A. Kara, S. Aksoy, N. Beşirli / Hacettepe J. Biol. & Chem., 2012, 40 (1), 37-44

Adsorption Properties of Cr(VI) onto Microspheres Carrying Imidazole Functional Groups: Kinetic and Isotherm Studies

İmidazol Fonksiyonel Grupları Taşıyan Mikrokürelerin Cr(VI) Adsorpsiyonunun Özellikleri: Kinetik ve İzoterm Çalışmaları

Research Article

Ali Kara, Suat Aksoy, Necati Beşirli
Uludağ University,Faculty of Science, Department of Chemistry, Bursa, Turkey

ABSTRACT

Poly(ethylene glycol dimethacrylate-n-vinyl imidazole) [poly(EGDMA-VIM)] microspheres (average diameter=150-200 μm) were prepared by copolymerizing of ethylene glycol dimethacrylate (EGDMA) with n-vinyl imidazole (VIM). Poly(EGDMA-VIM) microspheres were characterized by swelling studies and scanning electron microscope (SEM). The adsorption of Cr(VI) onto the poly(EGDMA-VIM) microspheres was examined in aqueous solutions. The adsorption of Cr(VI) from aqueous solutions was carried at different contact times, Cr(VI) concentrations, and pH. The amount of Cr(VI) adsorbed increased with increasing concentration and decreasing pH. The intraparticle diffusion rate constant was calculated. Adsorption isotherms poly(EGDMA-VIM) have been determined with common isotherm equations such as Langmuir and Freundlich isotherm models. The pseudo first-order kinetic model was used to describe the kinetic data. The Langmuir isotherm model appeared to fit the isotherm data better than the Freundlich isotherm model. Values of the dimensionless separation factor (RL) and the distrubition coefficient (KD) were evaluated.

Key Words
Adsorption kinetic, Adsorption isotherm, Adsorption thermodynamic, Cr(VI).

ÖZET

Poli(etilen glikol dimetakrilat-n-vinil imidazol) [poli(EGDMA-VIM)] mikroküreleri (ortalama çap=150-200 μm) etilen glikol dimetakrilat (EGDMA) ile n-vinil imidazol (VIM)ün kopolimerizasyonu ile elde edildiler. Poli(EGDMA-VIM) mikroküreleri, şişme çalışmaları ve taramalı elektron mikroskobu (SEM) ile karakterize edildiler. Poli(EGDMA-VIM) mikrokürelerinin Cr(VI) adsorpsiyonu sulu çözeltilerde çalışıldı. Sulu çözeltilerden Cr(VI) adsorpsiyonu farklı kontakt zamanlarında, Cr(VI) konsantrasyonlarında ve pH yapıldı. Adsorbe olan Cr(VI) iyonu miktarı başlangıç konsantrasyonunun artması ve pH azalmasıyla arttı. Partikül içi hız sabiti hesaplandı. Adsorpsiyon izotermleri Langmuir ve Freundlich gibi yaygın izoterm eşitlikleriyle belirlendi. Langmuir adsorpsiyon izoterminin Freundlich adsorpsiyon izoterminden daha uygun olduğu görüldü. Yalancı-birinci derece kinetik model kinetik verileri açıklamak için kullanıldı. Boyutsuz ayırma faktörü ve dağılım katsayısı değerleri incelendi.

Anahtar Kalimeler
Adsorpsiyon kinetik, Adsorpsiyon izoterm, Adsorpsiyon termodinamik, Cr(VI)

Article History: Received December 28, 2010; Revised July 23, 2011; Accepted September 12, 2011; Avaliable Online: March 5, 2012.

Correspondence to: Ali Kara, Uludağ University, Faculty of Science, Department of Chemistry, Bursa, Turkey
Tel: +90 224 294 17 33 Fax: +90 224 294 18 99 E-Mail: akara@uludag.edu.tr

Notation

C_e :Concentration of Cr(VI) at equilibrium ($mg.dm^{-3}$)

C_0 :Initial Cr(VI) concentration in solution ($mg.dm^{-3}$)

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_L :The Langmuir constant related to the affinity of binding sites ($dm^3.mg^{-1}$)

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 (mg/g $min^{0.5}$)

R^2: Linear regression coefficient

t:Time (min)

R_L :Dimensionless separation factor

K_D:Distribution coefficient ($dm^3.g^{-1}$)

INTRODUCTION

Chromium, detected in surface water and groundwater at sites associated with chemical manufacturing leather tanning, electroplating, painting and other industries, exists in both Cr(VI) and Cr(III) valance states. Cr(VI) anions are highly soluble in aquatic systems are severe contaminants to environment due to their carcinogenic and mutagenic features in biological systems. [1,2] The Agency for Toxic Substances and Disease Registry (ATSDR) classifies Cr(VI) as the top 16th hazardous substance. Due to its mutagenic and carcinogenic properties, the US EPA has set the maximum acceptable amount in contaminated water supply as 0.05 $\mu g/L$ [3].

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. In the past few decades, adsorption is considered a powerful technique that was extensively used for removal of heavy metal ions from domestic and industrial effluents. 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. 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, dithiocarbomate, polyaniline, thiazolidine, triazole and reactive amino acids have been used for the removal of heavy metal ions [4].

The aim of this work was to prepare a chelating adsorbent from imidazole monomer in the bead form. For this propose, poly(ethylene glycol dimethacrylate-n-vinylimidazole) [poly(EGDMA-VIM)] beads were prepared by copolymerizing of ethylene glycol dimethacrylate (EGDMA) with n-vinylimidazole (VIM). The Cr(VI) adsorption was tested in a batch system. The influences of contact time, initial Cr(VI) concentration and pH 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. N-Vinylimidazole (VIM, 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; Mw: 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 deionised water and dried in a dust-free environment. All water used in the chelation experiments 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.

Preparation of poly(EGDMA-VIM) beads

The poly(EGDMA–VIM) beads were selected for the synthesis of metal–chelate affinity adsorbent for chromium(VI) adsorption. The poly(EGDMA–VIM) beads were produced by suspension polymerization technique in an aqueous medium as described in our previous article [5].

EGDMA and VIM 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 examplified below. Continuous medium was prepared by dissolving PVAL (200 mg) in the purified water (50 mL). For the preparation of dispersion phase, EGDMA (6 mL; 30 mmol) and toluene (4 mL) were stirred for 15 minutes at room temperature. Then, VTAZ (3 mL; 30 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 90°C Final beads were extensively washed with ethanol and water to remove any unreacted monomer or diluent and then stored in distilled water at 4°C.

Adsorption experiments

Batch adsorption experiments were performed using 0.50 mg of poly(EGDMA-VIM) with 50 mL of aqueous metal ion solutions in 100 cm^3-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 cross-linked poly(EGDMA-VIM) beads in the spherical form in the size range of 150–200 μm. The surface morphology and internal structure of polymer beads are investigated by the scanning electron micrographs which were given in Figure 1. As clearly seen here, the beads have a spherical form and very rough surface due to the pores which formed during the polymerization. The

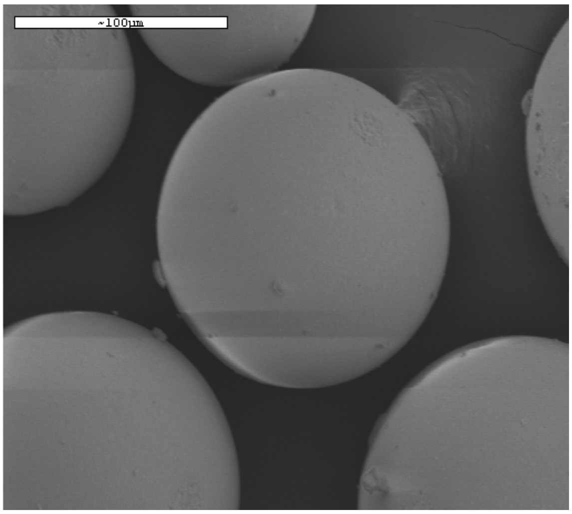

Figure 1. SEM photograph of poly(EGDMA-VIM) beads.

roughness of the surface should be considered as a factor providing an increase in the surface area. Specific surface area of the poly(EGDMA-VIM) beads was found to be 59.8 m^2/g. The equilibrium swelling ratio of the chelating beads used in this study is 78%. The water molecules penetrate into the entanglement polymer chains more easily, resulting in an increase of polymer water uptake in aqueous solutions [6]. It should be also noted that these beads are strong enough due to highly cross-linked structure therefore they are suitable for column applications.

Effect of pH on adsorption

The adsorption of the metal ions onto an adsorbent is varies generally with pH because pH causes to change the radius of hydrolyzed cation and the charge of the adsorbent surface. Therefore, in this study, the adsorption of Cr(VI) onto poly(EGDMA-VIM) 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-VIM) for initial solution concentrations of 600 mg.dm^{-3} for at 25°C and a contact time of 180 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 are decrease. 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 [7]. At acidic pH, the imidazole groups of poly(EGDMA-VIM) 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 imidazole groups on the poly(EGDMA-VIM) has become more positive.

Effect of Initial Chromium(VI) Concentration

Nine different concentrations for Cr(VI), i.e., concentrations of 25, 50, 75, 100, 200, 300, 400, 500, 600, 800 and 1000 mg.dm^{-3} are selected to investigate the effect of initial chromium(VI) concentration onto poly(EGDMA-VIM) beads, and the amounts of Cr(VI) adsorbed at equilibrium at 25°C and pH 2 are graphed in Figure 3. As shown in Figure 3, with increasing initial Cr(VI) concentration from 25 to 1000 mg dm^{-3}, the amount of Cr(VI) adsorbed by adsorbent increases from 18.31 to 122.34 of polymer at 25 °C. The adsorption capacities of the poly(EGDMA-VIM) obtained with Cr(VI) are comparable with values reported in the previous studies. Kara has used poly(EGDMA-VIM) for removal of Cr(VI) and adsorption capacity of the Cr(VI) obtained in the range of 12-48 mg.g^{-1}.[4] Panday et al. used fly ash for removal of Cr(VI) and adsorption capacity of the adsorbent was 2.91 mg.g^{-1} [8]. Sağ and Kutsal 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 [9]. Say et

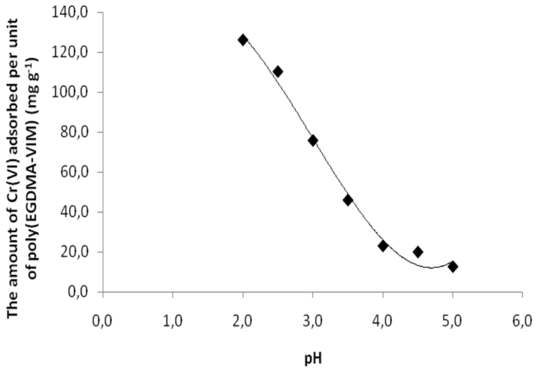

Figure 2. Effect of pH on adsorption of poly(EGDMA-VIM) beads: 600 mg dm^{-3} Cr(VI); 25 °C; 180 min.

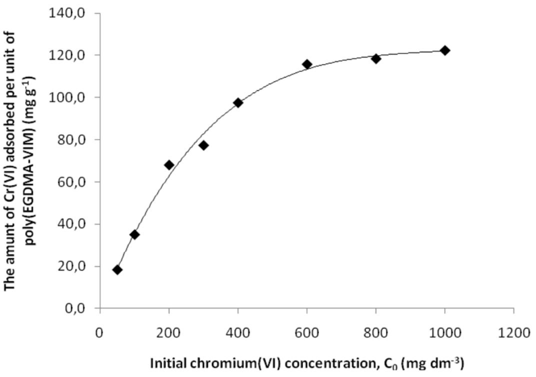

Figure 3. Effect of initial Cr(VI) concentration onto poly(EGDMA-VIM) beads: 25°C; pH:2.0; 180 min.

Table 1. Isotherm constants for the adsorption of Cr(VI) onto poly(EGDMA-VIM).

Adsorption Temperature	Langmuir isotherm			Freundlich isotherm			Dimensionless Parameter RL
(^{0}C)	q_m	K	R^2	n	K_f	R^2	
25	153,8	0,7662	0,9905	1,530	1,803	0,9333	0,0254- 0,0022

al. used the fungus *Penicillium purpurogenum* and the maximum adsorption capacity of the Cr(VI) was 36.5 mg.g^{-1}[10]. Aksu and Gönen reported 18.5 mg.g^{-1} adsorption for Cr(VI) by immobilized dried activated sludge [11]. Aggrawal et al. studied adsorption of chromium onto granulated active carbon and they obtained maximum adsorption capacity as 70 mg.g^{-1} [12]. The comparison of the adsorption capacities of poly(EGDMA-VIM) beads used in this work with those reported in the previous work shows that the adsorbent is suitable for this purpose.

Pore diffusion studies

The intraparticle diffusion equation can be described as follows:

$$q_t=k_i t^{0.5} \qquad (1)$$

Where k_i is the intraparticle diffusion rate constant (mg.g^{-1} min$^{0.5}$). q_t is the amounts of metal adsorbed on the adsorbent (mg g^{-1}) at time t. A plot of q_t versus $t^{0.5}$ may present multilinearity [13]. 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 [14]. When the adsorption of the exterior surface reached saturation, the Cr(VI) entered the poly(EGDMA-VIM) 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-VIM) beads, only one line for 25°C was obtained, and this indicates that both external surface and interior surface adsorption took place during the adsorption process. The intraparticle diffusion rate constant at 25°C was calculated (from Figure 4) as k_{298K} =10.23 mg.g^{-1}.min$^{0.5}$.

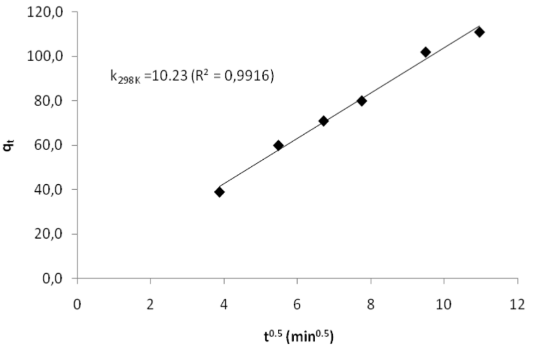

Figure 4. Effect of pore diffusion studies of Cr(VI) adsorption onto poly(EGDMA-VIM) beads: 25°C; pH:2.0; 600 mg.dm^{-3} Cr(VI).

Analysis of adsorption kinetics

To investigate the mechanism of adsorption, the pseudo-first-order model was used for testing dynamic experimental data [15,16]. The pseudo-first-order model of Lagergren is given as follows:

$$\log(q_e - q_t) = \log q_e - K_1 t / 2.303 \qquad (2)$$

where K_1 is the rate constant of pseudo-first-order adsorption (1/min). q_e and q_t are the amounts of metal adsorbed on the adsorbent (mg g^{-1}) at equilibrium and at time t, respectively. Figure 5 shows the linear transform of $\log(q_e- q_t)$ versus time at 25°C for the adsorption of Cr(VI). Linear

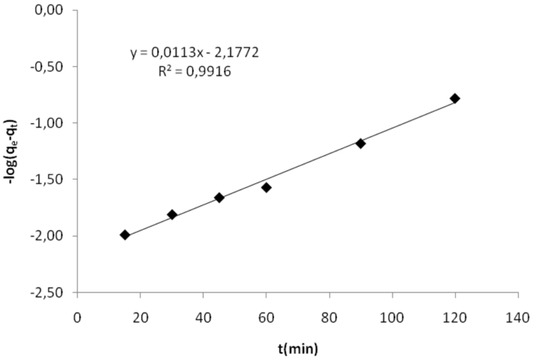

Figure 5. Linear transforms of $\log(q_e-q_t)$ versus time at various temperatures for the adsorption of Cr(VI): 600 mg.dm^{-3} Cr(VI); pH:2.0.

transform and regression coefficients were determined in Figure 5. Regression coefficients of points obtained from the pseudo-first-order relation were greater than 0.9916. The pseudo-first-order kinetic constant at 25°C was calculated (from Figure 5) as K_{298K}=26,52x10^{-3} (min^{-1}).

Analysis of adsorption isotherm

To determine the adsorption capacity, the experimental equilibrium data were fitted to Langmuir and Freundlich equations which are commonly used. The isotherm results indicate that the adsorption of Cr(VI) ions onto poly(EGDMA-VIM) is consistent with the Freundlich and Langmuir isotherms. Freundlich adsorption isotherm is given as [17]

$$q_e = K_f \, C_e^{1/n} \qquad (3)$$

In logarithmic form,

$$\ln q_e = \ln K_f + 1 / n \ln C_e \text{ (linear form)} \qquad (4)$$

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 coefficient from the plots of $\ln q_e$ against $\ln C_e$ for Cr(VI) at 298 K is 0.9333. (see Figure 6), 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 1. As shown in Table 1, the value of n 1.530. If the value of n is in the range 1<n<10, the adsorption is favorable [18]. The Langmuir isotherm is expressed as [17]

$$C_e / q_e = 1 / q_m K + C_e / q_m \qquad (5)$$

where q_m ($mg.g^{-1}$) is the maximum amount of Cr(VI) per unit weight of poly(EGDMA-VIM) 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 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 C_e / q_m versus C_e (Figure 7). Parameters of the Langmuir and Freundlich isotherms were computed in Table 2, Langmuir isotherm fits quite with the experimental data correlation coefficient ($R^2 > 0.99$), whereas the low correlation coefficients correlation coefficient ($R^2 > 0.93$) 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-VIM) surface, since the Langmuir equation assumes that the surface is homogeneous [19].

Furthermore, the essential characteristic of the Langmuir isotherm can be expressed by a dimensionless separation factor called equilibrium parameterR_L [20].

$$R_L = 1 / 1 + KC_e \qquad (6)$$

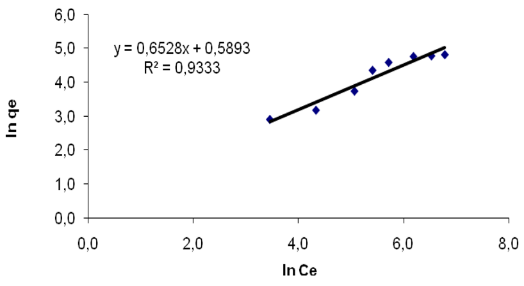

Figure 6. Freundlich plots of Cr(VI) at 298 K onto poly(EGDMA-VIM).

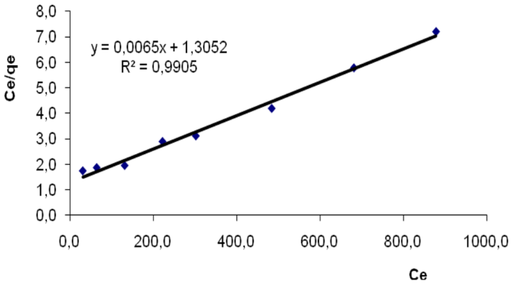

Figure 7. Establishment of the Langmuir monolayer adsorption constant for the adsorption of Cr(VI) at 298 K onto poly(EGDMA-VIM).

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

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

Parameter R_L indicates the shape of isotherm as follows:

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 1. The fact that all the R_L values for the adsorption of Cr(VI) onto poly(EGDMA-VIM) are in the ranges 0.0254-0.0022 shows that the adsorption process favorable.

Study of distribution coefficient

The variation of distribution ratio for Cr(VI) is estimated from the following equation [21, 22];

$$K_D = Q_e / C_e \qquad (8)$$

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 (in $mg\ g^{-1}$). The relationship between K_D and C_e is given in Figure 8. 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 been reported in another work equation [21,22]. 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} ($dm^3\ g^{-1}$).

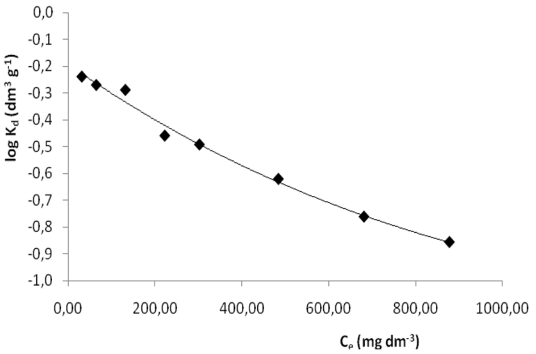

Figure 8. Distrubition coefficients of Cr(VI) as a function of equilibrium solution concentration at pH 2 and 298 K.

CONCLUSIONS

In this study, it was determined that poly(EGDMA-VIM) 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, and pH. The amount of Cr(VI) adsorbed increased with increasing concentration and decreasing pH. 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 dimensionless separation factor (R_L) showed that the adsorption of Cr(VI) onto poly(EGDMA-VIM) at 298 K was favorable. The values of distribution coefficient (K_D) for Cr(VI) at 298 K were between 10^{-2} and 10^{-1} $dm^3.g^{-1}$, meaning an effective adsorbent.

REFERENCES

1. B. Geng, Z. Jin, T. Li, X. Qi, Kinetics of hexavalent chromium removal from water by chitosan–Fe–0 nanoparticles, Chemosphere, 75 (2009) 825.
2. C. Quintelas, Z. Rocha, B. Silva, B. Fonseca, H. Figueiredo, T. Tavares, Removal of Cd(II), Cr(VI), Fe(III) and Ni(II) from aqueous solutions by an E.coli biofilm supported on kaolin, Chem. Eng. J., 149 (2009) 319.
3. US EPA, Ambient Water Quality Criteria for Chromium, EPA–440/5–80–035, PC31, 1980.
4. A. Kara, Adsorption of Cr(VI) ions onto Poly(ethylene glycol dimethacrylate–1–vinyl–1,2,4–triazole), J. App. Polym. Sci., 114 (2009) 948.
5. A. Kara, L. Uzun, N. Beşirli, A. Denizli, Poly(ethylene glycol dimethacrylate–n–vinyl imidazole beads for heavy metal removal, J. Hazard. Mat. 106B (2004) 93.
6. A. Denizli, E. Pişkin, Dye–ligand affinity systems, J. Biochem. Biophys. Methods, 49 (2001) 391.

7. Y. Sağ, T. Kutsal, Mass transfer and equilibrium studies for the sorption of chromium ions onto chitin, Process Biochem., 36 (2000) 157.
8. KK. Panday, G. Priasad, VM. Singh, Removal of Cr(VI) from aqueous solutions by adsorption on fly ash–wollastonite, J. Chem. Technol. Biotechnol., 34 (1984) 367.
9. Y. Sağ, T. Kutsal, Fully competitive biosorption of chromium(VI) and iron(III) ions from binary metal mixtures by R–arrhizus: Use of the competitive Langmuir model, Process Biochem., 31 (1996) 573.
10. R. Say, N. Yılmaz, A. Denizli, Removal of chromium(VI) ions from synthetic solutions by the fungus Penicillium purpurogenum, Eng. Life Sci., 4 (2004) 276.
11. Z. Aksu, F. Gönen, Binary biorsorption of phenol and chromium(VI) onto immobilized activated sludge in a packed bed: Prediction of kinetic paramters and breakthrough curves, Sep. Purif. Technol., 49 (2006) 205.
12. D. Aggrawal, M. Goyal, RC. Banzal, Adsorption of chromium by activated carbon from aqueous solution, Carbon, 37 (1999) 1989.
13. G. Arslan, E. Pehlivan, Batch removal of chromium (VI) from aqueous solution by Turkish brown coals, Bioresource Technol., 98 (2007) 2836.
14. SJ. Allen, G. McKay, KYH. Khader, Intraparticle diffusion of a basic dye during adsorption onto sphagnum peat, Environ. Pollut., 56 (1989) 39.
15. S. Lagergren, Zur theorie der sogenannten adsorption geloester stoffe, Kungliga Svenska, Vetenskapsakad. Handl. 24 (1898) 1.
16. MK. Donais, R. Henry, T. Rettberg, Chromium speciation using an automated liquid handling system with inductively coupled plasma–mass spectrometric detection, Talanta, 49 (1999) 1045.
17. N. Tekin, E. Kadıncı, Ö. Demirbaş, M. Alkan, A. Kara, Adsorption of polyvinylimidazole onto kaolinite, J. Col. Int. Sci., 296 (2006) 472.
18. A. Kara, B. Acemioğlu, MH. Alma, M. Cebe, Adsorbtion of Cr(III), Ni(II), Zn(II), Co(II) Ions on to Phenolated Wood Resin., J. Appl. Polym. Sci. 101 (2006) 2838.
19. M. Doğan, M. Alkan, Y. Onganer, Adsorption of methylene blue from aqueous solution onto perlite, Water Air Soil Pollut., 120 (2000) 229.
20. C. Namasivayam, D. Kavita, Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste, Dyes Pigment, 54 (2002) 47.
21. R. Apak, E. Tutem, M. Hugul, J. Hizal, Heavy metal cation retention by unconventional sorbents (red muds and fly ashes), Wat. Res., 32 (1998) 430.
22. X. Wang, W. Dong, Z. Tao, A multitracer study on the adsorption of 32 elements on a natural hematite (α–Fe_2O_3): effects of pH and fulvic acid, Colloid Surf. A: Physicochem. Eng. Aspects, 223 (2003) 135.