Kinetics, Isotherms and Thermodynamics of the Adsorption of Lead(II) Ions onto Porous Mono-sized Microspheres Possessing Imidazole Functional Groups

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ABSTRACT: A modified two-step seeded polymerization was used for the preparation of porous mono-sized microspheres of poly(ethylene glycol dimethacrylate-*co*-1-vinylimidazole) [poly(EGDMA-*co*-VIM)] of 7 μm in size. The specific surface area and the EGDMA/VIM molar ratio of the microspheres were determined as 64.5 m^2/g and 1.5:1.0 mol/mol, respectively. The adsorption of Pb(II) ions from aqueous solution onto the porous mono-sized poly(EGDMA-*co*-VIM) microspheres was examined. The maximum adsorption capacities of the microspheres towards Pb(II) ions were determined as 21.74, 30.52, 49.23 and 56.48 mg/g at 293 K, 303 K, 318 K and 338 K, respectively. The dynamic and equilibrium adsorption behaviours of the system were adequately described by the pseudo-second-order kinetic model and the Langmuir isotherm, respectively. The apparent activation energy was determined as 6.212 kJ/mol, which is characteristic of a chemically controlled reaction. The values of E_{fe} obtained from the Dubinin–Radushkevich equation in the non-linear form were 9.153 kJ/mol at 293 K, 10.34 kJ/mol at 303 K, 10.18 kJ/mol at 318 K and 10.91 kJ/mol at 333 K, thereby indicating that the adsorption of Pb(II) ions onto the porous mono-sized poly(EGDMA-*co*-VIM) microspheres occurred via a chemical process at all the temperatures studied. Various thermodynamic parameters, such as the Gibbs' free energy change (ΔG^0), the standard enthalpy change (ΔH^0) and the standard entropy change (ΔS^0) were also determined. The thermodynamic parameters obtained indicated that the adsorption process was endothermic in nature. These results demonstrate that the material studied could be used as a purifier for the removal of Pb(II) ions from water and wastewater.

1. INTRODUCTION

The presence of lead in the environment from industries such as mining, chemical, electroplating, petroleum refining, paper and pulp is a serious health hazard to living organisms at even relatively low concentrations (Stokinger 1981; Ma *et al*. 1995; Liu *et al*. 2008). Various methods have been applied for the removal of heavy metal ions from aqueous solutions. These include a number of traditional treatment techniques such as precipitation/neutralization, ultrafiltration, reverse osmosis, electrodeposition, solvent extraction, foam-flotation, cementation, complexation, filtration and evaporation. Adsorption is one of the most versatile methods for the removal of heavy metal ion

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contamination from aqueous systems. In recent years, the removal of toxic heavy metal ions such as lead, mercury, cadmium, nickel, etc. by polymeric resins has attracted significant attention (Peters and Ku 1985; Kara *et al*. 2004; Akgöl *et al*. 2006; Gurgel and Gil 2009; Yang *et al*. 2009).

Polymeric microspheres with different properties can easily be produced and converted into specific adsorbents of heavy metal ions by introducing different metal-complexing ligands. Thus, metal-complexing ligands such as triazole (Uzun *et al*. 2006; Kara *et al*. 2006), imidazole (Kara *et al*. 2004; Uğuzdoğan *et al*. 2009), acrylamide (Kesenci *et al*. 2002), thiazolidine (Sağlam *et al*. 2001) and ethylenediamine (Denizli *et al*. 1997) in polymeric microspheres can selectively interact with specific metal ions in aqueous media.

The aim of the present work was to prepare a cross-linked chelating adsorbent from ethylene glycol dimethacrylate and imidazole monomer in the form of porous mono-sized microspheres. For this propose, a modified two-step seeded polymerization was used for the preparation of the imidazole-carrying porous mono-sized micropheres [poly(ethylene glycol dimethacrylate-1-vinyl-imidazole)] [poly(EGDMA-*co*-VIM). The adsorption of Pb(II) ions from aqueous solution onto the porous mono-sized poly(EGDMA-*co*-VIM) microspheres was examined with respect to pH, initial Pb(II) ion concentration, contact time and temperature. The experimental data were analyzed in terms of the corresponding adsorption kinetic, equilibrium adsorption isotherm and thermodynamic parameters.

2. MATERIALS AND METHODS

2.1. Materials

Styrene (Yarpet As, Turkey) was distilled under vacuum before polymerization and stored in a refrigerator. Ethanol (Birpa As, Turkey) and 2-methoxyethanol (Aldrich Chemical Co., Milwaukee, WI, U.S.A., HPLC grade) were used as received. 2,2′-Azobisisobutyronitrile (AIBN, BDH Chemicals Ltd., Poole, U.K.) was recrystallized from methanol. Ethylene glycol dimethacrylate (EGDMA, Aldrich Chemical Co., Milwaukee, WI, U.S.A.) and vinylimidazole (VIM, Fluka Chemie AG, Germany) were used without further purification. Benzoyl peroxide, toluene and polyvinyl alcohol (87–89% hydrolyzed, M.W. 87 000–146 000) were supplied by the Aldrich Chemical Co., Milwaukee, WI, U.S.A. Polyvinylpyrolidone (PVP K-40) and sodium lauryl sulphate were obtained from the Sigma Chemical Co., St. Louis, MO, U.S.A.

2.2. Preparation of uniform polystyrene seed micropheres

Uniform polystyrene seed latex particles were synthesized by dispersion polymerization. Typically, 5 mℓ styrene was dissolved in a homogeneous mixture of 18 mℓ ethanol and 12 mℓ 2-methoxyethanol including 0.525 g PVP K-30. The initiator, 0.11 g of AIBN, was dissolved in the mixture of alcohols, monomer and steric stabilizer. The resulting mixture was poured into a polymerization reactor which was sealed and placed in a shaking water bath containing a heater and a temperature controller. Polymerization was conducted at 343 K for 24 h at a shaking rate of 150 rpm.

2.3. Preparation of porous mono-sized microspheres carrying imidazole functional groups

A modified two-step seeded polymerization procedure was used for the preparation of imidazole-carrying porous mono-sized micropheres (Tuncel *et al*. 2001). Typically, toluene (2 mℓ) was emulsified in an aqueous solution of sodium lauryl sulphate (30 mℓ, 0.25 w/w) using an ultrasonic

water bath (Bransonic 200, Krackeler Scientific, Albany, NY, U.S.A.). An aqueous dispersion of polystyrene particles (0.2 g) was then added to this emulsion. The dispersion thus obtained was stirred magnetically for 24 h at 400 rev/min. In the next stage, an aqueous emulsion of the monomer phase including EGDMA (2.0 mℓ), VIM (0.65 mℓ) and benzoyl peroxide (0.12 g) in 10 mℓ distilled water was prepared. The monomer emulsion was added to the toluene-swollen seed particles and the resulting mixture stirred at 300 rev/min for 24 h. An aqueous solution of polyvinyl alcohol (3 mℓ, 10% w/w) was then added to the emulsion and the mixture purged with nitrogen. Polymerization of the monomer phase to swollen seed particles was carried out at 343 K for 24 h at a shaking rate of 120 rev/min. The resulting large monodisperse particles were washed extensively with water, ethanol and tetrahydrofuran to remove the organic diluent and linear polystyrene. The resulting particles were re-dispersed in water.

2.4. Characterization of porous mono-sized microspheres carrying imidazole functional groups

The particles were mixed and dispersed with dry KBr and pressed into discs. FT-IR spectra were recorded on a Shimadzu 8000 series FT-IR spectrophotometer over the wavenumber range 4000–400 cm^{-1} employing 15 scans at 4 cm^{-1} resolution. To determine the degree of incorporation of VIM, the porous mono-sized poly(EGDMA-*co*-VIM) microspheres were subjected to elemental analysis using a model CHNS-932 Elemental Analyzer (Leco Industries, St. Joseph, MI, U.S.A.). The specific surface area of the monodisperse porous poly(EGDMA-*co*-VIM) microspheres was determined by nitrogen adsorption/desorption experiments employing usual BET methods. The average size and size distribution of the porous microspheres were determined by scanning electron microscopy (JEM 1200EX instrument, JEOL, Japan).

2.5. Batch adsorption studies

Batch adsorption experiments were performed by adding 0.050 g of the porous mono-sized poly(EGDMA-*co*-VIM) microspheres to 50 mℓ of an aqueous solution of Pb(II) ions contained in a series of 100 cm^3 Erlenmeyer flasks under controlled pH and temperature conditions. Each such mixture was shaken at 300 rpm for 1 h at the desired temperature, this time length having been established via preliminary experiments as being satisfactory for the establishment of adsorption equilibrium. The equilibrium Pb(II) ion concentration was then determined by means of an atomic absorption spectrophotometer (model 902, GBC, Adelaide, Australia) employing an air/acetylene flame. The spectral slit width used was 0.5 nm and deuterium background corrections were applied in all analyses. The working current/wavelength value for the determination of Pb(II) ion concentrations was 6 mA/217.0 nm, with the instrument response being checked periodically with known Pb(II) ion solution standards. An average of three replicate determinations is reported below for each adsorption system examined.

The amount of Pb(II) ions adsorbed onto the polymer microspheres at equilibrium, q (mg/g polymer), was calculated via the following relationship:

$$q = \frac{(C_0 - C)V}{m} \tag{1}$$

where C_0 and C are the initial and equilibrium metal ion concentrations (mg/ℓ), respectively, V is the volume of the aqueous phase (ℓ) and m is the mass of microspheres used (g).

2.6. Desorption and repeated use

The desorption of Pb(II) ions from the porous polymer microspheres was achieved by soaking them in 50 mℓ of a 0.1 M HNO$_3$ solution for 60 min. Thus, the microspheres containing the adsorbed Pb(II) ions were placed in the desorption medium and shaken at 300 rpm at room temperature. The final Pb(II) ion concentration in the aqueous phase was determined by atomic absorption spectrometry, the desorption ratio being calculated from the following expression:

$$\text{Desorption ratio } = \frac{\text{Amt. of Pb(II) ions desorbed to the elution medium}}{\text{Amt. of Pb(II) ions adsorbed onto the microspheres}} \qquad (2)$$

In order to determine the re-usability of the porous polymer microspheres, consecutive adsorption/elution cycles were repeated 10 times using the same porous polymer microspheres.

3. RESULTS AND DISCUSSION

3.1. Properties of the porous polymer microspheres

The chemical structure of the porous mono-sized poly(EGDMA-*co*-VIM) microspheres is depicted in Figure 1. A scanning electron micrograph of the microspheres (not depicted) showed that the modified two-step seeded polymerization provided mono-sized spherical cross-linked porous poly(EGDMA-*co*-VIM) microspheres which were ca. 7 μm in size. These microspheres were insoluble in a variety of solvents (ether, petroleum ether, chloroform, carbon tetrachloride, ethyl acetate, benzene, toluene). The specific surface area of the individual porous mono-sized poly(EGDMA-*co*-VIM) microspheres was determined as 64.5 m^2/g employing BET methods. The presence of the imidazole functionality in the structure of the porous microspheres was confirmed by the appearance of characteristic peaks at 2936 cm^{-1} (imidazole ring, C=C–H/N=C–H), 1454 cm^{-1} (C–C/N–C stretching), 1259 cm^{-1} (ring vibration) and 962 cm^{-1} (in-plane ring C–H bending) in the FT-IR spectrum of the microspheres.
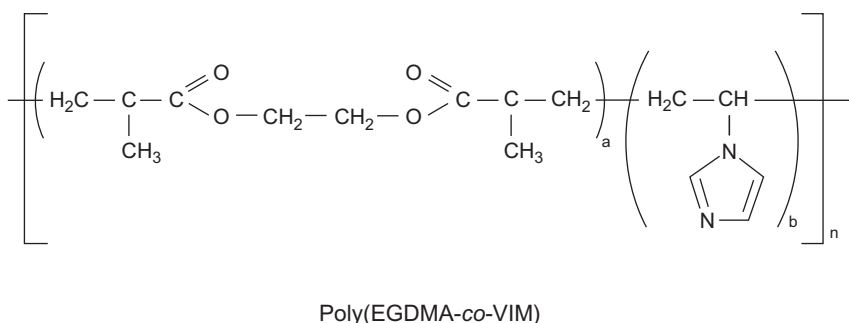

Poly(EGDMA-*co*-VIM)

Figure 1. Chemical structure of the porous mono-sized poly(EGDMA-*co*-VIM) microspheres.

The porous mono-sized poly(EGDMA-co-VIM) microspheres were synthesized by copolymerizing EGDMA with VIM at a 1.5:1.0 molar ratio. To evaluate the degree of VIM incorporation into the microspheres, elemental analysis (C: 57.81%; H: 7.39%; N: 2.29%) of the synthesized porous mono-sized poly(EGDMA-*co*-VIM) microspheres was performed. The resulting nitrogen stoichiometry indicated that 1.636 mmol VIM/g polymer had been incorporation into the microspheres. This indicates that most of the VIM charged into reactor was successfully incorporated into the microspheres by the polymerization procedure applied.

3.2. Adsorption of Pb(II) ions

3.2.1. Effect of pH on the adsorption of Pb(II) ions

The variation in the extent of Pb(II) ions adsorption onto the porous mono-sized poly(EGDMA-*co*-VIM) microspheres with pH is depicted in Figure 2. The initial Pb(II) ion concentration employed in these experiments was 300 mg/dm^3. The adsorbate and adsorbent were maintained in contact for 1 h at 293 K. It will be seen from the figure that the amount of Pb(II) ions adsorbed onto the porous microspheres increased significantly with increasing pH, probably as a result of the deprotonation of the VIM units in the particle structure. This may be explained by the decreasing competition
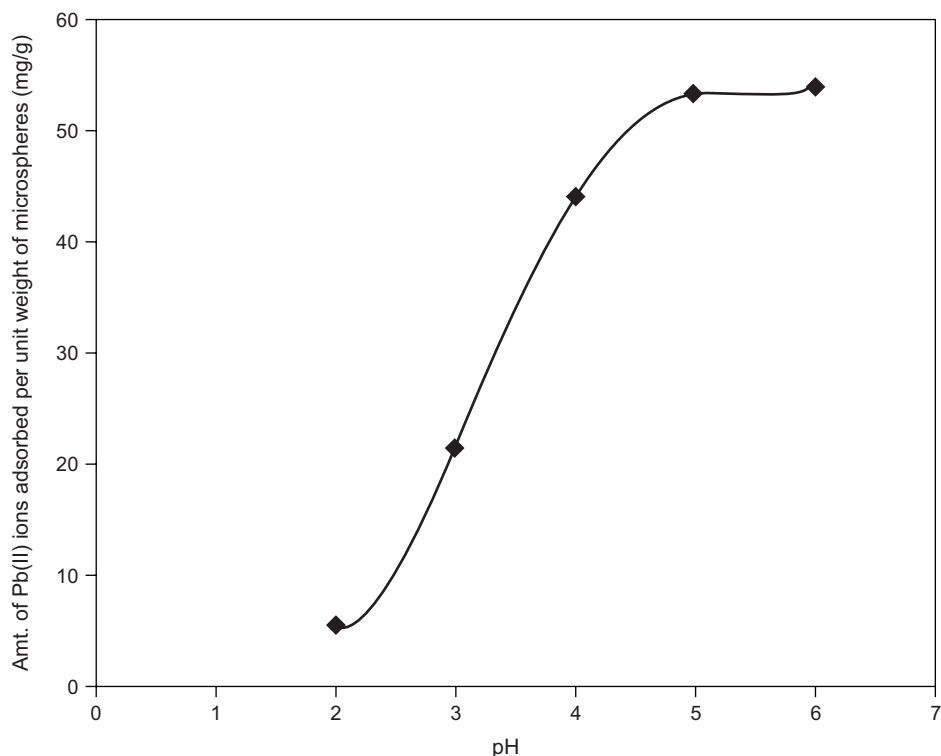

Figure 2. Influence of pH on the adsorption of Pb(II) ions from aqueous solution onto the porous mono-sized poly(EGDMA-*co*-VIM) microspheres. Experimental conditions employed: initial conc. of Pb(II) ions = 300 mg/dm^3; temp. = 293 K; contact time = 60 min.

between the hydrogen ions and Pb(II) ions in the solution for adsorption sites located at the nitrogen atoms of the adsorbate with increasing pH. The pH values investigated ranged up to 6.0; higher values were not examined since Pb(II) ions precipitated from the solution under these conditions.

3.2.2. Effect of temperature on the adsorption of Pb(II) ions

The uptake of Pb(II) ions (mg/g) onto the porous mono-sized poly(EGDMA-*co*-VIM) microspheres increased from 21.74 mg/g to 56.48 mg/g as the temperature was increased from 293 K to 333 K (see Figure 3). In all cases, the time required to attain equilibrium was 60 min, thereby indicating that the equilibrium time was independent of the temperature. These results also show that the adsorption process was endothermic in nature. The imidazole groups of the porous mono-sized poly(EGDMA-*co*-VIM) microspheres were partially protonated at all the temperatures employed, but their degree of deprotonation decreased at higher temperatures resulting in a slight increase in their adsorption capacity towards Pb(II) ions under these conditions. Where only the adsorption of Pb(II) ions is involved, the effect of temperature on the equilibrium time is relatively small, as has been shown in other studies (Miaou *et al*. 2009; Kong *et al*. 2010; Al-Haidary *et al*. 2011; Rashidi *et al*. 2010; Zhao *et al*. 2010; Kul and Koyuncu 2010).

3.2.4. Effect of initial Pb(II) ion concentration on the adsorption process

Nine different concentrations of Pb(II) ions, i.e. 25, 50, 75, 100, 200, 300, 400, 500 and 600 mg/dm^3, were selected for investigating the effect of the initial concentration of Pb(II) ions on
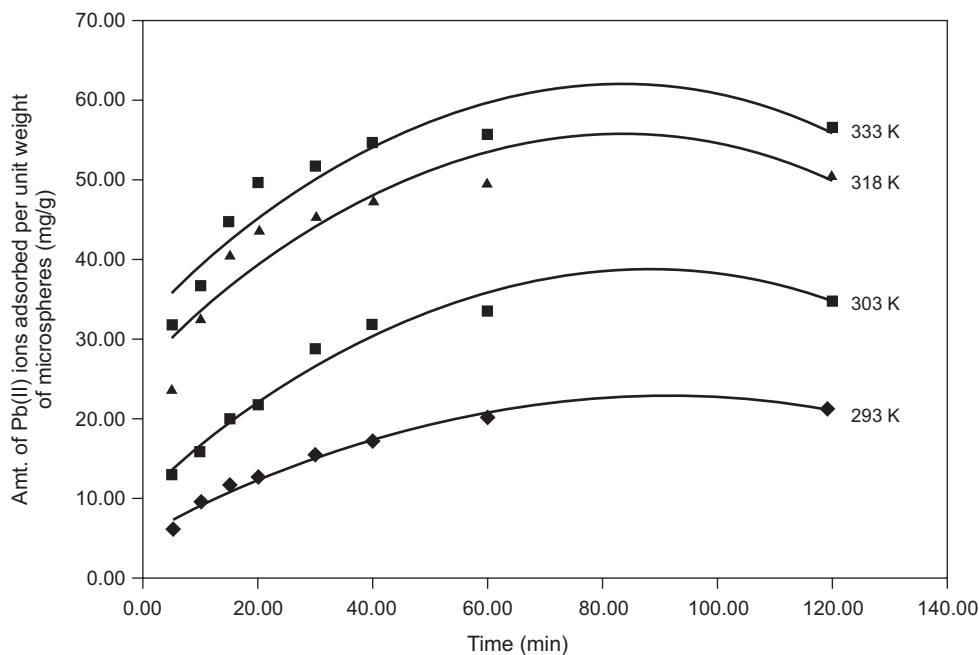

Figure 3. Effect of temperature on the adsorption of Pb(II) ions onto the porous mono-sized poly(EGDMA-*co*-VIM) microspheres.
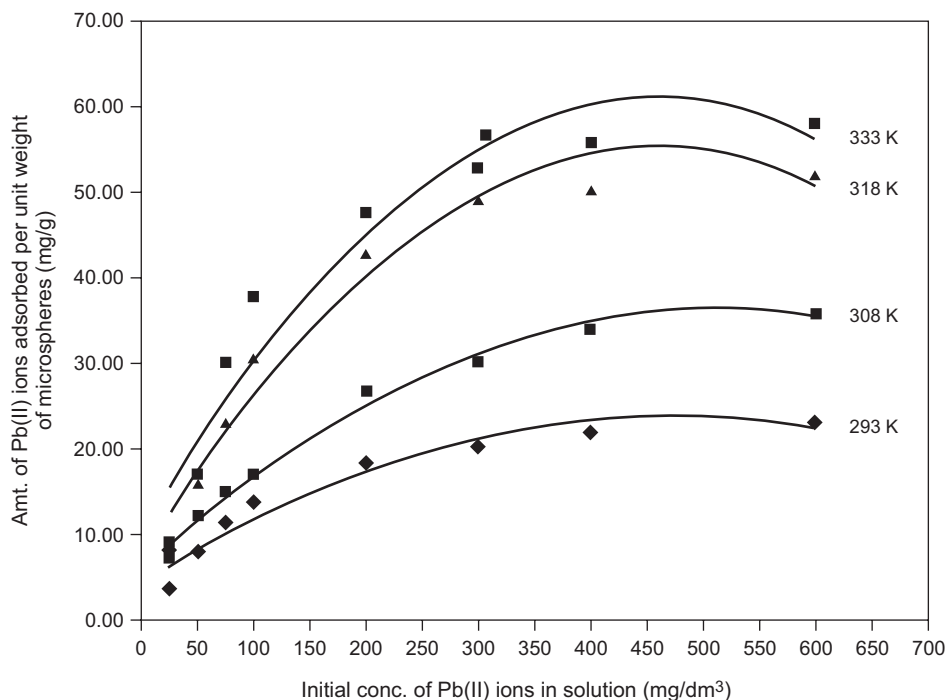
Figure 4. Effect of the initial concentration of Pb(II) ions in the aqueous solution on their adsorption onto the porous mono-sized poly(EGDMA-*co*-VIM) microspheres at various temperatures.

their adsorption onto the porous mono-sized poly(EGDMA-*co*-VIM) microspheres. The amounts of Pb(II) ions adsorbed at equilibrium at 293, 303, 315 and 333 K, respectively, and a pH of 6 are depicted in Figure 4. As shown, increasing the initial concentration of Pb(II) ions from 25 mg/dm^3 to 600 mg/dm^3 led to an increase in the amount of Pb(II) ions adsorbed from 3.56 mg/g polymer to 22.38 mg/g polymer at 293 K, from 7.27 mg/g polymer to 34.15 mg/g polymer at 303 K, from 8.61 mg/g polymer to 49.82 mg/g polymer at 318 K and from 9.35 mg/g polymer to 57.69 mg/g polymer at 333 K, respectively.

The adsorption capacities for Pb(II) ions exhibited by the porous mono-sized poly(EGDMA-*co*-VIM) microspheres are comparable with the values reported in other studies. Thus, Kara *et al*. (2004) reported that the adsorption capacity of poly(ethylene glycol dimethacrylate-n-vinyl imidazole) beads for Pb(II) ions was 114.8 mg/g. Uzun *et al*. (2006) using triazole-based beads for the adsorption of heavy metal ions reported an adsorption capacity of 134.9 mg/g for Pb(II) ions. Kesenci *et al*. (2002) used poly(ethylene glycol dimethacrylate-*co*-acrylamide) beads for the adsorption of heavy metal ions and obtained an adsorption capacity of 378.1 mg/g for Pb(II) ions. Sağlam *et al*. (2001) using thiazolidine-based microbeads for the adsorption of Pb(II) ions obtained an adsorption capacity of 69.5 mg/g. Denizli *et al*. (1997) using diamine-based beads treated by glow discharge obtained an adsorption capacity of 136.2 mg/g for Pb(II) ions, while Bulgariu *et al*. (2009) using lignin as an adsorbent obtained an adsorption capacity for Pb(II) ions of 32.36 mg/g. Oluyemi *et al*. (2009), using charcoal prepared locally from the burnt remnants of plantain peel with more conventional adsorbents such as industrial activated wood charcoal, technical charcoal animal powder and Amberlite resin for heavy metal ions adsorption from

synthetic wastewaters, obtained the following order for the adsorption of Pb(II) ions at a pH value of 7: Amberlite resin (99.98 ± 7.53%) > plantain peel charcoal (98.37 ± 7.95%) > technical charcoal animal powder (97.91 ± 6.83%) > activated wood charcoal (96.39 ± 7.06%). Faghihian and Yazdinejad (2009) used a local clay (bentonite) and a zeolite (clinoptilolite) for the removal of Pb(II) ions from aqueous solutions and obtained adsorption capacities of 106.6 mg/g and 90.3 mg/g, respectively. Nabi *et al.* (2008) used a new hybrid EDTA–zirconium iodate cation-exchanger and assessed its selectivity by examining its use for some important binary separations such as Mg^{2+}–Pb^{2+}, Cd^{2+}–Pb^{2+}, Hg^{2+}–Pb^{2+}, Zn^{2+}–Pb^{2+}, Cu^{2+}–Pb^{2+} and Al^{3+}–Pb^{2+} on a packed column of the material. Finally, Bhattacharyya and Gupto (2009) have examined the adsorptive accumulation of Cd(II), Co(II), Cu(II), Pb(II) and Ni(II) ions from water onto acid-activated kaolinite and obtained an adsorption capacity for Pb(II) ions in the range 11.1–12.1 mg/g.

3.3. Adsorption kinetics

The variation with time of the adsorption of Pb(II) ions onto the porous mono-sized poly(EGDMA-*co*-VIM) microspheres at various temperatures is depicted in Figure 3 above. As shown, the adsorption process levelled off after ca. 1 h. Similarly, for a constant time period, the adsorption of Pb(II) ions decreased with increasing temperature. Hence, the adsorption of Pb(II) ions onto the mono-sized porous poly(EGDMA-*co*-VIM) microspheres was favoured at higher temperatures.

Three different kinetic models, i.e. the Lagergren first-order, the pseudo-second-order and the intra-particle diffusion equations, were applied in an attempt to interpret the time-dependent adsorption data.

The Lagergren first-order rate expression (Lagergren 1898) may be expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (3)$$

where q_e and q_t are the amounts of Pb(II) ions (mg/g) adsorbed at equilibrium and a given time, t, respectively, while k_1 (min^{-1}) is the rate constant of the Lagergren first-order model.

The pseudo-second-order kinetic model equation (Ho and McKay 1999) may be written as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t \qquad (4)$$

where q_2 is the maximum adsorption capacity (mg/g) and k_2 is the rate constant [g/(mg min)].

The intra-particle diffusion model equation (Weber and Morris 1963) can be expressed by the following equation:

$$q_t = k_i t^{1/2} + C \qquad (5)$$

where C is the intercept of the linear plot of q_t versus $t^{1/2}$ and k_i is the intra-particle diffusion rate constant [mg/(g min$^{1/2}$)].

The kinetic parameters for the adsorption of Pb(II) ions onto the porous mono-sized poly(EGDMA-*co*-VIM) microspheres under different conditions were calculated from the corresponding plots and are listed in Table 1. Based on the correlation coefficients in Table 1, it may be concluded that the adsorption process was adequately described by the pseudo-second-order

TABLE 1. Kinetic Parameters for the Adsorption of Pb(II) Ions onto Mono-sized Poly(EGDMA-*co*-VIM) Microspheres

Temp. (K)	Experimental value of q_e (mg/g)	Langergren first-order			Pseudo-second-order			Intra-particle diffusion		
		$k_1 \times 10^3$ (min^{-1})	q_e (mg/g)	R^2	$k_2 \times 10^4$ [g/(mg min)]	q_e (mg/g)	R^2	k_i [mg/(g min$^{1/2}$)]	C (mg/g)	R^2
293	21.53	43.99	19.38	0.9830	23.47	25.13	0.9923	2.460	1.664	0.9862
303	30.52	57.11	33.98	0.9759	25.31	40.32	0.9961	4.182	3.826	0.9632
318	49.23	60.80	30.18	0.9521	30.42	55.25	0.9989	4.441	19.74	0.8268
333	56.48	71.39	36.07	0.9797	31.22	61.35	0.9988	4.509	25.27	0.8683

kinetic model. The pseudo-second-order rate constant increased with temperature over the range 293–333 K (Table 1), indicating that the adsorption of Pb(II) ions onto the porous mono-sized poly(EGDMA-*co*-VIM) microspheres was kinetically controlled.

The results were also analyzed by the intra-particle diffusion model to verify the rate-controlling step. If this model applies, a plot of the uptake, q_t, versus the square root of the time, $t^{1/2}$, should be linear and, if it passes through the origin, intra-particle diffusion will be the sole rate-controlling process (Özcan and Özcan 2005; Gök *et al*. 2008). In the present study, it was found that the plots of q_t versus $t^{1/2}$ (not shown) exhibited a linear tendency. However, probably due to the thickness of the boundary layer, none of the plots corresponding to different temperatures passed through the origin. However, values of the intercept should give an idea about the thickness of the boundary layer, i.e. the larger the intercept the greater is the boundary layer effect (Nadeem *et al*. 2006). These results indicate that although intra-particle diffusion was involved in the adsorption process, it was not the sole rate-controlling step for the whole adsorption process. The correlation coefficients for the intra-particle diffusion model (R^2) were between 0.9862 and 0.8268.

The pore diffusion coefficient (D) for the intra-particle transport of Pb(II) ions was calculated assuming a spherical geometry for the adsorbent particles (Uzun *et al*. 2006) and employing the following equation:

$$t_{1/2} = 0.03 r_0^2/D \tag{6}$$

where $t_{1/2}$ is the time for half-adsorption, r_0 is the diameter of the microspheres and D is the pore diffusion coefficient (cm^2/s). The value of D for Pb(II) ions was found to be 4.16×10^{-12} cm^2/s. This value indicates that pore diffusion was not significant.

The values of the pseudo-second-order rate constant, k_2, were found to increase from 1.269×10^{-3} g/(mg min) to 1.826×10^{-3} g/(mg min) as the solution temperature increased from 293 K to 333 K. In fact, there was a linear relationship between the temperature and the pseudo-second-order rate constant (see Figure 5). The adsorption rate constant is usually expressed as a function of solution temperature by the following Arrhenius-type relationship (Ho and Ofomaja 2006):

$$\ln k_2 = \ln k_0 - \frac{E_a}{RT} \tag{7}$$

where k_2 [g/(mg min)] is the rate constant for the pseudo-second-order adsorption process, k_0 [g/(mg min)] is a temperature-independent rate factor, R is the gas constant [8.314 J/(mol K)] and T is the solution temperature (K). In the present study, the relationship between k_2 and T could be represented in an Arrhenius form as:

$$\ln k_2 = 8.743 - \frac{747.2}{RT} \tag{8}$$

From this equation, the temperature-independent rate factor, k_0, was 6.270×10^3 g/(mg min) and the adsorption activation energy, E_0, was 6.212 kJ/mol.

The magnitude of the activation energy may be related to the type of sorption process involved. Two main types of adsorption can occur — physical or chemical. In physical adsorption, equilibrium is usually rapidly attained and is readily reversible because the energy requirements are small. The activation energy for physical adsorption is usually not greater than 4.184 kJ/mol because the forces
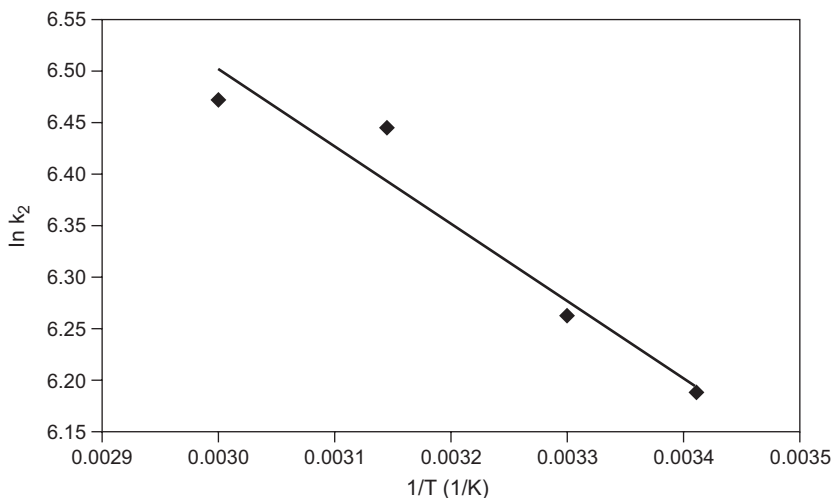
Figure 5. Arrhenius plot.

involved are weak. However, chemical adsorption is specific and involves forces which are much stronger than those for physical adsorption. Two kinds of chemisorption are encountered — activated and (less frequently) non-activated. Activated chemical adsorption means that the rate varies with temperature according to the Arrhenius equation with a finite activation energy (high value of E_a). However, chemical adsorption occurs very rapidly in some systems, suggesting that the activation energy is nearly zero. This is termed non-activated chemical adsorption.

By only taking activation energies into consideration, it was difficult to decide which mechanism was effective in the adsorption of Pb(II) ions onto the porous mono-sized poly(EGDMA-*co*-VIM) microspheres. As the observed value for the adsorption activation energy of Pb(II) ions onto the porous microspheres was slightly high (> 4.184 kJ/mol), the adsorption process could have involved both physical and chemical adsorption (Erturgay and Bayhan 2010; Sağ and Kutsal 2000).

3.4. Adsorption isotherms

The equilibrium adsorption data were analyzed using the Langmuir (1918), Freundlich (1906) and Dubinin–Radushkevich (Shibi and Anirudhan 2006) isotherm models. The linear forms of these models may be represented by the following equations:

$$\textit{Langmuir} \qquad \frac{C_e}{q_e} = \frac{1}{Q_L K_L} + \frac{C_e}{Q_L} \qquad\qquad (9)$$

$$\textit{Freundlich} \qquad \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad\qquad (10)$$

$$\textit{Dubinin–Radushkevich} \qquad \ln q_e = \ln Q_{D-R} - K_{D-R} \varepsilon^2 \qquad\qquad (11)$$

where q_e is the concentration of Pb(II) ions (mg/g) adsorbed onto the adsorbent at equilibrium, C_e is the concentration of Pb(II) ions remaining in solution at equilibrium (mg/dm^3), Q_L is the monolayer capacity of the adsorbent (mg/g), K_L is the Langmuir constant (dm^3/mg) related to the

free energy of adsorption, K_F (dm^3/g) is the Freundlich constant, n (dimensionless) is the heterogeneity factor, Q_{D-R} is the maximum adsorption capacity (mg/g), K_{D-R} is the D–R constant (mol^2/J^2) and ε is the Polanyi potential (J/mol) which can be calculated from the equation:

$$\varepsilon = RT \ln\left(1 + 1/C_e\right) \qquad (12)$$

where R is the gas constant [J/(mol K)], T is the absolute temperature (K) and C_e is the equilibrium concentration of adsorbate in the aqueous solution (mg/ℓ) (Laus *et al.* 2010; Chen *et al.* 2008; Tripathy and Raichur 2008). The calculated values of Q_{D-R} and K_{D-R} are listed in Table 2.

The plots of C_e/q_e versus C_e (Langmuir) for the adsorption of Pb(II) ions onto the porous mono-sized poly(EGDMA-*co*-VIM) microspheres were linear with slopes equal to $1/Q_L$ and intercepts equal to $1/Q_L K_L$. Similarly, by plotting $\ln q_e$ versus $\ln C_e$ (Freundlich) it was possible to obtain K_F and n from the intercept and slope, respectively, and by plotting $\ln q_e$ versus ε^2 (Dubinin–Radushkevich) it was possible to obtain the value of K_{D-R} from the intercept and the value of Q_{D-R} from the slope.

The values of all the isotherm constants were determined using the least-squares algorithm and are listed in Table 2. For the Freundlich isotherm, values of 1/n between 0.521 and 0.485 indicate the favourable adsorption of Pb(II) ions onto the porous mono-sized poly(EGDMA-*co*-VIM) microspheres (McKay *et al.* 1982; Kara *et al.* 2006). This means that the numerical values of n lie between 1.920 and 2.063, i.e. they are greater than unity, thereby indicating that Pb(II) ions were favourably adsorbed by the porous mono-sized poly(EGDMA-*co*-VIM) microspheres at all the temperatures studied.

The high R^2 values for the Langmuir isotherm suggest its applicability to the present system. The monolayer adsorption capacity, Q_L, increased from 27.62 mg/g to 67.11 mg/g as the temperature increased from 293 K to 333 K, indicating that the adsorption process was endothermic. The highest value for K_L obtained at 333 K was 13.92×10^{-3} dm^3/mg, demonstrating that the highest adsorption affinity occurred at the highest temperature. The highest value of Q_L (67.11 mg/g at 333 K) was comparable to values reported in the literature. Thus, the Q_L values for the adsorption of Pb(II) ions onto thiazolidine-immobilized polyhydroxyethylmethacrylate beads, polystyrene–divinylbenzene macroreticular resin functionalized with bis-(*N,N'*-salicylidine)-1,3-propandiamine and polyhydroxyethylmethacrylate beads carrying Cibacron Blue F3GA dye were 69.62, 80.81 and 16.78 mg/g, respectively (Sağlam *et al.* 2001; Dev and Rao 1996; Arpa *et al.* 2001).

The characteristics of the Langmuir isotherm can also be expressed by a dimensionless separation factor, R_L (Kara *et al.* 2006), viz.

$$R_L = \frac{1}{1 + K_L C_0} \qquad (13)$$

with a value of R_L between 0 and 1 indicating a favourable adsorption. The R_L values obtained in the present study are listed in Table 2. These were in the range 0.2564–0.1932, which again shows that the adsorption process was favoured at all temperatures.

Although the Langmuir and Freundlich isotherm models are widely employed, they do not provide any information regarding the adsorption mechanism. For this reason, the equilibrium data were also tested with the Dubinin–Radushkevich isotherm model (D–R isotherm). This isotherm model predicts the nature of adsorbate sorption onto the adsorbent and is used to

TABLE 2. Langmuir, Freundlich and Dubinin–Radushkevich (D–R) Isotherm Constants for the Adsorption of Pb(II) Ions onto Mono-sized Poly(EGDMA-*co*-VIM) Microspheres

Temp. (K)	Langmuir constants				Freundlich constants			Dubinin–Radushkevich constants			
	Q_L (mg/g)	$K_L \times 10^3$ (dm³/mg)	R^2	R_L	K_F	n	R^2	Q_{D-R} (mg/g)	$K_{D-R} \times 10^9$ (mol² J²)	E_{fe} (kJ/mol)	R^2
293	27.62	9.664	0.9906	0.2564	1.061	1.920	0.8793	3.559	−5.965	9.153	0.9163
303	42.55	9.866	0.9964	0.2524	2.132	2.135	0.9726	110.5	−4.680	10.34	0.9749
318	61.73	11.95	0.9938	0.2182	2.726	1.961	0.9102	213.4	−4.829	10.18	0.9410
333	67.11	13.92	0.9902	0.1932	3.560	2.063	0.8447	227.1	−4.203	10.91	0.8826

calculate the mean free energy of adsorption. The mean free energy of adsorption (E_{fe}) may be calculated from the K_{D-R} values via the equation:

$$E_{fe} = 1/\sqrt{-2K_{D-R}} \tag{14}$$

The magnitude of the E_{fe} value may be employed to ascertain the type of adsorption process under consideration. If this value is in the range 8–16 kJ/mol, the process can be assumed to involve chemical sorption. On the other hand, values lower than 8 kJ/mol indicate that the adsorption process is of a physical nature (Özcan *et al*. 2005; Ünlü and Ersoz 2006; Tassist *et al*. 2010). In the present study, the R^2 values obtained for the application of the D–R isotherm model were in the range 0.8826–0.9749 while the E_a values obtained using the D-R constant in the non-linear form were in the range 9.153–10.91 kJ/mol over the temperature range studied, thereby indicating that the adsorption of Pb(II) ions onto the porous mono-sized poly(EGDMA-*co*-VIM) microspheres occurred via a chemical process at all temperatures.

3.5. Adsorption thermodynamics

The temperature dependence of the equilibrium constant, K_L, can be used to determine the thermodynamic parameters (Yo and Ofomaja 2006) via the van't Hoff equation. The integrated form of this equation may be written as:

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{15}$$

The standard enthalpy change (ΔH^0) and the standard entropy change (ΔS^0) for the process can be determined from the slope and intercept of the linear plot of $\ln K_L$ versus 1/T. The standard Gibbs' free energy change for each temperature may then be obtained from the relationship:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{16}$$

The values of the standard Gibbs' free energy change for the adsorption of Pb(II) ions onto the mono-sized poly(EGDMA-*co*-VIM) microspheres obtained from the application of equation (16) were –18.52, –19.23, –20.66 and –22.06 kJ/mol at 293, 303, 318 and 333 K, respectively. The negative values for ΔG^0 indicate that the adsorption of Pb(II) ions onto the porous microspheres was both feasible and spontaneous from a thermodynamic standpoint. From the plot of $\ln K_L$ versus 1/T depicted in Figure 6 overleaf, the values of the standard enthalpy change (ΔH^0) and the standard entropy change (ΔS^0) were determined as 7.739 kJ/mol and 89.32 J/(mol K), respectively. The positive value of ΔH^0 indicates the endothermic nature of the adsorption process while the positive value of ΔS^0 shows the increasing randomness at the interface between the porous mono-sized poly(EGDMA-*co*-VIM) microspheres and the adsorption medium during the adsorption process.

3.6. Elution and repeated use

The practical use of an adsorbent in an adsorption process depends not only on its adsorptive capacity but also on how well the adsorbent can be regenerated and re-used. The re-usability of the porous mono-sized poly(EGDMA-*co*-VIM) microspheres was examined by employing the
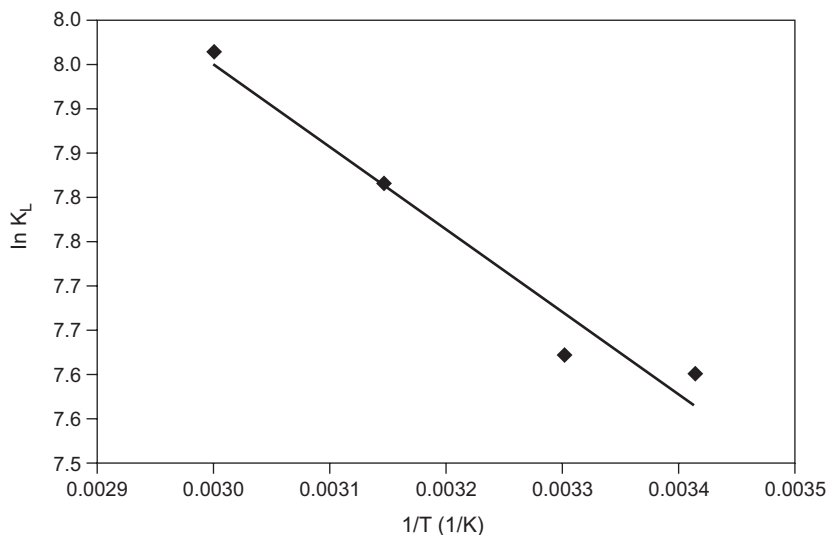
Figure 6. Plot of $\ln K_L$ versus 1/T to determine the magnitude of the standard Gibbs' free energy for the adsorption of Pb(II) ions onto the porous mono-sized poly(EGDMA-*co*-VIM) microspheres.

microspheres in an adsorption/desorption cycle which was repeated 10 times. In such studies, the eluant employed was HNO_3 solution and its repeated use with the porous mono-sized poly(EGDMA-*co*-VIM) microspheres demonstrated that the adsorption/desorption process was reversible. It was found that the adsorption capacity of the porous mono-sized poly(EGDMA-*co*-VIM) microspheres decreased by only 3% during the 10 adsorption/desorption cycles undertaken.

NOTATION

C_e	concentration of Pb(II) ions in the aqueous solution at equilibrium (mg/dm^3)
C_0	initial concentration of Pb(II) ions in the aqueous solution (mg/dm^3)
ΔG^0	standard Gibbs' free energy of adsorption (J/mol)
ΔH^0	isosteric enthalpy of adsorption (J/mol)
ΔS^0	standard entropy change for the adsorption process [J/(mol K)]
E_a	activation energy for the adsorption process (J/mol)
E_{fe}	free energy of adsorption (kJ/mol)
q_e	amount of Pb(II) ions adsorbed onto the adsorbent at equilibrium (mg/g)
q_t	amount of Pb(II) ions adsorbed onto the adsorbent at a time t (mg/g)
Q_L	maximum amount of Pb(II) ions adsorbed per unit mass of adsorbent (mg/g)
K_L	Langmuir constant related to the affinity of binding sites (dm^3/mg)
n	Freundlich constant
K_F	Freundlich constant
Q_{D-R}	maximum amount of Pb(II) ions adsorbed per unit mass of adsorbent (mg/g)
K_{D-R}	Dubinin–Radushkevich constant (mol^2/J^2)
ε	Polanyi potential (J/mol)
Q_S	maximum monolayer adsorption capacity (mg/g)

K_S	equilibrium adsorption constant
k_1	rate constant of the Lagergren first-order kinetic model (min^{-1})
k_2	rate constant for the pseudo-second-order kinetic model [g/(mg min)]
k_i	intra-particle diffusion rate constant [mg/(g $min^{1/2}$)]
r_0	diameter of microspheres (cm)
D	pore diffusion coefficient (cm^2/s)
R_L	dimensionless separation factor
R^2	linear regression coefficient
t	time (min)
T	temperature (K)

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REFERENCES

Akgöl, S., Kuşvuran, E., Kara, A., Şenel, S. and Denizli, A. (2006) *J. Appl. Polym. Sci.* **100,** 5056.

Al-Haidary, A.M.A., Zanganah, F.H.H., Al-Azawi, S.R.F., Khalili, F.I. and Al-Dujaili, A.H. (2011) *Water Air Soil Pollut.* **214,** 73.

Arpa, Ç., Alim, C., Bektaş, S., Genç, Ö. and Denizli, A. (2001) *Colloids Surf. A* **176,** 225.

Bhattacharyya, K.G. and Gupta, S.S. (2009) *Adsorpt. Sci. Technol.* **27,** 47.

Bulgariu, L., Bulgariu, D., Malutan, T. and Macoveanu, M. (2009) *Adsorpt. Sci. Technol.* **27,** 435.

Chen, A.H., Liu, S.C., Chen, C.Y., Szpoganicz, B. and Fávere, V.T. (2008) *J. Hazard. Mater.* **154,** 184.

Denizli, A., Salih, B. and Pişkin, E. (1997) *J. Chromatogr. A* **773,** 169.

Dev, K. and Rao, G.N. (1996) *Talanta* **43,** 451.

Erturgay, N. and Bayhan, Y.K. (2010) *Desalination* **255,** 137.

Faghihian, H. and Yazdinejad, M.N. (2009) *Adsorpt. Sci. Technol.* **27,** 107.

Freundlich, H.M.F. (1906) *Z. Phys. Chem. (Leipzig)* **57A,** 385.

Gök, Ö., Özcan, A., Erdem, B. and Özcan, A.S. (2008) *Colloids Surf. A* **317,** 174.

Gurgel, L.V.A. and Gil, L.F. (2009) *Water Res.* **43,** 4479.

Ho, Y.S and Ofomaja, A.E. (2006) *J. Hazard. Mater. B* **137,** 1796.

Ho, Y.S. and McKay, G. (1999) *Process Biochem.* **34,** 451.

Huang, Y.-H., Hsueh, C.-L., Huang, C.-P., Su, L.-C. and Chen, C.-Y. (2007) *Sep. Purif. Technol.* **55,** 23.

Kara, A., Acemioğlu, B., Alma, M.H. and Cebe, M. (2006) *J. Appl. Polym. Sci.* **101,** 2838.

Kara, A., Uzun, L., Beşirli, N. and Denizli, A. (2004) *J. Hazard. Mater. B* **106,** 93.

Kesenci, K., Say, R. and Denizli, A. (2002) *Eur. Polym. J.* **38,** 1443.

Kong, Q., Guo, C., Cheng, F., Ji, Q., Li, Y. and Xia, Y. (2010) *Adsorpt. Sci. Technol.* **28,** 363.

Kul, A.R. and Koyuncu, H. (2010) *J. Hazard. Mater.* **179,** 332.

Lagergren, S. (1898) *K. Sven. Vetenskapsakad. Handl.* **24,** 1.

Langmuir, I. (1918) *J. Am. Chem. Soc.* **40,** 1361.

Laus, R., Costa, T.G., Szpoganicz, B. and Fávere, V.T. (2010) *J. Hazard. Mater.* **183,** 233.

Liu, C., Bai, R. and Ly, Q.S. (2008) *Water Res.* **42,** 1511.

Ma, Q.Y., Logan, T.J. and Traine, S.J. (1995) *Environ. Sci. Technol.* **29,** 118.

McKay, G., Blair, H.S. and Gardner, J.R. (1982) *J. Appl. Polym. Sci.* **27,** 3043.

Miaou, D., Liu, F., Liu, Y. and Chen, H. (2009) *Adsorpt. Sci. Technol.* **27,** 785.

Nabi, S.A., Ganai, S.A. and Naushad, M. (2008) *Adsorpt. Sci. Technol.* **26,** 463.

Nadeem, M., Mahmood, A., Shahid, S.A., Shah, S.S., Khalid, A.M. and McKay, G. (2006) *J. Hazard. Mater. B* **138,** 604.

Oluyemi, E.A., Oyekunle, J.A.O. and Olasoji, S.O. (2009) *Adsorpt. Sci. Technol.* **27,** 493.

Özcan, A. and Özcan, A.S. (2005) *J. Hazard. Mater.* **125,** 252.

Özcan, A., Özcan, A.S., Tunali, S., Akar, T. and Kiran, I. (2005) *J. Hazard. Mater.* **124,** 200.

Peters, R.W. and Ku, Y. (1985) *AIChE Symp. Ser.* **81,** 9.

Rashidi, F., Sarabi, R.S., Ghasemi, Z. and Seif, A. (2010) *Superlattices Microstruct.* **48,** 577.

Sağ, Y. and Kutsal, T. (2000) *Process Biochem.* **35,** 801.

Sağlam, A., Bektaş, S., Patır, S., Genç, Ö. and Denizli, A. (2001) *React. Funct. Polym.* **47,** 185.

Shibi, I.G. and Anirudhan, T.S. (2006) *J. Chem. Technol. Biotechnol.* **81,** 433.

Stokinger, H.E. (1981) "Lead", in *Patty's Industrial Hygiene and Toxicology*, 3rd Revised Edn, Vol 2A, Clayton, G.D., Clayton, F.E., Eds, John Wiley & Sons, Inc., New York. pp. 1687–1728.

Tassist, A., Lounici, H., Abdi, N. and Mameri, N. (2010) *J. Hazard. Mater.* **183,** 35.

Tripathy, S.S. and Raichur, A.M. (2008) *J. Hazard. Mater.* **153,** 1043.

Tuncel, A., Tuncel, M., Çiçek, H. and Fidanboy, O. (2001) *Polym. Int.* **51,** 75.

Uğuzdoğan, E., Denkbaş, E.B., Öztürk, E. and Tuncel, S.A. (2009) *J. Hazard. Mater.* **162,** 1073.

Ünlü, N. and Ersoz, M. (2006) *J. Hazard. Mater. B* **136,** 272.

Uzun, L., Kara, A., Tüzmen, N., Karabakan, A., Beşirli, N. and Denizli, A. (2006) *J. Appl. Polym. Sci.* **102,** 4276.

Weber, W.J. and Morris, J.C. (1963) *J. Sanit. Eng. Div., Soc. Civil Eng.* **89,** 31.

Yang, D., Paul, B., Xu, W., Yuan, Y., Liu, E., Ke, X., Wellard, R.M., Guo, C., Xu, Y., Sun, Y. and Zhu, H. (2009) *Water Res.* **44,** 741.

Zhao, X., Jia, Q., Song, N., Zhou, W. and Li, Y. (2010) *J. Chem. Eng. Data* **55,** 4428.