

Poly[4-(4-vinylbenzyloxy)-2-hydroxybenzaldehyde] for Rapid Removal of Low Concentrations of Pb(II)

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ABSTRACT: Poly[4-(4-vinylbenzyloxy)-2-hydroxybenzaldehyde] was evaluated for removing low concentrations of lead(II) in ppb levels from aqueous media. The effects of the pH condition and the initial lead concentrations on removal were examined. It was found that the metal absorption is best described with the Langmuir model. The R_L values obtained between 0.01 and 0.23 indicate that favorable absorption occurs in the studied concentration ranges. The kinetic study revealed that the

metal removal proceeds at a very fast pace—less than 30 s—to reach the maximum capacity. The data fit the description of pseudo-second-order rate. The dynamic column study for real-time practical absorption also was investigated. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2096–2102, 2009

Key words: salicylaldehyde; chelating polymer; heavy metal removal; lead complex

INTRODUCTION

The mitigation of impact from environmental toxins is an important task in the effort to reduce mortality from various diseases and cancers. Heavy metal contamination due to mining, manufacturing, and disposal poses serious hazards to public health and ecosystems. Chronic exposure to contaminated air and water is harmful even in low concentrations. Among them, lead(II), for example, can lead to nerve damage in children and kidney damage as well as high blood pressure in adults. The contaminated drinking water is a particular concern. There is no known function of lead in the human biological system. Humans receive about 15–20% of their total Pb intake from drinking water.¹ The EPA sets the action level at 15 $\mu\text{g}/\text{L}$ and the maximum contaminant level goal (MCLG) for Pb in tap and drinking water at zero, in recognition of deleterious health effects from low Pb concentration distribution.²

The excessive Pb level in tap water in urban areas originates from corrosion of household plumbing systems. Replacing the old Pb-containing water piping system has an enormous cost issue, considering

the fact that there are too many houses still equipped with old piping systems. It is imperative to develop an alternative and cost-effective method to remove Pb(II) without overhauling the entire system. Recently, there has been an increasing interest in effective removal materials for a point-of-use device to remove low concentrations of lead from drinking water.³

Chelating polymers have been intensively studied for metal complexation, and such polymers may also hold a key to desirable materials for the low lead removal. Salicylaldehyde is a well-known bidentate ligand, and its chelating capability has been manifested with various metal ions including alkaline earth metal, transition metal, and heavy metal ions.^{4–8} It is a building block for other types of ligands for metal chelating as well.^{9–11} Salicylaldehyde is capable to chelate Pb(II) to form $\text{Pb}(\text{O})_4$ coordination chromophore core.^{12–14} Here we disclose results of low lead removal by poly[4-(4-vinylbenzyloxy)-2-hydroxybenzaldehyde], PVBH. Adsorption capacity, pH dependence, concentration dependence, and kinetics were studied for the removal. Finally, dynamic column for the removal also was evaluated.

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MATERIALS AND METHODS

Material synthesis

All chemicals and solvents were purchased and used as received unless indicated otherwise. For air- or moisture-sensitive reactions, solvents were

distilled under nitrogen using the following methods: tetrahydrofuran (THF) was dried from sodium/benzophenone ketyl, methylene chloride was distilled from calcium hydride, and 2,2'-azobis(isobutyronitrile) (AIBN) was purified by recrystallization from methanol.

4-(4-Vinylbenzyloxy)-2-hydrobenzaldehyde was prepared according to the literature method with a slight modification.¹⁵ Into 100 mL of dry DMF containing 5.00 g (0.036 mol) of 2,4-dihydroxybenzaldehyde was added 3.04 g (0.036 mol) of sodium bicarbonate at room temperature, followed by dropwise addition of 5.1 mL (0.036 mol) of 4-vinylbenzyl chloride at 0°C over a period of 5 min. The mixture was then heated at 100°C for 3 h. Upon work-up, the solvent was removed and the viscous crude product was obtained quickly, solidified, and was then recrystallized from ethanol to give the pure product. Yield was 72%; pale brown solid; mp. 95–96°C (lit: 99–101°C). ¹H-NMR (400 MHz, CDCl₃, ppm) 11.47 (1H, s), 10.38 (1H, s), 7.40 (1H, d, J = 8 Hz), 7.37 (1H, d, J = 6.8 Hz), 6.76–6.69 (1H, m, J = 10.8 Hz), 6.63 (1H, d, J = 8.8 Hz), 6.58 (1H, d, J = 11.2 Hz), 6.51 (1H, s), 5.78 (1H, d, J = 17.6 Hz), 5.28 (1H, d, J = 10.8 Hz), 5.10 (2H, s). GC-MS m/z: 254(M⁺). Anal. Calcd. for C₁₆H₁₄O₃: C, 75.57; H, 5.55; Found; C, 76.14; H, 5.58.

PVBH was synthesized according to Ref. 15, with a slight modification.¹⁵ Briefly, 10.0 g (0.039 mol) of the monomer and 0.051 g (0.304 mmol) of AIBN was charged into a 100 mL, pear-shaped flask under argon. The flask was vacuum-flushed one more time prior to addition of 70 mL of dry THF. The mixture was subjected to the standard freeze-thaw technique three times and then stirred at 60°C for 48 h. The resulting viscous solution was diluted with 100 mL of CHCl₃. The mixture was then transferred dropwise into 800 mL of methanol, forming a white solid that was filtered under vacuum. The crude product was dissolved in 100 mL of CHCl₃ and reprecipitated in 1000 mL methanol (twice). The pale white powder formed was filtered and dried. ¹H-NMR (400 MHz, CDCl₃, ppm) 11.48 (1H, s), 10.38 (2H, d), 9.65 (1H, s), 7.77 (2H, d), 7.36–7.07 (3H, m), 6.53 (s, CH₂—CH), 4.93 (2H, s).

Instrumentation

All ICP-MS measurements were carried out with an ICP-MS spectrometer (ELAN DR-e) equipped with an AS-90 autosampler, a cross-flow nebulizer, and a 4-channel peristaltic pump (Pump 1). Pump 1 was used for introduction of carrier solution (0.65% nitric acid) as well as spray chamber draining. Platinum sampler and skimmer cones were used throughout the experiments. All concentration determinations were duplicated under identical conditions using

this instrument. The values reported are averages of two determinations. The deviations are usually less than 3%.

Standard and stock solutions

All reagents used were of analytical grade unless indicated otherwise. All solutions were prepared with distilled de-ionized water (18 MΩ/cm) from a Milli-Q analytical reagent-grade water purification system. Calibration standard solutions and internal standards were prepared from commercial metal standard solutions (Spex Plasma, Fisher Scientific, Pittsburg, PA). Optimal grade nitric acid (Fisher) was used as acid for the preparation of all calibration standards solutions and analytical solutions.

Standard working solutions of lead were prepared from a 1000-mg/L standard solution (Titrisol, Merck, Darmstadt, Germany), and internal standard was added (10 μg/L) to all of the working standard solutions to ensure sensitivity and accuracy and, most importantly, to eliminate interferences. The pH measurements were made on a digital pH meter (Beckman, Fullerton, CA) equipped with a combined pH electrode. Before measurements the pH meter was calibrated with the buffers of 4, 7, and 10. A Burrell Wrist Action shaker was used as the shaking device for the batch experiments.

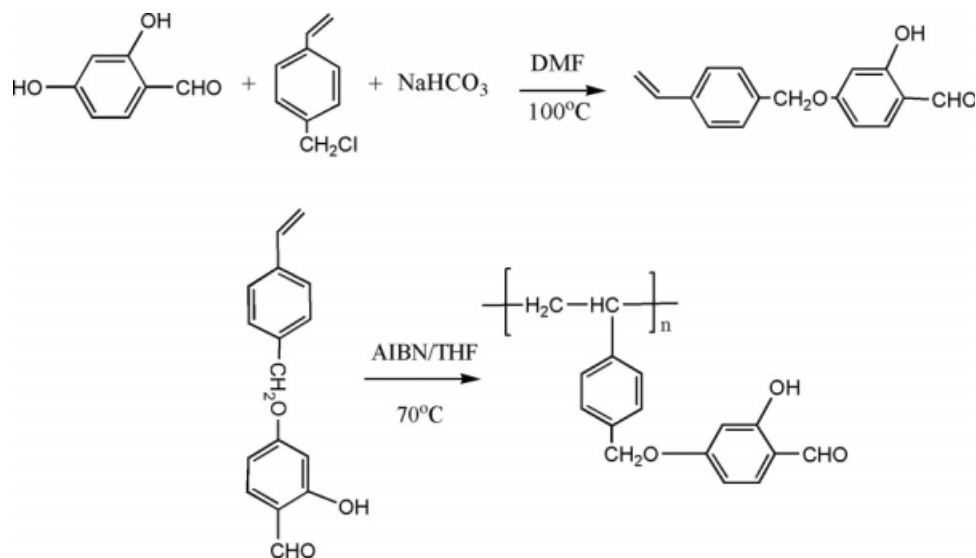
Stock solutions of lead were prepared using analytical grade nitrate salt (99.99% purity). Solutions of varying initial concentrations were prepared from a 1000-mL stock solution of 1000 mg/L in 2% nitric acid by serial dilution using distilled de-ionized water in 2% nitric acid.

Adsorption equilibrium

Equilibrium sorption studies were performed in the initial lead concentration in the ranges of 50–1000 μg/L. The adsorbent (50 mg) was equilibrated separately with 25-mL aliquots of lead solutions of different concentrations. The suspensions together with blank lead solutions were shaken on a mechanical shaker at 25°C for 2 h. The suspensions were filtered through Whatman filter paper (no. 42), and the filtrates were then analyzed for lead ion concentration using ICP-MS.

Adsorption kinetics

Three different concentrations (89.7, 261.8, and 437.1 ppb, determined by ICP) were used for kinetic studies. In each case, 0.025 g of the adsorbent polymer was treated separately with 12.5 mL aliquots at different time intervals between 5 and 10 s for a given concentration. The suspensions were filtered and the concentration of the filtrate was analyzed by ICP-MS.



Scheme 1 Synthesis of the chelating polymer.

Column adsorption experiment

Column adsorption experiment was performed using a 0.5×10 cm glass column packed with 0.20 g of the polymer. A lead solution (91.5 $\mu\text{g/L}$, pH 5.5) was passed through the column at a flow rate of 1.0 mL/min. The solution that was passed through the column was fractionated in 10-mL portions at regular intervals, and the concentration of lead was determined by ICP-MS.

RESULTS AND DISCUSSION

Synthesis

The synthesis of the precursor and the polymer is outlined in Scheme 1. The use of pure 4-vinylbenzyl chloride to react with 2,4-dihydroxybenzaldehyde gave the precursor, 4-(4-vinylbenzyloxy)-2-hydroxybenzaldehyde in 74% yield. This result is in marked contrast to that from the use of a mixture of 3- and 4-vinylbenzyl chloride isomers, which led to 17% yield for the desirable product.¹⁵

4-(4-Vinylbenzyloxy)-2-hydroxybenzaldehyde was polymerized using a radical initiation process.¹⁵ The obtained polymer showed that the vinyl proton signals at δ 5.31 ppm, δ 5.80 ppm, and δ 6.80 ppm in the precursor disappeared. The presence of hydroxyl and formyl groups was shown at δ 11.48 ppm and δ 10.38 ppm, respectively. The polymer is insoluble in aqueous media.

Effect of pH on lead uptake

The pH effect was examined in the pH range of 1.0–5.5. The desirable acidity was adjusted by the use of diluted nitric acid. It was found that the adsorption capacity is highly dependent on pH (Fig. 1). When

this is translated into the removal efficiency, the removal efficiency dependence is more obvious: at the low pH medium, less than 5% of Pb is removed. As the pH increases, so does the removal efficiency. At the intrinsic pH value of the solution, which is ca. 5.5, the removal efficiency reaches 99%. The carbonyl group is known to accept proton at strong acidic condition. This competitive protonation of carbonyl groups at the low pH media diminishes its chelating capability for the metal because the positively charged $\text{C}=\text{OH}^+$ induces an electrostatic repulsion to prevent the metal from approaching the chelating sites. In the nonprotonating condition at pH of 5.5, the free carbonyl becomes a part of effective chelating entity, and the removal becomes highly efficient.

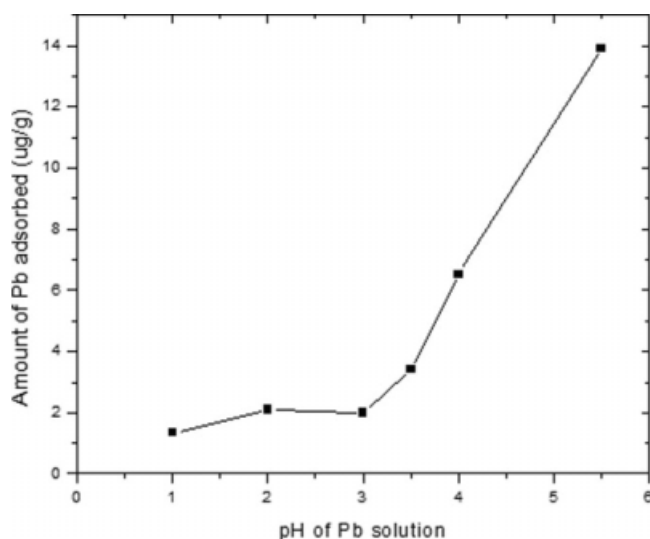


Figure 1 Effect of pH on the lead adsorption from solution on the polymer (lead ion concentration: 27.9 $\mu\text{g/L}$; polymer adsorbent: 25 mg).

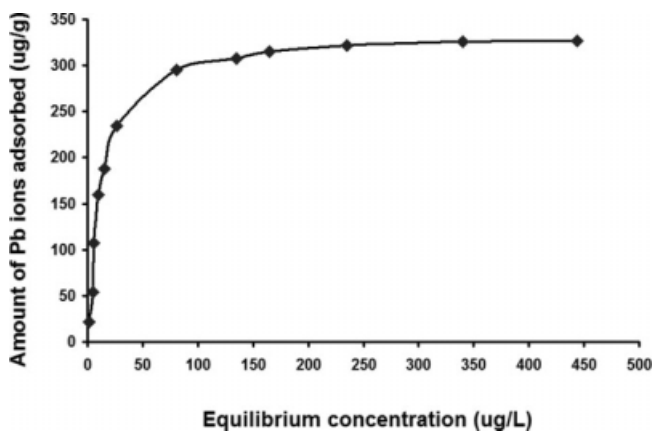


Figure 2 Effect of concentration on lead ion adsorption onto polymer.

This pH also ensures the Pb(II) ion to prevail in solution because it is known that the pH condition changes the nature of metal species in solution. Usually, other ion species emerge as the pH goes up.¹⁶ At pH of 6, for example, lead exists in a mixture of Pb(OH)⁺ and Pb²⁺ instead of Pb(II) only.¹⁷ For this consideration, pH of 5.5 is the pH condition used for all the other experiments as well.

Effect of lead concentrations on adsorption

The effect of Pb concentrations on adsorption was studied in the range between 44 and 1150 ppb at pH of 5.5. The equilibrium concentrations were obtained after 2 h of contact time. The plot of equilibrium concentration against adsorption capacity shown in Figure 2 indicates two distinct processes. First, the adsorption is a function of the initial concentration, but this concentration-dependent adsorption is only valid to a certain extent. Then, the adsorption reaches the maximum adsorption capacity, becoming a concentration-independent process. It was apparent that the adsorption saturation was reached within the studied concentration ranges.

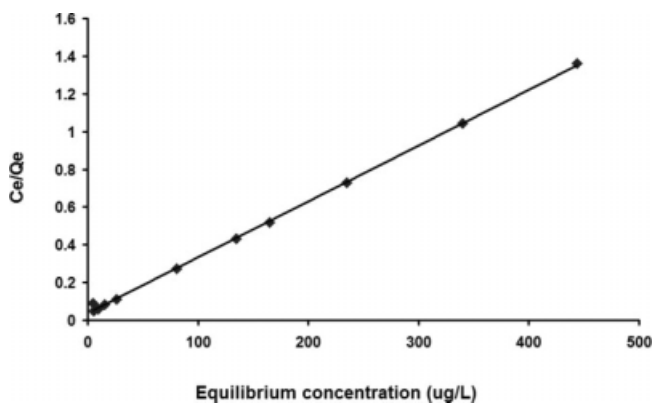


Figure 3 Langmuir plot for the adsorption of lead ions on polymer.

TABLE I
R_L Values from Various Initial C_is

C _i (μg/L)	R _L
44.37	0.23
112.91	0.10
219.47	0.06
329.28	0.04
391.72	0.03
494.99	0.02
672.52	0.02
734.84	0.02
797.48	0.02
879.45	0.01
993.07	0.01
1097.05	0.01
1151.13	0.01

The data were analyzed using two models to determine type of adsorption isotherm. One is the Langmuir isotherm model,¹⁸ defined as $C_e/Q_e = 1/(bQ_{max}) + C_e/Q_{max}$, where Q_e is the amount of lead ions adsorbed per unit weight of the polymer (μg/g) at equilibrium concentration, derived experimentally from $Q_e = (C_i - C_e)V/m$. C_i and C_e are the initial and equilibrium concentrations of metal ion in solution (μg/L), m is the mass of the adsorbent (g), and V is the volume of the sample solution (L). Q_{max} is the maximum adsorption at monolayer coverage (μg/g) and b is the Langmuir adsorption equilibrium constant (L/μg). A plot of C_e/Q_e versus C_e gave a straight line of slope for $1/Q_{max}$ and an intercept for $1/bQ_{max}$ (Fig. 3), from which the values of Q_{max} and b are deduced. A good fitness with the Langmuir model was manifested with the correlation coefficient of greater than 0.99. The maximum adsorption capacity Q_{max} was determined to be 333.3 μg/g.

One main aspect of a Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter, $R_L \times R_L = 1/(1 + bC_e)$. $R_L > 1$ is defined as unfavorable, $R_L = 1$ as linear, $0 < R_L < 1$ as favorable, and $R_L = 0$ as irreversible absorption,

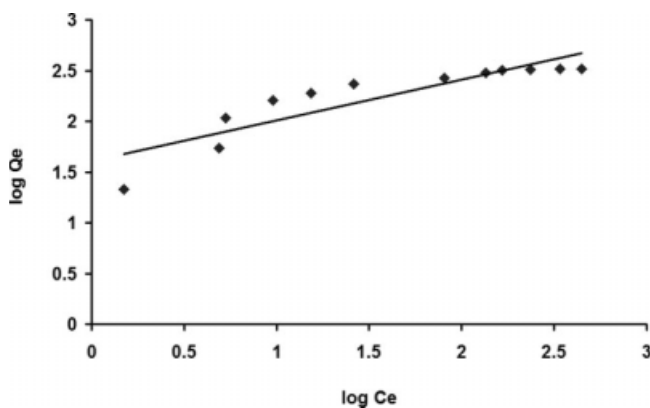


Figure 4 Freundlich plot for the adsorption of lead ions on polymer.

TABLE II
Langmuir and Freundlich Parameters for Adsorption

Langmuir model		
K	$1/n$	R^2
40.37	0.401	0.792
Freundlich model		
Q_m ($\mu\text{g/g}$)	B ($\text{L}/\mu\text{g}$)	R^2
333.3	0.077	0.993

respectively.^{19,20} The R_L values calculated from the equilibrium concentrations are listed to correspond to different initial Pb concentrations (C_i) in Table I, showing that favorable adsorption of lead took place in all the concentrations studied.

The data were assessed with the Freundlich isotherm, using the expression of $\log Q_e = 1/n \log C_e + \log K$, where K and $1/n$ are Freundlich constants, corresponding to the sorption capacity and sorption intensity, respectively.²¹ C_e is the equilibrium sorbate concentration in aqueous solution ($\mu\text{g/L}$) and Q_e is the sorption capacity ($\mu\text{g/g}$). Data from the Freundlich plot (Fig. 4) obtained by plotting $\log Q_e$ against $\log C_e$ are compiled in Table II, along with those from the Langmuir isotherm. The comparison of the correlation coefficients clearly indicates that the Langmuir model is the better one for description of adsorption isotherm, implying possible monolayer coverage of Pb(II) on the surface of the chelating polymer.

Effect of concentration on rates of adsorption

The kinetic behavior of lead uptake by the polymer was investigated at the pH of 5.5 in the concentration range of 89.7–437.1 $\mu\text{g/L}$. One of the characteristics emerging from the plots of Q_t , adsorption capacity at time t against time t for varying initial concentrations, is fast adsorption property. From all the three concentrations studied, the equilibrium is achieved within almost 30 s (Fig. 5). Furthermore, on close examination, the time for reaching equilibrium is even shorter for concentrations of 89.7 and 261.8 $\mu\text{g/L}$, only 15 and 20 s, respectively.

The fast equilibrium property from the present chelating polymer is complementary to those reported from various systems for the heavy metal removal. Several systems have been reported to have equilibrium achieved from 2 to 72 h.^{22–24} The

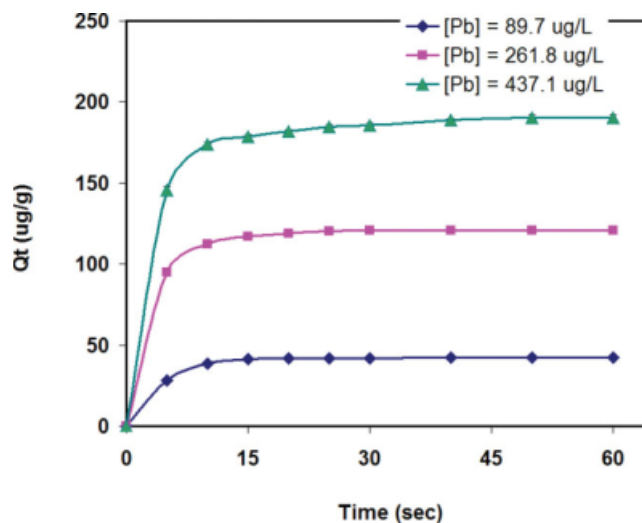


Figure 5 Amounts of lead ions adsorbed onto polymer at various initial concentrations with time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

short equilibrium adsorption time between 15 and 30 min has been observed for PEI-coated silica gel and ligands-modified gel beads.^{25,26} Biomass such as sawdust has also been reported to have a short equilibrium time of 2–10 min.²⁷ Since the equilibrium time is an important factor in practical systems, fast equilibrium is a desirable property for cost-effective application.

The adsorption rate was analyzed using two different kinetic models, namely the pseudo-first-order and the pseudo-second-order equations.^{28–30} The rate expression known as the Lagergren first-order equation is expressed as $\log(Q_e - Q_t) = \log Q_e - k_1 t / 2.303$, where k_1 (s^{-1}) is the rate constant of pseudo-first-order adsorption, Q_e ($\mu\text{g/g}$) is the amount of metal ion sorbed at equilibrium, and Q_t ($\mu\text{g/g}$) is the amount of metal ion sorbed at time t (s). The value of k_1 was determined experimentally by the slope of the linear plots of $\log(Q_e - Q_t)$ versus t . This approach led to low correlation coefficient values (Table III), indicating that the absorption less likely proceeds in this model.

A pseudo-second-order reaction is guided by the following expression: $t/Q_t = 1/(k_2 Q_e)^2 + t/Q_e$, where Q_e ($\mu\text{g/g}$) is the amount of metal ion sorbed at equilibrium, Q_t ($\mu\text{g/g}$) is the amount of metal ion on

TABLE III
Kinetic Parameters for Metal Adsorption

C_i ($\mu\text{g/L}$)	First order		Second order			
	k_1 (s^{-1})	R^2	k_2 , $\text{g}/(\text{s } \mu\text{g})$ [$\text{g}/(\text{min } \text{mg})$]	Q_e ($\mu\text{g/g}$)	R^2	
89.7	0.0721	0.772	0.01529 [9.17×10^2]	43.86	0.999	
261.8	0.0958	0.841	0.0852 [5.11×10^2]	123.46	0.999	
437.1	0.0677	0.863	0.0342 [2.05×10^2]	196.07	0.999	

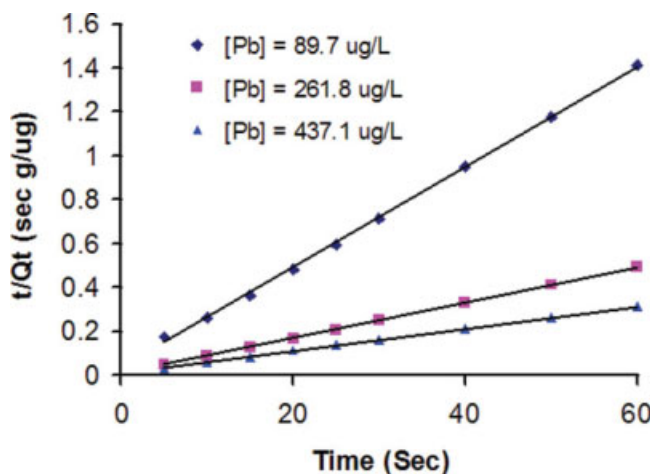


Figure 6 Second-order kinetic plot for the sorption of lead ions on polymer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the surface of the sorbent at time t (s), and k [$\text{g}/(\mu\text{g s})$] is the rate constant of pseudo-second-order adsorption. The values of $1/(k_2 Q_e)^2$ and $1/Q_e$ are derived experimentally from the intercept and slope of the linear plots of t/Q_t versus t , which eventually leads to values of k_2 and Q_e (cal) (Fig. 6). The obtained high correlation coefficients indicate that the adsorption indeed follows this pseudo-second-order kinetic model. Parameters derived from this approach are listed in Table III. Again, the fast adsorption process is manifested by fast kinetics with very large rate constants.

The fast equilibrium and large kinetic rate result from two factors. One is easy access by metal ions to the chelating units, and the other is fast complexation. The fast kinetics suggest that it is likely that the chelating polymer has most of their chelating groups on or near the surface for easy access. Once the metal ions reach the surface, the fast chelating process allows the chelating groups to quickly take in the metal ions. Lead ions are likely to form $\text{Pb}(\text{O})_4$ with oxygen-based ligands.¹²⁻¹⁴ As a bidentate ligand, salicylaldehyde units on or near the surface could form two kinds of lead complexes upon interacting with the metal ion. One has 1 : 1 ratio of lead ion to the ligand [Fig. 7(II)], and the other has 1 : 2 ratio of lead ion to the ligand [Fig. 7(I)]. The metal

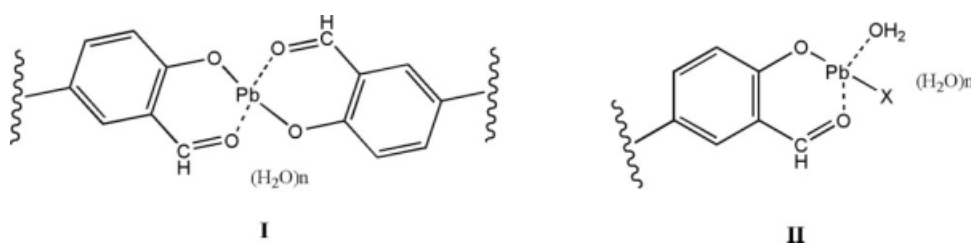


Figure 7 Two possible coordination modes for Pb(II).

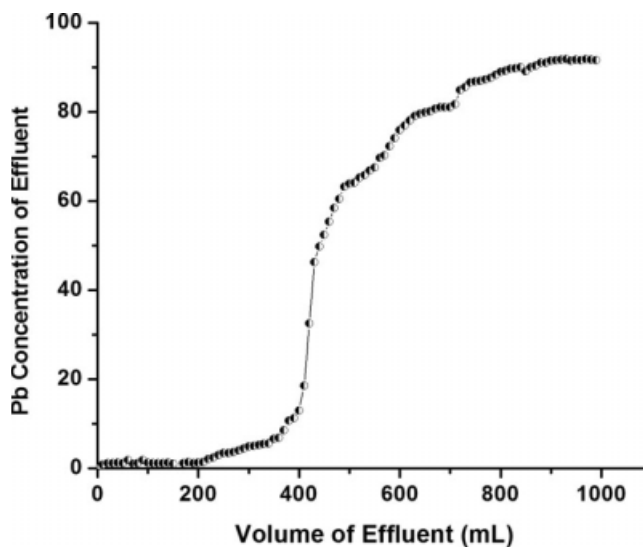


Figure 8 Column adsorption profile.

center in the former one is compensated with a water molecule and a counter ion to satisfy the coordination core chromophore. More water molecules could add to axial positions in both configurations.

Dynamic column adsorption

The chelating polymer as stationary phase in a packed column for lead ion uptake from aqueous solution was carried out using a solution with concentration of $91.5 \mu\text{g}/\text{L}$ at pH 5.5. The lead concentrations of series of eluents collected successively as 10-mL fractions were monitored by ICP-MS for a total elution of 1000 mL at the flow rate of 1 mL/min upon passing through a standing micro-column of internal diameter 0.5 cm, which was packed with 0.25 g of the chelating polymer.

Figure 8, a plot of effluent concentration vs. volume of effluent, shows that almost all the lead contents are removed when the first 200 mL of the lead solution are passed through the column. This high efficiency is only possible for materials with fast kinetics and fast complexation properties. Since it only requires 30 s at most to reach equilibrium for the chelating polymer, such short equilibrium time facilitates Pb(II) ions to complete equilibrium during mobile contact. Thus, without a need of concern

about equilibrium, the removal is more related to site availability. As more solution passes, more chelating sites are occupied and fewer chelating sites become available. Accordingly, further passing of an additional 200 mL of lead solution resulted in the removal of almost 90% of lead contents. The breakthrough volume is estimated to be ca. 500 mL, based on a polynomial fit of data ($R^2 = 0.962$). This is the volume of column effluent where the ratio of the effluent to influent concentration of a metal ion is equal to 0.5.³¹ It is worth mentioning that the chelating polymer can be recovered. The adsorption takes place when the polymer is treated with 0.1N HCl solution.

SUMMARY

This study presents the results of using a salicylaldehyde-based chelating polymer for removing low concentration of lead(II) from aqueous media. It was found that the metal absorption follows the Langmuir model. The R_L values have been determined, indicating the favorable absorption in a wide range of concentrations. The kinetic study revealed that the metal removal proceeds at a very fast pace—less than 20 s—to reach the maximum capacity. The data fits the description of pseudo-second-order rate. The dynamic column study for real-time practical absorption was investigated for effectiveness of the removal in stationary phase.

References

1. U.S. Environmental Protection Agency. Methods for the Determination of Metals in Environmental Samples, EPA 600-R-94/111; US EPA: Washington, DC, 1994.
2. U.S. Environmental Protection Agency. Drinking water regulations and health advisories, EPA 822-R-96-001; US EPA: Washington, DC, 1996.
3. Sublet, R.; Simonnot, M.-O.; Boireau, A.; Sardin, M. *Water Res* 2003, 37, 4904.
4. Chen, Q. *Acta Crystallogr Sect E* 2006, 62, m56.
5. Yu, Q.; Li, C.-Y.; Yang, X.-E.; He-Dong, B.; Liang, H. *Acta Crystallogr Sect E* 2006, 62, m391.
6. Papadopoulos, C. D.; Lalia-Kantouri, M.; Jaud, J.; Hatzidimitriou, A. G. *Inorg Chim Acta* 2007, 360, 3581.
7. Zhang, S.-H.; Li, G.-Z.; Feng, X.-Z.; Liu, Z. *Acta Crystallogr Sect E* 2007, 63, m1319.
8. Prasad, R. N.; Agrawal, M.; Ratnani, R.; Raju, K. *J Indian Chem Soc* 2005, 82, 1003.
9. Liang, S.; Bu, X. R. *J Org Chem* 2002, 67, 2702.
10. Liang, S.; Van Derveer, D.; Qian, S. Y.; Sturgeon, B.; Bu, X. R. *Polyhedron* 2002, 21, 2021.
11. Colon, M. L.; Qian, S. Y.; Vanderveer, D.; Bu, X. R. *Inorg Chim Acta* 2004, 67, 2702.
12. Tajima, Y. A. U.S. Pat. 4,226,792 (1980).
13. Gopinathan, C.; Pandit, S. K. *Indian J Chem* 1973, 11, 1069.
14. Mandal, S. K.; Nag, K. *J Org Chem* 1986, 51, 3900.
15. Kamogawa, H.; Sugiyama, K.; Hanawa, H.; Nanasawa, M. *J Polym Sci Polym Chem Ed* 1976, 14, 511.
16. Wan Ngah, W. S.; Endud, C. S.; Mayanar, R. *React Funct Polym* 2002, 50, 181.
17. Stumm, W.; Morgan, J. J. *Aquatic Chemistry*; Wiley: New York, 1996.
18. Langmuir, I. *J Am Chem Soc* 1916, 38, 2221.
19. McKay, G.; Blair, H. S.; Garden, J. R. *J Appl Polym Sci* 1982; 27: 3043.
20. Cooney, D. O. *Adsorption Design for Wastewater Treatment*; CRC Press LLC: Boca Raton, FL, 1999.
21. Freundlich, H. M. F. *Zeitsch Phys Chem* 1906, 57, 385.
22. Wang, C. C.; Chen, C. Y. *Macromol Chem Phys* 2001, 202, 882.
23. Reed, N. E.; Matsumoto, M. R. *Sep Sci Technol* 1993, 28, 2179.
24. Egawa, H.; Nakayama, M.; Nonaka, T.; Sugihara, E. *J Appl Polym Sci* 1987, 33, 1993.
25. Denizil, A.; Senel, S.; Alsancak, G.; Tüzman, N.; Say, R. *React Funct Polym* 2003, 55, 121.
26. Delacour, M. L.; Gailliez, E.; Bacquet, M.; Morcellet, M. *J Appl Polym Sci* 1999, 73, 899.
27. Taty-Costodes, V. C.; Fauduet, H.; Porte, C.; Delacroix, A. *J Hazard Mater* 2003, 105, 121.
28. Ho, Y. S.; McKay, G. *Process Biochem* 1999, 34, 451.
29. Allen, J. A.; Brown, D. A. *J Chem Technol Biotechnol* 1995, 62, 17.
30. Hullebusch, E. D.; Zandvoort, M. H.; Lens, P. L. *J Chem Technol Biotechnol* 2004, 79, 1219.
31. Oh, M.; Tshabalala, M. A. *Bioresources* 2007, 2, 66.