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Adsorption of Cr(VI) onto PEI immobilized acrylate-based magnetic beads: Isotherms, kinetics and thermodynamics study

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Abstract

Magnetic poly(GMA–EGDMA) beads were prepared from glycidylmetharylate (GMA) and ethyleneglycol dimethacrylate (EGDMA) in the presence of Fe_3O_4 nano-powder via suspension polymerization. After polymerization, the magnetic beads were coated with polyethyleneimine (PEI). Elemental analysis of PEI immobilized beads for the free amine group content was estimated as 258.8 μmol/g polymer. The magnetic beads were characterized by surface area measurement, electron spin resonance (ESR), and scanning electron microscopy (SEM). ESR data revealed that the beads were highly super-paramagnetic. The magnetic beads were used for the removal of Cr(VI) ions from aqueous solutions in batch mode. Adsorption equilibrium was established in about 120 min. The maximum adsorption of Cr(VI) on the magnetic beads was observed at around pH 2.0. The maximum adsorption capacity of the magnetic beads was 137.7 mg/g. The effects of adsorbent dosage, ionic strength and temperature have been also reported.

Keywords: Magnetic beads; PEI; Adsorption; Heavy metal; Cr(VI); Adsorption modelling; Kinetic characterization

1. Introduction

Growing attention is being paid to the health hazards presented by the existence of heavy metals in the environment; their accumulation in living tissues throughout the food chain poses a serious health problem [1]. Even a very small amount can cause severe physiological or neurological damage. Chromium, which is on the top-priority list of toxic pollutants defined by the U.S. Environmental Protection Agency (EPA), exists in nature mainly in two oxidation states and occurs most frequently as Cr(VI) or Cr(III) in aqueous solutions [2]. Major sources of contamination are electroplating, metal finishing industries (hexavalent chromium) and tanneries (trivalent chromium). Both valences of chromium are potentially harmful, while hexavalent chromium has high water solubility and, consequently, its high mobility poses a greater risk due to its carcinogenic properties [3–5].

The commonly used treatment methods for removing metal ions from wastewaters include adsorption, biosorption, complexation, chemical precipitation, solvent extraction, reverse osmosis, ion exchange, filtration and membrane processes [6–9]. Among them, adsorption is one of more popular methods for the removal of chromium from the wastewaters. Metal ions are adsorbed onto the solid adsorbent surface from the wastewater with the quantity of the removed pollutant depending on the adsorption capacity of the adsorbent [8], the chelating adsorbent is contacted with the contaminated solution and the adsorbed metal ions stripped with an appropriate eluent [10,11]. The need of more selective system for separation of metal ions has been increased the development of the synthesis of new adsorbents [12,13]. The acrylic-based adsorbents are almost ideal ones to perform for removal of toxic heavy metals, very stable in a range of buffers from pH 1.0 to 11.0 and were resistant to microbial degradation and several chemicals [9,11–15]. In addition, magnetic separation technique, using magnetic polymeric particles, is quick and easy method for sensitive and reliable capture of inorganic or organic pollutants. These methods are also non-laborious, cheap and often highly scalable. Moreover, techniques employing magnetism are more amenable to automation and miniaturization [16–18]. Much attention has been paid to improve the adsorptive performance of the adsorbent and, the main effort focused on the introduction of a second functional

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polymer via coating to the adsorbent surfaces [19–24]. Unnithan et al. studied the amino modified polyacrylamide grafted coir pith for removal of Cr(VI) from wastewater. The maximum adsorption capacity was 12.43 mg/g under specified experimental conditions [24]. The crosslinked alginate and gelatin was used as adsorbents for the removal of chromium ions from wastewater. The adsorption capacity of the biosorbent was around 0.83 mg/g [10]. Mesoporous SBA-15 was functionalized with imidazole groups by a facile two-step post-grafting method. The imidazole-functionalized material was used Cr(VI) adsorption from aqueous solutions, and the adsorption capacity was 113 mg/g for Cr(VI) [23]. In these studies, various kinetics and isotherm models were used to describe the adsorption kinetic and equilibrium of Cr(VI) removal by these adsorbents.

In this study, PEI immobilized metal chelating magnetic beads were prepared via suspension polymerization. The magnetic beads were characterized and their efficiency in toxic metal removal was investigated under a wide range of conditions, such as treatment time, initial pH of solution, solid/liquid ratio, ionic strength, initial metal ions concentrations using a batch method. The experimental adsorption data are tested for a number of theoretical kinetic and isotherm models and evaluated of thermodynamic parameters on Cr(VI) adsorption.

2. Materials and method

2.1. Materials

Glycidyl methacrylate methacrylic acid 2,3 epoxypropyl isopropyl ether; (GMA), ethyleneglycol dimethacrylate (EGDMA), polyethyleneimine (PEI), magnetite nano-powder (Fe_3O_4, diameter: 20–50 nm), α-α′-azoisobisbutyronitrile (AIBN), polyvinyl alcohol (PVA) and toluene were supplied from Sigma Chemical Co. (St Louis, MO, USA). The monomers distilled under reduced pressure in the presence of hydroquinone and stored at 4 °C until use. All other chemicals were of analytical grade and were purchased from Merck AG (Darmstadt, Germany). The water used in the present work was purified using a Barnstead (Dubuque, IA, USA) ROpure LP reverse osmosis unit with a high flow cellulose acetate membrane (Barnstead D2731) followed by a Barnstead D3804 NANOpure organic/colloid removal and ion exchange packed-bed system.

2.2. Preparation of poly(GMA–EGDMA) magnetic beads

The beads were prepared as previously described elsewhere [25]. The aqueous dispersion medium comprised from NaCl solution (0.1 M, 400 mL). The organic phase contained GMA (15 mL), EGDMA (7.5 mL), 1.0 g magnetite (Fe_3O_4) nanoparticles and 5.0% polyvinyl alcohol (20 mL, as stabilizer) were mixed together with 0.2 g of AIBN as initiator in 20 mL of toluene. The resulting medium was transferred into the reactor and sonicated for about 5 min at 200 W within an ultrasonic water bath (Bransonic 2200, England) for the complete dissolution of AIBN in the polymerization medium. The polymerization reactor was placed in a water bath and heated to 70 °C. It was then equipped with a mechanical stirrer, nitrogen inlet and reflux condenser. The polymerization reaction was maintained under nitrogen atmosphere at 70 °C for 2.0 h (stirring rate: 250 rpm) and then at 80 °C for 1.0 h. After the reaction, the resultant beads were filtered under suction and washed with distilled water and ethanol. Finally, the synthesized magnetic beads were separated from the reaction medium, washed in ethanol solution (70%; 250 mL) for 30 min, and then washed with purified water. The magnetic beads were finally dried in a vacuum oven at 50 °C and stored at room temperature until use.

2.3. Grafting of magnetic beads with PEI

In order to prepare polyethyleneimine grafted magnetic beads following procedure was applied. The magnetic poly(GMA–EGDMA) beads were incubated with PEI solution (5%, pH 10) at 65 °C in a reactor containing 20 g of dry magnetic beads and were shaken for 6 h. After this period, the PEI immobilized magnetic beads were removed from the medium by applying external magnetic force and washed with 1.0 M NaCl and then washed twice with purified water and dried in the oven at 55 °C under vacuum for 24 h.

The leakage of the PEI from the magnetic beads was followed by incubating the fully wetted beads with 10 mL of HCl solution at pH 1.0 for 24 h at room temperature. The leakage experiments were carried out 25 °C at a stirring rate of 50 rpm. PEI released after this incubation was measured at 233 nm in the liquid phase spectrophotometrically.

2.4. Characterization of magnetic beads

The amount of free amino group contents of the poly(GMA–EGDMA)–PEI beads was determined by potantiometric titration. Briefly, the magnetic beads (0.1 g) was allowed soak into water (10 mL) for 24 h. Then, HCl solution (0.1 M, 20 cm^3) was added to the mixture and it was then incubated in a shaking water-bath at 35 °C for 6 h. After this reaction period, the beads filtered and the final HCl concentration in the solution was assayed by a potentiometric titration with 0.05 M NaOH solution.

The average size and size distribution of the magnetic beads were determined by screen analysis performed by using molecular sieves. The specific surface area of the beads was measured by a surface area apparatus and calculated using the BET (Brunauer, Emmett and Teller) method. Scanning electron micrographs (SEM) of the dried magnetic beads were obtained using a JEOL, JMS 5600 scanning electron microscope, after coating with gold under reduced pressure. The FTIR spectra of the magnetic poly(GMA–EGDMA)–PEI and poly(GMA–EGDMA) beads were obtained using an FTIR spectrophotometer (Shimadzu, FTIR 8000 Series, Japan). Electron spin resonance (ESR) spectroscopy was carried out with a conventional X-band ($\nu = 9.75$ Hz) Bruker ESP 300E spectrometer at 100 kHz magnetic field modulation frequency, 31.7 G modulation amplitude and 0.1 mW microwave power. The magnetic beads about (50 mg) were placed into quartz tube and the measurements were performed at room temperature. The first derivative of the power absorption had been recorded as a function of the applied magnetic field.

2.5. Adsorption studies

A stock solution containing Cr(VI) ions were prepared from the analytical grade $K_2Cr_2O_7$ in Milli-Q water. The range of concentrations of Cr(VI) was prepared from this solution. The adsorption of Cr(VI) ions from aqueous solution on the magnetic poly(GMA–EGDMA)–PEI beads was investigated using plain poly(GMA–EGDMA) beads as a control system. Different quantities of magnetic beads, varying from 25 to 200 mg in each 50 mL of Cr(VI) (100 mg/L) solution were stirred 150 rpm for 2 h at 25 °C. Once the optimum magnetic beads dosage was determined, the effect of pH, temperature and ionic strength were conducted. The effect of pH on the adsorption capacity of the beads for Cr(VI) was investigated in the pH range 1.0–8.0 (which was adjusted with H_2SO_4 or NaOH at the beginning of the experiment and not controlled afterwards). The effect of temperature and ionic strength on Cr(VI) adsorption were studied at four different temperatures (i.e., 15, 25, 35 and 45) and at five different NaCl concentrations (between 25 and 1000 mM), respectively. All experiments were conducted in duplicates with 100 mg magnetic beads at pH 2.0 and the initial concentration of Cr(VI) was 100 mg/L in the medium. To determine the adsorption capacity of the magnetic poly(GMA–EGDMA)–PEI beads, the initial concentration of Cr(VI) was changed between 20 and 600 mg/L in the adsorption medium.

After the desired adsorption periods (about 2 h), magnetic poly(GMA–EGDMA)–PEI beads were separated from aqueous phases using a magnetic devise and the residual concentration of the Cr(VI) ions in the aqueous phases were measured at 540 nm by a double beam UV–vis spectrophotometer (Shimadzu, Tokyo, Japan, Model 1601) after complexation with 1,5 diphenyl carbazide. Before determination of the total quantity of chromium Cr(VI) in the adsorption medium, Cr(III) and Cr(II) were converted to Cr(VI) using $KMnO_4$ [27]. The amount of Cr(VI) adsorbed per unit mass of adsorbent (mg metal ions/g beads) and the percentage removal of chromium were calculated by using the determination data in described earlier [9].

2.6. Elution and regeneration of the sorbent

In order to determine the reusability of magnetic beads consecutive adsorption–desorption cycles were repeated five times by using the same magnetic poly(GMA–EGDMA)–PEI beads. Desorption of Cr(VI) ions was performed by 0.1 M NaOH solution. The magnetic poly(GMA–EGDMA)–PEI beads loaded with Cr(VI) ions was placed in desorption medium and stirred at 150 rpm for 2 h at 25 °C. The final Cr(VI) concentration in the aqueous phase was determined as described above. After each cycle of adsorption–desorption, the magnetic beads were washed and reconditioned for adsorption in the succeeding cycle. Desorption ratio was calculated from the amount of metal ions adsorbed on the magnetic beads and the final metal ions concentration in the adsorption medium.

3. Results and discussion

3.1. Characterization of magnetic beads

GMA monomer was use initially to incorporate epoxy groups on the polymer surface for further modification of the beads. The amount of available surface functional epoxy groups content of the poly(GMA–EGDMA) beads was determined by HCl–pyridine method and was found to be 3.17 mmol/g. The obtained value for epoxy groups was lower than that of the theoretical value (5.18 mmol/g) because some of the epoxy groups remain inside of the magnetic beads and are not accessible for subsequent reactions or analytical determinations. The beads were sieved and 75–150 μm size of fraction was used for immobilization of PEI. The free amino group content of the PEI immobilized magnetic beads was found to be as 258.8 μmol/g beads. The studies of immobilized PEI leakage from the magnetic beads showed that there was no PEI leakage in the medium used throughout this study, even in long storage period of time (more than 6 weeks). The specific surface area of the magnetic poly(GMA–EGDMA) beads was measured by BET method and was found to be 17.6 m^2/g beads. The low specific surface area (17.6 m^2/g) is likely to attributed to either low porosity or to rough external surface than to high porosity.

The water content is very important when use of the support material in chromatographic application is contemplated. The equilibrium-swelling ratio of the magnetic poly(GMA–EGDMA) and poly(GMA–EGDMA)–PEI beads was determined as 27.3% and 36.8%, respectively. The magnetic properties of the beads were confirmed with electron spin resonance spectroscopy (ESR) at room temperature and the intensity versus the magnetic field (Gauss) (Fig. 1). The spectrum has two components: (i) a typical low field high intensity ferromagnetic resonance signal (below 2000 G), and (ii) a broad line pick extended up to 5000 G. In this ESR spectrum, about 1500-G magnetic field was found to be sufficient to excite all of the dipole moments of the sample beads that consist of magnetite.

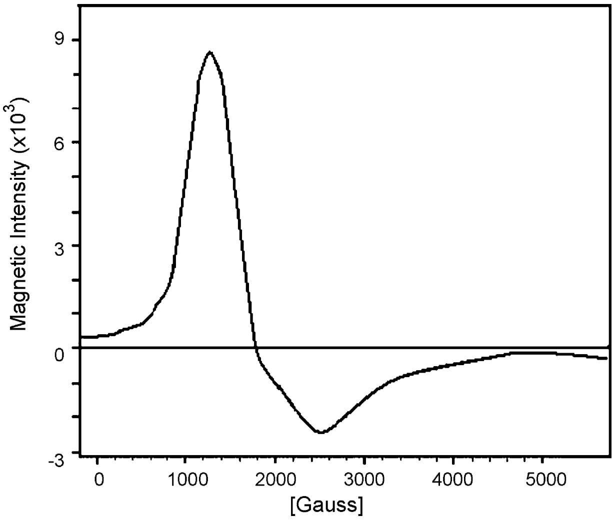

Fig. 1. Electron spin resonance (ESR) spectrum of magnetic poly(GMA–EGDMA) beads at room temperature.

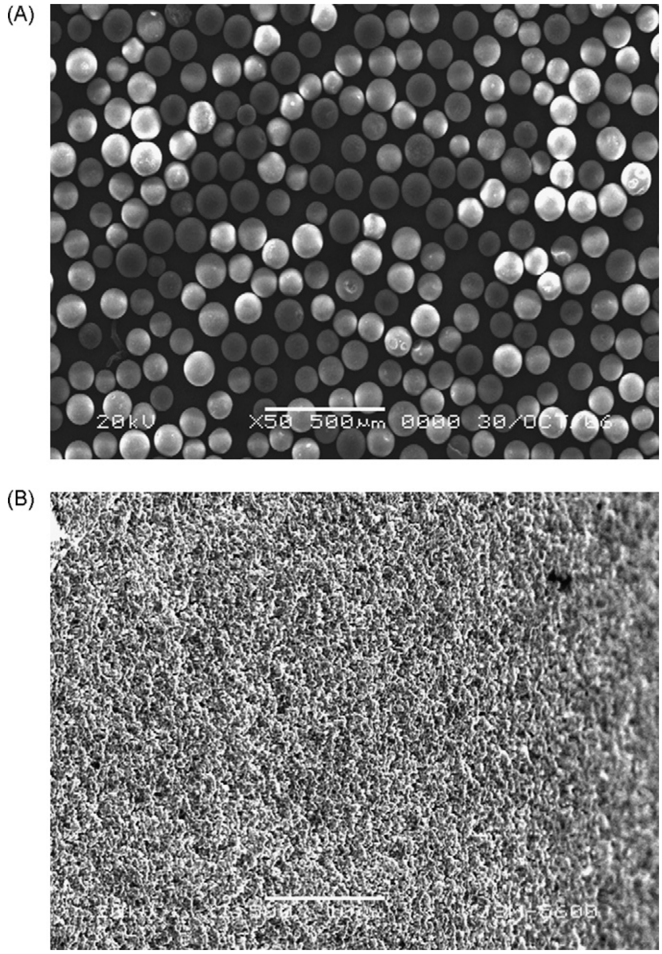

Fig. 2. SEM micrograph of the magnetic poly(GMA–EGDMA) beads; magnifications: (A) 50×; (B) 13,500×.

The value of this magnetic field is a function of the flow velocity, particle size and magnetic susceptibility of the beads to be displaced. In the literature, the value was reported between 1000 and 20,000 G [28], so the magnetic beads developed in this study will need less magnetic intensity for various reactor configurations. So, the magnetic beads can be easily separated within a few second by a conventional permanent magnet. When the applied magnetic force is removed, the magnetic beads can easily be dispersed by simple shaking. Thus, the magnetic beads can be removed or recycled in the adsorption medium.

Scanning electron microscopy (SEM) micrographs presented in Fig. 2 shows the porous surfaces structure of the magnetic beads. The beads have a spherical form and rough surface due to the pores, which formed during the polymerization process. The porous surface structure should be considered as a factor providing an increase surface area. In addition, these pores reduce the mass transfer resistance and facilitate the diffusion of metal ions because of high internal surface area with low diffusional resistance in the magnetic beads (imply high adsorption capacity and rate).

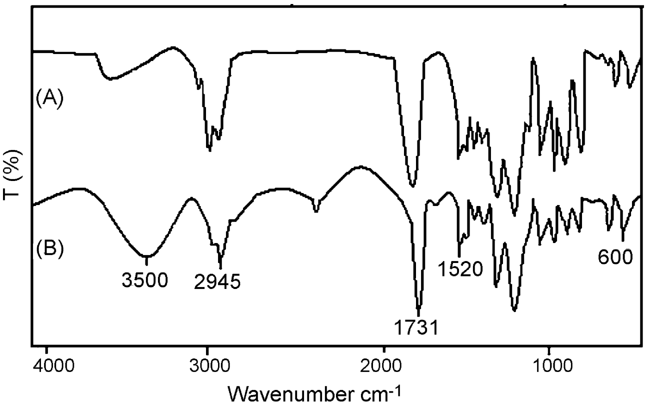

Fig. 3. FTIR spectra of the poly(GMA–EGDMA) and poly(GMA–EGDMA)–PEI.

The FTIR spectra of the magnetic poly(GMA–EGDMA) beads have the characteristic stretching vibration band of hydrogen-bounded alcohol at $\sim 3500\,\mathrm{cm}^{-1}$ (Fig. 3). Among the characteristic vibrations of both GMA and EGDMA is the methylene and ester configuration vibration at ~ 2945 and $1731\,\mathrm{cm}^{-1}$. The epoxide group gives the band between at $910\,\mathrm{cm}^{-1}$ (epoxy ring vibrations). The most important adsorption band at $1520\,\mathrm{cm}^{-1}$ representing N–H bending, is due to PEI bonded to the magnetic beads. The FTIR spectra of the magnetic beads have also characteristic N–H amine stretching bands at 3500 and $1655\,\mathrm{cm}^{-1}$ are is due to amino groups of the PEI immobilized on the magnetic beads. Fe_3O_4 has the characteristic band at $600\,\mathrm{cm}^{-1}$ and also this indicates that Fe_3O_4 molecules are successfully formed within the structure of the magnetic beads. The magnetic beads were also incubated in the pH ranges 1.0–10.0 for 48 h using 0.1N HCl and 0.1N NaOH for adjusting pH. After this period the magnetic material were dried and their Fe_2O_3 content was determined by gravimetrically. It was observed no significant change in Fe_2O_3 content and magnetization in the studied pH range 1.0–10.0.

3.2. *Influence of sorbent dosage*

The percentage removal of Cr(VI) was studied by varying the adsorbent dose between 25 and 200 mg at a Cr(VI) ions concentration of 100 mg/L (Fig. 4). The magnetic poly(GMA–EGDM)–PEI beads, the total chromium removal efficiency increases up to an optimum dosage beyond which the removal efficiency does not significantly change. This result was anticipated because for a fixed initial solute concentration, increasing adsorbent doses provides greater surface area (or adsorption sites), whereas the adsorbed metal ions quantity (q) per unit weight of the sorbent decreased by increasing the magnetic beads quantity [29].

3.3. *Effect of medium pH and ionic strength on adsorption*

As shown in Fig. 5, pH is an important parameter for the adsorption of Cr(IV) ions on the PEI immobilized magnetic beads. The functional amine groups of the PEI have a lone pair of electrons from nitrogen, which primarily act as an active site for the formation of PEI-metal-ion complex. As seen from Fig. 5, Cr(VI) adsorption on the magnetic beads is greater at low pH and decreases with increasing pH. The functional NH_2 groups

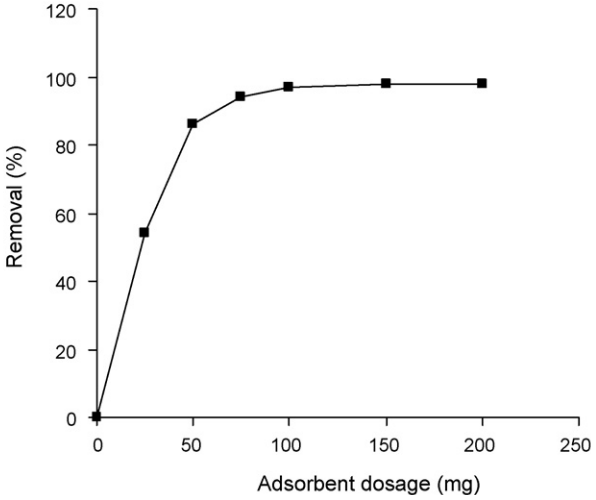

Fig. 4. Effect of sorbent dosage on the chromium ions adsorption onto magnetic beads; Volume of the medium: 50 mL; temperature: 25 °C; initial concentration of metal ions: 100 mg/L; contact time 2 h.

in PEI are considered active sites for the adsorption of Cr(VI). Depending on the solution pH, these amine groups of PEI can undergo protonation to NH_3^+ and the extent of protonation will be dependent on the solution pH. It should be noted that the distribution of Cr(VI) ions species is dependent on both the total concentration of Cr(VI) and pH of the aqueous solution. The oxy-anions of chromium are known to exist in the following equilibrium [30]:

$$H_2CrO_4 \leftrightarrow HCrO_4^- + H^+, \quad k_1 = 1.21 \tag{1}$$

$$CrO_7^{2-} + H_2O \leftrightarrow 2HCrO_4^-, \quad k_2 = 35.5 \tag{2}$$

$$HCrO_4^- \leftrightarrow CrO_4^{2-} + H^+, \quad k_3 = 3 \times 10^{-7} \tag{3}$$

$$HCrO_7^- \leftrightarrow CrO_7^{-2} + H^+, \quad k_4 = 0.85 \tag{4}$$

Since the distribution of anionic species of Cr(VI) is pH dependent, this could be the main variable for removal of Cr(VI) ions by adsorbent. Therefore, the functional amino groups on the surface of the magnetic beads will determine the type of electrostatic interaction between the metal ion and the sorbent surface for Cr(VI) adsorption. Chromium in industrial waste, primarily present in the form of hexavalent Cr(VI) as chromate ($HCrO_4^{1-}$, CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$, $HCr_2O_7^{1-}$), behaves as an oxyanion according to its aquatic chemistry and the fraction of any particular species is dependent on chromium concentration and solution pH [30–35]. At lower pH values, the protonated amine group of PEI which leads to an increased electrostatic attraction between NH_3^+ and the sorbate anion [25,36,37].

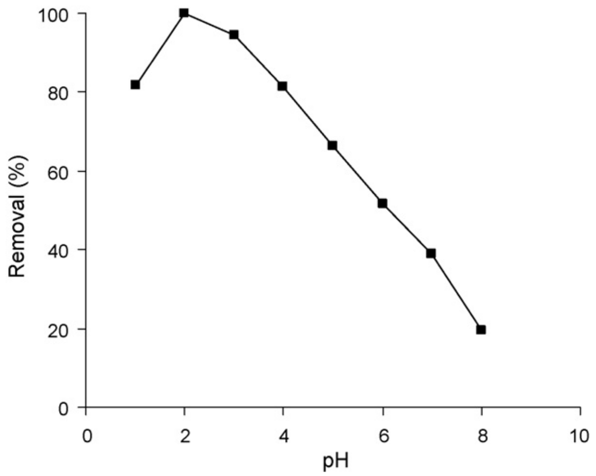

Fig. 5. Effect of pH on the chromium removal onto PEI immobilized magnetic beads; Initial concentration of metal ions: 100 mg/L; dose of adsorbent: 0.1 g; volume of the medium: 50 mL; contact time 2 h.

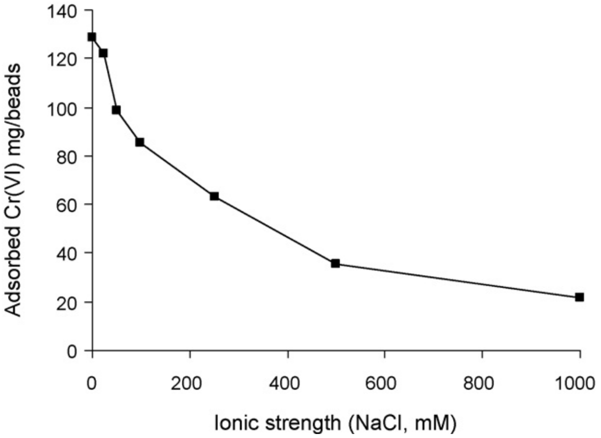

Fig. 6. Effect of ionic strength on the adsorption system; Initial concentration of metal ions: 100 mg/L; volume of the medium: 50 mL; dose of adsorbent: 0.1 g; contact time 2 h.

It appears that as the amount of salt increases, the adsorption efficiency of Cr(VI) ions decrease with increasing ionic strength though the decrease is insignificant at lower ionic strength (Fig. 6). This may also be due to the lowering in chromate anions (CrO_2^-), a reduction in columbic attraction, for chromate species on solid surfaces and/or to the presence of competing anions. The adsorption behavior of the PEI immobilized magnetic beads is suppressed in the presence of salt, which is in agreement with previous related publications [25,38].

3.4. Effect of initial metal concentration and temperature

As shown in Fig. 7, the adsorption capacity increased with increasing equilibrium metal ions concentration in the medium. As expected, an increase in the adsorption capacity of the magnetic beads after PEI immobilization was observed for Cr(VI) ions. The maximum adsorption capacity of Cr(VI) on the magnetic poly(GMA–EGDMA) and poly(GMA–EGDMA)–PEI beads was 11.6 and 137.7 mg/g dry beads, respectively. PEI immobilization caused in increase in the adsorption capacity of the magnetic beads about 11.8-folds compared to the plain poly(GMA–EGDMA) beads. As seen in figure, the experimental Cr(VI) adsorption isotherm is very steep at the beginning of adsorption and the gradually reached at a plateau about 300 mg/L initial Cr(VI) concentration.

The effect of temperature on the adsorption of Cr(VI) by the magnetic beads was investigated between 15 and 45 °C at pH 2.0. As shown in Fig. 8, the adsorption capacity increased with the increase in temperature. Enhancement of adsorption capacity

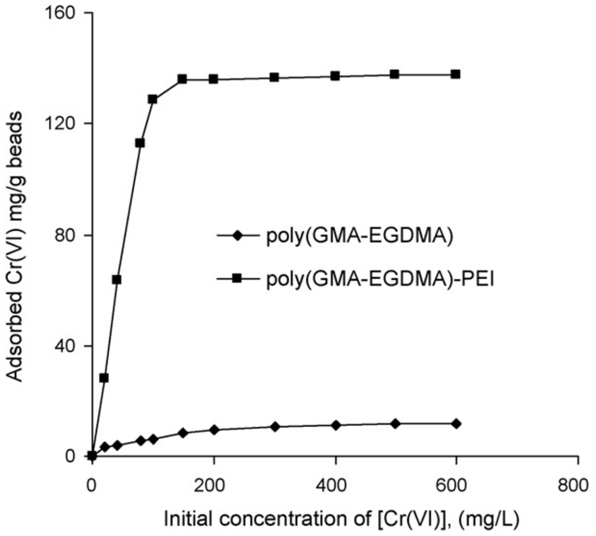

Fig. 7. Effect of initial metal ion concentration on the Cr(VI) adsorption; Volume of the medium: 50 mL; Temperature: 25 °C; pH: 2.0; dose of adsorbent: 0.1 g; contact time 2 h.

at higher temperatures may be attributed to enlargement of pore size and/or activation of the adsorbent surface [39].

3.5. Evaluation of adsorption isotherm models and thermodynamic parameters

It is known that equilibrium and kinetic analyses not only allow for the estimation of adsorption capacities and rates, but also lead to suitable rate expressions characteristic of possible reaction mechanisms. The adsorption isotherm models were used to characterize the interaction of chromium species with the magnetic poly(GMA–EGDMA)–PEI beads. The Langmuir model predicts the formation of an adsorbed solute monolayer, with no side interactions between the adsorbed ions. It also assumes that the interactions take place by adsorption of one ion per binding sites and that the adsorbent surface is homogeneous and contains only one type of binding site. The mathematical description of this model is as follows:

$$q_{\mathrm{eq}} = \frac{q_{\mathrm{m}} b C_{\mathrm{eq}}}{1 + bC_{\mathrm{eq}}} \tag{5}$$

where C_{eq} and q_{eq} also show the residual metal concentration and the amount of metal adsorbed on the adsorbent at equilibrium, respectively. q_{m} and b are the Langmuir constants of the system denoting maximum adsorption capacity and the affinity binding sites, respectively. Semi-reciprocal (C/q versus C) of the experiment data for the adsorption of chromium is plotted for the adsorbent and calculated the model parameters.

The Freundlich model does not predict surface saturation. It considers the existence of a multilayered structure. This empirical equation takes the form:

$$q_{\mathrm{eq}} = K_{\mathrm{F}}(C_{\mathrm{eq}})^{1/n} \tag{6}$$

where, K_{F} and n are the Freundlich constants indicating the adsorption capacity and adsorption intensity, respectively.

The Langmuir and Freundlich adsorption constants calculated from the corresponding isotherms (Fig. 9) with the correlation coefficients and model parameters are presented in Table 1. From the comparison of correlation coefficients, it was found that the data were fitted better by Langmuir equation than by Freundlich equation for Cr(VI) adsorption. The maximum adsorption capacity (q_{m}) was calculated to be 140.6 mg/g at 25 °C (Fig. 9).

The adsorption isotherms obtained at various temperatures were used to gain a better understanding of the adsorption mechanism. The dependency of the equilibrium association constant ($K_{\mathrm{a}} = b$) versus $1/T$ for the binding of chromium ions on the adsorbent was analyzed in terms of van't Hoff plots. From the van't Hoff plot for the adsorption process, the thermodynamic parameters such as free energy changes (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were then extracted. The value of the change in enthalpy during the binding process was determined from the gradient of the plots between $\ln K_{\mathrm{a}}$ versus

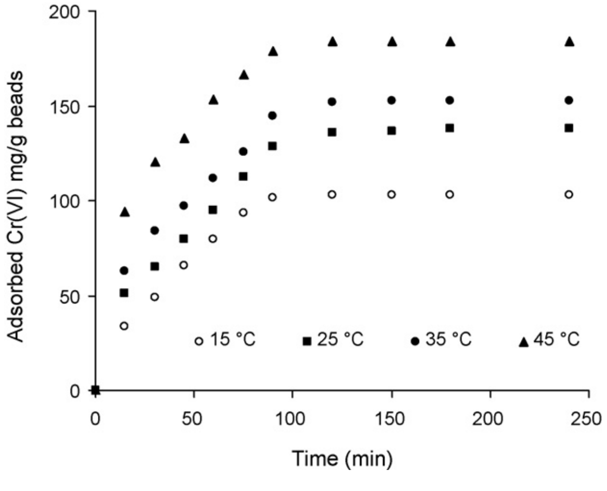

Fig. 8. Effect of temperature and contact time for adsorption of Cr(VI) on the PEI immobilized magnetic beads. Volume of the medium: 50 mL; temperature: 25 °C; pH: 2.0; dose of adsorbent: 0.1 g.

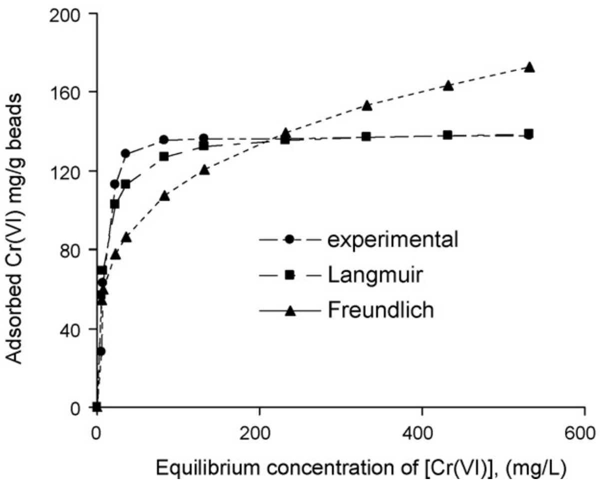

Fig. 9. Comparison of the equilibrium experimental and the adsorption isotherms obtained from the Langmuir and the Freundlich models for Cr(VI) adsorption on the magnetic beads.

Table 1
The isotherm model constants and correlation coefficients of Cr(VI) adsorption on the PEI immobilized magnetic beads

Temperature (K)	Experimental q_{exp} (mg/g)	Langmuir constant			Freundlich constant			ΔG (kJ/mol)
		q_{m} (mg/g)	b (M^{-1})	R^2	K_{F}	n	R^2	
288	103.2	108.2	2.65	0.996	16.39	3.01	0.831	−2.33
298	137.7	140.6	5.99	0.998	34.64	3.91	0.795	−4.43
308	152.4	153.9	11.03	0.999	46.17	4.44	0.830	−6.15
318	184.2	185.7	13.39	0.995	58.33	4.56	0.812	−6.86

$1/T$ ($\ln K_{\text{a}} = (\Delta S^\circ/R) - (\Delta H^\circ/RT)$). The value of ΔG° and ΔS° can be estimated from the relationships $\Delta G^\circ = -RT \ln K_{\text{a}}$ and $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$.

The thermodynamic parameters for the adsorption system at different temperatures are tabulated in Table 1. The negative values of ΔG° indicate that the adsorption of chromium on the PEI immobilized magnetic beads is feasible and spontaneous. The Gibbs energy of the interactions demonstrated that the processes are favorable for the formation of electrostatic interaction and/or chromium–adsorbent complexes. The magnitude of ΔG° for the adsorption of Cr(VI) on adsorbent increased with the ascend temperature. ΔH° for the adsorption of Cr(VI) onto PEI immobilized magnetic beads was found to be 41.95 kJ/mol while ΔS° was 154.76 J/mol K. The positive value of ΔH° shows that the Cr(VI) adsorption is an endothermic process. The positive value of ΔS° indicates that the randomness increases at the solid/solution interface during the adsorption of Cr(VI) on the magnetic poly(GMA–EGDMA)–PEI beads.

3.6. *Evaluation of equilibrium time and kinetic models*

In order to evaluate adsorption as a unit operation, it requires consideration of two important physico-chemical aspects of the process, the kinetics and the equilibrium of adsorption [40,41]. The Cr(VI) adsorption rate is high at the beginning of adsorption and saturation levels were completely reached at about 120 min and adsorption rate was obtained by following the decrease of the concentration of metal ions within the adsorption medium with time. A rapid removal of the metal ions by the adsorbent is desirable providing for a short solution adsorbent contact time in the actual process [21–45].

The kinetics of Cr(VI) adsorption on the PEI immobilized magnetic beads was determined with different kinetic models, i.e. the first- and second-order. The first-order rate equation of Lagergren is one of the most widely used for the adsorption of solute from a solution [46]. The model has the following form:

$$\log \frac{q_{\text{eq}}}{q_{\text{eq}} - q_{\text{t}}} = \frac{k_1 t}{2.303} \tag{7}$$

where k_1 is the rate constant of first-order adsorption (min^{-1}) and q_{eq} and q_{t} denote the amounts of adsorption at equilibrium and at time t (mg/g), respectively. In a true first-order process $\log q_{\text{eq}}$ should be equal to the intercept of a plot of $\log(q_{\text{eq}} - q_{\text{t}})$ against t.

Ritchie proposed a method for the kinetic adsorption of gases on solids [47]. If metal ion adsorption medium is considered to be a second-order reaction, Ritchie equation is:

$$\frac{1}{q_{\text{t}}} = \frac{1}{k_2 q_{\text{eq}} t} + \frac{1}{q_{\text{eq}}} \tag{8}$$

where k_2 (g/(mg min)) is the rate constant of the second-order adsorption. The rate constant (k_2) and adsorption at equilibrium (q_{eq}) can be obtained from the intercept and slope, respectively, and there is no need to know any parameter beforehand.

The second-order equation fitted well with the experimental data. The comparison made between the experimental adsorption capacity and the theoretical values estimated from the second-order equation is presented in Table 2. The theoretical q_{eq} values for the adsorbent were very close to the experimental q_{eq} values in the case of second-order kinetics. The second-order kinetics best described the data. On the other hand, the theoretical q_{eq} values estimated from the first-order kinetic model gave significantly different values compared to experimental values, and the correlation coefficients were also found to be slightly lower. These results showed that the first-order kinetic model did not well describe the adsorbent systems.

From the slop and intersection of the straight line obtained (data not shown), the corresponding constant values for the second-order kinetic model, for the studied temperature, provide the respective kinetic constants, k_2 and q_{e} parameters (Table 2).

Table 2
The first-order and second-order kinetics constants for adsorption of Cr(VI) on the PEI immobilized magnetic beads

	Experimental q_{exp} (mg/g)	First-order kinetic			Second-order kinetic		
		$k_1 \times 10^2$ (min^{-1})	q_{eq} (mg/g)	R^2	$k_2 \times 10^4$ (g/(mg min))	q_{eq} (mg/g)	R^2
288	103.2	5.82	362.7	0.963	3.49	119.0	0.994
298	137.7	3.55	233.8	0.914	2.99	156.3	0.987
308	152.4	4.69	373.3	0.920	3.78	166.7	0.990
318	184.2	5.99	563.77	0.918	5.56	199.8	0.989

Activation energy is determined according to the second-order rate constant is expressed as a function of temperature by the Arhenius equation, $k = A_0 \exp(-E_a/RT)$. A_0 is the temperature independent factor, k the second-order rate constant and R is the gas constant (8.314 J/(mol K)). Value of the activation energy, E_a, can be determined from the slope of $\ln k$ versus $1/T$ plot. The activation energy for chromium adsorption on the magnetic poly(GMA–EGDMA)–PEI beads were calculated and the value was found to be 13.6 kJ/mol for Cr(VI). The magnitude of E_a is useful for estimating the type of adsorption reaction. The E_a value is in the energy range of an ion-exchange reaction. This indicates that the adsorption of Cr(VI) ions onto magnetic beads may proceed through an ion-exchange reaction via amino groups of the beads.

3.7. Elution and regeneration

The use of an adsorbent in the wastewater treatment depends not only on the adsorptive capacity, but also on how well the adsorbent can be regenerated and used again. For repeated use of an adsorbent, adsorbed metal ions should be easily desorbed under suitable conditions. Desorption of the adsorbed chromium ions from the magnetic beads were studied in a batch system. The chromium ions adsorbed onto magnetic beads were eluded with 0.1 M NaOH. More than 95% of the adsorbed chromium ions were desorbed from the PEI immobilized magnetic beads. In order to show the reusability of the adsorbents adsorption–desorption cycle of chromium was repeated five times by using the same beads. The adsorption capacities for the tested magnetic beads did not noticeably change (only a maximum 7% change was observed) during the repeated adsorption–desorption operations.

4. Conclusions

Magnetic separation technologies have been applied in diverse field of the separation technology. In this study, the magnetic poly(GMA–EGDMA) beads were prepared via suspension polymerization. PEI was then immobilized onto poly(GMA–EGDMA) beads via epoxy ring opening reaction. One of the objectives for immobilization of PEI on the magnetic beads was to expose more amine groups on the surface in order to cerate active binding sites for chromium ions species. Furthermore, it is expected that PEI can be allowed regeneration and repeated use in batch and/or a column process. The magnetic analysis showed a high magnetic responsiveness in magnetic field, and no aggregation of the particles was observed after the particles had been treated in the magnetic field so its called super-paramagnetic. The adsorbent was evaluated for chromium by obtaining equilibrium adsorption data at different pH and temperatures. Results of batch equilibrium tests indicated that Langmuir isotherm describes well the Cr(VI) adsorption process. The adsorption process has been found to be endothermic for Cr(VI) (enthalpy change, $\Delta H^\circ = 41.95$ kJ/mol). Desorption experiments were conducted by employing NaOH showed that the loaded material could be regenerated satisfactorily. The magnetic support enhanced filtration/adsorption process shows promise as an improved, simple and inexpensive method for treating water and wastewater.

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