



The fast removal of low concentration of cadmium(II) from aqueous media by chelating polymers with salicylaldehyde units

Prince Addy Amoyaw, Myron Williams, Xiu R. Bu*

Department of Chemistry, Clark Atlanta University, Atlanta, GA 30314, USA

ARTICLE INFO

Article history:

Received 25 November 2008

Received in revised form 1 May 2009

Accepted 5 May 2009

Available online 15 May 2009

Keywords:

Heavy metal removal

Cadmium

Salicylaldehyde

Chelating polymer

4-Vinylbenzyl

ABSTRACT

Poly[4-(4-vinylbenzyloxy)-2-hydrobenzaldehyde], PVBH, a salicylaldehyde chelating functional group-based polymer has been found to be capable of the removal of low concentration of cadmium metal ion in ppb level from aqueous media. The adsorption fits best with the Langmuir model, indicating the monolayer coverage of the metal ion on the surface of chelating polymer. The R_L values have indicated the favorable adsorption in the range of all the ppb concentrations studied. The kinetic study has revealed a very fast adsorption process with the rate following the pseudo-second-order.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Cadmium is a toxin of environmental concern. The impact for non-cancer causes includes kidney, liver, and lung damage [1]. It is also classified as a probable human carcinogen for lung cancer. The association of cadmium with hormone-related cancers such as prostate and breast cancers has been actively investigated since the initial implication [2–4].

There is no known function of cadmium in the human biological system. The presence of such foreign metal ion in the human is likely a result of various exposures. In addition to direct exposure from air and drinking water, another potential exposure is to result from crops grown in the contaminated water and soil environment, which transports the metal into food chain where cadmium is accumulated in various parts of crops [5]. Electroplating, nickel–cadmium battery production and disposal, fossil fuels, pigments, fertilizers, certain electronic components are all potential sources of contamination to water [6].

The removal of heavy toxic metal from water has been explored with the use of solid support materials including activated carbon, metal oxides, silica and ion-exchange resins in addition to precipitation with bases (such as lime) and sulfides [7–10]. Bio-adsorbents have been also studied for the removal including plants, fruit components, rice polish, and various seeds [11–17]. The solid support materials furnished with ligands have received an increasing interest because of the defined chelating groups and the dedicated

ligand–metal complexation mechanism. Recently, we have set out to investigate salicylaldehyde-based polymers. Salicylaldehyde is a ligand with manifested chelating capability for various metal ions including alkaline earth metal, transition metal, and heavy metal ions [18–22]. It is an important building block for many other types of ligands for metal chelating as well [23]. The use of such ligands for metal removal would provide an insight into the design of better solid support materials. The present study is focused on the salicylaldehyde-containing chelating polymer PVBH (Fig. 1) and particularly on its capability and kinetic properties for removal of low concentration of cadmium from aqueous media.

2. Materials and methods

2.1. Instrumentation

All ICP-MS measurements were carried out with an ICP-MS spectrometer (ELAN DR-e) equipped with an AS-90 auto sampler, a cross flow nebulizer and a 4-channel peristaltic pump (pump 1), which 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. Each experiment was duplicated under identical conditions using this instrument for concentration determination.

2.2. Materials and standards

The chelating polymer, PVBH was prepared according to a published procedure [24].

* Corresponding author. Tel.: +1 404 880 6897; fax: +1 404 880 6890.
E-mail address: xbu@cau.edu (X.R. Bu).

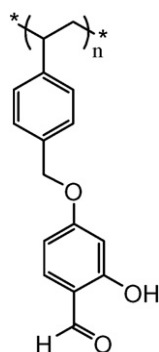


Fig. 1. Structure of the chelating polymer, PVBH.

All reagents used were of analytical-grade unless indicated otherwise. All laboratory wares used for analytical determination were cleaned first by trace metal grade nitric acid and hydrochloric acid, followed by repeated rinsing with de-ionized water. All the solutions were prepared with distilled de-ionized water ($18 \text{ M}\Omega \text{ cm}^{-1}$) 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). Optimal grade nitric acid (Fisher) was used as acid for the preparation of all the calibration standard solutions and analytical solutions.

Standard working solutions of cadmium were prepared from 1000 mg/L standard solution (Titrisol, Merck), and internal standard was added ($10 \mu\text{g/L}$) to all of the working standard solutions. The pH measurements were made on a digital pH meter (Beckman) equipped with a combined pH electrode. The 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 cadmium 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.

2.3. Batch equilibrium adsorption experiment

The initial cadmium concentrations used in equilibrium study are in the range of 50–1000 $\mu\text{g/L}$. At pH of 5.5, a series of batches of adsorbents (50 mg each) was equilibrated separately with 25 mL aliquots of cadmium solutions of different concentrations. The suspensions together with blank solutions were shaken on a mechanical shaker at 25°C for 2 h, and then filtered through Whatman filter paper (no. 42). The filtrates were then analyzed using ICP-MS.

2.4. Kinetic adsorption experiment

The kinetic study uses three different concentrations (86.9, 284.3, 505.4 ppb) at pH of 5.5. Data acquisition protocol includes the treatment of a series of 25 mg of the adsorbent polymer with 12.5 mL aliquots each for a given concentration, followed by shaking and separation (quenching). These series of samples are quenched at a different time intervals between 5 and 10 s by filtration. The concentrations of the filtrate were analyzed by ICP-MS.

3. Results and discussion

3.1. Adsorption isotherms

The initial Cd(II) concentrations in the range of 100–2000 $\mu\text{g/L}$ have been used for investigation of the adsorption isotherm. The

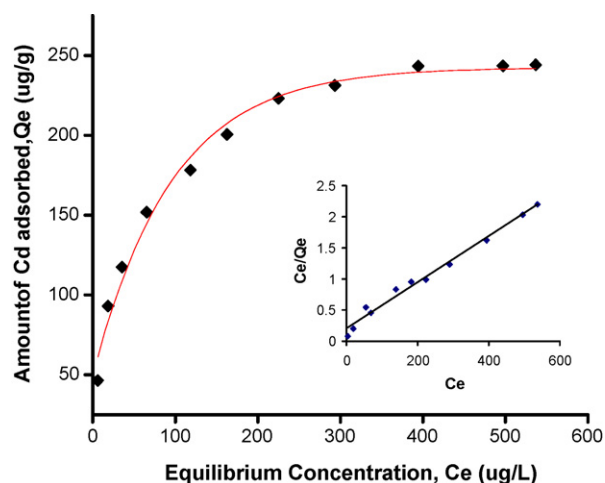


Fig. 2. Effect of the initial concentration on cadmium adsorption determined through equilibrium concentration vs. adsorption capacity. Inset: Langmuir plot.

equilibrium concentrations are obtained after 2 h of contact time, which is surely adequate since all the equilibria are achieved in just less than 1 min (vide infra). The amount of Cd(II) adsorbed on the chelating polymer was found to increase as the concentration went up. At ca. 400 $\mu\text{g/L}$ (C_e in Fig. 2), the adsorption leveled off.

Two models, both Langmuir [25] and Freundlich [26], are applied to analyze the data. The Langmuir isotherm (Fig. 2, inset) model is based on the equation of $C_e/Q_e = 1/(Q_m b) + C_e/Q_m$, where C_e is the equilibrium concentration obtained from the initial concentration upon a certain period of contact time with the chelating polymer, Q_e is the amount of Cd(II) ions adsorbed per gram of the chelating polymer ($\mu\text{g/g}$) at equilibrium, and Q_m is the maximum adsorption capacity ($\mu\text{g/g}$). b is the Langmuir parameter related to energy of adsorption. Q_e is derived from the formula of $Q_e = (C_i - C_e) \times V/m$ where C_i and C_e are initial and equilibrium concentration ($\mu\text{g/L}$), respectively. V (L) and m (g) are volume of the sample solution and mass of the chelating polymer, respectively. The linear plot of C_e/Q_e vs C_e gives the intercept and slope corresponding to $1/(Q_m b)$ and $1/Q_m$, respectively, from which both Q_m and b are derived.

On the other hand, the Freundlich isotherm (not shown) is analyzed based on the equation of $\log Q_e = 1/n \log C_e + \log K$, where K and $1/n$ are Freundlich constants, indicating the sorption capacity and sorption intensity, respectively [26]. C_e is the equilibrium concentration of Cd(II) in aqueous solution and Q_e is the sorption capacity. The plot of $\log Q_e$ against $\log C_e$ gives the intercept and slope corresponding to $\log K$ and $1/n$, respectively, from which both K and n are obtained.

Results from analyses of both models are listed in Table 1. The Langmuir model is more likely applicable because of higher correlation coefficient, indicating possible monolayer coverage of Cd(II) on the surface of the chelating polymer.

The equation $R_L = 1/(1 + bC_e)$ is to quantify favorability of an adsorption system [27]. The R_L value is a dimensionless parameter from the Langmuir isotherm. It is defined as unfavorable, linear, and irreversible, respectively, when R_L is greater than 1, equal to 1, and less than 1. The adsorption is defined as favorable when $0 < R_L < 1$. The values obtained for the present chelating polymer are between

Table 1
Langmuir and Freundlich parameters for metal adsorption.

Freundlich model			Langmuir model		
K	$1/n$	R^2	Q_m ($\mu\text{g/g}$)	b (L/ μg)	R^2
31.17	0.343	0.963	250.0	0.019	0.987

Table 2
 R_L values from various initial C_i 's.

C_i	R_L
98.921	0.93
204.666	0.75
270.446	0.50
368.985	0.44
475.184	0.28
563.846	0.23
671.601	0.19
756.042	0.16
881.176	0.12
984.152	0.10
1025.02	0.09

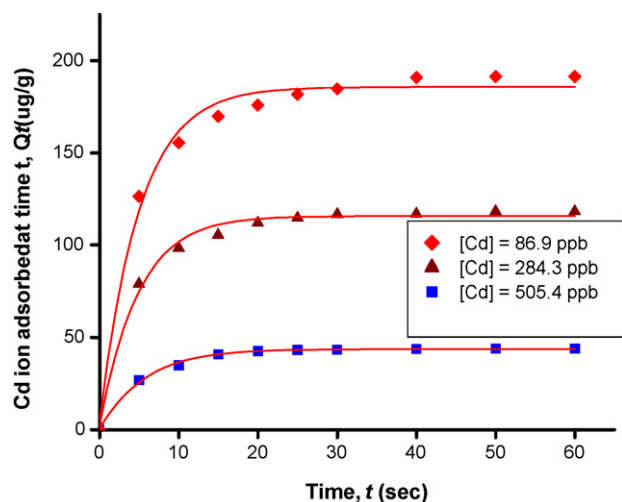


Fig. 3. The sorbed amounts of cadmium ion at varying initial concentrations with time.

0.93 and 0.09 (Table 2), suggesting that the favorable adsorption takes place in all the concentrations studied.

3.2. Adsorption kinetics

The kinetic property of Cd(II) adsorbed on the chelating polymer was assessed (Fig. 3). The adsorption rates were determined at pH of 5.5 in the range of Cd(II) concentrations from 85 to 510 ppb in aqueous media. The adsorption kinetics exhibit the following characters: (1) the adsorption is fast, and (2) the adsorption increases with increased concentration of the metal ion. At any given concentration, the Cd(II) adsorption quickly rose, and then reached the plateau, which is the equilibrium capacity. In all three cases, the adsorption reached the equilibrium capacity in less than 40 s. As a matter of fact, at Cd(II) concentrations of 86.9 and 248.5 µg/L, the time is ca. 20 and 30 s, respectively. This fast kinetics results from a high complexation process between the metal and the chelating units. At higher concentrations, more Cd(II) ions in liquid phase facilitate mass transfer to the solid surface as a result of great concentration gradient between the two phases [28].

Table 3
 Kinetic parameters for metal adsorption onto the polymer.

C_0 (µg/L)	First order		Second order		
	k_1 (s^{-1})	R^2	k_2 [$g/(s \mu g)$] ($g \text{ mg}^{-1} \text{ min}^{-1}$)	Q_e (µg/g)	R^2
86.9	0.0811	0.857	[0.0126] (7.56×10^2)	45.45	0.998
248.5	0.2537	0.831	[4.837×10^{-3}] (2.90×10^2)	121.95	0.999
505.4	0.0944	0.956	[2.575×10^{-3}] (1.54×10^2)	196.08	0.998

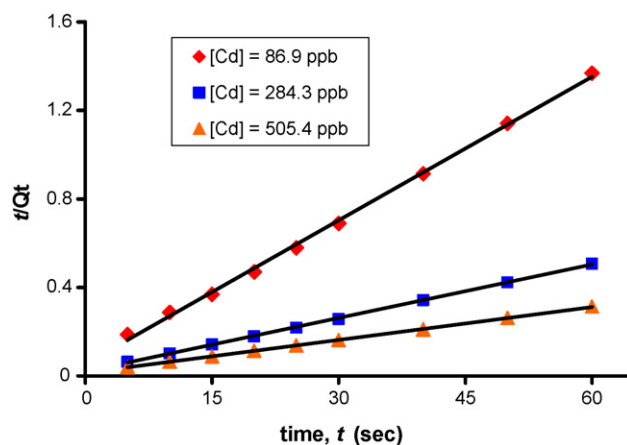


Fig. 4. Second-order kinetic plot for the sorption of cadmium.

The noticeably short time to reach the equilibrium for present kinetic study complements those reported from various systems for the heavy metal removal. Several systems have been reported to have equilibrium achieved between 2 and 72 h [29–31]. The short equilibrium adsorption time between 15 and 30 min has also been reported for PEI-coated silica gel and ligands-modified gel beads [28,32]. Sawdust has also been reported to have a short equilibrium time of 2–10 min in the removal of Cd(II) [33–34]. The equilibrium time is an important factor for cost-effective application in practical systems.

The adsorption kinetic mechanism was evaluated using two conventional models, namely the pseudo-first-order and the pseudo-second-order equations [35–37]. The rate expression, $\log(Q_e - Q_t) = \log Q_e - k_1 t/2.303$, is known as the Lagergren equation for the first-order assessment, where k_1 (min^{-1} or s^{-1}) is the rate constant of pseudo-first-order adsorption, Q_e (µg/g or mg/g) is the amount of metal ion sorbed at equilibrium, and Q_t (µg/g or mg/g) is the amount of metal ion sorbed at time t (min or s). The value of k_1 is derived experimentally from the slope of the linear plots of $\log(Q_e - Q_t)$ versus t . In this case, low correlation coefficient values were obtained, indicating that this absorption less likely proceeds in the first-order model.

A pseudo-second-order reaction is guided by the expression of $t/Q_t = 1/(k_2 Q_e)^2 + t/Q_e$ [35–36], where Q_e (µg/g or mg/g) is the amount of metal ion sorbed at equilibrium, Q_t (µg/g or mg/g) is the amount of metal ion on the surface of the sorbent at time t , and k_2 [$g/(\mu g \text{ s})$ or $g/(\text{mg min})$] 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. 4). It is found that this pseudo-second-order approach gives high correlation coefficient values, indicating that the pseudo-second-order is the model applicable to the present adsorption kinetics. The kinetic data for both pseudo-first-order and second-order assessment are listed in Table 3.

It is apparent that the high adsorption rate is corresponding to the fast equilibrium. This, coupled with the Langmuir monolayer adsorption coverage, suggests that the chelating polymer has most

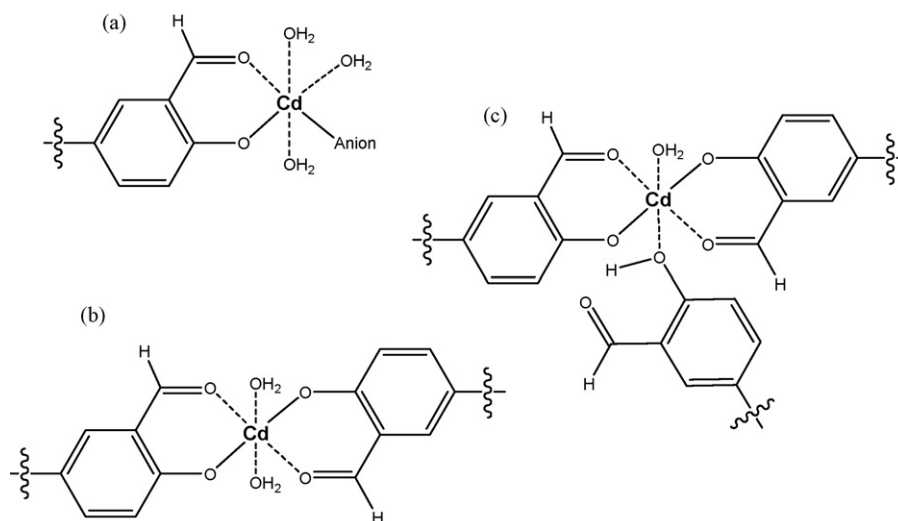


Fig. 5. Plausible coordination modes of metal and chelating units.

Table 4

Adsorption of other heavy metals from aqueous solution.

Metal ions	Percent removal (%) ^a	Q _e (μg/g) ^b
Cu(II)	64.0	278.7
Zn(II)	82.0	357.3
Co(II)	97.5	423.2
Ni(II)	92.7	312.5
Cr(III)	99.9	393.3

^a Initial metal ion concentration: 50 ppb, temperature: 25 °C, contact time: 2 h, and pH 5.5, mass of adsorbent: 0.05 g, volume of solution: 25 mL.

^b Initial metal ion concentration: ca. 1000 ppb, temperature: 25 °C, contact time: 2 h, and pH 5.5, mass of adsorbent: 0.025 g, volume of solution: 12.5 mL.

of their chelating groups on or near the surface for easy access. As pointed out earlier, the complexation is very fast between Cd(II) ions with the chelating groups. All these factors indicate the potential high efficiency of the adsorption process, in particular as far as the rate is concerned.

Six-coordinated cadmium has been found in oxygen-based bidentate ligands and other types of ligands [38–40]. This general tendency prompts us to speculate that three types of coordination modes would take place during the interaction of metal and polymer. They are based on number of chelating units involved (Fig. 5) to cover three scenarios: when three chelating units in the close proximity from the same chain and adjacent chains are available, they would complete six coordination (Fig. 5c); if only two units are available, additional coordination sites will be filled by water molecules (Fig. 5b); and if only one unit is available, an anion has to participate either in inner or outer coordination sphere to balance the charge (Fig. 5a).

4. Removal efficiency for other heavy metals

The batch screening studies were performed to study the uptake of other metals by the chelating polymer. For capacity study, the solutions of ca. 1000 μg/L of Cu(II), Ni(II), Co(II), Zn(II), and Cr(III) at pH of 5.5 were used. The Q_e values (Table 4) were obtained after 2 h contact time. For removal efficiency study, the solutions of ca. 50 μg/L were used with 2 h contact time. The percentage of removal was calculated by the equation

$$\text{removal efficiency (\%)} = \frac{C_i - C_e}{C_i} \times 100$$

where C_i and C_e are the initial and equilibrium concentrations of the metal ions.

It is found that removal efficiency in the following decreasing order: Cr(III) > Co(II) > Ni(II) > Zn(II) > Cu(II). But, in the initial concentrations of ca. 1000 ppb, the removal efficiency is in the following decreasing order: Cu(II) > Co(II) > Ni(II) > Zn(II) (data not listed), indicating that the order for Cu(II) is highly dependent on the initial concentration, but not for the rest of metal ions.

5. Conclusion

The present research establishes the ability of salicylaldehyde group-based chelating polymer to adsorb cadmium of low concentration with fast equilibrium rate. The investigation of poly[4-(4-vinylbenzyloxy)-2-hydrobenzaldehyde] for the removal has found the fast complexation capability for the metal ion of the ppb concentrations studied. The adsorption is best described with the Langmuir model, indicating the monolayer coverage of the metal ion on the surface of chelating polymer. The R_L values indicate that the adsorption in the range of all the concentrations studied is favorable. The kinetic study has revealed a very fast adsorption process, which is in less than 40 s to reach the equilibrium capacity. The adsorption rate follows the pseudo-second-order.

Acknowledgement

Supports from DOE (DE-FG52-05NA27040 & De-FC02-02EW15254) and NIH/NCRR (2G12RR003062-22) are acknowledged.

References

- [1] B. Volesky, *Biosorption of Heavy Metals*, RC Press, Boca Raton, FL, 1990.
- [2] M.P. Waalkes, S. Rehm, Cadmium and prostate cancer, *J. Toxicol. Environ. Health* 43 (1994) 251–269.
- [3] A. Åkesson, B. Julin, A. Wolk, Long-term dietary cadmium intake and post-menopausal endometrial cancer incidence: a population-based prospective cohort study, *Cancer Res.* 68 (2008) 6435–6441.
- [4] M. Filipič, Molecular mechanisms of cadmium induced mutagenicity, *Hum. Exp. Toxicol.* 25 (2006) 67–77.
- [5] T. Lebeau, D. Bagot, K. Jížiequel, B. Fabre, Cadmium biosorption by free and immobilised microorganisms cultivated in a liquid soil extract medium: effects of Cd, pH and techniques of culture, *Sci. Total Environ.* 291 (2002) 73–83.
- [6] R. Salim, M.M. Al-Subu, E. Sahrhage, Uptake of cadmium from water by beech leaves, *J. Environ. Sci. Health A27* (1992) 603–627.
- [7] X. Zhao, W.H. Höll, G. Yun, Elimination of cadmium trace contaminations from drinking water, *Water Res.* 36 (2002) 851–858.

- [8] W.D. Henry, D. Zhao, A.K. SenGupta, C. Lange, Preparation and characterization of a new class of polymeric ligand exchangers for selective removal of trace contaminants from water, *React. Funct. Polym.* 60 (2004) 109–120.
- [9] Y. Seida, Y. Nakano, Y. Nakamura, Rapid removal of diluted lead from water by pyroaurite-like compound, *Water Res.* 35 (2001) 2341–2346.
- [10] M.C. Basso, E.G. Cerrella, A.L. Cukierman, Activated carbons developed from a rapidly renewable biosource for removal of cadmium(ii) and nickel(ii) ions from dilute aqueous solutions, *Ind. Eng. Chem. Res.* 41 (2002) 180–189.
- [11] (a) J.L. Gardea-Torresdey, J.R. Peralta-Videa, M. Montes, G. de la Rosa, B. Corral-Diaz, Bioaccumulation of cadmium, chromium and copper by *Convolvulus arvensis* L.: impact on plant growth and uptake of nutritional elements, *Biore-sour. Technol.* 92 (2004) 229–235;
- (b) A.B. Perez-Marín, V. Meseguer Zapata, J.F. Ortuno, M. Aguilar, J. Saez, M. Llorens, Removal of cadmium from aqueous solutions by adsorption onto orange waste, *J. Hazard. Mater.* B139 (2007) 122–131.
- [12] (a) G. de la Rosa, J.R. Peralta-Videa, M. Montes, J.G. Parsons, I. Cano-Aguilera, J.L. Gardea-Torresdey, Cadmium uptake and translocation in tumbleweed (*Salsola kali*), a potential Cd-hyperaccumulator desert plant species: ICP/OES and XAS studies, *Chemosphere* 55 (2004) 1159–1168;
- (b) S. Al-Asheh, F. Banat, R. Al-Omari, Z. Duvnjak, Predictions of binary adsorption isotherms for the adsorption of heavy metals by pine bark using single isotherm data, *Chemosphere* 41 (2000) 659–665.
- [13] F.A. Pavan, I.S. Lima, C. Airoidi, Y. Gushikem, Use of pokan Mandarin Peels as biosorbent for toxic metals uptake from aqueous solutions, *J. Hazard. Mater.* 137 (2006) 527–533.
- [14] K.K. Singh, R. Rastogi, S.H. Hasan, Removal of cadmium from wastewater using agricultural waste “rice polish”, *J. Hazard. Mater.* A121 (2005) 51–58.
- [15] M.M. Rao, A. Ramesh, G.P. Chandra Rao, K. Seshiah, Removal of copper and cadmium from the aqueous solutions by activated carbon derived from *Ceiba pentandra* hulls, *J. Hazard. Mater.* 129 (2006) 123–129.
- [16] M. Ahmedna, W.E. Marshall, A.A. Husseiny, R.M. Rao, I. Goktep, The use of nut-shell carbons in drinking water filters for removal of trace metals, *Water Res.* 38 (2004) 1062–1068.
- [17] S.H. Min, J.S. Han, E.W. Shin, J.K. Park, Improvement of cadmium ion removal by base treatment of juniper fiber, *Water Res.* 38 (2004) 1289–1295.
- [18] Q. Chen, Bis(4-bromo-2-formylphenolato-*O,O'*)zinc(II), *Acta Cryst. E62* (2006) m56–m57.
- [19] Q. Yu, C.-Y. Li, X.-E. Yang, B. He-Dong, H. Liang, Aquabis(1-formyl-2-naphtholato-*O,O'*)copper(II), *Acta Cryst. E62* (2006) m391–m393.
- [20] C.D. Papadopoulos, M. Lalia-Kantouri, J. Jaud, A.G. Hatzidimitriou, Substitution effect on new Co(II) addition compounds with salicylaldehydes and the nitrogenous bases phen or neoc: crystal and molecular structures of [CoII(5-NO₂-salicylaldehyde)₂-(phen)], [CoII(5-CH₃-salicylaldehyde)₂(neoc)] and [CoII(5-Cl-salicylaldehyde)₂(neoc)], *Inorg. Chim. Acta* 360 (2007) 3581–3589.
- [21] S.-H. Zhang, G.-Z. Li, X.-Z. Feng, Z. Liu, Bis(4,6-dibromo-2-formylphenolato-*O,O'*)bis(dimethyl sulfoxide-*O*)nickel(II), *Acta Crystallogr. E63* (2007) m1319–m1320 (Section E: Structure Reports Online).
- [22] R.N. Prasad, M. Agrawal, R. Ratnani, K. Raju, Saraswat, Mixed ligand complexes of alkaline earth metals. Part-XIV. MgII, CaII, SrII and BaII complexes with 5-nitrosalicyl-aldehyde and salicylaldehyde or hydroxyaromatic ketones, *J. Indian Chem. Soc.* 82 (2005) 1003–1005.
- [23] (a) M.L. Colon, S.Y. Qian, D. Vanderveer, X.R. Bu, Chiral bimetallic complexes from chiral salen metal complexes and mercury(II) halides and acetates: the anionic groups interact with Cu(II) in apical position, *Inorg. Chim. Acta* 357 (2004) 83–88;
- (b) S. Liang, X.R. Bu, Tertiary-pentyl groups enhanced salen titanium catalyst for highly enantio-selective trimethylsilylcyanation of aldehydes, *J. Org. Chem.* 67 (2002) 2702–2704.
- [24] (a) H. Kamogawa, K. Sugiyama, H. Hanawa, M. Nanasawa, Syntheses of polymerizable phenol derivatives having a carbonyl-containing group as a ring substituent, *J. Polym. Sci. : Polym. Chem. Ed.* 14 (1976) 511–514;
- (b) P. Amoyaw, C. Ingram, F.-L. Hsu, X.R. Bu, Poly[4-(4-vinylbenzyloxy)-2-hydroxyl benzaldehyde] for rapid removal of low concentrations of Pb(II), *J. Appl. Polym. Sci.* 113 (2009) 2096–2102.
- [25] I. Langmuir, The constitution and fundamental properties of solids and liquids. Part 1. Solids, *J. Am. Chem. Soc.* 38 (1916) 2221–2295.
- [26] H.M.F. Freundlich, Adsorption in solids, *Z. Phys. Chem.* 57 (1906) 385–471.
- [27] G. McKay, H.S. Blair, J.R. Garden, Adsorption of dyes on chitin. I. Equilibrium studies, *J. Appl. Polym. Sci.* 27 (1982) 3043–3057.
- [28] A. Denizil, S. Senel, G. Alsancak, N. Tüzman, R. Say, Mercury removal from synthetic solutions using poly(2-hydroxyethylmethacrylate) gel beads modified with poly(ethyleneimine), *React. Funct. Polym.* 55 (2003) 121–130.
- [29] C.C. Wang, C.Y. Chang, C.Y. Chen, Study on aetal ion adsorption of bifunctional chelating/ion-exchange resins, *Macromol. Chem. Phys.* 202 (2001) 882–890.
- [30] N.E. Reed, M.R. Matsumoto, Modeling cadmium adsorption by activated carbon using the Langmuir and Freundlich isotherm expressions, *Sep. Sci. Technol.* 28 (1993) 2179–2195;
- S. Bahrami, A.S. Bassi, E. Yanful, Polyethyleneimine-containing sol-gels as novel sorbents for the removal of cadmium from aqueous solutions, *Can. J. Chem. Eng.* 77 (1999) 931.
- [31] H. Egawa, M. Nakayama, T. Nonaka, E. Sugihara, Recovery of uranium from sea water. IV. Influence of crosslinking reagent of the uranium adsorption of macroreticular chelating resin containing amidoxime groups, *J. Appl. Polym. Sci.* 33 (1987) 1993.
- [32] M.L. Delacour, E. Gailliez, M. Bacquet, M. Morcellet, Poly(ethyleneimine) coated onto silica gels: adsorption capacity toward lead and mercury, *J. Appl. Polym. Sci.* 73 (1999) 899.
- [33] S.Q. Memon, N. Memon, S.W. Shah, M.Y. Khuhawar, M.I. Bhangar, Sawdust-A green and economical sorbent for the removal of cadmium (II) ions, *J. Hazard. Mater.* 139 (2007) 116–121.
- [34] V.C. Taty-Costodes, H. Fauduet, C. Porte, A. Delacroix, Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of *Pinus sylvestris*, *J. Hazard. Mater.* 105 (2003) 121–142.
- [35] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, *Process Biochem.* 34 (1999) 451–465.
- [36] J.A. Allen, D.A. Brown, Isotherm analyses for single component and multi-component metal sorption onto lignite, *J. Chem. Technol. Biotechnol.* 62 (1995) 17–24.
- [37] E.D. Hullebusch, M.H. Zandvoort, P.L. Lens, Nickel and cobalt sorption on anaerobic granular sludges: kinetic and equilibrium studies, *J. Chem. Technol. Biotechnol.* 79 (2004) 1219–1227.
- [38] E.N. Maslen, T.M. Greaney, C.L. Raston, A.H. White, Crystal Structure of cafena-Di-p-acetylacetonato-cadmium, *J. Chem. Soc. Dalton* (1975) 400–402.
- [39] J. Chakraborty, B. Samanta, G. Pilet, S. Mitra, Tris(1-phenoxo) bridged Cd(II) polymer synthesised from asymmetrical tripodal ligand: A novel observation for heptadentate monocapped trigonal antiprismatic Schiff base complex, *Inorg. Chem. Commun.* 10 (2007) 40–44.
- [40] R. Kruszynski, A. Turek, A novel polymeric (4-chloro-2-methylphenoxy) acetate complex of cadmium(II), *J. Coord. Chem.* 57 (2004) 1089–1098.