Adsorption of Cr(VI) ions onto Poly(ethylene glycol dimethacrylate-1-vinyl-1,2,4-triazole)

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ABSTRACT: Poly(ethylene glycol dimethacrylate-1-vinyl-1,2,4-triazole) [poly(EGDMA-VTAZ)] beads (average diameter = 150–200 μm) were prepared by copolymerizing ethylene glycol dimethacrylate (EGDMA) with 1-vinyl-1,2,4-triazole (VTAZ). Poly(EGDMA-VTAZ) beads were characterized by swelling studies and scanning electron microscope (SEM). The adsorption of Cr(VI) from solutions was carried at different contact times, Cr(VI) concentrations, pH, and temperatures. High adsorption rates were achieved in about 240 min. The amount of Cr(VI) adsorbed increased with increasing concentration and decreasing pH and temperature. The intraparticle diffusion rate constants at various temperatures were calculated. Adsorption isotherms of Cr(VI) onto poly(EGDMA-VTAZ) have been determined and correlated with common isotherm equations such as Langmuir and Freundlich isotherm models.

The Langmuir isotherm model appeared to fit the isotherm data better than the Freundlich isotherm model. The pseudo first-order kinetic model was used to describe the kinetic data. The study of temperature effect was quantified by calculating various thermodynamic parameters such as Gibbs free energy, enthalpy, and entropy changes. The dimensionless separation factor (R_L) showed that the adsorption of metal ions onto poly(EGDMA-VTAZ) was favorable. It was seen that values of distribution coefficient (K_D) decreasing with Cr(VI) concentration in solution at equilibrium (C_e) indicated that the occupation of activate surface sites of adsorbent increased with Cr(VI). © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 948–955, 2009

Key words: adsorption; adsorption isotherms; adsorption kinetics; Cr(VI)

INTRODUCTION

Chromium is highly toxic pollutant generated from many industrial processes such as leather tanning process, electroplating, and manufacturing of dye, paint, and paper. Chromium is hazardous because it affects human physiology, accumulates in the food chain, and causes several diseases.[1] Chromium essentially exists in two forms namely chromium(VI) and chromium(III). Cr(III) is proved to be biologically essential to mammals as it maintains an effective glucose, lipid, and protein metabolism.[2] In contrast, Cr(VI) can diffuse as CrO_4^{2-} or $HCrO_4^-$ through cell membranes and oxidize biological molecules.[3] The Agency for Toxic Substances and Disease Registry (ATSDR) classifies Cr(VI) as the top 16th hazardous substance. Because of its mutagenic and carcinogenic properties, the US EPA has set the maximum acceptable amount in contaminated water supply as 0.05 μg/L.[4]

Many methods have been used for the removal of Cr(VI) from aqueous solutions, including chemical precipitation, chemical oxidation and reduction, ion exchange, filtration, electrochemical treatment, and evaporative recovery. However these high-technology processes have significant disadvantages, including incomplete metal removal, requirements for expensive equipment and monitoring systems, high reagent or energy requirements or generation of toxic sludge or other waste products that require disposal.[5] In the past few decades, adsorption is considered as a powerful technique that was extensively used for removal of heavy metal ions from domestic and industrial effluents.[6] Activated carbon, clay minerals, microbial biomass, metal oxides, and polymeric adsorbents have been used as adsorbents for removal of heavy metal ions from aqueous solutions. Polymeric adsorbents are generally preferred for the removal of heavy-metal ions due to their high efficiency, easy handling, and availability of different adsorbents, reusability, and cost effectiveness. Toxic metal-ion removal with chelating polymers would be of great importance in environmental applications.[7–9] Several criteria are important in the design of metal-chelating polymers with substantial stability for the selective removal of metal ions, including specific and fast complexation of the metal ions. Polymeric adsorbents incorporated with ethylenediamine, poly(ethyleneimine), amidoxime, acrylamide, dithiocarbamate, polyaniline, thiazolidine, and reactive amino acids have been used for the removal of heavy metal ions.[10,11]

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The aim of this work was to prepare a chelating adsorbent from triazole monomer in the bead form. For this propose, poly(ethylene glycol dimethacrylate-1-vinyl-1,2,4-triazole) [poly(EGDMA-VTAZ)] beads were prepared by copolymerizing of ethylene glycol dimethacrylate (EGDMA) with 1-vinyl-1,2,4-triazole (VTAZ). The Cr(VI) adsorption was tested in a batch system. The influences of contact time, initial Cr(VI) concentration, pH, and temperature were reported as well. The adsorption of Cr(VI) from aqueous solutions on the beads under different kinetic and equilibrium conditions were described in detail.

MATERIALS AND METHODS

Materials

Ethylene glycol dimethacrylate (EGDMA) was obtained from Merck (Darmstadt, Germany), purified by passing through active alumina and stored at 4°C until use. 1-Vinyl-1,2,4-triazole (VTAZ, Aldrich, Steinheim, Germany) was distilled under vacuum (74–76°C, 10 mmHg). 2,2′-Azobisisobutyronitrile (AIBN) was obtained from Fluka A.G. (Buchs, Switzerland). Poly(vinyl alcohol) (PVAL; M_w: 100,000, 98% hydrolyzed) was supplied from Aldrich Chem. Co. (USA). All other reagents, unless specified, were of analytical grade and were used without further purification. Laboratory glassware was kept overnight in a 5% nitric acid solution. Before use, the glassware was rinsed with deionized water and dried in a dust-free environment. All water used in the chelation experiments was purified using a Barnstead (Dubuque, IA) 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.

Preparation of poly(EGDMA-VTAZ) beads

The poly(EGDMA-VTAZ) beads were selected for the synthesis of metal-chelate affinity adsorbent for chromium(VI) adsorption. The poly(EGDMA-VTAZ) beads were produced by suspension polymerization technique in an aqueous medium as described in our previous article.[12]

EGDMA and VTAZ were copolymerized in suspension by using AIBN and PVAL as the initiator and the stabilizer, respectively. Toluene was included in the polymerization recipe as the diluent (as a pore former). A typical preparation procedure was exemplified later. Continuous medium was prepared by dissolving PVAL (200 mg) in the purified water (50 mL). For the preparation of dispersion phase, EGDMA (6 mL; 32 mmol) and toluene (4 mL)

TABLE I
Recipe and Polymerization Conditions for Preparation of the Poly(EGDMA-VTAZ) Beads

Aqueous dispersion phase	Organic phase
Distilled water: 50 mL	EGDMA: 6.0 mL
PVAL: 200 mg	VTAZ: 3 mL
	Toluene: 12 mL
	AIBN: 100 mg
Polymerization conditions	
Reactor volume: 100 mL	
Stirring rate: 600 rpm	
Temperature and time: first at 70°C for 4 h and then at 80°C for 2 h	

were stirred for 15 min at room temperature. Then, VTAZ (3 mL; 35 mmol) and AIBN (100 mg) were dissolved in the homogeneous organic phase. The organic phase was dispersed in the aqueous medium by stirring the mixture magnetically (400 rpm), in a sealed-cylindrical pyrex polymerization reactor. The reactor content was heated to polymerization temperature (i.e., 70°C) within 4 h, and the polymerization was conducted for 2 h with a 600 rpm stirring rate at 80°C. Finally, beads were extensively washed with ethanol and water to remove any unreacted monomer or diluent and then stored in distilled water at 4°C. Table I shows recipe and polymerization conditions for preparation of the poly(EGDMA-VTAZ) beads.

Adsorption experiments

Batch adsorption experiments were performed using 0.50 mg of poly(EGDMA-VTAZ) with 50 mL of aqueous metal ion solutions in 100 cm³-erlenmeyer flasks, of which concentrations, pH, and temperature have already been known. The sample was shaken at 300 rpm in a shaking water bath (Clifton, England). After desired contact time, suspension was filtered. The filtrate was analyzed for metal ions by using an UV–vis spectrophotometer (Shimadzu-2100 UV-vis, Japan). The concentrations of Cr(VI) in the solution is measured by using 1.5-diphenylcarbazide in an acid medium at 540 nm.[13] Blank solutions containing no metal ions were used for each series of experiments. The amount of metal ions adsorbed onto the resin was calculated from difference between initial and the final concentration. For each adsorption process, the average of three replicates was reported.

RESULTS AND DISCUSSION

Properties of polymer beads

The suspension polymerization procedure provided crosslinked poly(EGDMA-VTAZ) beads in the spherical form in the size range of 150–200 μm. The
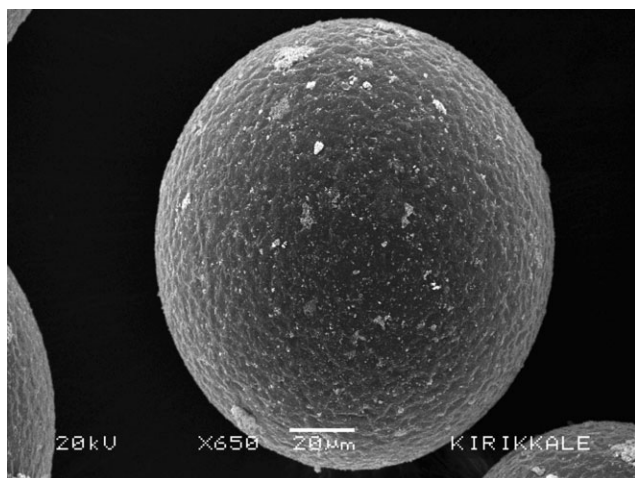
Figure 1 SEM photograph of poly(EGDMA-VTAZ) beads.

surface morphology and internal structure of polymer beads are investigated by the scanning electron micrographs that are given in Figure 1. As clearly seen here, the beads have a spherical form and very rough surface due to the pores that formed during the polymerization. The roughness of the surface should be considered as a factor providing an increase in the surface area. According to mercury porosimetry data, the average pore size of the poly (EGDMA-VTAZ) beads was 740 nm. This indicated that the beads contained mainly macropores. This macropore diameter range is possibly available for diffusion of Cr(VI). Specific surface area of the poly (EGDMA-VTAZ) beads was found to be 65.8 m^2/g. The equilibrium swelling ratio of the chelating beads used in this study is 84%. The water molecules penetrate into the entanglement polymer chains more easily, resulting in an increase of polymer water uptake in aqueous solutions.[14] It should be also noted that these beads are strong enough due to highly crosslinked structure; therefore, they are suitable for column applications.
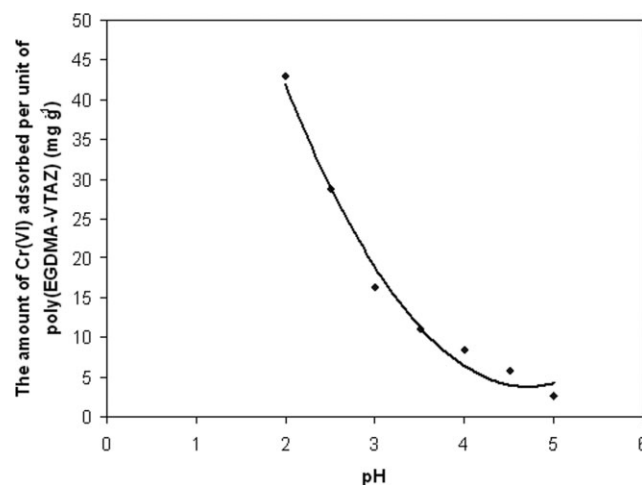
Effect of pH on adsorption

The adsorption of the metal ions onto an adsorbent varies generally with pH because pH changes the radius of hydrolyzed cation and the charge of the adsorbent surface. Therefore, in this study, the adsorption of Cr(VI) onto poly(EGDMA-VTAZ) is studied as a function of pH. The initial pH values of Cr(VI) solutions were kept between 2.0 and 5.0. The relationship between initial pH and the amounts of Cr(VI) adsorbed on poly(EGDMA-VTAZ) for initial solution concentrations of 400 mg dm^{-3} at 25°C and a contact time of 240 min is illustrated in Figure 2. When initial pH values of Cr (VI) solutions are increased from 2.0 to 5.0, the amounts of Cr(VI)

adsorbed per unit mass of adsorbent decreased. For example, the amounts of Cr(VI) adsorbed per unit adsorbent decrease from 42.95 to 2.55 mg g^{-1} for Cr(VI) when the pH value increase from 2.0 to 5.0. As seen in the Figure 2, pH 2 is a value for the maximum adsorption of Cr(VI). The metal adsorption depends on the protonation or unprotonation of functional groups on surface of the beads. Cr(VI) exists in anionic forms (i.e., $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2-}, and $HCr_2O_7^-$) in aqueous medium, and fraction of any particular species is depend on chromium concentration and pH.[15] At acidic pH, the triazole groups of poly(EGDMA-VTAZ) beads are positively charged, which leads to an electrostatic attraction for the negatively charged chromium species. The fact that a rise in the pH cause to the decrease of the adsorption of metal ions is attributed that protonation of triazole groups on the poly(EGDMA-VTAZ) has become more positive.

Effect of temperature on adsorption

The Cr(VI) uptake (mg g^{-1}) was decreased from 42.78 to 32.32 mg g^{-1} with the rise in temperature from 25 to 65°C (Fig. 3). Equilibrium time was found to be 240 min. indicating that the equilibrium time was independent of temperature. The earlier results also showed that the adsorption was exothermic in nature. The triazole groups of the poly(EGDMA-VTAZ) are partially protonated at all temperatures, but their deprotonation degree increases at higher temperatures resulting in a slight decrease in the metal capacities at high temperature. Where only metal adsorption is involved, the temperature effect on retention time is relatively small. Empirical studies show that temperature has a small effect on adsorption.[16–21]

Figure 2 Effect of pH on adsorption of poly(EGDMA-VTAZ) beads: 400 mg dm^{-3} Cr(VI); 25°C; 240 min.
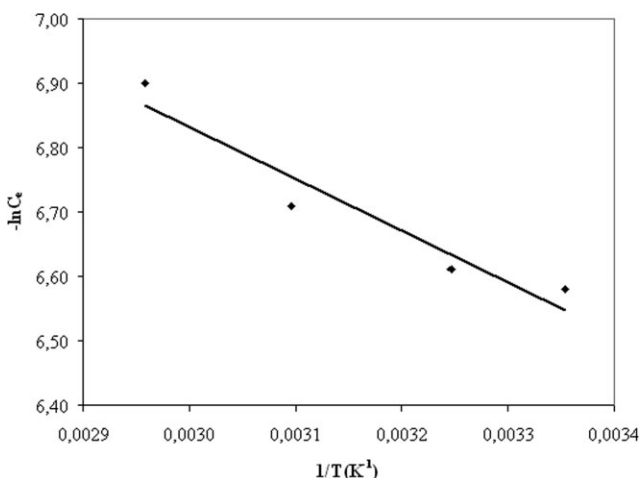
Figure 3 Plot of $-\ln C_e$ versus $1/T$ for Cr(VI) adsorption onto poly(EGDMA-VTAZ) beads.

It is noted that the isotherm data obtained at different temperatures are also well fitted by the Langmuir equation. Temperature dependence, K, can be used to determine the isosteric enthalpy of adsorption, ΔH^0. The enthalpy at a fixed surface coverage ($\theta = q_e/q_m$),

$$\left(\frac{\partial \ln K}{\partial T}\right)_\theta = -\left(\frac{\partial \ln C_e}{\partial T}\right)_\theta = \frac{\Delta H^0}{RT^2} \quad (1)$$

A plot of $-\ln C_e$ against $1/T$ should be a straight line. Figure 3 shows typical isotherms and reveals an approximately linear relationship. The value of ΔH^0 has been calculated to be -6.668 kJ mol^{-1} obviously; the negative value of ΔH^0 indicates that the Cr(VI)-poly(EGDMA-VTAZ) interaction is exothermic, and the product is energetically stable.[22]

The entropy change of adsorption process (ΔS^0) has been calculated from the intercept of the line in Figure 3. Gibbs free energy of adsorption (ΔG^0) can be found from

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (2)$$

The values of ΔG^0 and ΔS^0 were calculated as -29.57 kJ mol^{-1} and 9.238 J mol^{-1} K^{-1} at 25°C, respectively. A negative ΔG^0 value indicates the feasibility of the process and indicates the spontaneous nature of adsorption. Positive value of ΔS^0 suggests randomness at the solid-solution interface during adsorption.[23]
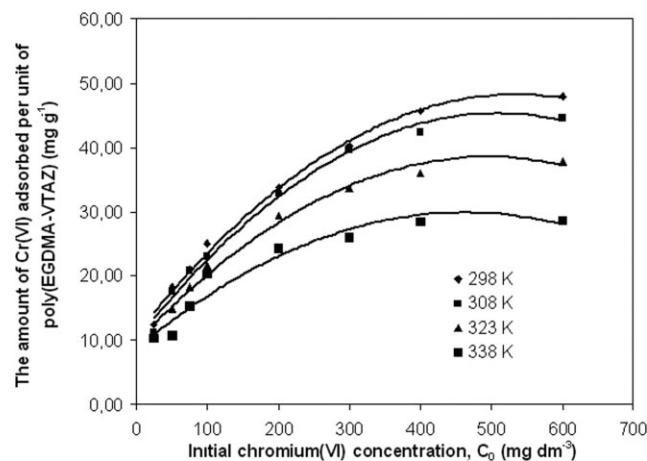
Effect of initial chromium(VI) concentration

Nine different concentrations for Cr(VI), i.e., concentrations of 25, 50, 75, 100, 200, 300, 400, 500, and 600 mg dm^{-3}, are selected to investigate the effect of initial chromium(VI) concentration onto poly(EGDMA-VTAZ) beads, and the amounts of Cr(VI) adsorbed

at equilibrium at 25, 35, 50, and 65°C, respectively and at pH 2 are graphed in Figure 4. As shown in Figure 4, with increasing initial Cr(VI) concentration from 25 to 600 mg dm^{-3}, the amount of Cr(VI) adsorbed by adsorbent increases from 12.45 to 47.93, from 11.23 to 44.62, from 11.12 to 37.77, from 10.28 to 25.56 mg g^{-1} of polymer at 25, 35, 50, and 65°C, respectively. The adsorption capacities of the poly (EGDMA-VTAZ) obtained with Cr(VI) are comparable with values reported in the previous studies. Panday et al.[24] used fly ash for removal of Cr(VI), and adsorption capacity of the adsorbent was 2.91 mg g^{-1}. Sağ and Kutsal[25] have used *Rhizopus arrhizus* microorganisms for Cr(VI) adsorption, and the adsorption capacity of Cr(VI) was obtained in the range of 21–90 mg g^{-1} dry weight of microorganisms. Say et al.[26] used the fungus *Penicillium purpurogenum* and the maximum adsorption capacity of the Cr(VI) was 36.5 mg g^{-1}. Aksu and Gönen[27] reported 18.5 mg g^{-1} adsorption for Cr(VI) by immobilized dried activated sludge. Aggrawal et al.[28] studied adsorption of chromium onto granulated active carbon and they obtained maximum adsorption capacity as 70 mg g^{-1}. The comparison of the adsorption capacities of poly(EGDMA-VTAZ) beads used in this work with those reported in the previous work shows that the adsorbent is suitable for this purpose.

Pore diffusion studies

According to previous studies, a plot of q_t versus $t^{0.5}$ may present multilinearity.[16] The first linear portion is the external surface adsorption stage. The second portion is the gradual adsorption stage, in which the intraparticle diffusion is rate controlled. The third portion is the final equilibrium stage.[29] When the adsorption of the exterior surface reached saturation,

Figure 4 Effect of initial Cr(VI) concentration onto poly (EGDMA-VTAZ) beads at various temperatures: pH: 2.0; 240 min.
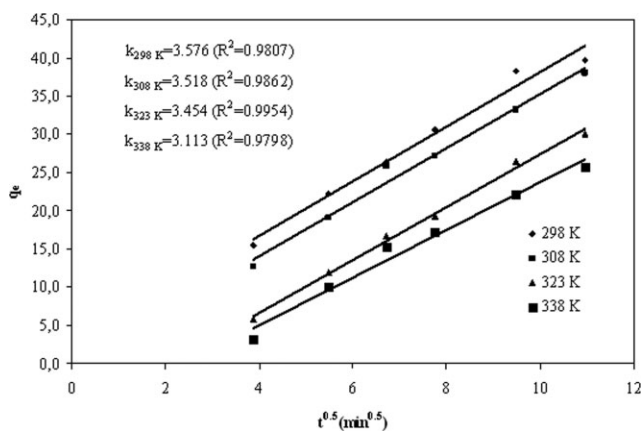
Figure 5 Effect of pore diffusion studies of Cr(VI) adsorption onto poly(EGDMA-VTAZ) beads at various temperatures: 400 mg dm^{-3} Cr(VI); pH: 2.0.

the Cr(VI) entered the poly(EGDMA-VTAZ) particles through the pores within the particle and were adsorbed by the interior surface of the particle. During the adsorption of Cr(VI) onto poly(EGDMA-VTAZ) beads, only one line for each temperature was obtained, and this indicates that both external surface and interior surface adsorption took place during the adsorption process. The intraparticle diffusion rate constants at various temperatures were calculated (from Fig. 5) as $k_{298K} = 3.576$ mg g^{-1} min$^{0.5}$, $k_{308K} = 3.518$ mg g^{-1} min$^{0.5}$, $k_{323K} = 3.454$ mg g^{-1} min$^{0.5}$, and $k_{338K} = 3.113$ mg g^{-1} min$^{0.5}$. When intraparticle diffusion rate constants were compared, inverse proportionality was observed. With increasing temperature, the kinetic energy of Cr(VI) in solution was enhanced, probably along with diffusion into pores, because Cr(VI) adsorption is exothermic with increasing temperature.
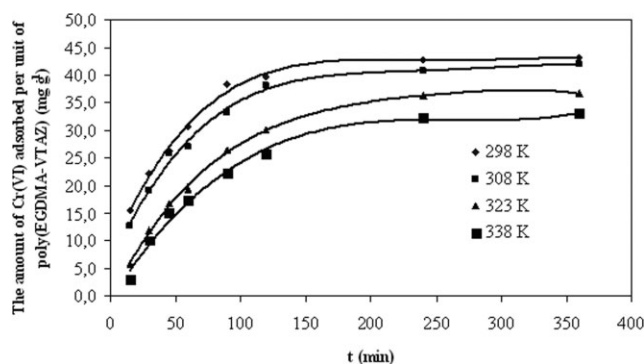
Analysis of adsorption kinetics

To investigate the mechanism of adsorption, the pseudofirst-order model, pseudosecond-order model, and intraparticle diffusion model were used for testing dynamic experimental data.[23,30–32] The pseudofirst-order model of Lagergren is given as follows:

$$\log q_e - q_t = \log q_e - K_1 t/2.303 \tag{3}$$

The intraparticle diffusion equation can be described as follows:

$$q_t = k_i t^{0.5} \tag{4}$$

where K_1 is the rate constant of pseudofirst-order adsorption (1/min), and k_i is the intraparticle diffusion rate constant (mg g^{-1} min$^{0.5}$). q_e and q_t are the amounts of metal adsorbed on the adsorbent (mg g^{-1}) at equilibrium and at time t, respectively. The change in the adsorption capacity with a rise in

temperature is examined (Fig. 6). As can be seen in Figure 6, the adsorption capacity and temperature were inversely proportional. At the end of 240 min, the amounts of Cr(VI) adsorbed onto poly(EGDMA-VTAZ) beads were 42.78, 40.81, 36.33, 32.32 mg g^{-1} of polymer at 25, 35, 50, and 65°C, respectively. Figure 7 shows the linear transforms of log $(q_e - q_t)$ versus time at various temperatures for the adsorption of Cr(VI). Linear transforms and regression coefficients were determined in Figure 7. Regression coefficients of points obtained from the pseudofirst-order relation were greater than 0.9710.

The adsorption kinetic constants as pseudofirst-order kinetic constants are given in Table II.

Analysis of adsorption isotherm

To determine the adsorption capacity, the experimental equilibrium data were fitted to Langmuir and Freundlich equations which are commonly

Figure 6 Adsorption Cr(VI) onto poly(EGDMA-VTAZ) beads at various temperatures: 400 mg dm^{-3} Cr(VI); pH: 2.0.
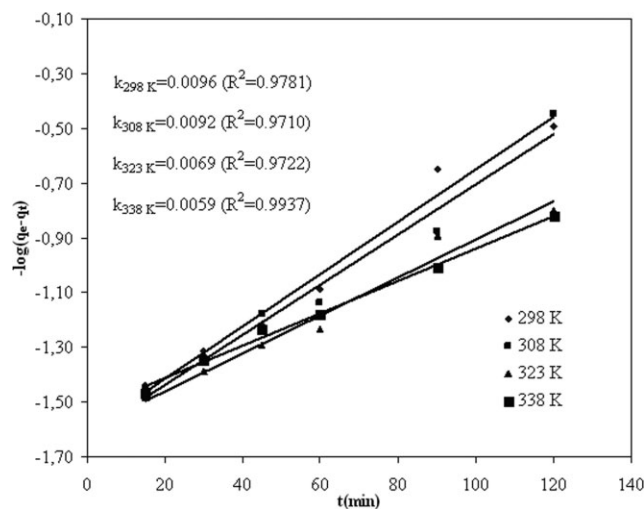
Figure 7 Linear transforms of log $(q_e - q_t)$ versus time at various temperatures for the adsorption of Cr(VI): 400 mg dm^{-3} Cr(VI); pH: 2.0.

TABLE II
Adsorption kinetic constants of Cr(VI)

	Pseudo-first-order kinetic constants	
T(K)	$K_1 \times 10^3$ (min^{-1})	R^2
298	22.11	0.9781
308	21.19	0.9710
323	15.89	0.9722
338	13.59	0.9937

used. The isotherm results indicate that the adsorption of Cr(VI) ions onto poly(EGDMA-VTAZ) is consistent with the Freundlich and Langmuir isotherms. Freundlich adsorption isotherm is given as[33]

$$q_e = K_f C_e^{1/n} \tag{5}$$

In logarithmic form,

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \text{(linear form)} \tag{6}$$

where q_e is the amount of metal ions adsorbed at equilibrium time (mg g^{-1}), C_e is the equilibrium concentration of the metal ions in solution (mg dm^{-3}). K_f and n are isotherm constants which indicate capacity and intensity of the adsorption, respectively. The correlation coefficients from the plots of $\ln q_e$ against $\ln C_e$ for Cr(VI) at 298, 308, 323, and 338 K are 0.9903, 0.9865, 0.9869, and 0.9796, respectively, (see Fig. 8), and the plots comply with Freundlich adsorption model. The values of K_f and n were calculated from the slope and intercept of the plot $\ln q_e$ versus $\ln C_e$. The value of K_f and n obtained is shown in Table III. As shown in Table II, the value of n range between 3.30 and 1.94. If the value of n is in the range $1 < n < 10$, the adsorption is favorable.[34]

The Langmuir isotherm is expressed as[33]

$$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{C_e}{q_m} \tag{7}$$

where q_m (mg g^{-1}) is the maximum amount of Cr(VI) per unit weight of poly(EGDMA-VTAZ) to form complete monolayer coverage on the surface bound at high equilibrium Cr(VI) concentration C_e, and K is Langmuir constant related to the affinity of
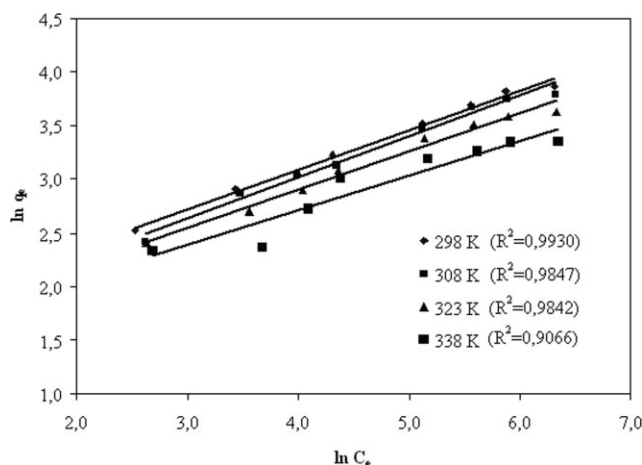
Figure 8 Freundlich plots of Cr(VI) at 298, 308, 323, and 338 K onto poly(EGDMA-VTAZ).

binding sites (L mg^{-1}). q_m represents a particle limiting adsorption capacity when the surface is fully covered with Cr(VI) and assists in the comparison of adsorption performance. q_m and K are calculated from the slopes and intercepts of the straight lines of plot of $\frac{C_e}{q_e}$ versus C_e (Fig. 9). Parameters of the Langmuir and Freundlich isotherms were computed in Table II, Langmuir isotherm fits quite with the experimental data correlation coefficient ($R^2 > 0.99$), whereas the low correlation coefficients correlation coefficient ($R^2 > 0.98$) show poor agreement of the Freundlich isotherm with the experimental data. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogenous distribution of active sites on the poly(EGDMA-VTAZ) surface, since the Langmuir equation assumes that the surface is homogeneous.[35]

Furthermore, the essential characteristic of the Langmuir isotherm can be expressed by a dimensionless separation factor called equilibrium parameter R_L.[36]

$$R_L = \frac{1}{1 + KC_e} \tag{8}$$

where, K is the Langmuir constant (dm^3 mg^{-1}), and C_e is the initial metal ion concentration (mg dm^{-3}).

TABLE III
Isotherm Constants for the Adsorption of Cr(VI) onto Poly(EGDMA-VTAZ)

Adsoption temperature (K)	Langmuir isotherm			Freundlich isotherm			Dimensionless Parameter R_L
	q_m (mg g^{-1})	K (dm^3 mg^{-1})	R^2	n	K_f	R^2	
298	53.48	0.0138	0.9907	2.71	5.005	0.9930	0.852-0.116
308	48.31	0.0155	0.9946	2.62	4.443	0.9847	0.824-0.104
323	41.84	0.0159	0.9965	2.83	4.444	0.9842	0.819-0.101
338	31.10	0.0191	0.9845	3.09	4.121	0.9066	0.781-0.084

Parameter R_L indicates the shape of isotherm as follows:

| Value of R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

R_L value between 0 and 1 indicates a favorable adsorption. Here in, the values of R_L between 0 and 1 indicate a favorable adsorption. Here, R_L obtained are listened in Table II. The fact that all the R_L values for the adsorption of Cr(VI) onto poly(EGDMA-VTAZ) are in the ranges 0.0075–0.838 shows that the adsorption process favorable.
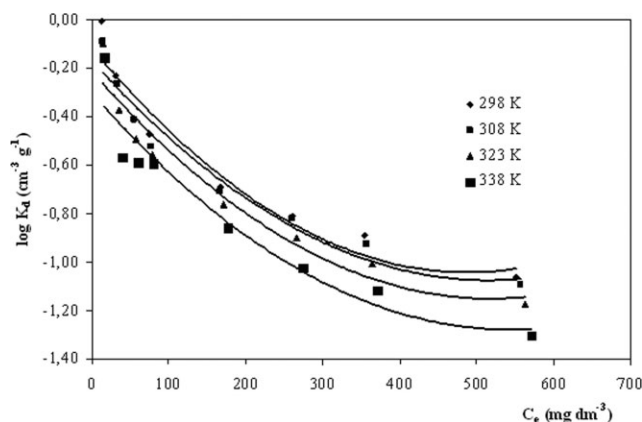
Study of distribution coefficient

The variation of distribution ratio for Cr(VI) is estimated from the following equation[37,38];

$$K_D = q_e / C_e \qquad (9)$$

where, K_D is the distribution coefficient of Cr(VI) (dm^3 g^{-1}). q_e and C_e are the amounts adsorbed on adsorbent and Cr(VI) remaining in solution (mg g^{-1}). The relationship between K_D and C_e is given in Figure 10. As illustrated in this figure, it is seen that K_D decreases with Cr(VI) concentration in the solution at equilibrium (C_e). This phenomenon indicates that the occupation of active surface sites of adsorbent increases with Cr(VI). The similar results have
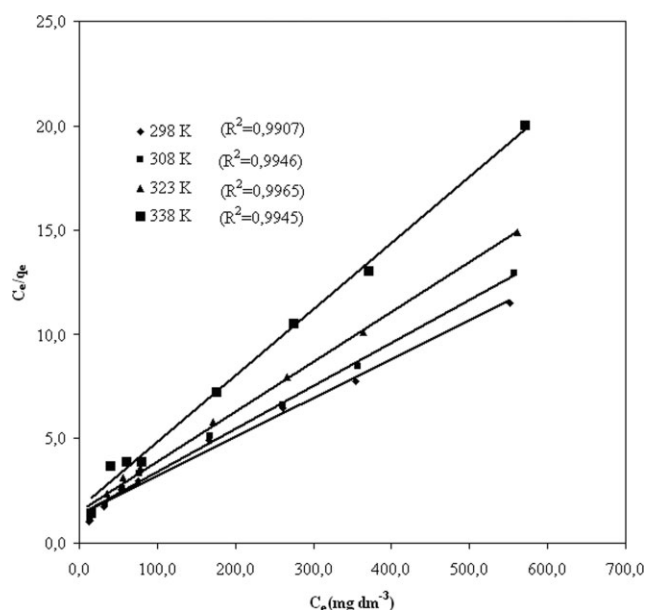
Figure 10 Distrubition coefficients of Cr(VI) as a function of equilibrium solution concentration at pH 2 and 298, 308, 323, 338 K.

been reported in another work equation.[37,38] The value of K_D for an effective adsorbent should be found between 10^{-2} and 10^{-1} (dm^3 g^{-1}). In this study, the values of K_D for Cr(VI) are between 10^{-2} and 10^{-1} (dm^3 g^{-1}).

CONCLUSIONS

In this study, it was determined that poly(EGDMA-VTAZ) beads could be utilized as an effective adsorbent for the removal of Cr(VI) from aqueous solution. The adsorption of Cr(VI) was found systematically at different contact times, initial Cr(VI) concentrations, pH, and temperatures. The amount of Cr(VI) adsorbed increased with increasing concentration and decreasing pH, temperature. The intraparticle diffusion rate constants at various temperatures were found. The Langmuir isotherm model appears to fit the isotherm data better than the Freundlich isotherm model. Adsorption equilibrium correlated reasonably well by Langmuir isotherm. The study of temperature was found by calculating various thermodynamic parameters such as Gibbs free energy, enthalpy, and entropy changes. The dimensionless separation factor (R_L) showed that the adsorption of Cr(VI) onto poly(EGDMA-VTAZ) at different temperatures was favorable. The values of distribution coefficient (K_D) for Cr(VI) at different temperatures were between 10^{-2} and 10^{-1} dm^3 g^{-1}, meaning an effective adsorbent.

NOMENCLATURE

C_e	concentration of Cr(VI) at equilibrium (mg dm^{-3})
C_0	initial Cr(VI) concentration in solution (mg dm^{-3})
ΔG^0	Gibbs free energy of adsorption (J mol^{-1})
ΔH^0	isosteric enthalpy of adsorption (J mol^{-1})

Figure 9 Establishment of the Langmuir monolayer adsorption constant for the adsorption of Cr(VI) at 298, 308, 323, and 338 K onto poly(EGDMA-VTAZ).

ΔS^0 entropy change of the adsorption process $(\text{J mol}^{-1} \text{ K}^{-1})$

q_e the amount of Cr(VI) adsorbed on the adsorbent at equilibrium (mg g^{-1})

q_t the amount of Cr(VI) adsorbed on the adsorbent at any time (mg g^{-1})

q_m the maximum amount of Cr(VI) adsorbed per unit mass adsorbent (mg g^{-1})

K the Langmuir constant related to the affinity of binding sites $(\text{dm}^3 \text{ mg}^{-1})$

n the Freundlich constant

K_f the Freundlich constant

K_1 the rate constant of pseudo first-order adsorption (min^{-1}).

K_i the intraparticle diffusion rate constant $(\text{mg/g min}^{0.5})$

R^2 linear regression coefficient

t time (min)

T temperature (K)

R_L dimensionless separation factor

K_D distribution coefficient $(\text{dm}^3 \text{ g}^{-1})$

References

1. Sitting, M. Hazardous and Toxic Effects of Industrial Chemicals; NDC Publication: USA, 1979; p 137.
2. Volkovic, V. Trace Element Analysis; Taylor and Francis: London, 1975.
3. Florence, T. M.; Bately, G. E. CRC Crit Rev Anal Chem 1980, 9, 219.
4. US EPA, Ambient Water Quality Criteria for Chromium, EPA-440/5-80-035 1980, PC31.
5. Patterson, J. W. Industrial Wastewater Treatment Technology; Butterworths: Stoneham, MA, 1985.
6. Tarasevich, Y. I.; Klimova, G. M. Appl Clay Sci 2001, 19, 95.
7. Saito, T. Sep Sci Technol 1991, 26, 1495.
8. Say, R.; Birlik, E.; Denizli, A., Ersöz, A. Appl Clay Sci 2006, 31, 298.
9. Gupta, R. K.; Singh, R. A.; Dubey, S. S. Sep Purif Technol 2004, 38, 225.
10. Sağlam, A.; Bektaş, S.; Patır, S.; Genç, Ö.; Denizli, A. React Funct Polym 2001, 47, 185.
11. Say, R.; Garipcan, B.; Emir, S.; Patır, S.; Denizli, A. Macromol Mater Eng 2002, 287, 539.
12. Uzun, L.; Kara, A.; Tüzmen, N.; Karabakan, A.; Beşirli, N.; Denizli, A. J Appl Polym Sci 2006, 102, 4276.
13. APHA. Standard methods for the examination of water and wastewater, 20th ed.; American Public Health Association: Washington, DC, 1998; p 3.
14. Denizli, A.; Pişkin, E. J Biochem Biophys Methods 2001, 49, 391.
15. Sağ, Y.; Kutsal, T. Process Biochem 2000, 35, 801.
16. Arslan, G.; Pehlivan, E. Bioresource Technol 2007, 98, 2836.
17. Donais, M. K.; Henry, R.; Rettberg, T. Talanta 1999, 49, 1045.
18. Biesuz, R.; Pesavento, M.; Gonzalo, A.; Valiente, M. Talanta 1998, 47, 127.
19. Jones, P.; Nesterenko, P. N. J Chromatogr A 1997, 789, 413.
20. Juang, R. S.; Shiau, L. D. Ind Eng Chem 1998, 37, 555.
21. Cooney, D. O. Adsorption Design for Wastewater Treatment; Lewis Publishers: London 1999; p 1.
22. Raji, C.; Anirudhan, T. S. Wat Res 1998, 32, 3772.
23. Lagergren, S. K. Svenska Vetenskapsakad Handl 1898, 24, 1.
24. Panday, K. K.; Priasad, G.; Singh, V. M. J Chem Technol Biotechnol 1984, 34, 367.
25. Sağ, Y.; Kutsal, T. Process Biochem 1996, 31, 573.
26. Say, R.; Yılmaz, N.; Denizli, A.; Eng Life Sci 2004, 4 176.
27. Aksu, Z.; Gönen, F. Sep Purif Technol 2006, 49, 205.
28. Aggrawal, D.; Goyal, M.; Banzal, R. C. Carbon 1989 1999, 37.
29. Allen, S. J; McKay, G.; Khader, K. Y. H. Environ Pollut 1989, 56, 39.
30. Öncel, Ş., Uzun, L., Garipcan, B., Denizli, A., Ind Eng Chem Res 2005, 44, 7049.
31. Hasan, S. H.; Singh, K. K.; Prakash, O.; Talat, M.; Ho, Y. S. J; Hazard Mater 2008, 152, 356.
32. Akgöl, S.; Kuşvuran, E.; Kara, A.; Şenel, S.; Denizli, A. J Appl Polym Sci 2006, 100, 5056.
33. Tekin, N.; Kadıncı, E.; Demirbaş, Ö.; Alkan, M; Kara, A. J Colloid Interface Sci 2006, 296, 472.
34. Kara, A.; Acemioğlu, B.; Alma, M. H.; Cebe, M. J. Appl Polym Sci 2006, 2838.
35. Doğan, M.; Alkan, M.; Onganer, Y. Water Air Soil Pollut 2000, 120, 229.
36. Namasivayam, C.; Kavita, D. Dyes Pigment 2002, 54, 47.
37. Apak, R.; Tutem, E.; Hugul, M.; Hizal, J. Wat Res 1998, 32, 430.
38. Wang, X.; Dong, W.; Tao, Z. Colloid Surf A: Physicochem Eng Aspects 2003, 223, 135.