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ORIGINAL PAPER

Aqueous heavy metals removal by adsorption on β-diketone-functionalized styrene–divinylbenzene copolymeric resin

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Abstract An investigation was undertaken regarding the adsorption of different heavy metal ions from aqueous solutions using β-diketone-functionalized styrene divinylbenzene resin under different experimental conditions such as initial concentration of metal ions, contact time, pH, and chelating capacity. The functionalization of resin was carried out by the condensation reaction of sodium salt of β-diketones (pentane-1,3-dione) and chloromethylated styrene–divinylbenzene resin in dichloromethane. Functionalized resin beads were characterized by Fourier transform infrared spectroscopy. The batch method was employed using different metal ions solution from 5 to 15 mg/L at different contact times. The adsorption kinetics was tested for the pseudo-first order, pseudo-second order reaction at different experimental conditions. The rate constant of adsorption kinetic models were also calculated and good correlation coefficient ($R^2 > 0.9941$) was obtained for pseudo-second order kinetic model. The maximum adsorption value obtain for lead (0.725728 mg/g), chromium (0.9199 mg/g), nickel (0.4974 mg/g), cobalt (0.6196 mg/g) and cadmium (0.6519 mg/g) at equilibrium condition, which shows that β-diketone-functionalized styrene divinylbenzene resin is an effective adsorbent for toxic metal ions.

Keywords Adsorbent · Batch method · Chelating agents · Pollutants · Resin beads

Introduction

Recently, heavy metals are among the most important pollutants in the treated water and are becoming severe public health problem. Industrial wastewater is the major source of various kinds of metal pollution in natural water (Demirbas 2004; Mohan and Sreelakshmi 2008). The heavy metal ions are stable with persistent environment contaminations, since they cannot degrade and nor be destroyed. These metals are mostly toxic even at very low concentration. Heavy metal toxicity can cause hypertension, nephritis, abdominal pain, nausea, vomiting, behavioral changes and development defects (Ake et al. 2001; Tunali et al. 2006). These pollutants are present in water from industrial applications such as in the manufacture of pesticides, batteries, alloys, electroplated metal parts, mining, refining and production of textiles, paints and dyes (Patterson 1985; Roberts 1999; Abdel-Ghani et al. 2009). Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. Pb^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Hg^{2+}, Cr^{6+}, Cd^{2+} and Zn^{2+} are especially common metals that tend to accumulate in organisms, causing numerous diseases and disorders (Inglezakis et al. 2003; Rivera-Utrilla and Sanchez-Polo 2003). A wide variety of techniques to remove heavy metals from water is available such as ion exchange (Dizge et al. 2009; Rafati et al. 2010), reverse osmosis and nanofiltration (Fatin-Rouge et al. 2006), precipitation, coagulation/co-precipitation and adsorption (Freeman 1989; Cheremisinoff 2002; Aguado et al. 2009). This last technique is very popular due to simplicity and low cost. Although activated carbon (Bailey et al. 1999; Babel and Kurniawani 2003) is frequently used as general adsorbent of inorganic and organic compounds, alternative adsorbents have been developed to improve the effectiveness at very low

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pollutant concentration. Recently, chelating resins with various functionalities have also been widely used for removal of heavy metals from pollutant water. A chelating resin or polymer essentially consists of two components: the chelate forming functional group and the polymeric matrix or the support (Bilba et al. 1998; Camel 2003; Jeon and Holl 2003). Chelating or coordinating resins are polymers with covalently bound functional groups containing one or more donor atoms that are capable of forming complexes directly with metal ions. In these resins, functional group atoms most frequently used are nitrogen (e.g., N presents in amines, azo groups, amides, nitriles), oxygen (e.g., O presents in carboxylic, hydroxyl, phenolic, ether, carbonyl, phosphoryl groups), and sulfur (e.g., S presents in thiols, thiocarbamates, thioethers) (Zuo and Muhammed 1990, 1995; Donia et al. 2005). The chelating resins with functional groups including oxygen and nitrogen donor atoms are very efficient at chelating with metals according to hard–soft acid–base (HSAB) theory by Pearson (1963). Soft metal ions show affinity to soft bases with donor atoms as $O < N < S$. On the other hand, hard metal ions, for instance show affinity hard bases with donor atoms as $O > N > S$ (Aydin et al. 2008; Wuana et al. 2010). Moreover, β-diketone resins as chelating resins have ionic interaction properties by coordination. Oxygen atoms in a chelating resin can show ionic interaction with metal ions. Oxygen atoms are effective in coordinating with hard metals (Atia et al. 2005).

This study was undertaken to characterize the adsorption and removal of heavy metals as Pb^{2+}, Cr^{6+} Ni^{2+}, Co^{2+} and Cd^{2+} by batch method, using β-diketone-functionalized styrene–DVB copolymeric resin beads. β-Diketone-functionalized resin has oxygen atom as an electron donor which helps the formation of coordination complex with metal ions. The synthesis of novel β-diketones and their heterocyclic compounds for antibacterial properties were already reported (Kumar and Joshi 2007, 2008, 2009). In continuation of our ongoing research program, in this paper the potential use of β-diketone-functionalized styrene–DVB resin for removal of heavy metals from contaminated water was explored. All research work was performed in the laboratory of Water Quality Monitoring, Defence laboratory, Jodhpur, during 2009 and 2010.

Materials and methods

Chemicals

Chloromethylated styrene–DVB beads were procured from Thermax limited, India. The reagents used in the synthesis of functionalized resin were from Sigma Aldrich, USA. Atomic absorption standard solution (1,000 mg/L) was purchased from Merck, Germany. The other reagents were analytical grade.

Instruments

All atomic absorption spectrometer (AAS) (Analytik-Jena-Nova-400) measurements were carried out on flame mode with single beam. AAS equipped with 100 mm burner, a cross-flow nebulizer 5.0 mL/min and 1.2 mm slit were used throughout the experiments. Each experiment was duplicated under identical conditions using this instrument for concentration determination. IR spectra were recorded on Jasco FT-IR spectrometer model 610 by using KBr pellets. The pH measurements were made on a digital pH meter (HACH, sension 1, model 51935-00) equipped with a gel-filled pH electrode. The meter was calibrated with the buffers of 4, 7 and 10.

Functionalization of the resins

Functionalization of resin has been carried out in two steps, first salt formation of β-diketones with sodium methoxide and second condensation of sodium salt of β-diketones and chloromethylated styrene–DVB beads (Fig. 1).

Formation of sodium salt of β-diketones

Sodium methoxide (0.54 g, 0.01 M) and β-diketones (0.01 M) were placed in a dry round bottom flask (fitted with a guard tube) and stirred it for 2 h on a magnetic stirrer at a temperature of 50°C, to obtain the sodium salt of β-diketones. The salt was washed with dry ether for removal of unreacted β-diketones.

β-Diketone-functionalized styrene–DVB copolymeric resin

Synthesized sodium salt of β-diketone and chloromethylated styrene–DVB beads and dichloromethane were

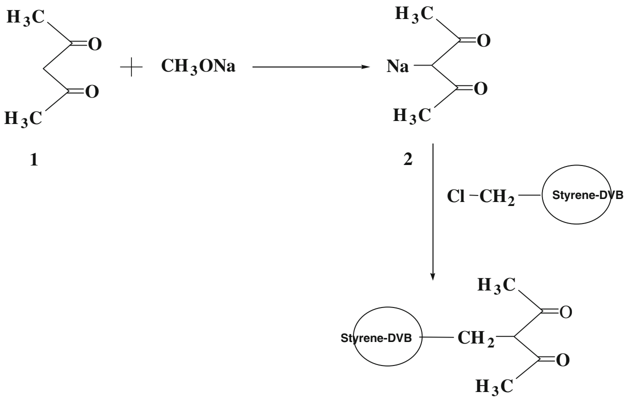

Fig. 1 Functionalization of resin

placed in a two-neck round bottom flask. The reaction mixture was refluxed at a temperature of 60°C for 8 h with continuous stirring. The completion of the reaction was monitored through FT-IR. After the reaction was completed, the reaction mass was cooled and dichloromethane was removed under reduced pressure. The crude product was washed with ultrapure water (resistivity, 18.2 MΩ cm, Elix) till the neutral pH and then dried. The product was then characterized by FT-IR.

Preparation of the solutions

Stock solutions of 1,000 mg/L of the metals ions under study were prepared by dissolving 1.560 g of $Pb(NO_3)_2$, 2.827 g of $K_2Cr_2O_7$, 4.050 g of $NiCl_2 \cdot 6H_2O$, 4.037 g of $CoCl_2 \cdot 6H_2O$ and 1.630 g of $CdCl_2$ separately in 1,000 mL ultra pure water. These solutions were diluted to prepare standard solutions of required concentration. All the solutions were prepared with ultrapure water (resistivity: 18.2 MΩ cm,) from Elix analytical reagent-grade water purification system.

Adsorption studies with batch method

Pretreatment of functionalized resin was done by soaking it in ultrapure water to increase it surface area for 24 h.

Batch experiments were carried out in glass bottles containing pretreated chelating resin beads (100 mg) with 10 mL of the metal ion solutions of concentration 10 mg/L at different pH (1–7) at 30 ± 1°C. Five milliliters of the solution from each glass bottle was taken at different time interval (20, 40, 60, 80, 100 and 120 min) to determine the optimum contact time where the maximum adsorption was accomplished for metal ions. The residual concentration of metal ions was determined using AAS. The amount of metal ion adsorbed by β-diketone-functionalized styrene–DVB resin (Q_e mmol/g) was calculated according to the following equation:

$$Q_e = (C_i - C_e) \times V/m \tag{1}$$

where C_i and C_e are initial and equilibrium concentration (mg/L), respectively. V (L) and m (g) are volume of the sample solution and mass of the chelating resin beads (100 mg), respectively.

The optimum contact time was determined as Pb^{2+} (60 min), Cr^{6+} (60 min), Ni^{2+} (100 min), Co^{2+} (60 min), and Cd^{2+} (100 min) and used throughout all adsorption experiments. Uptake experiments of metal ions at different pHs (1–7) were carried out by placing 100 mg chelating resin beads containing 10 mL solution of metal ions with an initial concentration of 10 mg/L. The pH was adjusted using 0.1 M NaOH and 0.1 M HCl. The residual concentration of lead ions was determined using AAS. The amount of metal ion adsorbed by chelating resin beads (Q_e mmol/g) was calculated according to Eq. 1.

Metal ion concentration 5, 10 and 15 mg/L were prepared and used to determine the effect of initial concentration of metal ions on adsorption. 100 mg chelating resin beads was placed in a series of glass bottles containing 10 mL of metal ions solution with above-mentioned concentration at optimum pH for different metal ions for above-mentioned optimum time. After equilibration, 5 mL of the solution was taken for the determination of residual concentration of metal ions by AAS. The amount of metal ions adsorbed by chelating resin beads (Q_e mmol/g) was calculated according to Eq. 1.

Kinetic adsorption experiment

The kinetic study of all metal ions were carried out at 10 mg/L concentrations at optimum pH (different for different metal ions reported in "Results and discussion") for each metal. Data acquisition protocol includes the treatment of a series of 100 mg of the chelating resin beads with 10 mL of metal ions solution. These series of samples are quenched for each bottle at above-mentioned optimum time by filtration. The concentrations of the filtrate were analyzed by AAS.

Results and discussion

Characterization of functionalized resin beads

IR spectra of the compound I (Fig. 1) show 2,914 and 2,851/cm bands due to C–H stretching vibration and a band at 1,750/cm due to C=O group. The presence of these groups in the FT-IR of functionalized resin shows that the condensation reaction takes place between chloromethylated styrene–DVB beads and β-diketone.

Batch method studies

Effect of contact time

The influence of contact time on the adsorption of Pb^{2+}, Cr^{6+}, Ni^{2+}, Co^{2+}, and Cd^{2+} ions onto β-diketone-functionalized styrene–DVB copolymeric resin (Fig. 2) was investigated at constant concentration of metal ions at different time (min). It is easily seen from Fig. 2 that the amount of adsorption increased with increasing the contact time (Abdel-Ghani et al. 2007). For Pb^{2+} the removal capacities increased up to contact time 60 min and after this time, no change is observed in the removal. The speed of removal can be explained by the presence of chelating groups that present good coordinating centers. This was

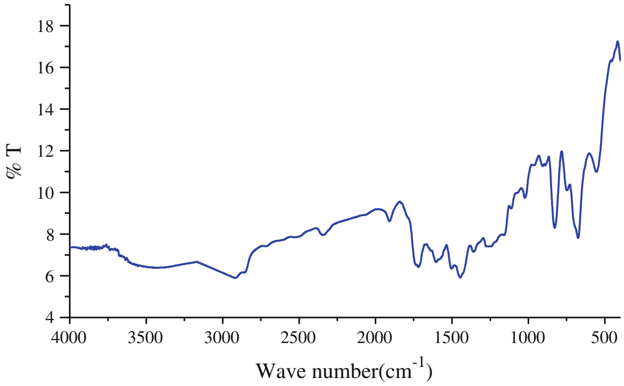

Fig. 2 IR spectra of resin functionalized with pentane-1,3-dione

therefore fixed as the equilibrium contact time. Similarly, equilibria were obtained for metal ions at different contact time such as Cr^{6+} (60 min), Ni^{2+} (100 min), Co^{2+} (60 min), and Cd^{2+} (100 min).

Effect of pH

The pH of aqueous solution has been known as the most important variable governing heavy metal adsorption onto adsorbent. This is partly because hydrogen ions themselves are strongly competing with metals (Forstner and Wittman 1981). The dependence of amount of adsorption of Pb^{2+}, Cr^{6+}, Ni^{2+}, Co^{2+}, and Cd^{2+} ions on pH is shown in Fig. 3. The removal of ions increased with increase of pH. For a Pb^{2+} concentration of 10 mg/L, the rates of removal capacities increased up to pH 4.0. After pH 4.0, salt of lead precipitated out. Moreover, at lower pH, protonation of chelating group takes place. Thus, complexation with available ligands is reduced and hence the percentage uptake decreases. But at higher pH, deprotonation takes place and percentage uptake increases. Experiments were not carried out with the pH values above 5 due to the fact that lead precipitation appeared at higher pH values. Similarly, the optimal removal is obtained at Cr^{6+} (pH = 5), Ni^{2+} (pH = 6), Co^{2+} (pH = 5), and Cd^{2+} (pH = 6); different pH for different metal ions.

Effect of initial ions concentration

The results of the experiments with varying initial concentrations of metal ions (5, 10 and 15 mg/L) at optimum pH are illustrated in Fig. 4. It shows a significant increase in the removal of lead with an increase in the initial concentration of metal ion from 5 to 10 mg/L. This observation is in accordance with the open available literature data. In the range of initial concentration from 10-15 mg/L the increase in extraction is less significant. These results are probably related to a saturation of the chelating agents. Similar results are also obtained for other metals.

Adsorption kinetics of metal ions

The kinetic characters of metal ions Pb (II), Cr (VI), Ni (II), Co (II) and Cd (II) adsorbed on the chelating resin beads were assessed (Fig. 5). The adsorption rates were determined at optimum pH in the metal ion concentrations 10 mg/L 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 metal ion adsorption quickly rose, and then reached the plateau, which is the equilibrium capacity. In all cases, the adsorption reached the equilibrium capacity in 60–100 min. This fast kinetics results from a high complexation process between the metal and the chelating units. At higher concentrations, more metal ions in liquid phase facilitate mass transfer to the solid surface as a result of high concentration gradient between the two phases.

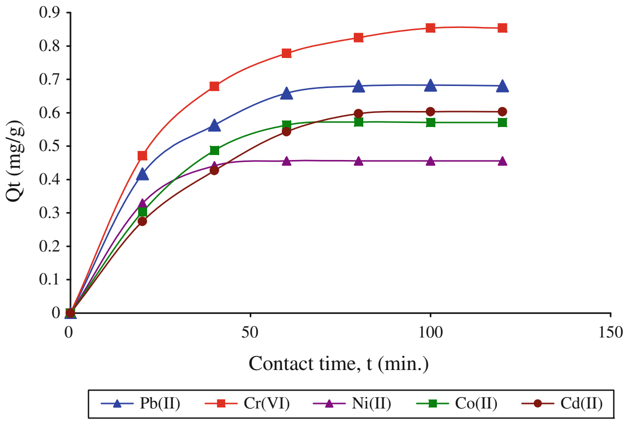

Fig. 3 Effect of contact time on the removal of metal ions at constant metal ion conc. 10 mg/L

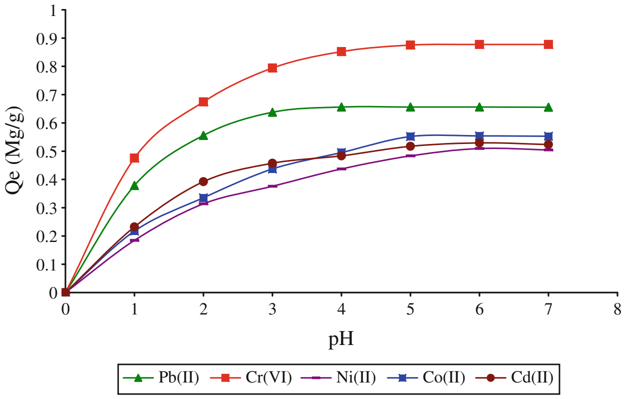

Fig. 4 Effect of pH on the removal of metal ions at constant metal ion conc. 10 mg/L

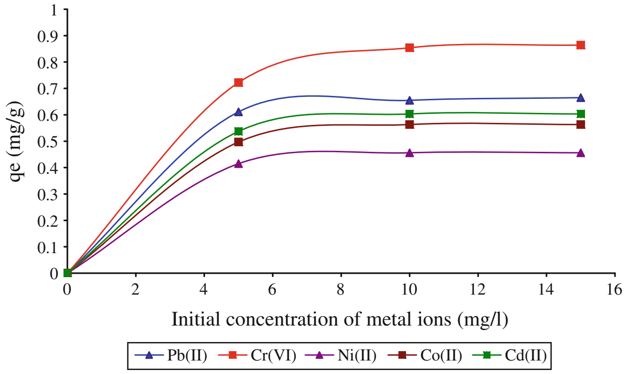

Fig. 5 Effect of initial concentration on removal of metal ions

The adsorption kinetic mechanism was evaluated using one conventional model, namely the pseudo-second-order equations (Ho and Mckay 2000). In this case of pseudo-first-order, very low correlation coefficient values were obtained, so that this model was not reported for absorption kinetic studies.

A pseudo-second-order reaction is guided by the expression of $t/Q_t = 1/(k_2Q_e)^2 + t/Q_e$ (Ho and McKay 1999; Allen and Brown 1995, where Q_e (mg/g) is the amount of metal ion sorbed at equilibrium, Q_t (mg/g) is the amount of metal ion on the surface of the sorbent at time t and k_2 [g/(mg min)] is the rate constant of pseudo-second-order adsorption. The values of $1/(k_2Q_e)^2$ 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 (Fig. 6).

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 (Horsfall et al. 2004). The kinetic data for second-order assessment are listed in Table 1.

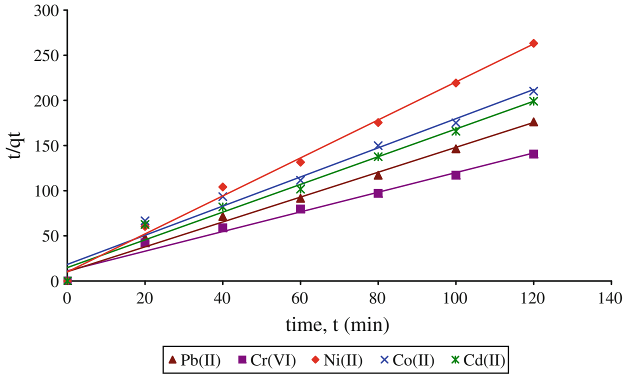

Fig. 6 Second order kinetic plot for the adsorption of metal ions

Table 1 Kinetic parameters for metal ions adsorption onto the chelating resin

Metal	k_2 [g/(min mg)]	Q_e (mg/g)	R^2
Pseudo-second-order reaction			
Pb (II)	0.4310	0.7257	0.9882
Cr (VI)	0.3247	0.9199	0.9815
Ni (II)	0.6354	0.4974	0.9941
Co (II)	0.3764	0.6196	0.9756
Cd (II)	0.3973	0.6519	0.9785

Resin stability and reusability

The stability of β-diketone-functionalized resin was studied in acid (1.0–6 mol L^{-1}). It was shaken with acid solutions of varying concentration for 4 h and filtered. The solid was washed with distilled water until free from acid and air dried, and its sorption capacity was determined using a batch method. The sorption capacity of the acid-treated resin was found to be similar (variation, 5%) to that of the untreated one. This shows that the present resin can resist an acid concentration up to 6 mol/L. It can also be reused for more than five cycles of sorption–desorption without any significant change in the sorption capacity (<5%).

Conclusion

In conclusion, it has been shown that the use of functionalized resin beads with compound I for heavy metals removal from aqueous solution appears to be technically feasible with high efficiency. The experimental data establishes the ability of β-diketone-functionalized styrene–DVB copolymeric resin to adsorb Pb (II), Cr (VI), Ni (II), Co (II) and Cd (II) of low concentration with fast equilibrium rate. The resin shows high removal efficiency because of fast complexation with above metal ions. The adsorption is best described with the pseudo-second-order model, indicating the monolayer coverage of the metal ion on the surface of β-diketone-functionalized styrene–DVB copolymeric resin. Although the removal studies were carried out by batch method, these molecules may be good functionalized resin beads for treatment of waste water contaminated by toxic metals.

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