



Research article

Adsorption of Cr(VI) from aqueous solution by hydrous zirconium oxide

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ABSTRACT

A type of $ZrO_2 \cdot nH_2O$ was synthesized and its Cr(VI) removal potential was investigated in this study. The kinetic study, adsorption isotherm, pH effect, thermodynamic study and desorption were examined in batch experiments. The kinetic process was described by a pseudo-second-order rate model very well. The Cr(VI) adsorption tended to increase with a decrease of pH. The adsorption data fitted well to the Langmuir model. The adsorption capacity increased from 61 to 66 $mg\ g^{-1}$ when the temperature was increased from 298 to 338 K. The positive values of both ΔH° and ΔS° suggest an endothermic reaction and increase in randomness at the solid–liquid interface during the adsorption. ΔG° values obtained were negative indicating a spontaneous adsorption process. The effective desorption of Cr(VI) on $ZrO_2 \cdot nH_2O$ could be achieved using distilled water at pH 12.

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1. Introduction

Removal of hazardous metal ions especially in low concentrations from industrial effluent is of great interest due to the large quantity of material processed. Metals ions, such as Cr, Hg, Cd, Ni, As, Pb, etc., have a harmful effect on human physiology and other biological systems [1].

Hexavalent chromium Cr(VI) is one of the most dangerous heavy metal and a major pollutant in wastewaters, because it is a strong oxidizing agent which irritates plant and animal tissues and it is carcinogenic and mutagenic [2–4].

Cr(VI) is commonly used in the preparation of a great variety of industrial products, such as pigments for the manufacture of paints, inks, rubber, ceramics, corrosion inhibitors, fungicides [5,6]. It is found naturally in rocks, soil, plants, animals, volcanic dust and gases [6].

The recommended limit of Cr(VI) in potable water is only 0.05 $mg\ dm^{-3}$ [7]. But the industrial effluents contain much higher concentrations compared to the permissible limit. Thus, treatment of the effluent to reduce/remove the pollutant before discharging into the environment becomes inevitable [8,9].

Numerous studies concerning its removal from aqueous solutions have been attempted. Chemical precipitation is one of the most common conventional treatment methods to effectively decrease metal to acceptable levels. It requires large excess of chemicals and generates volumetric sludge and increases the cost.

Other available treatment methods, such as electrolysis and reverse osmosis require high capital investment and running cost [10,11]. Adsorption is one of the techniques that would be comparatively more useful and economical for this aim [12]. The application of low-cost and easily available materials has been widely used for Cr(VI) removal. These include metal oxides [6,13], hydrous metal oxides [9,14], hybrid materials [15], biomaterials [11,16,17], activated carbon [1,18], carbon nanotubes [19], boehmite [20] and maghemite [21].

Hydrous zirconium oxide has been known to have a remarkable selectivity to certain ions. In addition, it has good resistance to oxidant agents, low solubility, high thermal stability and amphoteric character. It is easier and cheaper to prepare than the organic resins. However, hydrous zirconium oxide is not amenable to efficient regeneration [22–24].

In view of the health problems caused by Cr(VI), the present work describes the kinetics, isotherm and thermodynamics of Cr adsorption from aqueous solutions onto hydrous zirconium oxide ($ZrO_2 \cdot nH_2O$).

2. Experimental

2.1. Synthesis of hydrous zirconium oxide by co-precipitation method

The hydrous zirconium oxide was prepared by dissolution of zirconium oxychloride in 0.5M HCl solution. Excess of ammonium hydroxide (ca. 28%) solution (1:3) was added dropwise to the solution with constant stirring at room temperature until precipitate hydrous zirconium oxide. After precipitation, it is filtered

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and washed several times until complete Cl^- removal with distilled water and dried in an oven at 323 K until a constant weight was achieved.

2.2. Characterization

Thermogravimetry measurement (TG/DTG) was carried out with a Shimadzu TGA-50 thermal analyzer from 298 to 1073 K at a heating rate of 293 K min^{-1} in N_2 atmosphere.

BET surface area measurement was carried out using Quantachrome NOVA 1200. The samples were degassed at 323 K for 16 h in vacuum prior to analysis. The nitrogen adsorption was carried out at 77 K.

2.3. Determination of the point of zero charge

The point of zero charge of the hydrous zirconium oxide was determined by a previously described batch equilibration technique [25]. Initial pH values (pH_i) of 25 cm^3 of KNO_3 solutions (concentrations 10^{-1} and 10^{-2} M) were adjusted in pH range of 2–8 using 0.1 M of HCl or NaOH. Then, 0.05 g of hydrous zirconium oxide was added to each sample. Equilibration was carried out by shaking, in a thermostated orbital shaker for 24 h at 298 K. The dispersions were then filtered and the final pH of the solutions (pH_f) was determined, point of zero charge was found from a plot of ($\text{pH}_i - \text{pH}_f$) versus pH_i .

2.4. Adsorption studies

All adsorption studies were carried out in polyethylene flasks of 100 cm^3 by subjecting a given dose of hydrous zirconium oxide to a period of shaking with 50 cm^3 of Cr(VI) solution on a thermostated orbital shaker. The pH of Cr(VI) solution was adjusted using dilute HCl and NaOH solutions by using pH meter. The supernatant solution was separated from the adsorbent by filtration. Cr(VI) concentration in the supernatant was estimated spectrophotometrically by diphenyl carbazide method, monitoring the absorbance at 540 nm on UV–vis spectrophotometer [26]. The adsorption studies with Cr(VI) synthetic solutions were performed using the following conditions.

2.4.1. Kinetic study

Hydrous zirconium oxide dose 2 g dm^{-3} ; initial Cr(VI) concentrations 100 and 200 mg dm^{-3} ; pH 2; shaking time 0–240 min; $T = 298 \text{ K}$.

2.4.2. Effect of pH

Hydrous zirconium oxide dose 2 g dm^{-3} ; initial Cr(VI) concentration 200 mg dm^{-3} ; pH 2–7; predetermined shaking time value; $T = 298 \text{ K}$.

2.4.3. Adsorption isotherms

Hydrous zirconium oxide dose 2 g dm^{-3} ; initial Cr(VI) concentrations 100– 200 mg dm^{-3} ; predetermined pH; predetermined shaking time value; temperature range 298–338 K.

2.4.4. Thermodynamic study

Hydrous zirconium oxide dose 2 g dm^{-3} ; initial Cr(VI) concentrations 200 mg dm^{-3} ; predetermined pH; predetermined shaking time value; temperature range 298–338 K.

2.4.5. Desorption

The adsorbent that was used for the adsorption of 200 mg dm^{-3} of Cr(VI) solution was separated from the solution by filtration and washed gently with water to remove any unadsorbed Cr(VI). Then the spent adsorbent was mixed with 50 cm^3 of distilled water at

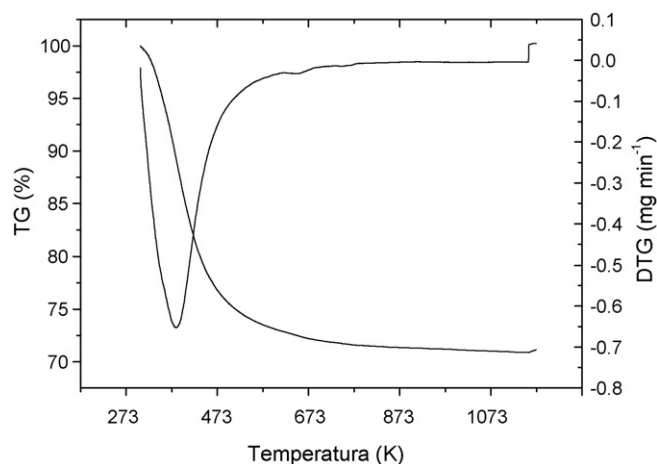


Fig. 1. TG/DTG curves of hydrous zirconium oxide synthesized.

pH 5 and 12, adjusted using dilute HCl and NaOH solutions, and agitated at time intervals not longer than the equilibrium time. The desorbed Cr(VI) was estimated as before.

3. Results and discussion

3.1. Thermal analysis and BET measurements

The TG curve (Fig. 1) revealed that the weight loss (about 29%) was caused by the desorption of physically adsorbed water [27,28]. The degree of hydration in the hydrous zirconium oxide was determined from the weight loss between 298 and 1073 K. TG data indicated that the chemical formula of the hydrous zirconium oxide prepared was $\text{ZrO}_2 \cdot 3\text{H}_2\text{O}$.

The BET specific surface area was $254 \text{ m}^2 \text{ g}^{-1}$ bigger than the $78.1 \text{ m}^2 \text{ g}^{-1}$ observed on the aluminium oxide reported literature data for Cr(VI) removal [13], and $185 \text{ m}^2 \text{ g}^{-1}$ reported for Cr(VI) removal onto hydrous titanium oxide [14].

3.2. Kinetic study

The kinetic curves obtained for the Cr(VI) removal from aqueous solutions onto hydrous zirconium oxide are shown in Fig. 2. These curves clearly show that the time required to reach equilibrium depends on the initial Cr(VI) concentration. For the highest

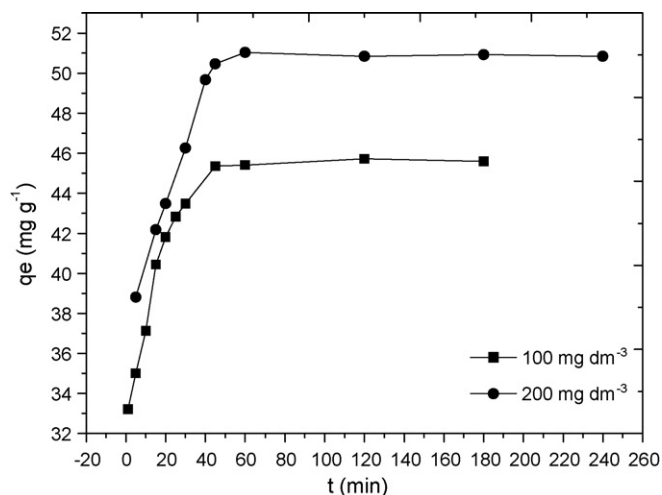


Fig. 2. The variation of adsorption capacity with adsorption time at various initial Cr(VI) concentrations ($T = 298 \text{ K}$; adsorbent dose = 2 g dm^{-3} ; pH 2).

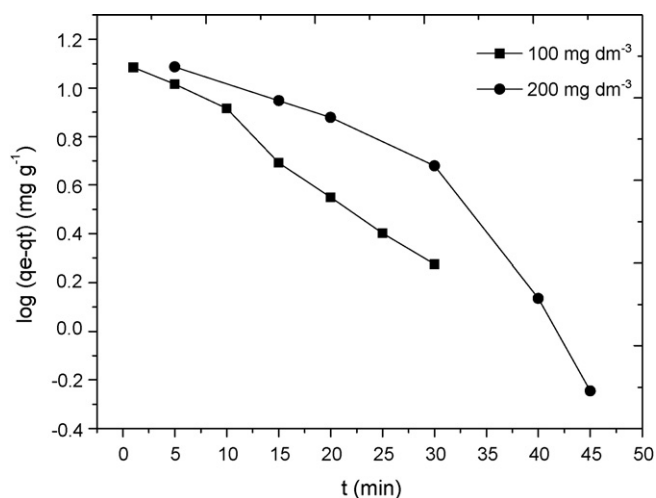


Fig. 3. Pseudo-first-order kinetics for adsorption of Cr(VI) onto $ZrO_2 \cdot nH_2O$.

value (200 mg dm^{-3}) adsorption increased sharply at short contact times; 60 min of interaction were needed to attain values above 50% of the Cr(VI) amount adsorbed at equilibrium. For the lowest concentration (100 mg dm^{-3}), the adsorption process took place very quickly, being almost completed (>90%) after 45 min of interaction.

Up to now, several kinetic models, such as the pseudo-first- and second-order equations and intraparticle diffusion equation are used to examine the controlling mechanism of adsorption process [12].

The linear pseudo-first-order equation is given as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (1)$$

where q_t and q_e are the amounts of Cr(VI) adsorbed at time and at equilibrium (mg g^{-1}), respectively, and k_1 is the rate constant of pseudo-first-order adsorption process (min^{-1}). The slopes and intercepts of plots of $\log(q_e - q_t)$ versus t (Fig. 3) were used to determine the first-order rate constant k_1 and equilibrium adsorption density q_e . A comparison of the results with the correlation coefficients is shown in Table 1. The correlation coefficients for the first-order kinetic model obtained at all the studied concentrations were low. It was also observed in the present work that q_e values computed from the Lagergren plots deviated considerably from the experimental q_e values. This indicates that pseudo-first-order equation might not be sufficient to describe the mechanism of Cr(VI)–hydrrous zirconium oxide interactions.

The linear pseudo-second-order equation is given as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where k_2 is the pseudo-second-order rate constant ($\text{min}^{-1} \text{ g mg}^{-1}$). The slopes of the plots t/q_t^{-1} versus t give the value of q_e , and from the intercept k_2 can be calculated.

The plot of t/q_t^{-1} versus t (Fig. 4) yields very good straight lines for different initial Cr(VI) concentrations. Table 1 lists the computed results obtained from the second-order equation. The correlation coefficients for the second-order kinetic equation were 1.00 for all

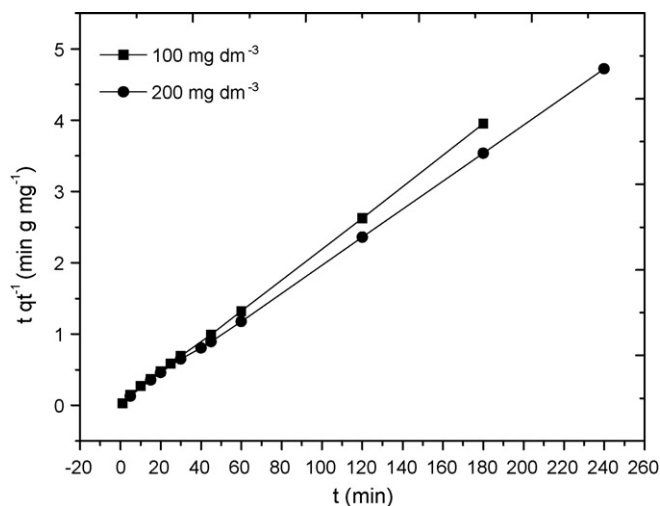


Fig. 4. Pseudo-second-order kinetics for adsorption of Cr(VI) onto $ZrO_2 \cdot nH_2O$.

concentrations. The calculated q_e values also agree very well with the experimental data. These indicate that the adsorption system studied belongs to the second-order kinetic model.

The variation in the amount of adsorption with time at different initial Cr(VI) ion concentrations can be used to evaluate the role of diffusion in the adsorption process.

The intraparticle diffusion rate constant (k_{dif}) is given by the equation:

$$q_t = k_{dif} t^{0.5} \quad (3)$$

where k_{dif} is intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{ min}^{-1/2}$). Such plots may present a multilinearity, indicating that two or more steps take place. The first, sharper portion is attributed to the diffusion of adsorbate through the solution to the external surface of adsorbent or the boundary layer diffusion of solute molecules or ions. The second portion describes the gradual adsorption stage, where intraparticle diffusion is rate limiting. The third portion is attributed to the final equilibrium stage where intraparticle diffusion starts to slow down due to extremely low adsorbate concentrations in the solution [29]. Fig. 5 shows a plot of the linearized form of the intraparticle diffusion model at all concentrations studied. It can be seen that the plots are not linear over the whole time range, implying that more than one process affects the Cr(VI) removal. The rate parameters, k_{dif} , together with the correlation coefficients are also listed in Table 1.

The pseudo-second-order kinetic model provides the best correlation for all of the adsorption process.

3.3. Effect of pH

The pH of the aqueous solution is an important variable, which influences the adsorption of both anions and cations at the solid–liquid interface. The anion–exchange capacity is strongly governed by the pH of the solution and by the surface chemistry of the solids. The effect of pH on Cr(VI) adsorption onto the hydrrous zirconium oxide is shown in Fig. 6. It is found that while the adsorbed amount of Cr(VI) increased from 6.35 to 59.24 mg g^{-1}

Table 1
Kinetic parameters for Cr(VI) adsorption onto $ZrO_2 \cdot nH_2O$.

C_0 (mg dm^{-3})	First-order-model			Second-order-model			Intraparticle diffusion	
	k_1 (min^{-1})	q_1 (mg g^{-1})	r^2	k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$)	q_2 (mg g^{-1})	r^2	k_{in} ($\text{mg g}^{-1} \text{ min}^{-1/2}$)	r^2
200	0.08	26.20	0.87	0.01	51.47	1.00	2.68	0.98
100	0.08	14.13	0.99	0.02	46.10	1.00	2.50	0.97

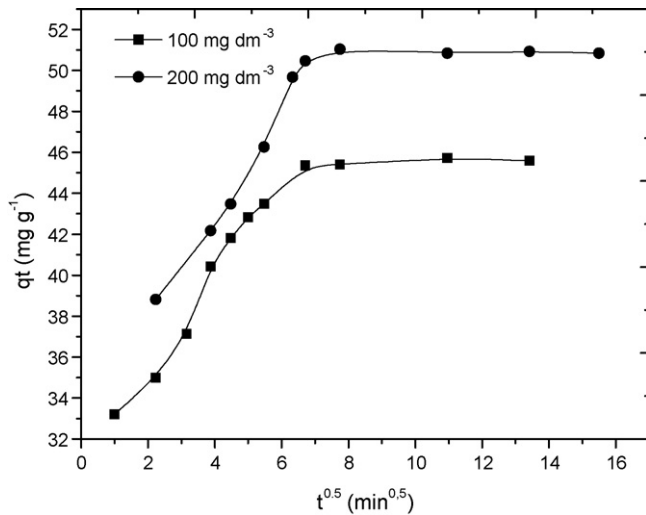
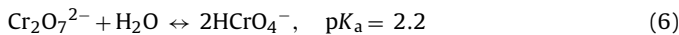
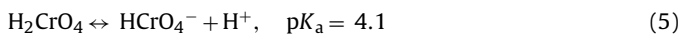
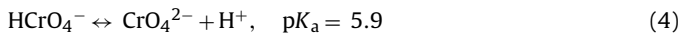


Fig. 5. Intraparticle diffusion kinetics for adsorption of Cr(VI) onto $ZrO_2 \cdot nH_2O$.

with a decrease in pH from 7 to 2. The results showed that the Cr(VI) adsorption is strongly pH dependent. The pH dependency is both related to the amphoteric properties of the hydrous zirconium oxide surface and chromium speciation in solution [30]. The Cr(VI) species may be represented in various forms, such as H_2CrO_4 , $HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^{2-}$ in the solution phase as a function of pH. Cr(VI) speciation is affected by solution pH through the following equilibrium [31,32]:



The value of zero point charge (PZC) of hydrous zirconium oxide (figure not shown) was found to be 2.2. The pH dependence of the uptake is likely attributable to the fact that a lower pH (<2.2) causes the hydrous zirconium oxide surface to carry a more positive charge, and thus would more significantly attract the negatively charged monovalent $HCrO_4^-$ ions in solution, which indicated that the physicochemical adsorption due to Coulombic attraction was the predominant process of Cr(VI) removal. In the lower pH range, Coulombic attraction can readily occur in conjunction with spe-

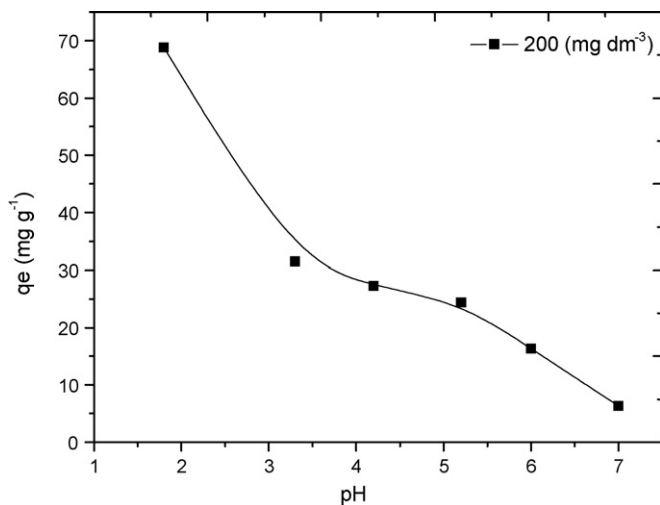


Fig. 6. Effect of solution pH on the adsorption of Cr(VI) onto $ZrO_2 \cdot nH_2O$ ($C_0 = 200 \text{ mg dm}^{-3}$; $T = 298 \text{ K}$; adsorbent dose = 2 g dm^{-3} ; $t = 60 \text{ min}$).

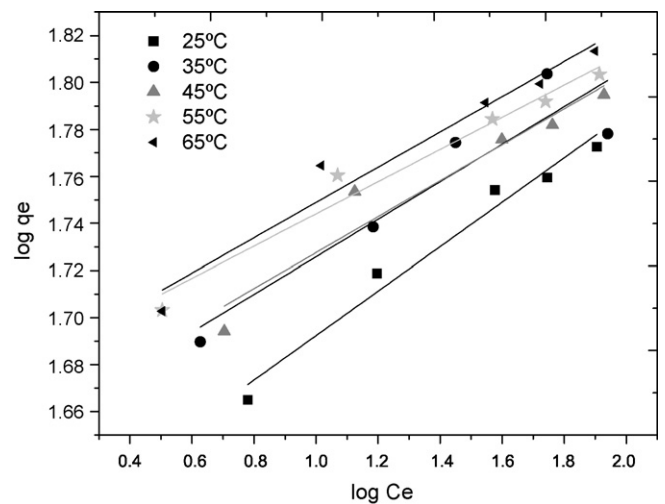


Fig. 7. Freundlich isotherm for Cr(VI) adsorption onto $ZrO_2 \cdot nH_2O$ (pH 2; adsorbent dose = 2 g dm^{-3} ; $t = 60 \text{ min}$).

cific chemical adsorption due to an exchange reaction [20,30,33]. When pH of the solution increases, the surface becomes negatively charged and the adsorption capacity for Cr(VI) decreases. Because negatively charged surface sites on the adsorbent unfavors of Cr(VI) due to the electrostatic repulsion. Therefore, maximum Cr(VI) adsorption occurred at pH 2.

3.4. Adsorption isotherms

The equilibrium adsorption isotherm is fundamental in describing the interactive behavior between adsorbates and adsorbent, and is important in the design of adsorption systems.

The linear equation of the Freundlich adsorption model is expressed by

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

where K_F and $1/n$ are the Freundlich constants.

The linear equation of the Langmuir adsorption model is expressed by

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (8)$$

where Q_0 (mg g^{-1}) is the maximum adsorption capacity and b is the binding constant which is relate to the heat of adsorption.

The essential characteristics of the Langmuir equation can be expressed in term of a dimensionless separation factor, R_L , defined as:

$$R_L = \frac{1}{1 + bC_0} \quad (9)$$

Adsorption isotherms were obtained at pH 2. The pH of Cr(VI) solution (before and after adsorption) was estimated using pH meter. The pH value remained constant during the adsorption process.

The linearized Freundlich and Langmuir plots are given in Figs. 7 and 8, respectively. The slopes of the linearized Freundlich and Langmuir plots were used to calculate the adsorption constants tabulated in Table 2. From Table 2, higher correlation coefficients indicate that the Langmuir model fits the adsorption data better than the Freundlich model. R_L values indicated favorable adsorption. The results revealed that the adsorption capacity increased from 61 to 66 mg g^{-1} when the temperature was increased from 298 to 338 K.

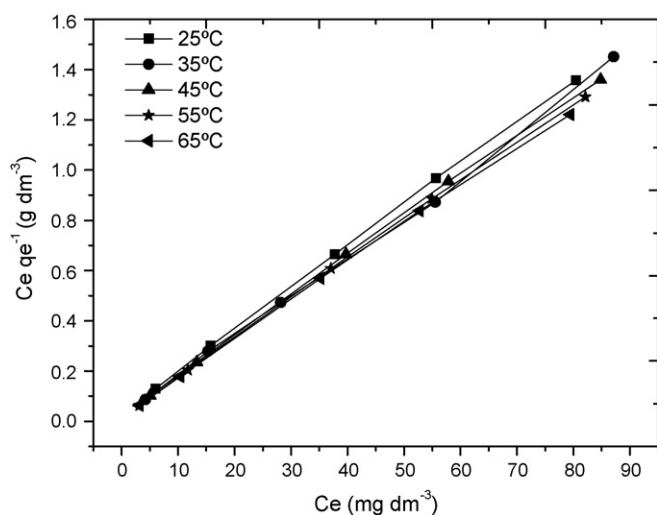


Fig. 8. Langmuir isotherm for Cr(VI) adsorption onto $ZrO_2 \cdot nH_2O$ (pH 2; adsorbent dose = 2 g dm^{-3} ; $t = 60 \text{ min}$).

The difference in shape of the curve at 308 K (Fig. 7) was attributed to the hydrous zirconium oxide used (same product but of a different lot).

Table 3 shows the maximum capacity values reported in literature for the adsorption of Cr(VI) on different materials; such adsorption data were also derived from the Langmuir equation. Except for amorphous aluminium oxide, the chromium retention capacities displayed by these materials are in general much lower than that achieved on hydrous zirconium oxide. Although the chromium retention capacity displayed by hydrous zirconium oxide is lower than that achieved on amorphous aluminium oxide, the contact time required for reaching equilibrium (60 min) by hydrous zirconium oxide is much lower than that one required by amorphous aluminium oxide (1440 min) [13]. The value of removal attained by this product appears high enough to consider its use in the purification of chromium industrial wastewaters.

3.5. Thermodynamic study

The thermodynamic parameters, such as change in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined by using the following equations:

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

$$R_L = \frac{1}{1 + bC_0} \quad (11)$$

where R ($\text{kJ mol}^{-1} \text{K}^{-1}$) is the gas constant, T (K) the absolute temperature and K_c ($\text{cm}^3 \text{g}^{-1}$) is the standard thermodynamic equilibrium constant defined by $q_e C_e^{-1}$. By plotting a graph of $\ln K_c$ versus T^{-1} (Fig. 9) the values ΔH° and ΔS° can be estimated from the slopes and intercepts [39]. Table 4 shows the negative values of ΔG° and positive ΔH° obtained indicated that the Cr(VI) adsorp-

Table 2
Langmuir, Freundlich isotherm constants for adsorption of Cr(VI) onto $ZrO_2 \cdot nH_2O$.

Temperature (K)	Langmuir constants				Freundlich constants		
	Q_0 (mg g^{-1})	b ($\text{dm}^3 \text{mg}^{-1}$)	R_L	r^2	K_F (mg g^{-1})	$1/n$	r^2
298	61	0.43	0.01	1.00	7.05	0.87	0.87
308	62	1.03	0.01	1.00	6.97	0.86	0.77
318	63	0.57	0.01	1.00	6.51	0.92	0.86
328	64	0.72	0.01	1.00	5.12	1.06	0.82
338	66	0.67	0.01	1.00	4.94	1.12	0.83

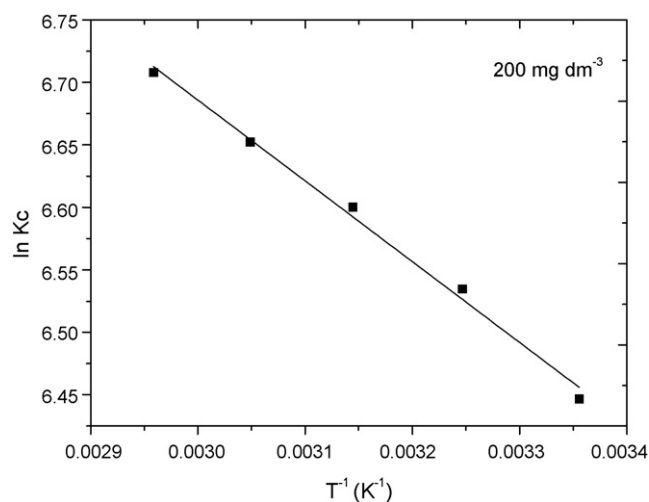


Fig. 9. Plot of $\ln K_c$ versus T^{-1} for Cr(VI) adsorption onto $ZrO_2 \cdot nH_2O$ (pH 2; $C_0 = 200 \text{ mg dm}^{-3}$; adsorbent dose = 2 g dm^{-3} ; $t = 60 \text{ min}$).

Table 3

Summary of adsorption capacity values of Cr(VI) on different adsorbent materials reported in literature.

Adsorbent	Q_0 (mg g^{-1})	Reference
Amorphous aluminium oxide	78	[13]
Iron oxide	23	[34]
Iron–nickel oxide	30	[35]
Hydrous stannic oxide	3	[36]
Hydrous titanium oxide	30	[37]
Hydrous ferric oxide	36	[38]
Hydrous titanium oxide	14	[9]
Hydrous titanium oxide	5	[14]
Activated alumina	7	[6]
Activated charcoal	13	[6]
Activated carbon	8	[1]
Carbon nanotubes	4	[19]
Maghemite	19	[21]

Table 4

Thermodynamic parameters for Cr(VI) adsorption onto $ZrO_2 \cdot nH_2O$.

T (K)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° ($\text{kJ mol}^{-1} \text{K}^{-1}$)
298	−16.00	5.36	0.0717
308	−16.71		
318	−17.43		
328	−18.15		
338	−18.86		

tion process is a spontaneous and an endothermic [40]. The ΔH° value is found to be less than 40 kJ mol^{-1} which indicates the Cr(VI) removal onto hydrous zirconium oxide is physisorption [41,42]. The decrease in ΔG° with the increase of temperature indicated more efficient adsorption at higher temperature. This effect is due to an increase in the driving force of Cr(VI) adsorption. The positive value of ΔS° suggests increased randomness at the solid/solution

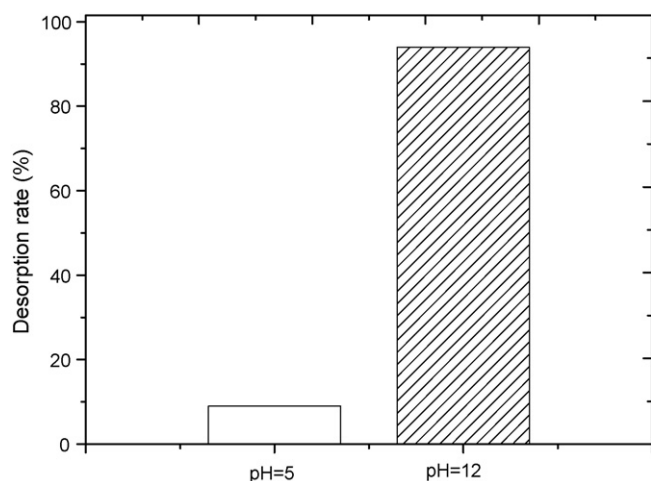


Fig. 10. Desorption of Cr(VI) from hydrous zirconium oxide (adsorbent dose = 2 g dm^{-3} ; $t = 60 \text{ min}$; $T = 298 \text{ K}$).

interface occur in the internal structure of the Cr(VI) removal onto hydrous zirconium oxide [39].

3.6. Desorption

Repeated availability is an important factor for an advanced adsorbent. Such adsorbent not only possesses higher adsorption capability, but also shows better desorption property, which will significantly reduce overall cost for adsorbent. According to the results of desorption studies (Fig. 10), the amount of the desorbed Cr(VI) increased with the increase of pH. When pH value is 5 only extracted 9% Cr(VI) immobilized on the adsorbent. If pH reached 12, 94% could be liberated into the liquid. The results of these desorption studies indicate that the Cr(VI) adsorption on the hydrous zirconium is not completely reversible and Cr(VI) can be desorbed from the surface of hydrous zirconium oxide by adjusting the pH values of the solution. Effects of pH and desorption studies show that chemisorptions, physisorptions and ion-exchange mechanisms are operative in the adsorption process. Chemisorption involves zirconium–Cr(VI) complex formation ($\equiv\text{Zr}-\text{OH}_2^+-\text{HCrO}_4^-$). Only the Cr(VI) ions that are adsorbed by physisorption and ion-exchange are desorbed and the Cr(VI) ions that are removed by complex formation are not desorbed [43].

4. Conclusion

The adsorption equilibrium time was 60 min, and Cr(VI) adsorption process onto $\text{ZrO}_2 \cdot 3\text{H}_2\text{O}$ could be best described by the pseudo-second-order model. The Cr(VI) removal tended to increase with a decrease of pH. Langmuir dimensionless separation factor calculation results indicated that a favorable adsorption. The adsorption capacity increased from 61 to 66 mg g^{-1} when the temperature was increased from 298 to 338 K. Thermodynamic parameters suggested that the adsorption process was spontaneous and governed by physisorption interaction, the adsorption was a spontaneous process at high temperature and endothermic in nature. A Cr(VI) desorbability of approximately 94% was observed with water at pH 12. Due to its high adsorption capacity, this type of hydrous zirconium oxide has the potential for application to control Cr(VI) pollution.

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