Synthesis, Characterization and Application of a New Chelating Resin Containing 2-(4-Methylbenzylidene)hydrazone

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ABSTRACT: The functionalization of 2-(4-methylbenzylidene)hydrazone onto chloromethylated styrene–divinylbenzene copolymeric resin has been explored in this study. The structure of the functionalized resin was confirmed by FT-IR spectroscopy and its use for the adsorption of Ni(II) and Co(II) ions from aqueous solution studied. The effects of pH, initial concentration of metal ion and contact time on the adsorption process were examined using batch experiments. The Langmuir and Freundlich models were applied to the equilibrium adsorption data obtained, when it was found that both isotherms gave a reasonable fit. For initial concentrations of 1000 µg/ℓ, maximum adsorption capacities for Ni(II) and Co(II) ions of 6.67 mg/g and 9.985 mg/g, respectively, were obtained. The adsorption kinetics followed the pseudo-second-order model and the rate constants for this kinetic model were calculated. The experimental results indicated that the functionalized resin has the potential for use as a good adsorbent for the removal of Ni(II) and Co(II) ions from contaminated water.

INTRODUCTION

The removal of heavy metal ions from polluted water has become one of the most important challenges worldwide. According to recent surveys, the most common contaminations reported in ground water are heavy metal ions. The World Health Organization (WHO) has reported that the metal ions of immediate concern are those of aluminium, chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, mercury and lead (WHO 1984). In particular, cobalt and nickel ions are especially dangerous and highly toxic at low concentrations. Nickel and cobalt are used mainly in the production of stainless steels, non-ferrous alloys, corrosion-resistant alloys and super-alloys. Other uses of these metal salts are in electroplating, as catalysts, in nickel–cadmium batteries, in coins, in welding products, and in certain pigments and electronic products (Ake et al. 2001; Tunali et al. 2006). The toxicity of cobalt ions contributes to a large number of health conditions, including major killer diseases such as heart disease, cancer and diabetes. Cobalt concentrates in the kidney, liver and various other organs. It is considered more toxic than either lead or mercury since it is toxic at levels which are one-tenth those of lead, mercury, aluminium or nickel (Linder 1985). Equally, nickel is also a toxic heavy metal with nickel compounds suspected of causing cancer. Health effects that are a direct result of the uptake of high concentrations of these

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Metals include vomiting and nausea, vision problems, heart problems, thyroid damage, diarrhoea, coma, cancer and even death (Patnaik 1999).

The concentrations of these pollutants must be reduced by means of treatment to meet legislative standards. Several methods have been reported for the removal of heavy metal ions such as ion exchange (Dizge et al. 2009), filtration (Fatin-Rouge et al. 2006), coagulation (El-Samrani et al. 2008), adsorption (Aguado et al. 2009) and electrochemical deposition (Chen and Lim 2005). Adsorption has become one of most commonly used treatment methods for the removal of nickel and cobalt ions. Many adsorbents have been developed and used to remove metal ions from wastewater, such as hybrid EDTA/zirconium phosphate cation-exchanger (Nabi et al. 2009), hazelnut activated carbon (Koby et al. 2002), peanut hulls (Hashem et al. 2005), montmorillonite (Miao et al. 2009), kaolinite (Bhattacharyya et al. 2009), titania gel (Yacoub et al. 2005), crab shell particles (Vijayaghavan et al. 2005) and chelating resin (Abuilaiwi et al. 2009). However, the removal efficiencies of these adsorbents towards metal ions were low and the adsorbents themselves were expensive. Hence, further attention and research are required to develop novel adsorbents for heavy metal ions which demonstrate high efficiency and low cost.

The aim of the present work was to explore the adsorption behaviour of Ni(II) and Co(II) ions onto a chelating resin containing 2-(4-methylbenzylidene)hydrazine. Such a resin can be synthesized both simply and productively via a condensation reaction. In this regard, chloromethylated styrene-DVB beads were treated with hydrazine and condensed with 4-methylbenzaldehyde. The effects of pH, contact time, initial metal ion concentration and the amount of resin were systematically studied to optimize the adsorption of Ni(II) and Co(II) ions onto the chelating resin. The adsorption equilibrium and kinetic data were fitted using different models and their parameters were evaluated.

MATERIALS AND METHODS

Chemicals

Chloromethylated styrene-DVB beads were obtained from Thermax Ltd., India. The reagents used in the synthesis of the functionalized resin were supplied by Sigma Aldrich, U.S.A. The standard solution (1000 mg/l) for atomic absorption measurements was purchased from Merck, Germany. All other reagents employed were of A.R. grade and all experiments were performed at room temperature (30 ± 1 °C).

Instruments

Atomic absorption measurements were undertaken on a single-beam atomic absorption spectrometer (Analytik-Jena-Nova-400) in flame mode, employing a 100 mm burner, a cross-flow nebulizer at 5.0 ml/min and 1.2 mm slit width in all experiments. Each experiment was undertaken twice under identical conditions using this instrument for concentration determinations. IR spectra were recorded on a JASCO FT-IR spectrometer model 610 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 at pH values of 4, 7 and 10 using appropriate buffer solutions.
Preparation of the resins: general procedure

To 20 g of resin (chloromethylated styrene–divinylbenzene copolymer, 6.5% divinylbenzene) was added 100 mL of dichloromethane and the resulting mixture stirred for 2 h at room temperature to allow swelling. Then, 10 mL of hydrazine (95%) was added to this reaction mixture and the resulting mixture refluxed with continuous stirring for 3 h. The product was filtered off and washed with de-ionized water and methanol. The hydrazine-containing resin was obtained on drying in a vacuum desiccator. Ethanol (50 mL) was then added to 10 g of the hydrazine-containing resin and the resulting mixture stirred for 1 h. After this time, 5 mL of 4-methyl benzaldehyde was added to the mixture which was then refluxed for a further 5 h with continuous stirring. The final reaction product was washed with ultrapure water (Elix: resistivity, 18.2 MΩ cm) until a neutral pH was obtained when the solid was dried. This dried material was then characterized by FT-IR spectroscopy.

Adsorptive studies

Standard stock solutions of Co(II) and Ni(II) ions (1000 mg/L) were purchased from Merck, Germany. These stock solutions were subsequently diluted with de-ionized water to obtain the desired test concentrations of the metal ions concerned. The adsorption of both Ni(II) and Co(II) ions onto the functionalized resin was studied in batch mode. Thus, a number of glass bottles containing a definite volume (10 mL in each case) of solutions of the metal ions of desired concentration and pH were placed in a thermostatted water bath at a known temperature. For equilibrium studies, 100 mg of adsorbent was treated with 10 mL of 1000 µg/L metal ion solutions and the resulting mixtures maintained for 2 h at a constant temperature to ensure that equilibrium had been attained. For the kinetic studies, samples (2 mL) were taken from the solutions at different time intervals and filtered through a 0.45 µm filter and the concentration of the corresponding metal ion determined using AAS in the flame mode. The effect of pH on the adsorption was studied at constant time, constant initial ion concentration (1000 µg/L) and constant amount of functionalized resin. Similarly, the effects of the initial concentration of metal ion and amount of resin were also studied in detail.

All the experiments were carried out in duplicate and the average of the values was used for further calculations. For the calculation of the average value, the percentage relative standard deviation for each sample was calculated. Data for samples having standard deviations greater than 5% were not employed. The samples were analyzed three times and the mean values were used for different isotherm models and adsorption kinetics. The amount of metal ion adsorbed per unit mass of the functionalized resin at equilibrium was evaluated using following equation:

\[
Q_e = \frac{(C_i - C_e)V}{m}
\]  

(1)

where \(C_i\) is the initial metal ion concentration (µg/L), \(C_e\) is the metal ion concentration at equilibrium (µg/L), \(V\) is the volume of the metal ion solution (mL) and \(m\) is the mass of functionalized resin (g). The percentage metal ion removal was evaluated from the equation:

\[
\%\text{Removal} = \left(\frac{C_i - C_e}{C_i}\right) \times 100
\]  

(2)
RESULTS AND DISCUSSION

Characterization of functionalized resin beads

A schematic representation of the functionalization of the styrene–DVB copolymeric resin is given in Scheme 1. The FT-IR spectrum of the functionalized resin (Figure 1) showed absorption bands at 3550, 3060, 2910, 1705, 1570–1400, 1073 and 840 cm⁻¹ due to NH stretching, Ar–H stretching, C–H stretching, C=N stretching, C=C stretching in the aromatic system, N–N stretching and C–H bending, respectively. The appearance of the characteristic IR absorption bands of these groups provides proof for the functionalization of the resin.

![Scheme 1. Schematic representation of the functionalization process employed for the resin.](image)

![Figure 1. FT-IR spectrum of functionalized resin.](image)

Adsorption studies

Effect of contact time

The influence of contact time on the adsorption of Ni(II) and Co(II) ions onto functionalized styrene–DVB copolymeric resin was investigated employing an initial constant concentration
(1000 µg/ℓ) of the metal ions and determining their concentrations in solution after 30, 60, 90, 120, 150 and 180 min, respectively. The corresponding data are depicted in Figure 2. It will be seen from the figure that the adsorption of the metal ions increased with time and then attained an equilibrium value (Abdel-Ghani et al. 2007; Kumar et al. 2008). At equilibrium, the metal ion uptake for Ni(II) ions was 73.3% after 120 min while that of Co(II) ions was 82.5% after a similar time interval. After this time, no further adsorption was observed for both ions and this time was therefore regarded as the equilibrium contact time. The speed of the adsorption process may be attributed to the presence of chelating groups which provide good coordinating centres on the surface of the functionalized resin.

**Effect of pH**

The pH of the aqueous solution is one of the important factors governing the adsorption of metal ions. In the present work, adsorption studies for both Ni(II) and Co(II) ions were carried out under similar conditions at pH values of 3, 6 and 10, respectively. The initial pH of the solution has a significant influence on the amount of metal ion adsorbed. It was observed that the percentage adsorption of both Ni(II) and Co(II) ions from aqueous solution was low at lower pH values but increased as the initial pH value of the solution increased. The influence of pH can be related to the fact that, at low pH, hydrogen ions strongly compete with metal ions for the available adsorption sites on the surface of the functionalized resin and metal ion adsorption under such conditions is not significant. However, with increasing pH, electrostatic repulsion between the metal ions in solution and the sorption sites on the resin decreases due to the reduction in the positive charge density on these sites, thereby resulting in an increase in metal ion adsorption (Bhattacharya et al. 2006). From the experimental results listed in Table 1, it is seen the maximum adsorption was achieved at pH 6 for both the Ni(II) and Co(II) ions.

**Figure 2.** Adsorption of (●) Ni(II) and (▲) Co(II) ions onto the functionalized resin at different time intervals. Experimental conditions: initial metal ion conc. = 1000 µg/ℓ; amount of functionalized resin employed = 100 mg; temperature = 30 ± 1 °C; pH = 6.0.
Metal ion uptake from aqueous solution is particularly dependent on the initial metal ion concentration in the system. At low concentrations, metal ions are adsorbed by specific active sites whilst, at higher concentrations, saturation of such sites leads to a lower uptake of metal ions. Though an increase in metal ion uptake was observed in the present studies, the decrease in percentage adsorption may be attributed to lack of sufficient surface area to accommodate much more of the metal ions available in the solution. This appears to be due to the increase in the number of ions competing for the available active sites on the surface. The experimental results obtained using varying initial concentrations of metal ions (500–1200 µg/ℓ) at optimum pH are illustrated in Figure 3. This shows that a significant increase occurred in the adsorption of Ni(II) and Co(II) ions as the initial concentration of the metal ions was increased from 500 µg/ℓ to 1000 µg/ℓ.

**TABLE 1.** Effect of pH on the Adsorption of Ni(II) and Co(II) Ions from Aqueous Solution

| pH | % Adsorption | Ni(II) ions | Co(II) ions |
|----|--------------|-------------|-------------|
| 3  | 56.8         | 67.8        |             |
| 6  | 73.3         | 82.5        |             |
| 10 | 52.3         | 61.7        |             |

*Experimental conditions: initial metal ion conc. = 1000 µg/ℓ; contact time = 120 min; temperature = 30 ± 1 °C.*

**Effect of initial metal ion concentration**

**Figure 3.** Effect of the initial concentration of metal ions on the adsorption of (♦) Ni(II) and (▲) Co(II) ions onto the functionalized resin. Experimental conditions: amount of functionalized resin employed = 100 mg; temperature = 30 ± 1 °C; pH = 6.0.
Adsorption isotherms

Initial Ni(II) and Co(II) ion concentrations in the range 500–1100 µg/ℓ were employed to investigate the adsorption isotherms for the metal ions onto functionalized styrene–DVB copolymeric resin. In both cases, equilibrium was attained after 120 min contact time. The amounts of Ni(II) and Co(II) ions adsorbed onto the functionalized resin were found to increase as the initial metal ion concentration in the solution increased. This continued up to an initial concentration of 1000 µg/ℓ but levelled off at higher initial concentrations. Two isotherm models, viz. the Langmuir model (Langmuir 1916) and the Freundlich model (Freundlich 1906), were used to analyze the experimental data.

The Langmuir isotherm model may be expressed by the equation:

\[
\frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m}
\]  

where \(C_e\) is the equilibrium concentration in the solution (µg/ℓ) obtained after contact with the chelating resin for a given period of time, \(Q_e\) is the amount of Ni(II) or Co(II) ions adsorbed per g of functionalized resin (µg/g) at equilibrium, \(Q_m\) is the maximum adsorption capacity (µg/g) and \(b\) is the Langmuir parameter related to the energy of adsorption. The magnitude of \(Q_e\) may be derived from equation (1). Linearity of the plot of \(C_e/Q_e\) versus \(C_e\) indicates that the adsorption data corresponded to the equilibrium values (Gupta and Babu 2009), allowing the values of \(1/(Q_m b)\) and \(1/Q_m\) to be obtained from the intercept and slope, respectively. The corresponding values obtained for \(Q_m\), \(b\) and the correlation coefficient, \(R^2\), are all listed in Table 2.

The Freundlich isotherm can be expressed as:

\[
\log Q_e = \frac{1}{n} \log C_e + \log K_F
\]  

where \(K_F\) and \(1/n\) are Freundlich constants indicating the sorption capacity and the sorption intensity, respectively, while \(C_e\) is the equilibrium concentration of Ni(II) or Co(II) ions in the aqueous solution and \(Q_e\) is the sorption capacity. The intercept and slope of the plot of \(\log Q_e\) against \(\log C_e\) correspond to \(\log K_F\) and \(1/n\), respectively. The values obtained for these quantities in the present studies are also listed in Table 2.

| Table 2. Langmuir and Freundlich Parameters for the Adsorption of Ni(II) and Co(II) Ions onto Functionalized Styrene–DVB Copolymeric Resin |
|---|---|---|---|---|---|---|
| Metal ion | Langmuir model | Freundlich model |
| | \(Q_m\) (µg/g) | \(b\) (µg/ℓ) | \(R^2\) | \(K_F\) | \(1/n\) | \(R^2\) |
| Ni(II) | 6666 | 0.01363 | 0.9805 | 6.323 | 0.6048 | 0.9373 |
| Co(II) | 9985 | 0.01785 | 0.9915 | 3.952 | 0.4829 | 0.9742 |

It will be seen from data listed in the table that application of the Langmuir model to the experimental data gave a higher correlation coefficient, thereby suggesting possible monolayer coverage of Ni(II) and Co(II) ions on the surface of the functionalized resin.

Adsorption kinetics

The kinetic studies of the adsorption of Ni(II) and Co(II) ions from aqueous solution onto the functionalized resin were undertaken at initial ion concentrations of 1000 µg/ℓ and a pH value
of 6. The corresponding kinetic data were evaluated using one conventional model, viz. the pseudo-second-order equation (Ho and McKay 2000), since very low correlation coefficients were observed when the first-order model was applied which indicated its low applicability.

A pseudo-second-order reaction may be described mathematically by the expression (Ho and McKay 1999; Allen and Brown 1995):

$$\frac{t}{Q_t} = \frac{1}{(k_2Q_e)^2} + \frac{t}{Q_e}$$

where $Q_e$ ($\mu$g/g) is the amount of metal ion sorbed at equilibrium, $Q_t$ ($\mu$g/g) is the amount of metal ion on the surface of the sorbent at time $t$ and $k_2$ [g/(μg min)] is the rate constant for the pseudo-second-order adsorption process. The values of $1/(k_2Q_e)^2$ and $1/Q_e$ may be derived experimentally from the intercept and slope of the linear plots of $t/Q_t$ versus $t$, thereby allowing the values of $k_2$ and $Q_e$ to be obtained (see Figure 4).

The kinetic data for the pseudo-second-order assessment are listed in Table 3. It will be observed that the pseudo-second-order approach gave high correlation coefficient values,
thereby indicating that the pseudo-second-order model was applicable to the present adsorption kinetics.

**CONCLUSIONS**

The use of functionalized resin as an adsorbent for Ni(II) and Co(II) ions has been studied. It was observed that the functionalized resin provided an effective adsorbent for the two metal ions, the maximum adsorption capacities for Ni(II) and Co(II) ions being 6.67 mg/g and 9.985 mg/g, respectively. Such maximum adsorption capacities were obtained under optimum conditions, viz. initial concentration of metal ions = 1000 µg/ℓ, pH = 6 and contact time = 120 min. The sorption capacity was strongly dependent on the adsorbent dosage, the initial concentration of metal ions employed and the initial pH of the aqueous system. The experimental data were well fitted by the Langmuir and Freundlich equations, as demonstrated by the good correlation coefficients obtained. Detailed kinetic studies of the rapid adsorption process revealed that equilibrium adsorption was attained within 120 min. The adsorption rate was pseudo-second-order and gave reaction rate constants, $k_2$, of 0.2561 g/(min µg) and 0.0748 g/(min µg)] for the adsorption of Ni(II) and Co(II) ions, respectively, onto 100 mg of functionalized resin from solutions with an initial ion concentration of 1000 µg/ℓ at a pH value of 6.0 and a temperature of 30 ± 1 °C. Although the adsorption studies were carried out by the batch method, functionalized resin may be a good adsorbent for the treatment of wastewater contaminated by dangerous and highly toxic metal ions, i.e. Ni(II) and Co(II).

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