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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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To cite this Article Laurino, Joseph P.(2008) 'Removal of Lead (II) Ions by Poly(2-octadecyl butanedioic acid): Isothermal and Kinetic Studies', *Journal of Macromolecular Science, Part A*, 45: 8, 612 – 619

To link to this Article: DOI: 10.1080/10601320802168736

URL: <http://dx.doi.org/10.1080/10601320802168736>

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Removal of Lead (II) Ions by Poly(2-octadecyl butanedioic acid): Isothermal and Kinetic Studies

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Received and accepted April, 2008

Poly(2-octadecyl-butanedioic acid), prepared from polyanhydride PA-18, possesses novel heavy metal adsorption characteristics. The adsorption capacity of this water insoluble polymer for lead (II) was substantially higher than other heterogeneous adsorbents and is equivalent to those obtained with homogeneous sorbents. The polymer exhibited pseudo-second-order kinetics and nearly complete adsorption of lead occurred in 15 min with initial lead (II) concentrations greater than $100 \text{ mg} \cdot \text{L}^{-1}$. Adsorptive behavior was accurately predicted by the Dubinin-Radushkevich isotherm model. The mean free energy of adsorption of lead (II) onto poly(2-octadecyl-butanedioic acid) was determined to be $31.6 \text{ kJ} \cdot \text{mol}^{-1}$, suggesting an ion exchange component to the adsorption mechanism. Gibb's free energy values for this process indicate that it is spontaneous. Adsorption was relatively independent of pH in the range of 3–5, due to the utilization of the sodium carboxylate form of the chelating groups, and was not influenced by high Na^+ concentration and moderate concentrations (up to $200 \text{ mg} \cdot \text{L}^{-1}$) of Ca^{+2} . Lead (II) solutions containing $2000 \text{ mg} \cdot \text{L}^{-1} \text{Ca}^{+2}$ did reduce the adsorption of $2000 \text{ mg} \cdot \text{L}^{-1}$ lead (II) by 28%.

Keywords: heavy metal; removal; polymer; lead

1 Introduction

Heavy metal exposure currently represents a serious worldwide environmental hazard. Of the 23 commonly classified heavy elements, excessive amounts of lead, cadmium, mercury, arsenic, chromium, zinc, and copper are of the greatest concern, as they frequently result in compromised mental and central nervous system function, alterations in blood composition, nausea and vomiting, damage to organs such as the lungs, kidneys, and liver, and an overall reduced level of energy. Degenerative processes that mimic Alzheimer's disease, muscular dystrophy, Parkinson's disease, and multiple sclerosis, along with various types of cancer, are associated with chronic exposure to heavy metal toxins. Exposure often results from ingestion of food, water, non-food materials, such as contaminated soil or paint chips, or adsorption through the skin in occupational or residential settings (1). Physiologically, the high degree of toxicity after ingestion or adsorption directly results from the ease with which these metals bind to essential cellular components, such as nucleic acids, enzymes, and structural proteins, and alter their function (2).

Lead has been classified as a priority pollutant by the United States Environmental Protection Agency and is considered one of the most toxic heavy metals in the environment today. Industrial sources of lead contaminated waste water include production and processing operations such as metal plating, lead battery, glass, and paint and dye manufacturing, fossil fuel combustion, acid mine drainage, and sulfide ore smelting. Its presence in drinking water above the EPA limit has been associated with anemia, encephalopathy, hepatitis, and nephritic syndrome (3).

Several methods have been employed to remove lead and other heavy metals ions from aqueous media. These include chemical precipitation, ion exchange, reverse osmosis, solvent extraction, complexation-ultrafiltration using soluble metal chelating polymers, and sorption on various materials such as polymer films, activated carbon, hydrogels, nanocomposites, polymeric flocculants, sargassum, chitosan, metal oxide gel, sawdust, humus-boehmite complex, animal bone powder, ceramics, polymerized banana stems, cellulose, *Caladium bicolor*, *Cephalosporium aphidicola*, titanium silicate zeolites, and pectin (4–24). Each of the aforementioned methods, however, is accompanied by one or more physical characteristic(s) that limit their widespread use. For example, hydrogels and ion exchange resins have relatively slow uptake kinetics, are expensive, and have limited metal ion capacity. Complexation – ultrafiltration with poly-chelators requires highly controlled polymer synthesis and

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the use of costly ultrafiltration equipment. Biosorption processes are limited by their regional distribution and problems associated with the consistency and complete characterization of raw materials. Additionally, most separation methods can only be successfully employed around a relatively narrow pH range.

A copolymer composed of maleic anhydride and 1-octadecene has been described in the literature (25). We observed this polymer, known as PA-18, to partially bind various aqueous metal ions. Conversion of the anhydride functionality to a dicarboxylic acid moiety dramatically increased the affinity of this polymer toward several mono-, di-, and tri-valent metal ions. The objective of this study is to characterize the lead (II) binding properties of this newly developed polymer of 2-octadecyl-butanedioic acid.

2 Experimental

2.1 Analysis and Spectroscopy

FT-IR spectra were recorded in KBr pellets (400–4000 cm^{-1}) on a ThermoNicolet Avatar 360 spectrometer. The ion concentrations of the filtrates were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Perkin Elmer Optima 2100). The concentration values reported represent the mean of duplicate determinations.

2.2 Preparation of Polymer

Poly(2-octadecyl-butanedioic acid) was prepared from the corresponding poly-anhydride copolymer. 10 g of poly-anhydride PA-18 (Archimica Fine Chemicals, Inc.) were dissolved in 200 ml of 4 M NaOH and stirred at 85°C for 2 h. The reaction mixture was cooled, the pH adjusted to 6 to 6.5, and filtered. The solid polymer was washed with cold analytical grade methanol (ThermoFisher) and dried under vacuum. IR: 2923 cm^{-1} (C-H stretch), 2852 cm^{-1} (C-H stretch), 1569 cm^{-1} (COO^- stretch), 1468 cm^{-1} (C-H bend), 1411 cm^{-1} (COO^- stretch), 1035 cm^{-1} (CO stretch).

2.3 Determination of Sorption Kinetics

Analytical grade $\text{Pb}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, and NaNO_3 (ThermoFisher) were used to prepare various concentrations of stock solutions. Solution pH was adjusted with trace metal grade HNO_3 or NaOH. A series of batch sorption experiments were conducted by adding 0.0500 g of poly(2-octadecyl-butanedioic acid) to 5.0 ml of stock solutions of varying lead (II) concentrations. The heterogeneous mixtures were agitated at 150 rpm at 22°C for 15 min, 30 min, 1 h, 2 h, 6 h, and 24 h and the samples gravity filtered.

2.4 Desorption and Regeneration of Polymer

Dilute (2%) trace metal grade nitric acid was added to 0.0500 g metal-bound polymer samples and stirred at 150 rpm for 30 min. The heterogeneous solutions were filtered and the metal ion concentration of the filtrate determined by ICP-AES. The solid polymer was washed with 10 ml of deionized water and 5 ml of analytical grade methanol, and dried under vacuum for 3 h. Each sorption and desorption cycle included a 6 h contact time with the metal ion solution and a 30 min desorption incubation with 2% trace metal grade nitric acid.

3 Results and Discussion

3.1 Kinetics

The influence of reaction time, initial lead concentration, pH, temperature, and the presence of a secondary metal ion on the sorption kinetics of lead (II) ions by this polymer was investigated. The percent removal of the metal ion by the polymer was determined from the following Equation (1):

$$\%R = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

where %R is the amount removed at time t and C_o and C_t are the initial and residual (at time t) metal ion concentrations, respectively. The percent removal of lead at various reaction times and initial lead concentrations at 22°C and pH of 4 is given in Figure 1. At 15 min, the rapid uptake of lead ions (80% to 99%) from lead solutions with initial concentrations greater than 100 $\text{mg} \cdot \text{L}^{-1}$ was observed. The uptake of lead ions from the lead solution with an initial concentration of 25 $\text{mg} \cdot \text{L}^{-1}$ was somewhat slower and reached equilibrium at 6 h. As such, all equilibrium studies were conducted at a contact time of 6 h.

The amount of adsorption (q_t) at various times was calculated using the following Equation (2):

$$q_t = \frac{C_o - C_t}{m} V \quad (2)$$

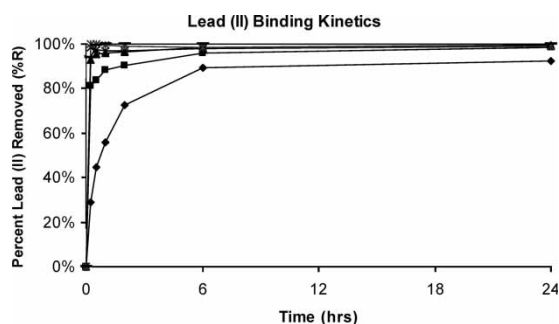


Fig. 1. Lead binding kinetics at 22°C and pH 4. [◆ = 25 $\text{mg} \cdot \text{L}^{-1}$, ■ = 100 $\text{mg} \cdot \text{L}^{-1}$, ▲ = 200 $\text{mg} \cdot \text{L}^{-1}$, × = 500 $\text{mg} \cdot \text{L}^{-1}$, * = 1000 $\text{mg} \cdot \text{L}^{-1}$ and – = 2000 $\text{mg} \cdot \text{L}^{-1}$].

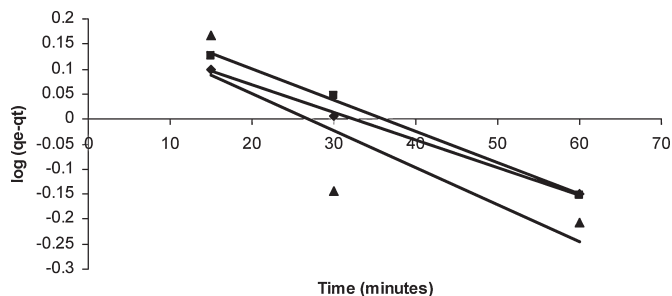


Fig. 2. Pseudo-first-order plots for lead ion solutions at 22°C and pH 4. [$\diamond = 25 \text{ mg} \cdot \text{L}^{-1}$, $\blacksquare = 100 \text{ mg} \cdot \text{L}^{-1}$, and $\blacktriangle = 200 \text{ mg} \cdot \text{L}^{-1}$].

where q_t is the amount of adsorption ($\text{mg} \cdot \text{g}^{-1}$ or $\text{mmol} \cdot \text{g}^{-1}$) at time t (min), C_o and C_t are the initial and residual (at time t) metal ion concentrations ($\text{mg} \cdot \text{L}^{-1}$ or $\text{mmol} \cdot \text{L}^{-1}$), respectively, V is the solution volume (L), and m is the amount (g) of polymer used. In order to clarify the kinetics of the adsorption process, two models, Lagergren's (26) pseudo-first order kinetic model and a pseudo-second order kinetic model were used to evaluate the experimental data.

The linear form of the Lagergren pseudo-first-order rate Equation (3) is given by:

$$\log(q_e - q_t) = \log q_e - \frac{k}{2.303} \times t \quad (3)$$

where q_t and q_e are the amounts of metal ion adsorbed ($\text{mg} \cdot \text{g}^{-1}$) at time t (min) and at equilibrium, respectively, and k is the adsorption rate constant (min^{-1}). Lagergren plots of the $\log(q_e - q_t)$ vs. t for solutions with initial lead concentrations of 25, 100 and 200 $\text{mg} \cdot \text{L}^{-1}$ are given in Figure 2. The values of the slope and y-intercept of the regression lines, R^2 , k , q_e (experimental), q_e (theoretical), and are given in Table 1. The poor agreement between experimental and theoretical q_e values suggests that the adsorption of lead (II) by this polymer is not a first-order reaction.

The empirical data was evaluated by a pseudo-second-order kinetic adsorption model (27) represented by the following Equation (4):

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

Plots of t/q_t vs. t for solutions with initial lead (II) concentrations of 25, 100, and 200 $\text{mg} \cdot \text{L}^{-1}$ are given in Figure 3 and the values for the slope and y-intercept of the regression lines, R^2 , k , q_e (experimental) and q_e (theoretical) are given in

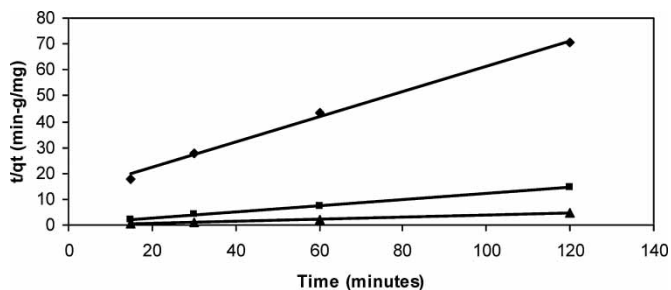


Fig. 3. Pseudo-second-order plots for lead solutions at 22°C and pH 4. [$\diamond = 25 \text{ mg} \cdot \text{L}^{-1}$, $\blacksquare = 100 \text{ mg} \cdot \text{L}^{-1}$, and $\blacktriangle = 200 \text{ mg} \cdot \text{L}^{-1}$].

Table 2. The linearity of the plots and the concordance of experimental and theoretical q_e values, are highly suggestive of a second-order-type adsorption process. Since ion exchange reactions are generally considered to be instantaneous upon contact and are controlled only by the diffusion of the ion, reactions involving only an ion exchange process can be appropriately modeled using first-order kinetics (16). The second-order kinetics observed for lead (II) adsorption onto poly(2-octadecyl-butanedioic acid) suggests a combination of both ion exchange and chelation mechanisms.

3.2 Adsorption Isotherms

The effect of the initial lead (II) concentration on the uptake of metal ions by the polymer was investigated by determining the concentration of lead ions remaining in solution after 6 h of adsorption time at 22°C and pH 4. As shown in Figure 4, the amount of lead ions adsorbed per unit mass of the polymer increased with the initial concentration of the lead ions. This is attributed to the increased driving force to overcome mass transfer resistance between the solution and the polymer provided by the increased initial metal ion concentration (28). The maximum adsorption capacity of the polymer was determined by incubating increasing volumes of 2000 $\text{mg} \cdot \text{L}^{-1}$ lead(II) solution with 0.0500 g of the polymer for 6 h at 22°C and pH 4, and was determined to be 290 $\text{mg} \cdot \text{g}^{-1}$ of adsorbent. This capacity is comparable with soluble adsorbents and substantially greater than those associated with heterogeneous separations using ion exchange resins, activated carbon, or biosorbents. (Table 3)

In order to further understand the mechanism of ion exchange and/or chelation associated with this polymer, experimental data obtained from the determination of the maximum adsorption capacity with lead (II) solutions of

Table 1. Regression and sorption values and for pseudo-first-order plots

[Pb ⁺²]	Slope	y-Intercept	R ²	k (min ⁻¹)	q_e (exp) $\text{mg} \cdot \text{g}^{-1}$	q_e (theor) $\text{mg} \cdot \text{g}^{-1}$
25 $\text{mg} \cdot \text{L}^{-1}$	-0.0055	0.1770	0.9971	0.01267	2.0229	1.5031
100 $\text{mg} \cdot \text{L}^{-1}$	-0.0063	0.2268	0.9965	0.01451	8.7116	1.6858
200 $\text{mg} \cdot \text{L}^{-1}$	-0.0074	0.1975	0.7193	0.01704	26.285	1.5758

Table 2. Regression and sorption values and for pseudo-second-order plots

[Pb ⁺²]	Slope	y-Intercept	R ²	k (g · mg ⁻¹ · min ⁻¹)	q_e (exp) mg · g ⁻¹	q_e (theor) mg · g ⁻¹
25 mg · L ⁻¹	0.4911	12.243	0.9958	0.01970	2.093	2.036
100 mg · L ⁻¹	0.1195	0.3028	0.9999	0.04716	8.712	8.368
200 mg · L ⁻¹	0.0385	0.0232	1.000	0.06389	26.285	25.974

varying initial concentrations were used to evaluate three equilibrium adsorption isotherm models: Langmuir, Freundlich, and Dubinin-Radushkevich (D-R).

The Langmuir model (29) is a two-parameter adsorption model that makes several assumptions regarding both the adsorption mechanism and the sorbent itself. This model assumes a structurally homogeneous adsorbent with specific energetically identical binding sites and suggests ion adsorption as a partial monolayer. Further, the intermolecular forces between the metal ion and the adsorbent are assumed to decrease rapidly with increasing distance between the ion and the adsorption surface, and interactions between adsorbed molecules or ions are absent. Thus, the presence of an adsorbed ion or molecule on a site does not impact the adsorption of an ion or molecule on an adjacent binding site. The linear form of the Langmuir Equation (5) is:

$$\frac{1}{q_e} = \frac{1}{Q^\circ} + \frac{1}{bQ^\circ C_e} \quad (5)$$

where q_e is the amount of adsorbed solute (mmol · g⁻¹), C_e is the equilibrium metal ion concentration of the solution (mmol · L⁻¹), Q° (mmol · g⁻¹) is the maximum surface density associated with a monolayer coverage and represents the limiting adsorption capacity of the adsorbent when fully covered with metal ions, and b is the Langmuir adsorption constant (L · mmol⁻¹) and is related to the free energy of adsorption. Langmuir constants and correlation coefficients are given in Table 4.

The Freundlich model (30) is a two-parameter model that assumes a heterogeneous adsorption surface with sites that differ in their binding energies. These energy differences

may reflect the potential availability of these sites on the adsorbent for the metal ion. Thus, the stronger binding sites are occupied first and subsequent binding energies decrease as the number of ions adsorbed increases. The linear form of the Freundlich Equation (6) is:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (6)$$

where q_e is the amount of adsorbed solute at equilibrium (mmol · g⁻¹), C_e is the equilibrium metal ion concentration of the solution (mmol · L⁻¹), K_F is the Freundlich constant (mmol · g⁻¹) and indicates both the adsorption capacity and the strength of the adsorptive bond, and n is the heterogeneity factor which represents the binding distribution. Freundlich constants and correlation coefficients for this process are given in Table 4.

The Dubinin-Radushkevich (31) (D-R) isotherm is a two-parameter analogue of the Langmuir isotherm model, but it is more general as it does not assume energetically equivalent binding sites or require a homogeneous surface structure. This isotherm model is particularly useful for the characterization of the adsorptive behavior of porous materials and assumes a layer-by-layer coverage of the pore surfaces (32). The linear form of this isotherm is Equation (7):

$$\ln q = \ln q_m - k\varepsilon^2 \quad (7)$$

where ε is the Polanyi potential and is given by the expression $[RT \ln(1 + (1/C_e))]$ where R (J mol⁻¹ · K⁻¹) is the gas constant and T (K) is the absolute temperature, q is the amount of adsorbed solute per unit weight of adsorbent (mol · g⁻¹) at equilibrium, q_m is the maximum adsorption

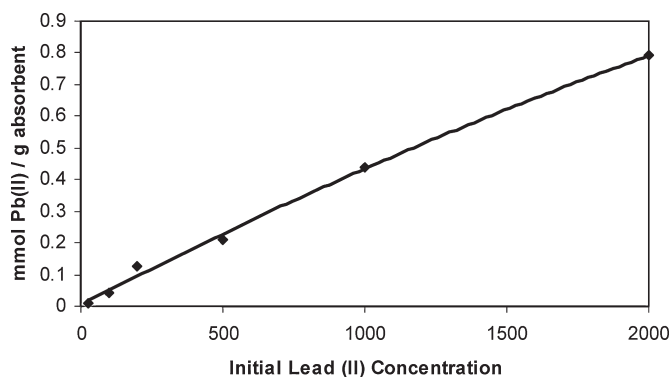


Fig. 4. Effect of initial lead (II) concentration (in mg · L⁻¹) on adsorption capacity at 22°C and pH 4.

Table 3. Adsorption capacities of various adsorbents

Adsorbent	Homegeneous/heterogeneous	Adsorption capacity (mg · g ⁻¹)	Reference
Polymer	Heterogeneous	290	This study
Banana stem	Heterogeneous	91.74	12
Tin oxide gel	Heterogeneous	16.3	7
Sporopollenin	Heterogeneous	8.52	22
XAD-4 Copolymer resin	Heterogeneous	12.2	10
Macroreticular resins	Heterogeneous	2.05	23
Sargassum sp.	Heterogeneous	244	5
Polyethyleneimine	Homogeneous	120–470	24

Table 4. Langmuir, Freundlich and D-R isotherm constants

Langmuir		Freundlich		D-R	
Q° (mmol · g ⁻¹)	1.6958	K_F (mmol · g ⁻¹)	1.5157	q_m (mmol · g ⁻¹)	1.8503
b (L · mmol ⁻¹)	2949	N	16.23	k (mmol ² · kJ ⁻²)	5×10^{-10}
R^2	0.9942	R^2	0.9925	R^2	0.9999
				E (kJ · mol ⁻¹)	31.6
Δq	7.31%	Δq	2.51%	Δq	1.70%

capacity (mol · g⁻¹), C_e is the equilibrium lead (II) concentration in the solution (mol · L⁻¹), and k is a constant related to the adsorption energy (mol² · kJ⁻²). This adsorption model also allows for the calculation of the mean free energy of adsorption (E , kJ · mol⁻¹) from the D-R constant k using the following Equation (8):

$$E = (-2k)^{-0.5} \quad (8)$$

The parameter E provides some information about the mechanism of adsorption. If the magnitude of E is greater than 8 kJ · mol⁻¹, the process can be characterized as an ion-exchange mechanism. If the magnitude of E is less than 8 kJ · mol⁻¹, the adsorption process is physical in nature (33, 34). The mean free energy of adsorption of lead (II) onto poly(2-octadecyl-butanedioic acid) was determined to be 31.6 kJ · mol⁻¹, suggesting an ion exchange component to the adsorption mechanism. Similar adsorption energies were reported for carbon adsorbents obtained from brown coal (35). D-R isotherm constants are given in Table 4.

In order to compare the three isotherm equations, normalized standard deviations (Δq) for q_e for each isotherm were calculated (Table 4) using the following Equation (9):

$$\Delta q(\%) = 100x \sqrt{\frac{\sum[(q_e^{\text{exp}} - q_e^{\text{cal}})/q_e^{\text{exp}}]^2}{N - 1}} \quad (9)$$

where q_e^{exp} and q_e^{cal} are the experimental and calculated values for q_e , respectively and N is the number of different concentrations tested. While all three models generally described the behavior of the adsorption process, based on both the R^2 and Δq values, the Dubinin-Radushkevich isotherm model best predicted the behavior of lead (II) adsorption onto poly(2-octadecyl-butanedioic acid).

3.3 Thermodynamic Parameters

The Gibb's free energies for the adsorption process at various initial lead concentrations were determined using the following Equations (9) and (10):

$$K_c = \frac{C_A}{C_S} \quad (10)$$

$$\Delta G^\circ = -RT \ln K_c \quad (11)$$

where K_c is the equilibrium constant, C_A is the concentration (mg · L⁻¹) of lead (II) adsorbed at equilibrium, C_S is the

equilibrium concentration (mg · L⁻¹) of lead (II) remaining in solution. The large negative values obtained for the change in free energy (Table 5) suggest that this adsorption is spontaneous, and similar Gibb's free energies have been reported for the adsorption of lead on sea nodule residues (36) and siderite (37).

3.4 Effect of pH on Adsorption

The effect of pH on the removal of lead (II) was investigated in solutions with initial concentrations of 25 mg · L⁻¹, 200 mg · L⁻¹ and 2000 mg · L⁻¹ over the pH range of 3.0 to 5.0 at 22°C. Above pH 5.5, the lead solutions became cloudy due to the formation of lead (II) hydroxide. Plots of percent lead removed vs. time at various pH values (Figures 5a–c) and the amount of adsorbed solute at equilibrium, q_e , (Figure 6) indicate that, with the exception of a possible slight decrease in initial adsorption rates at 15 and 30 minutes for the 2000 mg · L⁻¹ solution and a possible decrease in the amount of adsorbed ion at equilibrium at pH 3 for the 2000 mg · L⁻¹ solution, the adsorption process is relatively insensitive to pH over this range for the initial concentrations tested. Since the carboxylic acid groups on the polymer exist as sodium carboxylate groups, rather than the free acid, the lack of pH sensitivity likely results from the release of sodium ions rather than hydrogen ions upon adsorption of the lead (II) ion.

3.5 Effect of Competing Cations on Lead Adsorption

Freshwater, groundwater, and industrial wastewater sources may contain high amounts of Na⁺ and Ca⁺². In order to determine the effectiveness of the adsorption of lead (II) ions by poly(2-octadecyl-butanedioic acid), both the binding of Na⁺ and Ca⁺² in the absence of competing ions and the binding of lead (II) in the presence of various concentrations of Na⁺

Table 5. Gibb's free energy and equilibrium constants

Initial [Pb ⁺²] mg · L ⁻¹	K_c	ΔG (kJ · mol ⁻¹)
	14.83	-6.50
100	23.97	-7.65
200	56.55	-9.72
500	50.54	-9.45
1000	66.66	-10.12
2000	123.76	-11.61

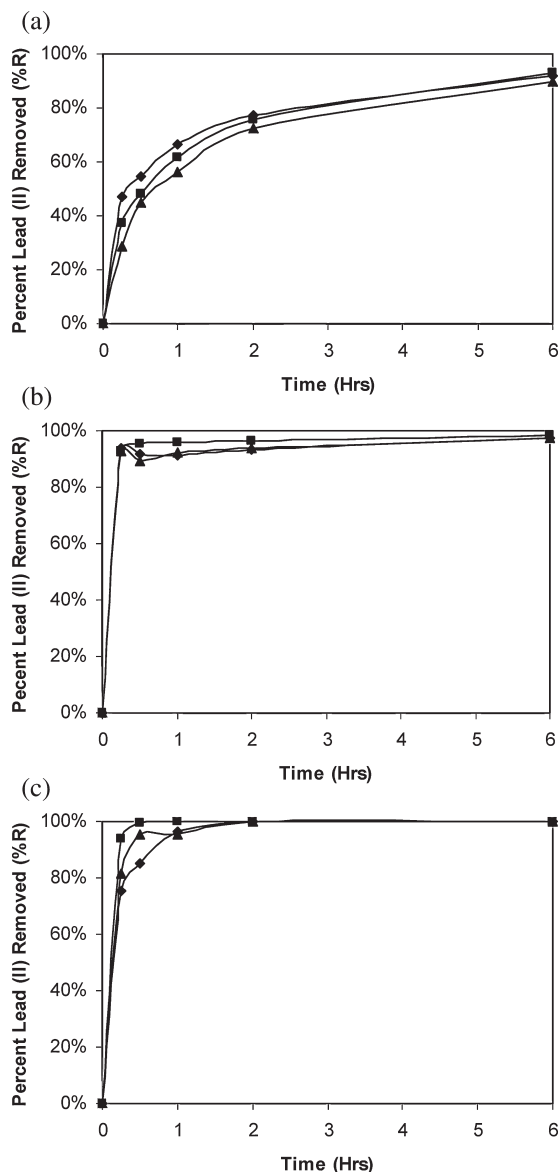


Fig. 5. (a) Binding kinetics for 25 mg · L⁻¹ lead (II) (initial) at 22°C and pH 3, 4, and 5. [◆ = pH 3, ■ = pH 4, ▲ = pH 5]; (b) Binding kinetics for 200 mg · L⁻¹ lead (II) (initial) at 22°C and pH 3, 4, and 5. [◆ = pH 3, ■ = pH 4, ▲ = pH 5]; (c) Binding kinetics for 2000 mg · L⁻¹ lead (II) (initial) at 22°C and pH 3, 4, and 5. [◆ = pH 3, ■ = pH 4, ▲ = pH 5].

and Ca⁺² were investigated. As shown in Figure 7, less than 10% of a 2000 mg · L⁻¹ Na⁺ solution was adsorbed after a 6 h incubation at 22°C. (This suggests that the majority of the carboxylic acid functional groups in the polymer exist as sodium carboxylates.) Additionally, the affinity of the polymer for Ca⁺² ions (33% adsorption after 6 h at 22°C) is substantially less than that observed for the corresponding lead (II) solution.

To determine the effect of Na⁺ and Ca⁺² on the adsorption of lead (II), the polymer was incubated with lead (II) solutions of various concentrations containing 200 mg · L⁻¹ or 2000

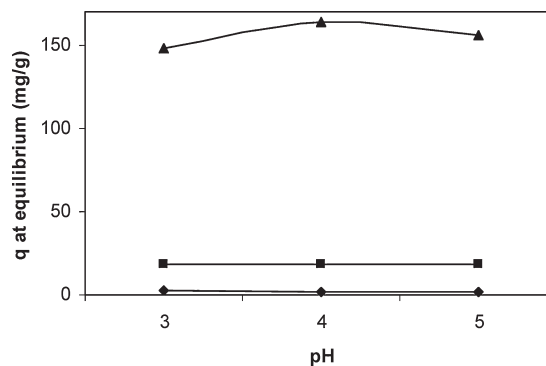


Fig. 6. Effect of pH on the adsorption of lead (II) at 22°C. [◆ = 25 mg · L⁻¹, ■ = 200 mg · L⁻¹, ▲ = 2000 mg · L⁻¹].

mg · L⁻¹ of Na⁺ or Ca⁺² for 6 h at 22°C. As shown in Figure 8, Na⁺ concentrations up to 2000 mg · L⁻¹ did not alter the adsorption of lead (II) onto poly(2-octadecyl-butanedioic acid). Similarly, Ca⁺² concentrations up to 2000 mg · L⁻¹ did not adversely impact the adsorption of either 25 mg · L⁻¹ or 200 mg · L⁻¹ lead (II) (Figure 8 a and b). However, 2000 mg · L⁻¹ Ca⁺² did reduce the adsorption of 2000 mg · L⁻¹ lead (II) by 28% (Figure 8c). These observations suggest that Ca⁺² is only able to interact with a limited number of adsorption sites on the polymer and that the adsorption to these sites is favored over lead (II). It has been reported that in the absence of spatial restrictions, divalent cations with low hydration energies are adsorbed preferentially on sorbents (38). The relative Gibbs free energies of hydration (39) for Pb⁺² (-1425 kJ · mol⁻¹) and Ca⁺² (-1505 kJ · mol⁻¹) in conjunction with the saturation of metal ion adsorption sites on the polymer may explain the observed competition at high concentrations of Pb⁺² and Ca⁺².

3.6 Desorption and Polymer Regeneration

Lead (II) ions adsorbed onto poly(2-octadecyl-butanedioic acid) were effectively desorbed with 2% trace metal grade

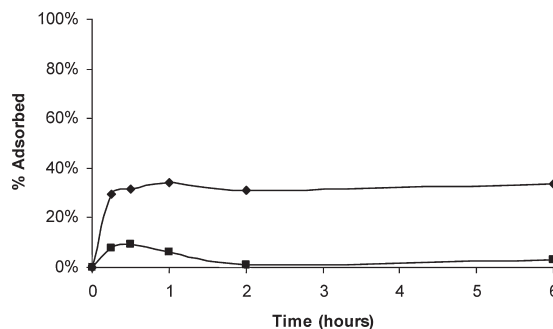


Fig. 7. Adsorption of Na⁺ and Ca⁺² onto poly(2-octadecyl-butanedioic acid) [■ = 2000 mg · L⁻¹ Na⁺, ◆ = 2000 mg · L⁻¹ Ca⁺²].

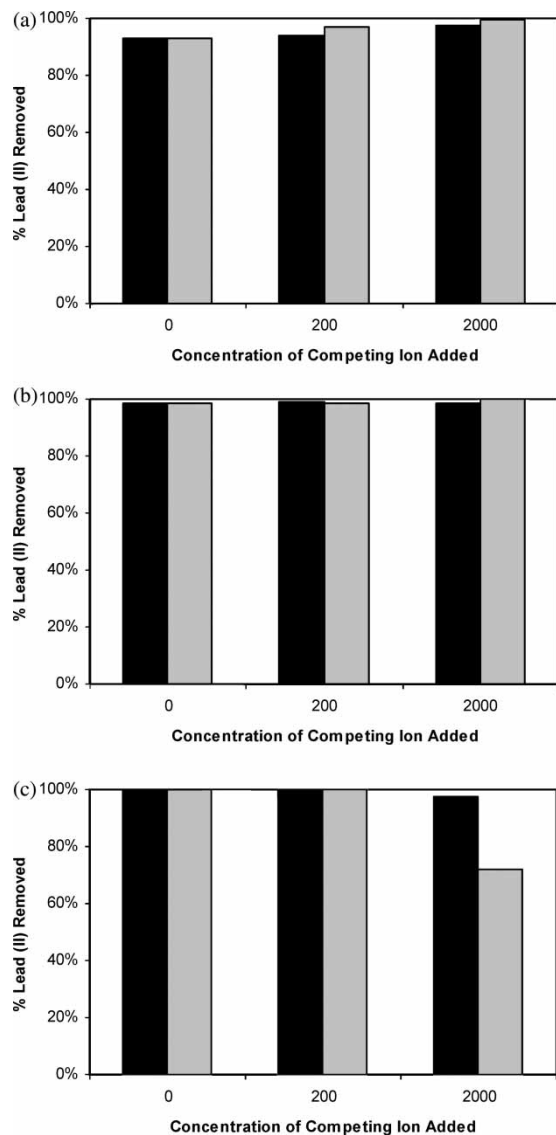


Fig. 8. (a) Effect of Na^+ and Ca^{+2} on the adsorption of $25 \text{ mg} \cdot \text{L}^{-1} \text{ Pb}^{+2}$ ($\blacksquare = [\text{Na}^+]$ in $\text{mg} \cdot \text{L}^{-1}$, $\blacksquare = [\text{Ca}^{+2}]$ in $\text{mg} \cdot \text{L}^{-1}$); (b) Effect of Na^+ and Ca^{+2} on the adsorption of $200 \text{ mg} \cdot \text{L}^{-1} \text{ Pb}^{+2}$ ($\blacksquare = [\text{Na}^+]$ in $\text{mg} \cdot \text{L}^{-1}$, $\blacksquare = [\text{Ca}^{+2}]$ in $\text{mg} \cdot \text{L}^{-1}$); (c) Effect of Na^+ and Ca^{+2} on the adsorption of $2000 \text{ mg} \cdot \text{L}^{-1} \text{ Pb}^{+2}$ ($\blacksquare = [\text{Na}^+]$ in $\text{mg} \cdot \text{L}^{-1}$, $\blacksquare = [\text{Ca}^{+2}]$ in $\text{mg} \cdot \text{L}^{-1}$).

HNO_3 . Percent recoveries (%R) of lead were calculated using the following expression:

$$\%R = \frac{\text{Concentration of lead ions desorbed to the elution solution}}{\text{Concentration of lead ions adsorbed onto the polymer}}$$

The ability to remove adsorbed metals from the polymer and the reusability of the adsorbing functional groups was demonstrated using successive adsorption/desorption trials with a $1000 \text{ mg} \cdot \text{L}^{-1}$ lead (II) solution (Figure 9).

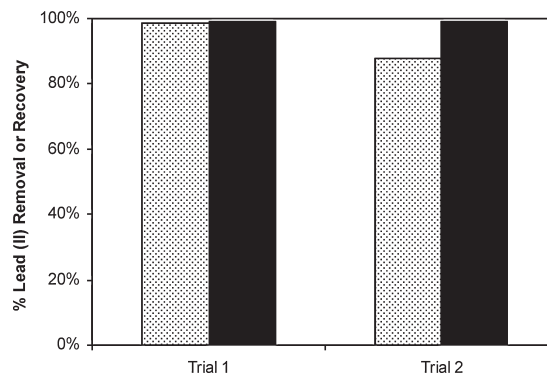


Fig. 9. Adsorption/desorption studies using $1000 \text{ mg} \cdot \text{L}^{-1} \text{ Pb}^{+2}$ and $2\% \text{ HNO}_3$ [$\blacksquare = \% \text{ removal}$, $\blacksquare = \% \text{ recovery}$].

4 Conclusions

Poly(2-octadecyl-butanedioic acid) exhibits novel heavy metal adsorption characteristics, as the adsorption capacity of this water insoluble polymer for lead (II) was substantially higher than other heterogeneous adsorbants and is equivalent to those obtained with homogeneous sorbants. Adsorption was rapid and spontaneous, and the ion-exchange behavior accurately predicted by the Dubinin-Radushkevich isotherm model.

5 Acknowledgments

The author thanks Drs. Steve Hendrix and Scott Allen (The University of Tampa) for comments on the manuscript and Dr. Hendrix for ICP-AES assistance. PA-18 was provided by Archimica Fine Chemicals, Inc.

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