantly ion exchange. Effect of other anions such as phosphate, selenite, molybdate, nitrate, chloride, and sulfate on adsorption of vanadium has been examined.

Keywords Vanadate · Adsorption · Kinetics · Isotherms · Temperature
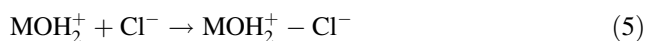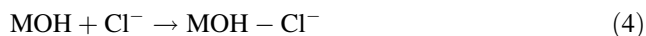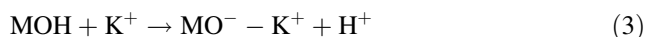
Introduction

Vanadium is widely distributed in Earth's crust and has been recognized as a potentially dangerous pollutant and it is listed on the United States Environment Protection Agency (USEPA) candidate contaminant list (Naeem et al. 2007). Vanadium is mostly found along with phosphorus ores (Jansson-Charrier et al. 1996). The production of phosphoric

acid using these minerals results in the extraction of large amount of vanadate. Vanadium compounds are also present in significant concentration in fuel oil (Jansson-Charrier et al. 1996) and combusting this in thermal power plants produces toxic fly ash. These wastes cannot be disposed directly into the environment because rain water easily leaches vanadate (Naeem et al. 2007). It has been reported that contamination of groundwater occurs with vanadate from industrial mining and natural sources (Ortiz-Bernard et al. 2004). Vanadium/phosphoric acid system is also used as corrosion inhibitor in the place of Cr(VI) in steel industries (Blackmore et al. 1996). Vanadium compounds have shown harmful effects on the circulatory system and can disturb the metabolism of human (Zagulski et al. 1980) and lower the food glucose, cholesterol, and triglycerides in diabetic rats (Nukatsuka et al. 2002).
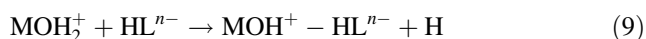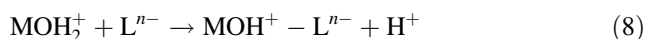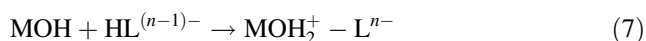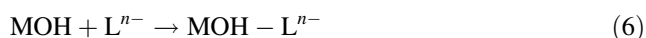
Various biological and chemical treatments have been studied to remove vanadate (Kunz et al. 1976). Blackmore et al. (1996) have shown that vanadium could be removed chemically through adsorption and co-precipitation with FeO(OH). Guzman et al. (2002) also reported that vanadium was removed by chitosan through adsorption process. Although many studies have been conducted in treating vanadium, few studies are available to clearly depict the removal mechanism.

Baes and Mesmer (1976) have extensively studied vanadium species at different pH values. Speciation diagram suggests that vanadium exists in cationic form below pH 3.0 and anionic form between pH 3.5 and 11. Adsorption of oxyanions onto metal(oxy)hydroxide can be described by inner sphere or outer sphere anion surface complexation (Hayes et al. 1988). Surface complex mechanism of anionic species onto metal(oxy)hydroxide can be represented as follows (Su and Suarez 2000; Kreller et al. 2002):
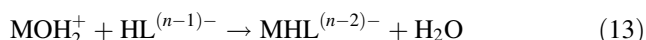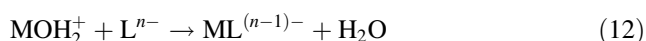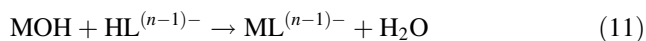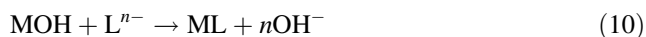
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$$MOH_2^+ \rightarrow MOH + H^+ \tag{1}$$

$$MOH \rightarrow MO^- + H^+ \tag{2}$$

$$MOH + K^+ \rightarrow MO^- - K^+ + H^+ \tag{3}$$

$$MOH + Cl^- \rightarrow MOH - Cl^- \tag{4}$$

$$MOH_2^+ + Cl^- \rightarrow MOH_2^+ - Cl^- \tag{5}$$

Outer sphere complex mechanism

$$MOH + L^{n-} \rightarrow MOH - L^{n-} \tag{6}$$

$$MOH + HL^{(n-1)-} \rightarrow MOH_2^+ - L^{n-} \tag{7}$$

$$MOH_2^+ + L^{n-} \rightarrow MOH^+ - L^{n-} + H^+ \tag{8}$$

$$MOH_2^+ + HL^{n-} \rightarrow MOH^+ - HL^{n-} + H \tag{9}$$

Inner sphere complex mechanism

$$MOH + L^{n-} \rightarrow ML + nOH^- \tag{10}$$

$$MOH + HL^{(n-1)-} \rightarrow ML^{(n-1)-} + H_2O \tag{11}$$

$$MOH_2^+ + L^{n-} \rightarrow ML^{(n-1)-} + H_2O \tag{12}$$

$$MOH_2^+ + HL^{(n-1)-} \rightarrow MHL^{(n-2)-} + H_2O \tag{13}$$

where M is the hydroxylated mineral surface and OH is a reactive surface hydroxyl group. L^{n-} is the oxyanion. Protonation of the reactive hydroxyl group of metal(oxy) hydroxide is represented by Eqs. 1 and 2. Complex formation of background electrolyte ions and the surface is shown in Eqs. 3–5. Outer sphere complex mechanism is represented by Eqs. 6–9, which shows that anion reacts similar to the background electrolyte. Inner sphere coordination mechanism of anions is shown in Eqs. 10–13.

Chemical industries use hexavelant chromium compounds as corrosion inhibitors in the cooling water systems. Periodically fresh Cr(VI) solutions are injected and the spent cooling water is let out. Chromium(VI) in the water is toxic and is reduced to less toxic Cr(III) using ferrous ion produced through an electrolytic process or ferrous sulfate under acidic conditions. The trivalent chromium and iron are precipitated as chromium hydroxide and ferric hydroxide under alkaline conditions. The resultant Fe(III)/Cr(III) hydroxide settles as sludge in lagoons and is removed periodically. The Fe(III)/Cr(III) hydroxide sludge is discarded as waste in the industries. The re-use of solid waste from wastewater treatment plants may reduce the cost of treating vanadate. The use of this solid waste has been applied to removing heavy metals (Namasivayam and Senthilkumar 1998), dyes (Namasivayam et al. 1994), phenol (Namasivayam and Sumithra 2004), phosphate (Namasivayam and Prathap 2005), selenite (Namasivayam and Prathap 2006), and silica (Namasivayam and Prathap 2007). The purpose of this study was to use the solid waste

Fe(III)/Cr(III) hydroxide to remove vanadate(V). Effects of contact time, pH, and temperature were also studied. In this study, effects of the competitive ions such as phosphate, selenite, and molybdate on adsorption of vanadate(V) were also investigated.

Materials and methods

'Waste' Fe(III)/Cr(III)hydroxide was obtained from the Southern Petrochemical Industries Corporation Limited (SPIC), Tuticorin, Tamil Nadu, India. It was grinded and washed with deionized water to remove very fine powder. Then it was dried at 65°C for 12 h. The dried material was sieved to 75–150 μm size and used as adsorbent. The characteristics of waste Fe(III)/Cr(III) hydroxide are shown in Table 1 (Namasivayam and Ranganathan 1994). This material has a fractal dimension usually known for mineral surfaces. The specific surface area (SSA) is made of very small non-micro pores particles. The pore size distribution shows that the particles alone are not porous but the total pore volume for pores is mostly due to interparticle pores. A broad distribution with pores larger than the estimated particle diameter (a maximum around 3 nm) was observed, which most likely corresponds to the small pores created by spheres with a diameter of 10 nm adjacent to each other and such building makes a porous aggregate. Table 1 shows that neither Fe^{3+} nor Cr^{3+} goes into solution in the pH range 3.5–10.0. Ammonium vanadate was obtained from s.d. Fine Chemicals, Mumbai, India.

Table 1 Characteristics of Fe(III)Cr(III) hydroxide

Physical parameters	
SSA ($m^2 g^{-1}$)	147.4
Total pore volume ($cm^3 g^{-1}$)	0.2918
Average pore diameter (nm)	7.9
Apparent density (g ml^{-1})	0.895
Acid (HNO_3) insoluble matter (%)	9.7
Water soluble matter	
(pH range 3.5–10.0)	
Fe(III) (mg l^{-1})	<0.05
Cr(III) (mg l^{-1})	<0.008
Mechanical moisture content (%)	16.8
Loss on ignition (%)	32.8
Total Fe (%)	29.3
Total Cr (%)	5.3
Total Ca (%)	5.0
pH of 0.2% solution	8.11
Conductivity of 0.2% (μS cm^{-1})	68
Particle size (μm)	75–150
pH_{zpc}	8.1

Batch mode adsorption experiments

An aliquot of 500 mg of untreated adsorbent and 50 ml of ammonium vanadate solution of desired concentration were transferred into 250 ml high-density polyethylene bottles and agitated at 160 rpm, 32°C on a mechanical shaker. At the end of the predetermined time intervals, the bottles were withdrawn and the supernatant was centrifuged at 20,000 rpm for 20 min. Then the residual vanadate(V) was analyzed by colorimetric method (Jansson-Charrier et al. 1996) on UV–Vis spectrophotometer (Hitachi, Model U-3210, Japan and/Analytik Jena AG, Specord 200, Germany). Effect of pH was studied in the range 4.0–10.0 using 1 M HCl and 1 M NaOH solutions by means of a pH meter (Elico, Mode LI-107, Hyderabad, India).

Treated adsorbent was also used to study the adsorption process. Treated adsorbent was prepared by shaking the adsorbent, Fe(III)/Cr(III) hydroxide, with distilled water at pH 4.0 adjusted using 1 M HCl. Shaking and adjustment of the supernatant pH to 4.0 were continued until the supernatant pH remained at 4.0. Then the wet adsorbent was separated from the solution and used for adsorption experiments.

In the case of untreated adsorbent, the equilibrium pH (final pH after agitation) was 7.9–8.7 for the initial pH range 4.0–10.0. Since the pH_{zpc} of the adsorbent is 8.1, the surface sites are mostly negatively charged at pH > 8.1, which is less favorable for the adsorption of vanadate anion due to the electrostatic repulsion between the negatively charged surface and vanadate anion. In the case of treated adsorbent, equilibrium pH was found to be 6.5–7.8 for the initial pH range 4.0 to 10.0. At this condition, surface sites of the adsorbent exist mostly as positively charged, which favors the adsorption of vanadate anion by electrostatic attraction between the positively charged adsorbent surface and negatively charged adsorbate. This surface property of the treated adsorbent enhances the adsorption capacity. Effect of foreign anions on adsorption was studied using equimolar concentrations (0.78 mmol l^{-1}) of vanadate(V) and foreign anions.

Desorption studies

The adsorbent that was used for the adsorption of 10 and 20 mg l^{-1} of vanadate(V) solution was separated from the solution by suction–filtration using Whatmann filter paper and washed gently with water to remove unadsorbed vanadate(V). Then the spent adsorbent was agitated for equilibrium time with 50 ml of desorption media. The desorption media were prepared with water at different pH values (4.0–12.0) adjusted using HCl/NaOH solutions. Then the desorbed vanadate(V) was estimated as before.

Temperature study

An aliquot of 50 ml of vanadate solution was added into 500 mg of the untreated adsorbent in a 100-ml conical flask. The concentrations of vanadate solution used are 10, 20, 30, 40, and 50 mg l^{-1} at initial pH 4.0 and the experiments were carried out at 32, 40, 50, and 60°C in a thermostated rotary shaker. The final pH ranged from 7.9 to 8.2.

Effect of foreign ions

Solutions of NO_3^-, SO_4^{2-}, Cl^-, PO_4^{3-}, SeO_3^{2-}, and MoO_4^{2-} were prepared from their sodium salts. To study the effect of these ions on the removal of vanadate, the sorption of vanadate alone and in the presence of foreign anion were determined. Equimolar quantities (0.78 mM) of vanadate(V) and foreign anions were used to study the foreign ion effect.

Preliminary experiments showed that there was no adsorption of vanadate(V) due to container walls. Experiments were carried in duplicates and mean values were used for calculations. Maximum deviation was found to be 3.5%.

Results and discussion

Adsorption kinetics

In order to investigate the mechanism of adsorption and rate-controlling steps, the kinetic data were modeled using Lagergren first-order (Lagergren 1898) and second-order models (Mckay and Ho 1998)

The Lagergren first-order model can be represented as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{14}$$

where q_e and q_t are the amounts of vanadate(V) adsorbed (mg g^{-1}) at equilibrium and at time t, respectively, and k_1 is the rate constant of first-order adsorption (min^{-1}). Values of q_e and k_1 were calculated from the slope and intercept of the plots of $\log(q_e - q_t)$ versus t (Fig. 1).

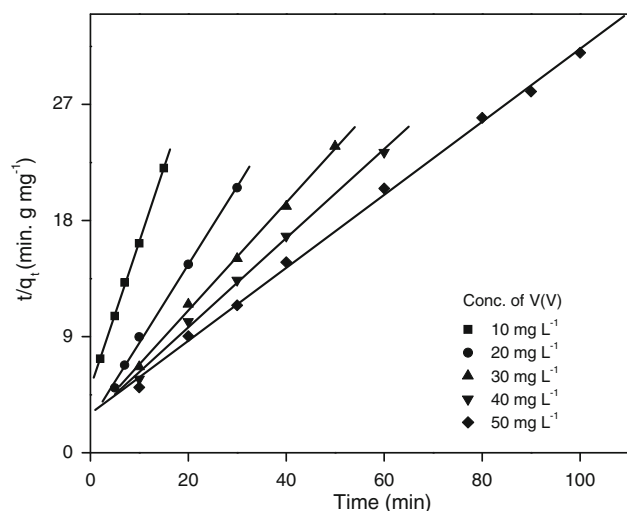The second-order kinetic model is represented as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{15}$$

Values of the second-order rate constant, k_2 and q_e, were calculated from the slope and intercept of the plots of t/q_t versus t (Fig. 2).

Table 2 shows that q_e values calculated using the first-order kinetic model do not agree with the experimental q_e values even though the plots have high correlation coefficients. This suggests that the adsorption of vanadate(V) does not follow first-order kinetic model. It was found that the q_e
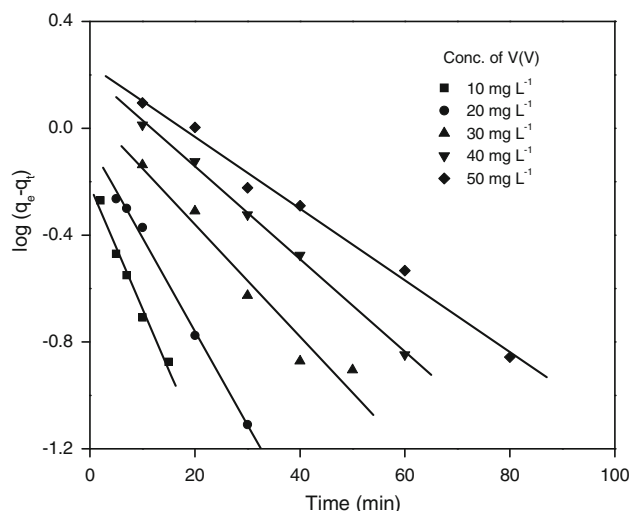
Fig. 1 Plot of the first-order kinetic model for the absorption of vanadate(V) onto untreated Fe(III)/Cr(III) hydroxide at different initial vanadate(V) concentrations: adsorbent dose, 500 mg, 50 ml^{-1}; pH 4.0; temperature 32°C

Fig. 2 Plot of the second-order kinetic model for the absorption of vanadate(V) onto untreated Fe(III)/Cr(III) hydroxide at different initial vanadate(V) concentrations: adsorbent dose, 500 mg, 50 ml^{-1}; pH 4.0; temperature 32°C

values calculated using the second-order model agree with the experimental q_e values with high correlation coefficients (Table 2). So, the adsorption system studied belongs to the second-order kinetic model. Similar results have been observed in the adsorption of phosphorus on alunite (Ozacar 2003) and Fe(III)/Cr(III)hydroxide (Namasivayam and Ranganathan 1994).

Adsorption isotherms

The equilibrium of a solute separated between liquid and solid phase is described by various models of adsorption

isotherms such as the Langmuir (Langmuir 1918) and Freundlich (Freundlich 1906) models. The Langmuir iso-therm has widely been used to describe single-solute sys-tems. It is based on the assumption that intermolecular forces decrease rapidly with distance and consequently it predicts monolayer coverage of the adsorbate on the outer surface of the adsorbent. This model also suggests that there is no lateral interaction between the sorbed mole-cules. Once a molecule occupies a site, no further adsorption can take place at that site.

The Langmuir isotherm can be expressed as:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \qquad (16)$$

where q_e is the solid-phase adsorbate concentration at equilibrium (mg g^{-1}), C_e is the concentration of vanadate(V) solution (mg l^{-1}) at equilibrium. The constant Q_0 gives the theoretical monolayer adsorption capacity (mg g^{-1}) and b is related to the energy of adsorption (l mg^{-1}). A linear expression for the Langmuir equation is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \qquad (17)$$
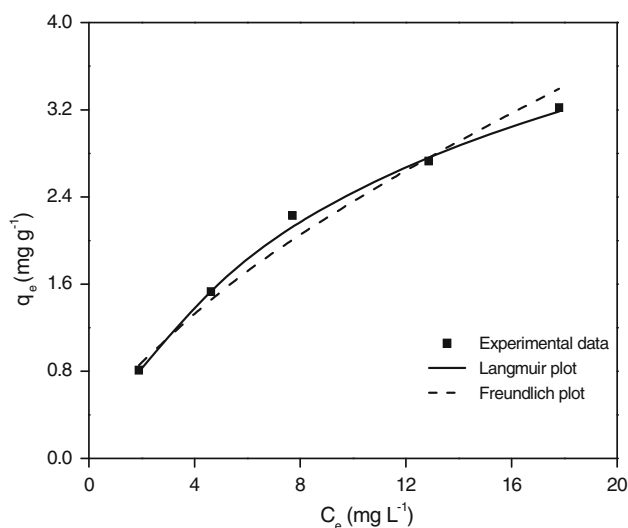
Langmuir isotherms are shown in Figs. 3 and 4 for untreated and treated adsorbents, respectively. Langmuir constants are given in Table 3. In the case of untreated adsorbent, the monolayer adsorption capacity, Q_0, was found to be 4.93 mg g^{-1} and b was 0.10 l mg^{-1} at room temperature (Table 3), whereas for the treated adsorbent the Q_0 and b were found to be 11.43 mg g^{-1} and 0.82 l mg^{-1}, respectively. Low adsorption capacity of the untreated adsorbent is due to the higher equilibrium pH (final pH > 8.1) compared to the treated adsorbent. Above pH 8.1, the adsorbent surface modified with hydroxide ions does not favor adsorption of oxyanion, since the pH$_{zpc}$ of the adsorbent is 8.1 (Namasivayam and Sumithra 2004). In the case of treated adsorbent, the equilibrium pH (final pH) is 6.5, and positively charged adsorbent surface favors the adsorption of vanadate anion. The value of Q_0 obtained in this study was lower than that reported by Guzman et al. (2002) for chitosan (400–450 mg g^{-1}). The high adsorption capacity of chitosan may be due to lower particle size (0–125 μm), surface functional groups, and maintenance of the equilibrium pH (final pH) at 3–3.5. In this study, final pH was not maintained during adsorption. For all the different initial pH values studied, the final pH was >8.0 and 7.0 for the untreated and treated adsorbents, respectively. At pH >8.0, chitosan gave Q_0 values of less than 20 mg g^{-1}. Guibal et al. (1998) reported adsorption capacity for the adsorption of vanadate onto chitosan beads of varying particles size: 402.5, 250.4, 165.2, and 146.8 mg g^{-1} for particle size, 0.95 mm, 0–125, 125–250,

Table 2 Comparison of first-order and second-order rate constants and calculated and experimental q_e values for different initial vanadate(V) concentrations and temperatures: untreated adsorbent

	First-order kinetic model				Second-order kinetic model		
	Q_e (exp) (mg g^{-1})	k_1 (min^{-1})	q_e (cal) (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e (cal) (mg g^{-1})	R^2
Initial V(V) conc. (mg l^{-1})[a]							
10	0.811	0.12	0.666	0.9916	0.25	0.892	0.9999
20	1.537	0.08	0.865	0.9943	0.15	1.642	0.9968
30	2.230	0.04	1.146	0.9546	0.05	2.394	0.9977
40	2.717	0.03	1.599	0.9977	0.02	2.891	0.9965
50	3.22	0.03	0.12	0.9948	0.02	3.53	0.9975
Temperature (°C)[b]							
32	2.230	0.04	1.146	0.9546	0.05	2.394	0.9977
40	2.318	0.05	1.151	0.9512	0.05	2.521	0.9976
50	2.340	0.07	1.290	0.9536	0.08	2.504	0.9988
60	2.464	0.07	1.143	0.9808	0.11	2.596	0.9993

[a] Adsorbent dose, 500 mg, 50 ml^{-1}; initial pH, 4.0; final pH range 7.9–8.2; temperature 32°C

[b] Adsorbent dose, 500 mg, 50 ml^{-1}; initial pH, 4.0; final pH range 7.9–8.2; initial conc. 30 mg l^{-1}

Fig. 3 Adsorption isotherms of vanadate(V) onto untreated Fe(III)/Cr(III) hydroxide

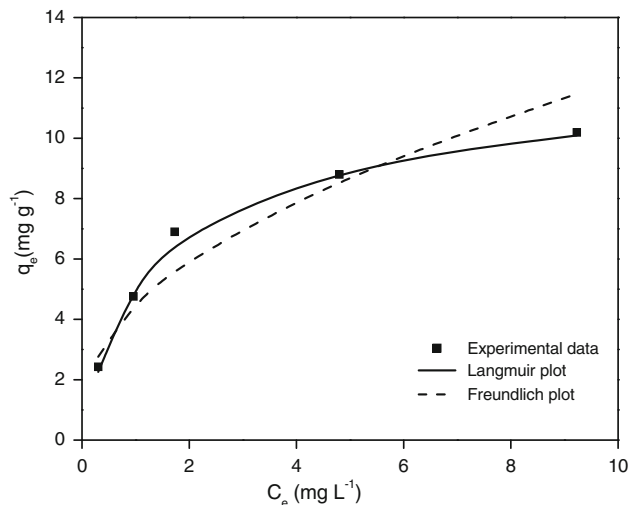**Fig. 4** Adsorption isotherms of vanadate(V) onto treated Fe(III)/Cr(III) hydroxide

and 250–500 μm, respectively. So, it is expected that combined influence of functional groups, particle size, and system pH is responsible for good adsorption.

Freundlich model assumes heterogeneous adsorption due to the diversity of sorption sites or the diverse nature of the metal ions sorbed, free, or hydrolyzed species.

The Freundlich model equation is expressed as:

$$\log q_e = \log k_f + \frac{1}{n}\log C_e \qquad (18)$$

where k_f denotes adsorption capacity and n is related to intensity of adsorption. Freundlich isotherms are shown in Figs. 3 and 4. Values of the Freundlich constants, k_f and n, were found to be higher for treated adsorbent compared to

untreated adsorbent (Table 4). Experimental equilibrium data appear to fit better with Langmuir isotherm than with Freundlich isotherm for both the untreated and treated adsorbents.

Effect of temperature

Effect of temperature on the adsorption isotherm was investigated in the temperature range 32–60°C. Figure 5 shows the temperature dependence of vanadate adsorption on to untreated Fe(III)/Cr(III) hydroxide. Values of the Langmuir constants obtained from the best fit of Langmuir adsorption isotherm are listed in Table 3. Results show that the value of b increases with increase in temperature. Value

Table 3 Langmuir constants

Temperature (°C)	Treated Fe(III)/Cr(III) hydroxide			Untreated Fe(III)/Cr(III) hydroxide		
	Q_0 (mg g^{-1})	b (l mg^{-1})	R^2	Q_0 (mg g^{-1})	b (l mg^{-1})	R^2
32	11.43	0.82	0.9990	4.93	0.10	0.9973
40				5.30	0.12	0.9991
50				5.08	0.15	0.9884
60				5.08	0.20	0.9989

Table 4 Freundlich constants

Treated Fe(III)/Cr(III) hydroxide			Untreated Fe(III)/Cr(III) hydroxide		
k_f (mg$^{1-1/n}$ l$^{1/n}$ g^{-1})	n	R^2	k_f (mg$^{1-1/n}$ l$^{1/n}$ g^{-1})	n	R^2
4.56	2.40	0.9730	0.58	1.63	0.9931
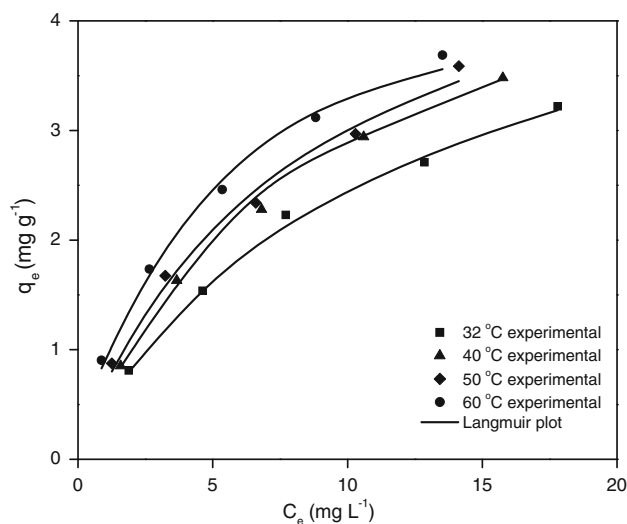
Fig. 5 Langmuir adsorption isotherm of vanadate(V) onto untreated Fe(III)/Cr(III) hydroxide at various temperatures

of Q_0 remains more or less same with increase in temperature (Sontheimer et al. 1988). Similar results have been reported for the adsorption of Zn(II) from aqueous solution by fly ash (Weng and Huang 2004).

Using the Lagergran rate equation, the first-order rate constants (k_1) and correlation coefficients were calculated. The calculated q_e values obtained from the first-order kinetics do not agree with the experimental q_e values at different temperatures (Table 2). These results indicate that the system does not follow first-order kinetic model. Second-order kinetic model shows that the calculated q_e values agree with the experimental q_e values at different temperatures (Table 2). This indicates that the adsorption follows second-order kinetic model at different temperatures used in this study. On increasing the temperature from 32 to

60°C, the amount adsorbed at equilibrium, q_e, increased from 2.23 to 2.46 mg g^{-1}. The increase in the equilibrium sorption of vanadate(V) with temperature indicates that high temperature favors vanadate(V) removal. Thermodynamic parameters such as change of Gibbs free energy (ΔG^o), entropy (ΔS^o), and enthalpy (ΔH^o) were calculated using the following thermodynamic equations (Sontheimer et al. 1988):

$$\Delta G^o = -RT \ln b \tag{19}$$

$$\ln b = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{20}$$

where R is the gas constant in J K^{-1} mol^{-1}, T is the temperature in K, and b is equilibrium constant (Langmuir constant in l mol^{-1}). Figure 6 shows van't Hoff plot of ln b versus $1/T$ and the values of ΔS^o and ΔH^o were determined from the intercept and slope, respectively. The thermodynamical parameters are listed in Table 5. The negative values of ΔG^o indicate the spontaneous nature of adsorption. ΔG increased with increase in temperature from 32 to 60°C, which shows that the process is favorable at higher temperature. The positive value of ΔH confirms the endothermic nature of adsorption. The positive value of ΔS shows the increased randomness at the solid/solution interface during the adsorption of vanadate(V) (Dursun et al. 2005).

The activation energy for the adsorption process was calculated using Arrhenius equation.

$$\log k = \log A - \frac{E_a}{2.303RT} \tag{21}$$

where k is the rate constant at given temperature, T, E_a is the activation energy for the overall adsorption process (kJ mol^{-1}), which must be overcome before adsorption takes place, A is the exponential factor, which is the measure
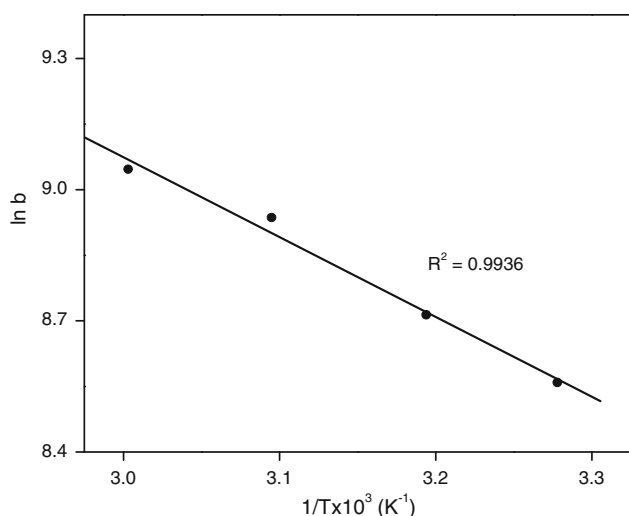
Fig. 6 Van't Hoff plot for vanadate(V) adsorption onto untreated Fe(III)/Cr(III) hydroxide

Table 5 Thermodynamic parameters for the adsorption of vanadate(V) on untreated Fe(III)/Cr(III) hydroxide

Temperature (°C)	ΔG^o (kJ mol^{-1})	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})
32	−21.7	14.9	120
40	−22.7		
50	−24.0		
60	−25.0		

of the accessibility of the reactive sites of the adsorbent, R is the universal gas constant (8.314 J K^{-1} mol^{-1}), and T is the absolute temperature. A plot of log k versus $1/T$ yields a straight line, from which the E_a and A were calculated based on the slope and intercept, respectively (data not shown). Value of E_a was found to be 23.9 kJ mol^{-1}, which is lower than 40 kJ mol^{-1} for chemical adsorption process (Ozcan and Ozcan 2004).

Effect of pH

The species distribution of vanadium was studied by Baes and Mesmer (1976). According to their study, various forms of vanadium existed in solution. They were cationic VO_2^+, neutral $VO(OH)_3$, and anionic species, $V_{10}O_{26}(OH)^{3-}$, $V_{10}O_{27}(OH)^{5-}$, $V_{10}O_{28}^{6-}$, and other mono or poly vanadate species, $VO_2(OH)_2^-$, $VO_3(OH)^{2-}$, VO_4^{3-}, $V_2O_6(OH)^{3-}$, $V_2O_7^{4-}$, $V_3O_9^{3-}$, and $V_4O_{12}^{4-}$. The distribution of these forms was found to be pH dependent. In the pH range 4.0–10.0, vanadium(V) exists mainly as VO_3^- (Blackmore et al. 1996). Figure 7 shows the adsorption of vanadate onto treated Fe(III)/Cr(III) hydroxide in the pH range 4.0–10.0. It was found that with increase in pH the removal of vanadate(V) decreases. Similar behavior has been reported for
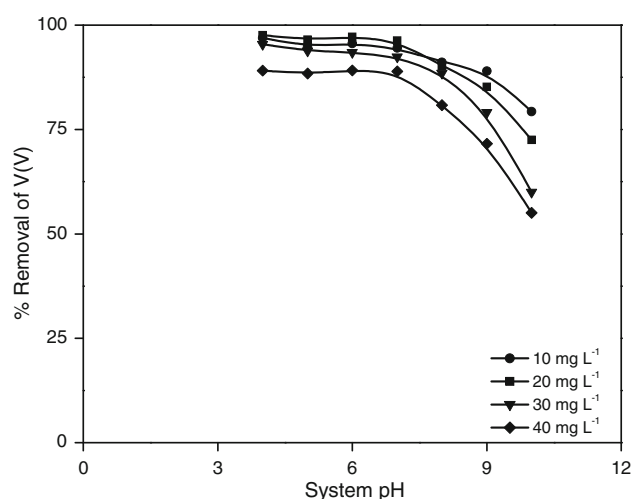
Fig. 7 Effect of pH on removal of vanadate(V) by treated Fe(III)/Cr(III) hydroxide. Adsorbent dose, 200 mg, 50 ml^{-1}; vanadate(V) concentration, 10 mg l^{-1}; agitation time, 20 min; vanadate(V) concentration, 20 mg l^{-1}; agitation time, 40 min; vanadate(V) concentration, 30 mg l^{-1}; agitation time, 60 min; vanadate(V) concentration, 40 mg l^{-1}; agitation time, 80 min; temperature 32°C

the adsorption of vanadate by iron hydroxide (Blackmore et al. 1996) and chitosan (Guzman et al. 2002). pH$_{zpc}$ plays an important role in adsorption process. The pH$_{zpc}$ of the Fe(III)/Cr(III) hydroxide used in the study is 8.1, below which the surface is positively charged. The removal efficiency is higher in acidic pH than that in basic pH conditions (Fig. 7). In the lower pH the adsorbent surface is modified by H$^+$ ions. Due to the electrostatic attraction between the anionic vanadate species and the adsorbent surface, removal is maximum at pH 4.0. On increasing the pH, the electrostatic repulsion occurs between adsorbed OH$^-$ ions and anionic vanadate species, which hinder the adsorption of vanadate.

Desorption studies

Desorption studies were carried out with two different initial concentrations of vanadate(V) (10 and 20 mg l^{-1}) in the initial pH range 4.0–12.0 for both untreated and treated adsorbents. It was found that desorption of vanadate increased with increase in pH for both untreated and treated adsorbents (Table 6). Very high desorption shows that the adsorption of vanadate on Fe(III)/Cr(III) hydroxide is reversible and ion exchange mechanism seems to predominate (Eqs. 11–13). Similar observation was reported for the adsorption of vanadate(V) onto chitosan (Guibal et al. 1998). Inner sphere complex mechanism was reported for the adsorption of vanadate(V) onto iron oxyhydroxide (Blackmore et al. 1996).

Vanadate anion was adsorbed onto Fe(III)/Cr(III) hydroxide through exchange of OH$^-$ or SO$_4^{2-}$ ions of the

Table 6 Desorption studies for vanadate(V): untreated and treated adsorbents

pH	Untreated adsorbent (mg l^{-1})		Treated adsorbent (mg l^{-1})	
	10	20	10	20
4	9.86	5.20	6.55	5.25
5	9.88	5.56	6.18	5.42
6	9.04	4.88	5.07	5.37
7	9.04	4.33	5.68	5.78
8	9.58	5.35	5.19	6.21
9	8.45	4.69	5.06	6.45
10	8.77	5.35	5.44	6.87
12	86.66	79.39	75.33	61.21

Table 7 Effect of foreign anions on the sorption of VO_3^-

Species	Removal of VO_3^- (%)	
	Treated Fe(III)/Cr(III)hydroxide[a]	Untreated Fe(III)/Cr(III)hydroxide[b]
VO_3^-	86	77
$VO_3^- + PO_4^{3-}$	70	63
$VO_3^- + SeO_3^{2-}$	78	67
$VO_3^- + MoO_4^{2-}$	75	73
$VO_3^- + SO_4^{2-}$	84	75
$VO_3^- + Cl^-$	85	78
$VO_3^- + NO_3^-$	85	78

[a] Adsorbent dose 200 mg, 50 ml^{-1}

[b] Adsorbent dose 500 mg, 50 ml^{-1}

adsorbent. Release of the sulfate ions was experimentally observed and it is represented by:

$$M_2SO_4^{2-} + L^{n-} \rightarrow M_2L^{n-} + SO_4^{2-} \qquad (22)$$
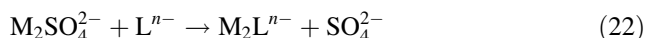
However, there was no detectable pH increase after adsorption. This may be attributed to a small increase in OH^- concentration in the system, due to low concentration of vanadate(V) used (Jackson and Miller 2000) (Eq. 10) or due to the release of water molecules (Eqs. 11–13). The adsorbent Fe(III)/Cr(III) hydroxide is similar to iron oxyhydroxide (Kreller et al. 2002). Since the final pH for the untreated adsorbent ranged from 7.99 to 8.8 for the initial pH range 4.0–10.0, the adsorbent surface is dominated with –MOH species. Hence adsorption of vanadate follows Eqs. 10–12. Since the final pH for the treated adsorbent ranged from 6.2 to 7.8 for the initial pH range 4.0–10.0, the adsorbent surface is dominated with $-MOH_2^+$ species. Hence, adsorption of vanadate follows Eq. 13. Chemisorption plays a minor role in the adsorption of vanadate(V). This is substantiated by the fact that ΔH for adsorption was found to be less than 40 kJ mol^{-1}

(Alkan et al. 2004) and desorption was high at pH 12.0. Also FTIR spectrum of vanadate(V)-loaded adsorbent did not show any band specific for chemisorbed vanadate(V) species.

Effect of foreign anions

The extent of vanadate adsorption by untreated and treated Fe(III)/Cr(III) hydroxide in the presence of other ions is shown in Table 7. Anions, PO_4^{3-}, MoO_4^{2-}, and SeO_3^{2-} interfered with the adsorption of vanadate for both the adsorbents. This agrees with the result proposed by Blackmore et al. (1996) in the adsorption of vanadate by iron oxyhydroxide. The order of adsorption among the oxyanions studied was $V(V) > PO_4^{3-} > SeO_3^{2-} > MoO_4^2$ based on the percent removal of anions at equimolar concentrations (0.78 mM). This may be due to the preference of the adsorbent sites for those anions in that order (Rayden et al. 1987). Competition between the anions occurs for the common sites and results will be published elsewhere. Anions—SO_4^{2-}, Cl^-, and NO_3^-—showed no effect on the adsorption of vanadate, because these ions were not adsorbed onto both the untreated and treated adsorbents. Hingston et al. (1971) studied the adsorption of phosphate, selenite, and arsenate on goethite, and proposed that there are a number of sorption sites available to a particular anion on goethite. The adsorption of vanadate onto the adsorbent surface can be described by inner sphere surface coordination mechanism, since the adsorption was not affected by change in ionic strength using KNO_3 in the concentration range 0.5–50 mM (Blackmore et al. 1996).

Conclusions

This study demonstrates that the solid waste Fe(III)/Cr(III) hydroxide is effective in removing vanadate(V) from aqueous solutions. The vanadate adsorption was found to be spontaneous and endothermic in nature. The adsorption mechanism was primarily associated with ion exchange, which was best predicted by second-order kinetic model. The experimental data appeared to fit better with Langmuir isotherm than Freundlich isotherm. High temperature favored adsorption and maximum adsorption occurred at pH 4.0. Although SO_4^{2-}, Cl^-, and NO_3^- did not interfere with vanadate adsorption, other ions like selenite, molybdate, and phosphate showed negative effect on the adsorption for both treated and untreated Fe(III)/Cr(III) hydroxides.

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