

Synthesis of some ferromagnetic composite resins and their metal removal characteristics in aqueous solutions

R.R. Sheha^{*}, A.A. El-Zahhar

Nuclear Chem. Department, Hot Labs. Center, Atomic Energy Authority, P.C. 13759, Cairo, Egypt

Received 12 February 2007; received in revised form 9 May 2007; accepted 11 May 2007

Available online 18 May 2007

Abstract

In this study, a procedure for synthesis of new organic-inorganic magnetic composite resins was established. The procedure was based upon immobilization of magnetite (Mag) as a ferromagnetic material within the polymer poly(acrylic acid acrylonitrile) P(AA-AN) and the ion exchange resin (Amberlite IR120). The produced magnetic resins, IR120-PAN-Mag (R1) and P(AA-AN)-Mag (R2) were assessed as sorbents for Cr(VI). Various factors influencing the sorption of Cr(VI), e.g., pH, equilibrium time, initial concentration and temperature were studied. The sorption process was very fast initially and maximum sorption was achieved within 3 h and pH 5.1. The kinetic of the system has been evaluated with pseudo first order model, second order model, Elovich model, intra-particle diffusion model and liquid film diffusion model. Chromium interaction with composite particles followed second-order kinetics with a correlation coefficient extremely high and closer to unity and rate constant (k_s) has the values 1.68×10^{-4} and 1.9×10^{-4} g (mg⁻¹ min⁻¹) for R1 and R2, respectively. The values of equilibrium sorption capacity (q_e) are consistent with the modeled data and attain the range 893–951 mg g⁻¹. Kinetically, both pore diffusion and film diffusion are participating in ruling the diffusion of Cr(VI) ions. The sorption data gave good fits with Temkin and Flory–Huggins isotherm models. The isotherm parameters related to the heat of sorption are in the range 8–16 kJ mol⁻¹ which is the range of bonding energy for ion exchange interactions and so suggest an ion exchange mechanism for removal of Cr(VI) by the composite sorbents. The adsorption process was exothermic with ΔH in the range of –73 to –97 kJ mol⁻¹. The negative values of Gibbs free energy confirm the feasibility and the spontaneous nature of Cr(VI) removal with these novel composites.

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Keywords: Ferromagnetic composites; Synthesis; Sorption; Cr(VI); Kinetics

1. Introduction

Transition metals are generated as a by product in various industries creating serious environmental problems. Many research efforts were done to develop more effective processes for treatment of waste containing such metals [1]. As eco-toxins, Cu(II), Cd (II), Zn(II), Cr(VI) have increasing significance and great interest due to their tendency to accumulate in vital organs in human and animals [2]. These metals do not degrade into harmless end products in the metabolic cycle and are accumulated in the food chain causing great hazard to the living organs [3]. Removal of these metal ions from aqueous effluent requires developed technologies [4]. Varied technologies were applied for treatment of heavy metals such as chemical

precipitation, sorption and ion exchange [5–9]. Ion exchangers have been widely used in liquid waste treatment and most of them were commercially mass produced organic resin [10]. The applicability of these organic resins has few limitations, of them the poor thermal stability and mechanical strength in addition to the depression in their removal potential at high temperature and radiation doses [11]. However, the inorganic sorbents have higher thermal and radiation stability as well as higher selectivity towards certain metal ions, they have also their own limitations. For instance, it is quite difficult to obtain inorganic sorbents in form of granular bead-type resins suitable for column operation [1]. The above limitations of organic resins and inorganic sorbents could be overcome by introducing composite resins consisting of inorganic sorbents and organic binding matrices. Phenolic resins, phenolsulphonic formaldehyde (PSF) resin, sulphonated poly styrene-divinyl benzene (SPS-DVB), hydrophilic poly-acrylic hydrazid (PAH) and polyacrylonitrile (PAN) are the major organic binding matrices used in preparation

^{*} Corresponding author. Tel.: +2 10 529 15 48.

E-mail address: rsheha68@yahoo.com (R.R. Sheha).

of composite resins [12,13]. Also, a wide variety of inorganic sorbents were adopted in preparation of composite resins (e.g. zeolites, metal hydrates, metal phosphonates, etc.). Magnetite has been introduced in composite particles to be applied in different work area (e.g. biosciences, medicine, and wastewater treatment) [14,15]. In this concern, composite particles have been synthesized by combining functionalized polymer with micro particles of magnetite using a modified process [16]. The obtained particles have large surface area and ion exchange properties due to the presence of carboxylic groups in their acrylic composition [17]. They comprise a magnetite part which facilitates their separation from aqueous solutions. Recently, a method was developed for preparation of ion exchange sorbents comprising one anion exchange resin, ferromagnetic substance and a water permeable organic polymer [18]. The sorbent component in these composites could be a weakly basic anion exchange resins as polymeric amines. While the second component is a ferromagnetic material in powder form whose purpose is to enhance the physical properties of the product (granular strength, thermal stability, etc.) and also to restrict the movement of the produced resin if a magnetic field was applied. The third component in these composite sorbents is a water permeable organic polymer binder whose purpose is to hold the anion exchange resin with the ferromagnetic material together in a granular form applicable in removal of different contaminants from waste streams. These composites were successfully applied in removal of anions from waste streams [19]. In addition, magnetite polymer resins were also prepared and effectively used in separation of actinide elements and remediation of water contaminated with heavy metals [20]. These resins contain polyamine-epichlorohydrin resin beads with ferrites attached to the surface of the beads. The regeneration of the used composites was studied. The novelty of these types of sorbent was deduced from their unique properties when compared with the known sorbents used (organic ion exchangers, inorganic ion exchangers, natural sorbents, etc.). They exhibit a good physical properties facilitating their usage under different conditions, exhibit a good flow-through properties when used in column operation and their contaminants removal efficiency could be enhanced by applying an external magnetic field.

This study deals with the preparation of two polymeric ferromagnetic composite sorbents contain magnetite and polymeric binder and have ion exchange characteristics. The produced particles were subjected, in batch reactor, with Cr(VI) ions to investigate their comparative sorption characteristics in aqueous solution under different experimental conditions.

2. Experimental

2.1. Materials

All chemicals used in this study were of analytical grade reagent and were used as received. Magnetite was supplied from NMA, Egypt. IR120 ion exchange resin (Amberlite IR120, its matrix component is styrene-divinyl benzene (gel type) and the matrix active group is sulfonic acid) was a BDH product. While acrylic acid (AA) was obtained from BDH and acrylonitrile (AN) was obtained from Merck. Acetone used as a solvent was Adwic product. The solution was sufficiently agitated using magnetic stirrer device of type Nuova, USA product.

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2.2. Composites preparation

The IR120-PAN-magnetite composite (R1) was prepared using the following procedure. Firstly, IR120 ion exchanger was heated at 100 °C for 3 days and then ground to the appropriate size. Polyacrylonitrile PAN was prepared by gamma radiation polymerization of 20% acrylonitrile at 20 kGy. The magnetite and IR120 were poured into PAN according to the procedure reported by Kochen and Navratil [20]. The produced material was chopped into small pieces and placed in a 50 °C oven overnight, then ground and stocked for further work. The final composite was 4:1:1.5 for IR120: magnetite: PAN, respectively.

Poly(acrylic acid acrylonitrile) P(AA-AN)-magnetite composite (R2) was prepared in two stages. In the first one, the polymeric part (P(AA-AN)) was prepared by gamma radiation initiated polymerization of AA and AN monomers at 20 kGy with monomer ratio of 60:40 with 20% concentration. Secondly, the composite matrix was prepared by adding 5 g of magnetite powder to the polymeric content with 5% weight content according to the procedure of Phanapovudhikul et al. [17].

2.3. Sorption studies

Batch sorption studies were performed by mixing 0.1 g composite particles with 10 mL potassium chromate K_2CrO_4 solution of 10 mg L^{-1} initial concentration in a 50 mL stopper conical flask. The mixtures were shaken in a thermostatic shaker at room temperature of 29 °C and 120 rpm for 6 h. Aliquot samples were taken from the flask at appropriate time intervals as necessary. The resin was separated from the solution by the aid of a magnet, then the concentrations of chromium were analyzed using the pink color complex developed between diphenylcarbazide and chromium ions in an acidified solution with a spectrophotometer at 540 nm using a Shimadzu UV/V-double beam spectrophotometer (UV/V—210A, Tokyo, Japan). An investigation for the effect of solution pH values on chromium sorption was performed to determine the pH value at which maximum uptake of metal occurs. The process was evaluated using both composite sorbents in the range of pH 2–10 and adjusted when necessary, with 0.1 M HCl and/or 0.1 M NaOH solutions using MA-235 digital pH meter from Mettler Toledo, UK. Sorption isotherm studies were conducted by Cr(VI) concentration from 10 to 50 mg L^{-1} at pH ~5. After sorption reached equilibrium, the mixtures were separated by aid of a magnet and the supernatant was separated and subjected for metal concentration measurements. The amount of Cr(VI) sorbed onto composite particles (q , mg g^{-1}) and uptake percent were calculated using the relations:

$$q = (C_0 - C_e) \frac{V}{m} Z \quad (1)$$

$$\text{Uptake (U)\%} = \frac{C_0 - C_e}{C_e} \times 100 \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations of Cr(VI) in the solution (mg L^{-1}), V is the volume of solution (ml), m is the weight of the resin (g), and Z is the charge of the studied cation. All experiments were performed at room temperature of 29 ± 1 °C, and pH of ~ 5 in duplicate and the averaged values were taken.

3. Results and discussion

3.1. Sorption performance

3.1.1. Effect of pH

The pH value of the working system plays an important role on sorption extent due to its influence on the surface properties of the applied sorbents and the degree of ionization and speciation chromium ions in aqueous solution. The variation in removal potential of Cr(VI) with pH using R1 and R2 resins is shown in Fig. 1. It is noticed that the sorbed amount keeps a high level when pH value within the range 3–5, then it decreases distinctly in the range of pH 5–10. This indicates that the solution pH greatly affects the sorption of Cr(VI). This is because chromium ions exist in different species with stability depends upon pH of the system [21]. At pH 1.0, chromium exists in the form H_2CrO_4 , while in the range 2–5, different species coexist such as $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , $\text{Cr}_3\text{O}_{10}^{2-}$, $\text{Cr}_4\text{O}_{13}^{2-}$ of which HCrO_4^- predominates. As pH increases these forms shift to CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ [22]. In aqueous solution, these different species attain equilibrium according the following reactions:

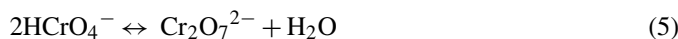


Fig. 1 exhibits a maximum Cr(VI) sorption at pH 5.1 may be significantly referred to a strong electrostatic attraction between positively charged sites in composite surface and HCrO_4^- anions. At pH less than 3.0, a decrease is observed in removal efficiency that may be ascribed to the presence of chromium predominantly as H_2CrO_4 . However, at higher pH values, the removal was found to exponentially decrease with increase in the pH. This may be due to the dual competition of both CrO_4^{2-}

and OH^- anions to be sorbed on the surface of the sorbent of which OH^- predominates. Another factor affecting the variation in sorptive capacity at different pH values may be the sorption free energy of various chromium species (HCrO_4^- , H_2CrO_4 and CrO_4^{2-}) existing at different pH values [23]. At pH of 2–5, the predominant Cr(VI) species mainly exists in the monovalent HCrO_4^- form, which is then gradually converted to the divalent CrO_4^{2-} form as pH increases. The sorption free energy is ranged from -2.5 to -0.6 kcal mol^{-1} for HCrO_4^- and ranged from -2.1 to -0.3 kcal mol^{-1} for CrO_4^{2-} [24]. The sorption free energy of HCrO_4^- is lower than that of CrO_4^{2-} , and consequently HCrO_4^- is more favorably sorbed than CrO_4^{2-} at the same concentration. The removal of Cr(VI) at lower pH is mainly due to sorption of HCrO_4^- , which is expected to be sorbed in larger quantities than CrO_4^{2-} under the same sorption affinity. When the concentration of CrO_4^{2-} is much higher than that of HCrO_4^- at higher pH values, the sorption free energy of CrO_4^{2-} is lower, and only under such a circumstance CrO_4^{2-} sorption can be more favorable than HCrO_4^- . This behavior is consistent with that revealed by other investigators [25,26]. Maximum sorption occurs at pH 5.1 was taken as the optimal value for further sorption studies.

3.1.2. Effect of time

The effect of time on the removal efficiency of Cr(VI) is shown in Fig. 2. It can be seen that the rate of Cr(VI) uptake was initially quite high, followed by a much slower subsequent removal rate leading gradually to an equilibrium condition. About 90% of Cr(VI) was removed during the first hour of reaction, while only a very small part of the additional removal occurred during the following hour of contact. The initial rapid sorption gives a way to a slow approach to equilibrium at higher ion concentrations. These results reflect the high efficiency of the prepared resins for removal of Cr(VI) from aqueous solution in a wide range of concentrations.

The rapid sorption of Cr(VI) by the applied composites is perhaps attributed to the surface site initially available for Cr(VI) sorption is very large compared to the concentration of Cr(VI) ions and consequently, the rate of sorption was very high. However, with increasing coverage, the fraction of sorption sites in

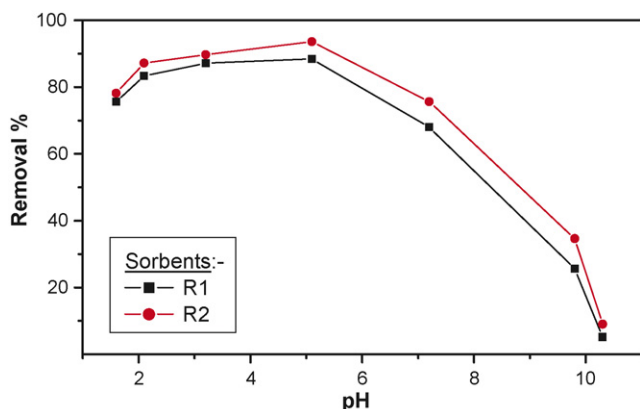


Fig. 1. Effect of pH on sorption of Cr(VI) ions on R1 and R2 resins.

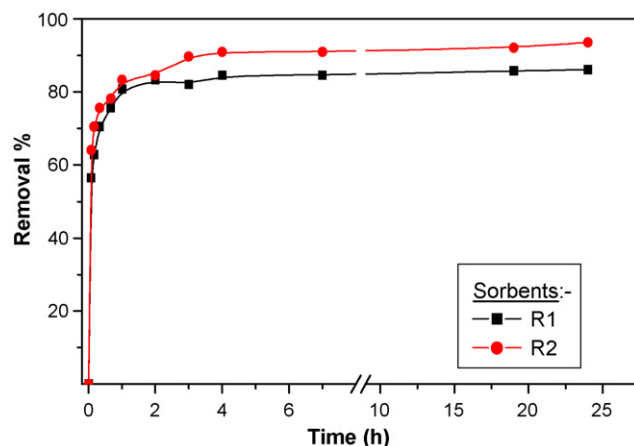


Fig. 2. Effect of contact time on sorption of Cr(VI) ions on R1 and R2 resins.

composite surface rapidly diminished and Cr(VI) ions had to compete among themselves for the sorption sites. This competition leads to slow down the interaction and the rate limiting step becomes predominantly dependent on the rate at which Cr(VI) ions are transported from the bulk to the sorbent–adsorbate interface. The kinetics of the interactions is thus likely to be dependent on different rate processes as the interaction time increases [27]. Generally, an efficiency amounted to 86.2 and 93.6% for Cr(VI) removal using R1 and R2 was attained after ~3 h of contact. In comparison, sorption of Cr(VI) onto other sorbents attains equilibrium after a longer time where equilibrium was reached in more than 6 h for sorption onto peat [7] and around 10–50 h for uptake onto activated carbon [28].

3.2. Sorption kinetics

The kinetics of sorption process were studied by carrying out a set of Cr(VI) sorption experiments between Cr(VI) and composite sorbents at constant temperature and monitoring the amount sorbed with time. The sorption kinetics normally include two phases: a rapid removal stage followed by a much slower stage before the equilibrium is established. Assuming pseudo first order kinetics, the rate of the sorptive interactions can be evaluated by using the simple Lagergren equation [29]:

$$\log(q_e - q_t) = \log q_e - \frac{k_f t}{2.303} \quad (6)$$

where q_e and q_t are the values of amount sorbed per unit mass (mg g^{-1}) at equilibrium and at any time t , respectively and k_f is the pseudo first order sorption rate constant (min^{-1}). The k_f values could be obtained by plotting $\log(q_e - q_t)$ versus t for sorption of Cr(VI) at 29°C and $\text{pH} \sim 5.0$ and the data are represented in Fig. 3. The plots show straight lines have a good linearity. The values of first order rate constant (k_f) and correlation coefficient (R^2) obtained from these plots are listed in Table 1. The sorbents differ very little in the rates of uptake of Cr(VI) ions. The differences in the kinetics between the two sorbents can thus be attributed to the structural differences existing between them. The first order mechanism suffered from inadequacies when applied to Cr(VI) sorption on the composite sorbents. One of the major discrepancies was observed when

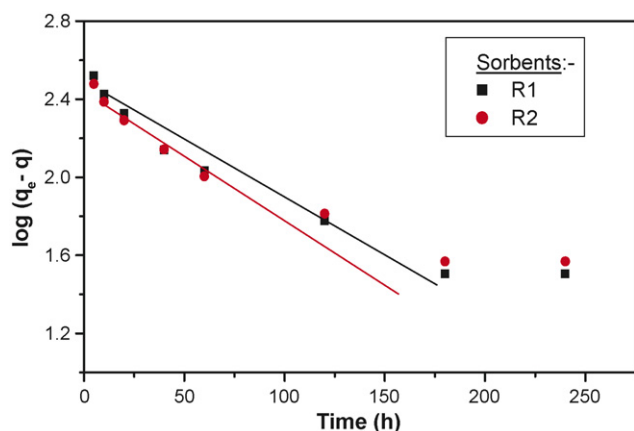


Fig. 3. Lagergren plots for sorption of Cr(VI) ions onto R1 and R2 resins.

Table 1
Kinetic parameters for sorption of Cr(VI) ions by different synthesized composite sorbents

Kinetic parameters	Parameters	Composite sorbents	
		R1	R2
Pseudo first order (Lagergren)	k_f (min^{-1})	0.0198	0.0195
	R^2	0.985	0.991
	S.D.	0.038	0.029
Pseudo second order	k_s ($\text{g mg}^{-1} \text{min}^{-1}$)	1.68×10^{-4}	1.90×10^{-4}
	h ($\text{mg g}^{-1} \text{min}^{-1}$)	138.83	169.1
	R^2	0.999	0.999
	S.D.	0.003	0.003
Elovich	α ($\text{g mg}^{-1} \text{min}^{-2}$)	5.69	5.41
	β ($\text{mg g}^{-1} \text{min}^{-1}$)	75.47	67.39
	R^2	0.989	0.992
	S.D.	17.75	13.48

q_e values obtained from Lagergren plots were compared with the experimental q_e values, Table 2. The experimental q_e values differed from the corresponding theoretical values for both R1 and R2 sorbents. Thus, good linearity of Lagergren plots is not guarantee that the interactions of Cr(VI) with the synthesized sorbents will follow first order kinetics. It is worth to mention that the magnetic resins R1 and R2 give a sorption capacity for Cr(VI) (893.7 and 951.4 mg g^{-1} , respectively) comparatively higher than other resins as Lewatite anion exchanger that gives a sorption capacity of 20 mg g^{-1} [30]. Also R1 and R2 show higher sorption capacity than other magnetic resins used for sorption of Hg(II), Cu(II) and Ni(II) and give sorption capacity of 455.3 , 141.6 and 75.9 mg g^{-1} , respectively [31].

In order to find a more reliable description of the kinetics, second order kinetic equation was applied. The pseudo second order kinetics can be represented by the following linear equation [32]:

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \left(\frac{1}{q_e}\right) t \quad (7)$$

where k_s is the second order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$). The kinetic plots of t/q_t versus t for Cr(VI) removal are shown in Fig. 4. The relationship is linear and the correlation coefficient (R^2) suggests a strong relationship between the model parameters and explains that the sorption process follows pseudo second order kinetics. The equilibrium sorption capacity (q_e), the initial sorption rate (h) that represented as $h = k_s q_e^2$, the pseudo-second-order constant (k_s) along with correlation coefficient were determined and listed in Table 1. From these data, it was observed that, the calculated correlation coefficient is

Table 2
Experimental and modeled values of equilibrium sorption capacity (q_e) of the synthesized composites towards Cr(VI) ions

Sorbent	q_e (mg g^{-1})		
	Experimental	Lagergren	Second order
R1	893.7	332.66	909.09
R2	951.4	304.79	943.39

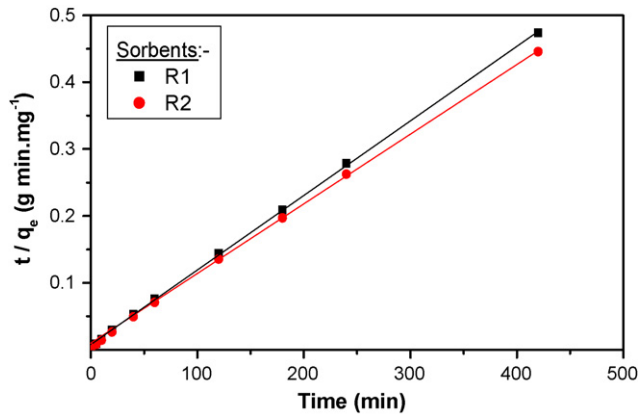


Fig. 4. Pseudo-second order plots for sorption of Cr(VI) ions onto R1 and R2 resins.

extremely high and closer to unity for pseudo second order kinetic model than for pseudo first order kinetic model. The calculated equilibrium sorption capacity (q_e) is consistent with the experimental data, Table 2. Therefore, the sorption reaction can be approximated more favorably by the pseudo second order kinetic model. These results suggest that a pseudo second order sorption is the predominant mechanism and the overall rate constant of Cr(VI) ions appears to be controlled by the chemisorption process [33].

Elovich equation is often used to interpret the kinetics of sorption and successfully describe the predominantly chemical sorption on highly heterogeneous sorbents. The linear form of this equation is given by [34]:

$$q_t = 2.303\beta \log(\alpha\beta) + 2.303\beta \log t \quad (8)$$

where α and β are Elovich coefficients represent the initial sorption rate ($\text{g mg}^{-1} \text{min}^{-2}$) and the desorption constant ($\text{mg g}^{-1} \text{min}^{-1}$), respectively. The relation between q_t and $\log t$ for sorption of Cr(VI) on the prepared composites is illustrated in Fig. 5. The plots exhibit good linear relations from their slopes and intercepts Elovich constants were determined and given in Table 1. Elovich constant α has the values 5.69 and $5.4 \text{ g mg}^{-1} \text{min}^{-2}$ for R1 and R2 resins, respectively. It represents the initial rate of sorption and depends significantly on the

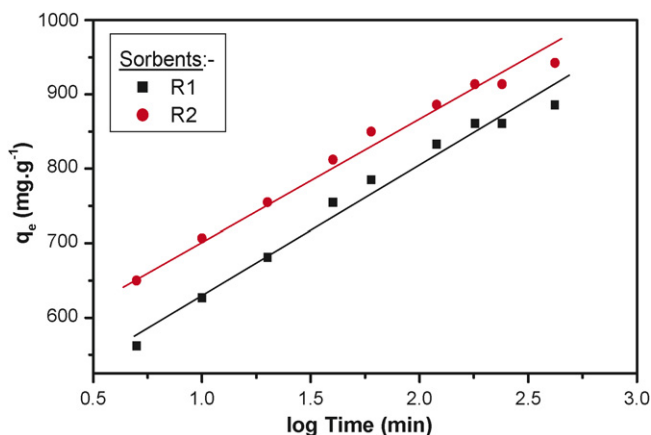


Fig. 5. Elovich plots for sorption of Cr(VI) ions onto R1 and R2 resins.

amount of sorbent subjected in the working system. The integral values of α indicate that the sorption rate could be enhanced many times by increasing the applied amount of composites due to providing a large surface area for solute-sorbent interactions. Although Elovich equation is useful in describing the chemical sorption on heterogeneous systems, no definite mechanism for Cr(VI)-composite interaction could be suggested. Thus, it is predicted that Cr(VI) ions are held strongly to the composite surface by chemisorptive bonds.

The solute transport from the solution phase to the surface of sorbent particles occurs in several steps. The overall sorption process may be controlled either by one step, e.g. film diffusion, pore diffusion, surface diffusion and adsorption on the pore surface, or a combination of more than one step. In a rapidly stirred batch sorption, the diffusive mass transfer can be related by an apparent diffusion coefficient, which will fit the experimental sorption-rate data. Generally, a process is diffusion controlled if its rate is dependent upon the rate at which components diffuse towards one another. The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model given by Weber–Morris and represented by the equation [35]:

$$q_t = k_{id}t^{0.5} + C \quad (9)$$

where k_{id} is the intra-particle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-0.5}$) and C is a constant (mg g^{-1}) gives an idea about the thickness of the boundary layer, i.e., the value of C is indicative for the boundary layer effect. By other words as higher the value of C the greater is the boundary layer effect. If the Weber–Morris plot of q_t versus $t^{0.5}$ gives a straight line, then the sorption process is controlled by intra-particle diffusion only. However, if the data exhibit multi-linear plots, then two or more steps influence the sorption process. Weber–Morris plots of Cr(VI) sorbed per unit mass of sorbent versus $t^{0.5}$ for both sorbents are given in Fig. 6. The slope of these plots is defined as a rate parameter, characteristic of the rate of sorption in the region where intra-particle diffusion is rate controlling. The graphs reveal data points related by two straight lines, the first portion depicting macro-pore diffusion and the second representing micro-pore diffusion. Extrapolation of the linear portions of the plots back to the y-axis gives the intercepts, which provide the

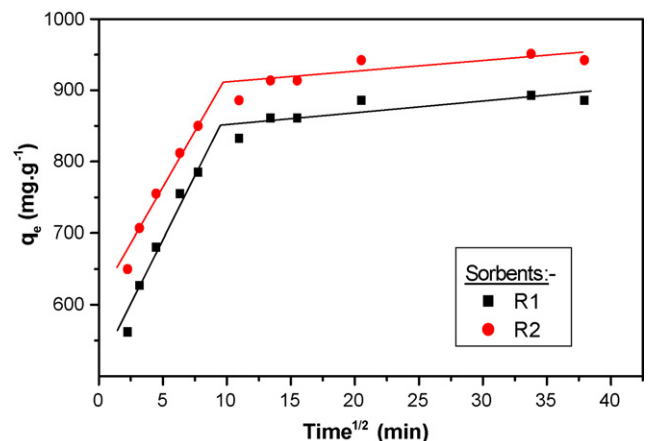


Fig. 6. Weber–Morris plots for sorption of Cr(VI) ions onto R1 and R2 resins.

measure of the boundary layer thickness. The deviation of single straight lines from the origin may be due to difference in rate of mass transfer in the initial and final stages of sorption. Further, such deviation of straight line from the origin indicates that the pore diffusion is not the sole rate-controlling step. The sorption data for q_e versus $t^{0.5}$ for the initial period show curvature, usually attributed to boundary layer diffusion effects or external mass transfer effects. The values of rate parameters ($k_{id,1}$ and $k_{id,2}$) were calculated from the slopes of the linear plots obtained and given in Table 3. The regression coefficient (R^2) has values ranged from 0.926 to 0.998. The intra-particle diffusion rate constant for the first linear portion ($k_{id,1}$) has the values 35.17 and 31.11 $\text{mg g}^{-1} \text{min}^{-0.5}$ for R1 and R2, respectively while $k_{id,2}$ attains the values 1.65 and 1.31 min^{-1} in Cr(VI) sorption on these sorbents. It is likely that a large number of Cr(VI) ions diffuse into the pores before being sorbed. Significantly, the plots did not have a zero intercept as proposed by Eq. (9) indicating that intra-particle diffusion may not be the controlling factor in determining the kinetics of the process.

When the transport of the solute molecules from liquid phase up to solid phase boundary plays the most significant role in sorption, the liquid film diffusion model may be applied using the equation described by Boyd et al. [36]:

$$\log(1 - F) = -\frac{k_{fd}}{2.303} t \quad (10)$$

where F is the fractional attainment of equilibrium ($F = q_t/q_e$) and k_{fd} is the film diffusion rate constant. A linear plot of $\log(1 - F)$ versus t with zero intercept would suggest that the kinetics of the sorption process is controlled by diffusion through the liquid film surrounding the solid sorbents. The plot of $\log(1 - F)$ versus t is illustrated in Fig. 7. The curves exhibit linear plots with a correlation coefficient value ($R^2 = 0.959$) and intercepts of -0.552 and -0.617 for R1 and R2 resins, respectively. The rate constant for liquid film diffusion, k_{fd} , is in the range of 0.0089 – 0.0101 min^{-1} , Table 3. The non-zero intercepts show that, despite giving linear plots, the predictions of the model will have limited applicability in sorption of Cr(VI) on the synthesized composites. The kinetics of Cr(VI) interaction with the composite surfaces does not appear to be straight forward. Second order mechanism is the more likely sorption kinetics and both pore diffusion and film diffusion are participating in ruling the diffusion of solute ions.

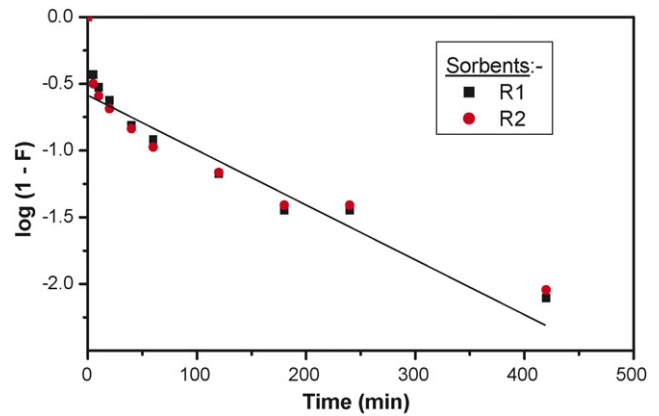


Fig. 7. Boyd plots for sorption of Cr(VI) ions onto R1 and R2 resins.

3.3. Sorption isotherms

Two equilibrium isotherm models were used to find out the relation between the equilibrium concentrations of Cr(VI) ions in liquid and solid phases. These isotherms are Temkin and Flory–Huggins models. The logarithmic form of these isotherm equations may be written as [37]:

$$q_e = \frac{2.303RT}{b_T} \log k_T + \frac{2.303RT}{b_T} \log C_e \quad (11)$$

$$\log \frac{\theta}{C_0} = \log k_{FH} + n \log(1 - \theta) \quad (12)$$

where C_0 and C_e are the initial and equilibrium concentration of Cr(VI) in the liquid phase, q_e is the corresponding concentration of the adsorbate in the solid phase (mg g^{-1}), b_T is a constant related to the heat of sorption, k_T is Temkin isotherm constant indicates the sorption potential of composites, θ is the degree of surface coverage and defined as $\theta = (1 - C_e/C_0)$ and k_{FH} is Flory–Huggins equilibrium constant. The different isotherm parameters for sorption of Cr(VI) ions on the prepared composite samples were evaluated by plotting q_e versus $\log C_e$ and $\log(\theta/C_0)$ versus $\log(1 - \theta)$ for Temkin and Flory–Huggins models and data are presented in Figs. 8 and 9. The straight lines obtained for the two-sorption isotherms indicate that the sorption of Cr(VI) ions fit with the two investigated models. The corresponding isotherm parameters along with correlation coefficients are given in Table 4.

Table 3
Intra-particle and liquid film diffusion models rate constants for sorption of Cr(VI) ions by different synthesized composite sorbents

Sorbents	Intra-particle diffusion				Liquid-particle diffusion			
	k_{id} ($\text{mg g}^{-1} \text{min}^{-0.5}$)	Intercept	R^2	S.D.	k_{fd} (min^{-1})	Intercept	R^2	S.D.
R1								
1	35.17	521.13	0.992	10.93	0.0101	-0.552	0.959	0.12
2	1.650	833.62	0.969	14.71				
R2								
1	31.11	612.21	0.998	4.77	0.0089	-0.617	0.959	0.11
2	1.310	900.88	0.926	11.41				

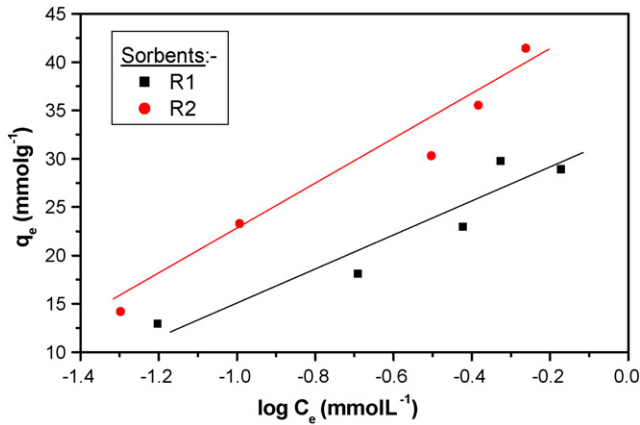


Fig. 8. Temkin plots for sorption of Cr(VI) ions onto R1 and R2 resins.

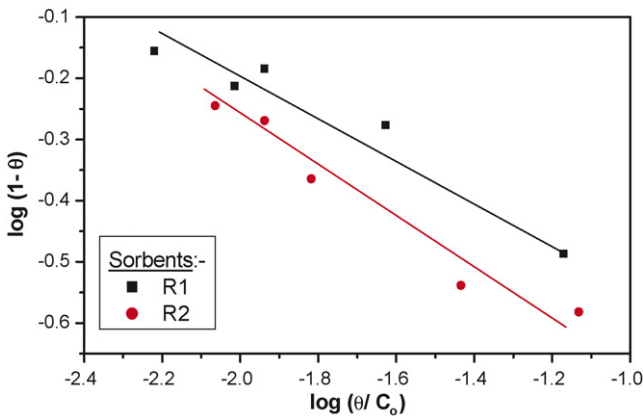


Fig. 9. Flory–Huggins plots for sorption of Cr(VI) ions onto R1 and R2 resins.

Temkin sorption potential constant (k_T) attains the values 81.01 and 81.75 L g⁻¹ for Cr(VI) sorption onto R1 and R2, respectively. The values of b_T , Temkin constant related to heat of sorption are 7.28 and 10.27 kJ mol⁻¹ for R1 and R2, respectively. These values are in the range 8–16 kJ mol⁻¹ which is the range of bonding energy for ion exchange interactions. Therefore, Temkin constant value suggests an ion exchange mechanism for removal of Cr(VI) by the composite sorbents.

Flory–Huggins model accounts for the degree of surface coverage characteristics of Cr(VI) on the surface of composite samples. The isotherm data, listed in Table 4, show that the apparent number of Cr(VI) ions (n) occupying sorption sites on composite surface is greater in case with R2 than with R1. The overall coverage processes clarify that more than 50%

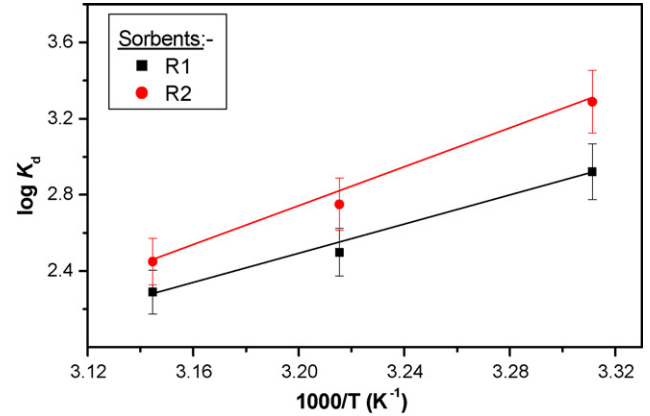


Fig. 10. Van't Hoff plots for sorption of Cr(VI) ions onto synthesized composites.

of the sorption sites on composite surfaces were covered by Cr(VI) during sorption process. The equilibrium constant (k_{FH}) attains the values 0.148 and 0.188 for sorption on R1 and R2, respectively.

3.4. Sorption thermodynamics

The effect of sorption temperature on uptake of Cr(VI) ions by composite sorbents was carried out in temperature ranged from 302 to 318 K. An increase in temperature resulted in a decrease in the amount of Cr(VI) sorbed per unit mass of sorbents showing an exothermic nature of the sorption process. The extent to which the Cr(VI) sorption capacity decreases with increasing temperature might be attributed to the change in surface properties of the sorbent, solubility of the solute species and exothermic nature of the sorption process. Therefore, thermodynamic parameters were evaluated to assess the thermodynamic feasibility and to confirm the nature of the sorption process. The thermodynamic parameters corresponding to Cr(VI) sorption on composite samples were assessed using Van't Hoff equation [38]:

$$\log k_d = \frac{\Delta S^\circ}{2.303R} - \left(\frac{\Delta H^\circ}{2.303R} \right) \frac{1}{T} \quad (13)$$

where k_d is the distribution coefficient of the solute ions and equals to (q_e/C_e) , ΔS° is the entropy change (J mol⁻¹ K⁻¹), R is the ideal gas constant (8.314 J mol⁻¹ K⁻¹) and T is the absolute temperature in Kelvin. A plot of $\log k_d$ versus $1/T$ was constructed and shown in Fig. 10. The figure shows straight lines with slopes equal to the value of apparent enthalpy (ΔH°) for the overall system. The magnitude of the other thermodynamic

Table 4

Temkin and Flory–Huggins isotherm parameters for sorption of Cr(VI) ions by different synthesized composite sorbents

Sorbents	Temkin isotherm model				Flory–Huggins isotherm model			
	k_T (L g ⁻¹)	b_T (kJ mol ⁻¹)	R^2	S.D.	k_{FH} (L g ⁻¹)	n	R^2	S.D.
R1	81.01	7.28	0.947	2.63	0.148	0.614	0.968	0.038
R2	81.75	10.27	0.979	2.44	0.188	0.639	0.978	0.037

Table 5
Thermodynamic parameters for sorption of Cr(VI) ions by different synthesized composite sorbents

Temperature	Thermodynamic parameters					
	$-\Delta H^\circ$ (kJ mol ⁻¹)		$-\Delta G^\circ$ (kJ mol ⁻¹)		$-\Delta S^\circ$ (J mol ⁻¹ K ⁻¹)	
	R1	R2	R1	R2	R1	R2
302	73.36	97.06	16.91	19.04	187	258
311			14.89	16.39	188	259
318			13.96	14.93	187	258

parameters was calculated at different temperatures, using the following equations, and listed in Table 5.

$$\Delta G^\circ = -2.303RT \log k_d \quad (14)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (15)$$

The negative ΔG° values confirm the spontaneous nature and feasibility of the sorption process. With the increase of temperature, the ΔG° value decreased from 16.91 to 13.96 kJ mol⁻¹ for R1 and from 19.04 to 14.93 kJ mol⁻¹ for R2. This indicates that favorable Cr(VI) sorption takes place with decreasing temperature. The negative ΔH° values indicate the exothermic nature of Cr(VI) sorption onto prepared resins. The negative ΔS° values suggest the decrease in sorbate concentration in solid–solution interface indicating thereby the increase in sorbate concentration onto the solid phase. This is the normal consequence of the chemical sorption phenomenon, which takes place through ion exchange interactions as suggested earlier [39]. Also, the negative values of ΔS° specifies an increased randomness at the composite/solution interface during the progress of sorption process.

4. Conclusion

New composite sorbents containing magnetite particles and IR120 ion exchange resin or prepared P(AA-AN) were developed for separation of Cr(VI) from wastewaters. The presence of magnetite particles in these sorbents increase their granular strength, thermal stability and facilitate their separation from aqueous solutions beside the sorption behavior of magnetite. The potential of these sorbents for removal and recovery of Cr(VI) from wastewater was verified under different conditions in batch reactor. In order to optimize the sorption conditions for hexavalent chromium removal from wastewaters, extensive kinetic and thermodynamic studies have been performed resulting in reliable sorption data (rate constants, thermodynamic equilibrium constants, entropies, enthalpies, and free energies). These data indicate that sorption of Cr(VI) on the studied composite samples is a rather complex process. It could be either a chemisorption or simple ion-exchange, in which the transport of metal ions through the solution–solid interface into the porous matrix and their adsorption on the available surface sites are both responsible for the Cr(VI) uptake. By other words the rate of the sorption reaction was suggested to be controlled by second order mechanism (chemical sorption) while particle diffusion and film diffusion are participating in ruling the diffusion of Cr(VI) ions.

The sorption was found to be exothermic process follows pseudo second order kinetics with initial rates being higher for sorption on Mag sorbent. The negative values of Gibbs free energy confirm the feasibility and the spontaneous nature of the sorption process using these novel composites.

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