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Sequestering of Cd (II) and Ni (II) from aqueous solutions onto chelex 100

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ABSTRACT

The chelating exchange resin Chelex 100, with functional group iminodiacetic acid (IDA), was used to remove Cd (II) and Ni (II) from aqueous solutions. Batch elution experiments using Cd (II) and Ni (II) solutions were compared. Experiments were finally performed at different pH values (2.0–7.0), metal ion concentrations (10–500 mg/l), and resin dose (1 g–15 g/l of metal ion solution), stirring speed (50–250 rpm) and contact time (10–120 min) at 25 ± 5°C. Maximum metal removal was observed at pH 5.0 to 6.0. The removal efficiency of Chelex 100 for Cd (II) and Ni (II) removal were found to be 100% and 82.5% respectively for dilute solutions at 15 g/l resin dose under optimized conditions. The results revealed that Cd (II) and Ni (II) can be considerably removed by chelex 100 and it could be a potential material for the removal of these heavy metals from aqueous systems.

Keywords: Ion exchange; Iminodiacetic acid; Kinetic studies

1. Introduction

Water plays an important role in natural environment, and social development, but the subsequences of water use are municipal wastewaters and industrial wastewaters. Heavy metals are released into the environment due to rapid industrialization and have created a major global concern. Heavy metal pollution is currently of great concern due to increased awareness of the hazardous effects of the elevated levels of these chemicals in the environment [1]. Cadmium, nickel, chromium, copper, lead and mercury are often detected in industrial wastewaters, which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic, radiator manufacturing, alloy industries, storage batteries industries, etc. [2,3] and these usually contain metal-ion concentrations much higher than the permissible levels and do not degrade easily into harmless end products [4]. The Ni (II) concentration in wastewater from mine drainage, tableware plating, metal finishing and forging has been reported up to 130 mg/l. The permissible limits of cadmium for the discharge of wastewater are 0.1 mg/l in India. Separation of heavy metals from wastewater has received a considerable amount of attention in recent years due to the concern that heavy metals can be readily absorbed by organisms. These absorbed heavy metals consequently enter human food chains, and thus exert a high health risk to the community and biosphere in general [5]. Due to their high toxicity, industrial wastewaters containing heavy metals are strictly regulated and must be treated before being discharged in the environment. Industrial wastewaters containing heavy metals are generally treated by adjusting solution pH to form metal precipitates followed by coagulation, clarification and filtration. Although the chemical precipitation method is quite effective for heavy metal

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removal, the resultant heavy metal sludge is classified as a hazardous solid waste and needs to be adequately treated. Sometimes, treatment and final disposal of metal laden sludge is more problematic than treating heavy metal-containing wastewaters. Other methods such as electrodialysis [6], reverse osmosis [7,8], biosorption including some economic bio-adsorbent [9–15] and adsorption [16–21] are also feasible with certain limitations.

Among the heavy metal removal processes, ion exchangers are very effective to remove various heavy metals and can be easily recovered and reused by regeneration operation. Ion-exchange resins have a variety of different types of exchange materials, which are distinguished into natural or synthetic resin. The use of the ion exchangers to remove metals from wastewater has been extensively studied. Previous researches focused on the equilibrium relationship between the ion exchange resin and exchanged ions [22,23]. However, selective recovery or removal of one or more heavy metals from multimetal mixtures using common organic cation exchange resins is generally not feasible, particularly for those metal ions with the same valency [24,25]. In yesteryears, use of chelating resins for this purpose has been extensively examined [26–28]. For such studies, the resins with IDA (Imminodiacetic Acid) ligand such as Chelex 100, Amberlite IRC 748, and Purolite S930 have been often used due to their high selectivity and low manufacturing cost [29]. The IDA ligand could provide electron pairs so that the binding forces for alkaline earth metals is 5,000 times than those for alkali metals such as Na^+; i.e., the IDA ligand can readily react with heavy metal ions to form a stable coordination covalent bond [25–29].

The removal behaviors of Cd (II) and Ni (II) with Chelex 100 cation exchange resin were investigated in this study. The effects of pH, adsorbent dose, concentration of metal ions and contact time have been investigated. The data obtained may be useful for environmental engineers in designing heavy-metal-containing wastewater treatment systems.

2. Materials and methods

2.1. Preparation and conditioning of resin

The chelating resin, Chelex 100 (Fluka chemicals, USA), containing iminodiacetic acid functional ligand was used. The physical properties and specifications of Chelex 100 as reported by the suppliers are given in Table 1. Prior to use, the resins were washed with 1 mol/dm^3 HCl and 1 mol/dm^3 NaOH to remove possible organic and inorganic impurities, washed with double distilled water for three times, and converted to Na^+ form with 1 mol/dm^3 NaCl for 12 h. Chelex 100 was finally washed with double distilled water and dried in vacuum oven at 60°C.

2.2. Reagents

Stock metal solutions of Cd (II) (1000 mg/l) and Ni (II) (1000 mg/l) were prepared by dissolving cadmium nitrate and nickel nitrate (Merck, AR Grade) respectively in double distilled water. The stock solutions were diluted with distilled water to obtain the desired concentration range for all the metal ions. pH of the solutions was adjusted by 0.01 mmol NaOH/0.01 mmol HCl using pH meter (Thermo-Orion, 420A). Ni (II) concentration was determined using standard methods [Double Array UV–Vis Spectrophotometer, Agilent 8453] using standard methods [30]. The Cd (II) concentration was determined potentiometrically using Thermo Orion 920A ion selective meter.

2.3. Experimental

Batch experiments were carried out at various pH (2–8), resin dose (0.1 –1.5 g), for a contact time of 60 min. For each batch experiment, 100 ml metal ion solution of 50 mgl^{-1} concentration was used. After adding desired amount of resin, pH was adjusted and the mixture was agitated on a mechanical shaker for 60 min. After that the mixture was centrifuged at 4000 rpm for 10 min to separate the resin from supernatant. The residual concentration of metal ion in supernatant was determined as stated in the reagent section. All experiments were replicated thrice for all the metal ion solutions and results were averaged. The percentage removal (R %) of the metal ions was calculated for each run by following expression:

$$R(\%) = \frac{C_i - C_e}{C_i} \times 100$$

where C_i and C_e were the initial and final concentration of metal ion in the solution. Under the experimental

Table 1
Physical and chemical properties of the chelating resins used (As provided by the supplier)

Properties	Chelex 100
Grade	Industrial Grade
Physical form	Opaque, beige beads
Functional group	Paired Iminodiacetic acid
Matrix	Styrene-divinylbenzene
Structure	Macroporous
Particle size (mm, dry)	50–100 Mesh
Capacity (equiv/m^3 of resin)	1250
Bulk density ρs (kg/m^3)	968
pH range	0–14
Maximum operating Temperature	80–90°C

conditions, the removal capacities of Chelex 100 for each concentration of studied metal ions at equilibrium were calculated by following equation:

$$q_e(mgg^{-1}) = \left[\frac{C_i - C_e}{W_R}\right] \times V$$

where W_R is the Weight of dry resin and V is the volume of solution.

3. Results and discussion

Chelex 100 resin is composed of styrene divinylbenzene copolymers (Fig. 1a) with imminodiacetate functional groups (Fig. 1b). Iminodiacetate ions act as chelator for binding polyvalent metal ions. Chelex 100 is very effective in binding metal contaminants with a high selectivity for divalent ions, without altering the concentration on non-metal ions. At low pH, the imines, nitrogen and the carboxyl groups are protonated. The protonated nitrogen is positively charged, and can attract anions; the carboxyl groups are neutral and unreactive. As pH increases, anion sorption decreases and cation sorption increases until at pH > 12 the resin functions solely as a cation exchanger. In the case of iminodiacetic acid type resin, the distribution coefficient value reaches a maximum around pH 5 [31].

3.1. Effect of pH

The pH of the aqueous solution is an important variable, which controls the removal of the metal at Chelex–water interfaces. To determine the pH effect on removal capacity of materials, solutions were prepared at different pH levels from 2 to 7 before adding Chelex 100. The effect of pH on metal exchange was determined in batch experiments and the results are given in Fig. 2. The percentage removal followed increasing trend with increasing pH values for all the metals. The removal efficiency of Cd (II) and Ni (II) increases from 39 to 100% and 22 to 82% respectively for Chelex 100 resin with increase in the pH from 3.0 to 5.0 for Cd (II) and 3.0 to 6.0 for NI (II). At lower pH, the removal was less, may be because of the surface area of the resin was more protonated and competitive exchange of ions occurred between H⁺ protons and free metal ions towards the fixation sites [32]. Metal exchange starts when the pH rises to the range where most acidic ion exchange sites start to exchange hydronium ion for metal and the capacity reaches the maximum value in the pH range where all the ion exchange sites take part in the reaction and the

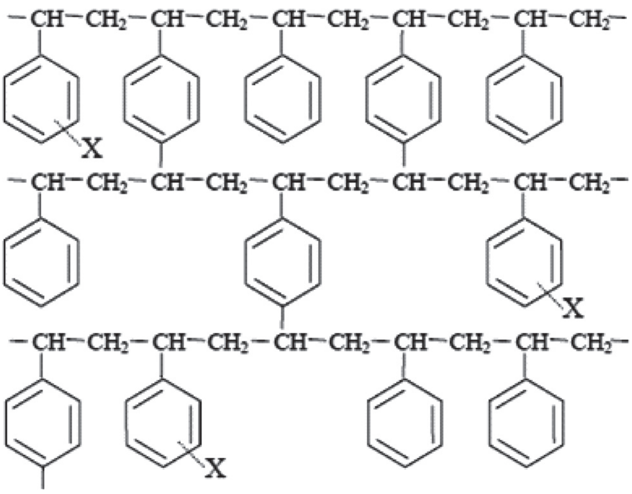

Fig. 1a. Styrene divinylbenzene copolymers.

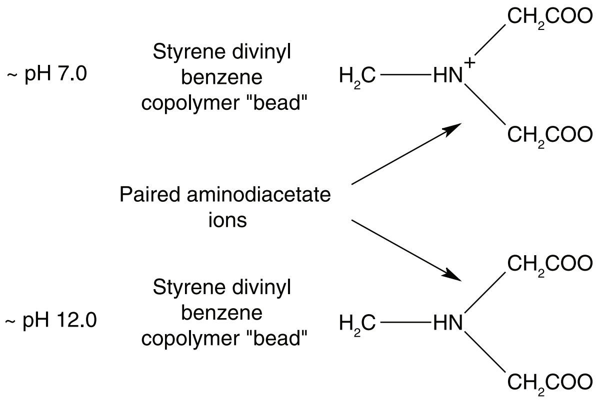

Fig. 1b. Styrene divinylbenzene copolymers with paired iminodiacetate ions.

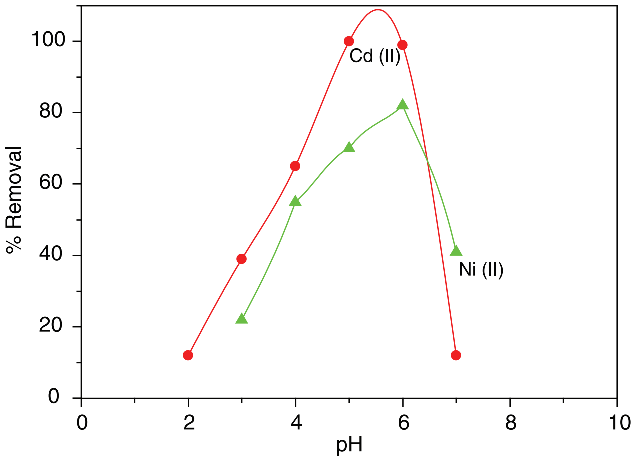

Fig. 2. Effect of equilibrium pH on the amount of metal ions exchanged with chelex 100 resin.

functional group is able to form chelate rings with the metal cations. The pH has a strong effect on the competing complexation. In waste solutions there are complex forming agents, which dissociate and become reactive as hydronium ion concentration decreases. In the neutral region the autoprotolysis of water produces hydroxide ions, and in the alkaline pH range hydrolysis of cations and complexation with dissolved atmospheric carbonate takes place, which interferes with metal sorption at trace concentrations. For avoiding precipitation of metals high pH values were not preferable and the optimum pH was chosen as in the region of pH 5–6 for all the three metals [33].

3.2. Effect of resin dose

The removal of Cd (II) and Ni (II) with Chelex 100 was studied at different resin dosages [0.1 to 1.5 g / 100 ml of Cd(II) solution] keeping metal ion concentration (50 mg/l), stirring speed (250 rpm), pH (6.0 for Ni (II) and 5.0 for Cd (II)) and contact time (60 min) constant. The results (Fig. 3) indicate that increase in resin dose resulted in a higher removal of Cd (II) and Ni (II). Maximum removal was observed with resin dose of 15 g/l Chelex 100. The increase in the percentage removal with increase in the resin dose is due to the increase in the number of exchange sites. The removal capacity was lesser at higher resin doses (Table 2). This may be attributed to overlapping or aggregation of exchange sites resulting in decrease in total Chelex 100 surface area available to metal ions and an increase in diffusion path length.

3.3. Effect of contact time

Chelex 100 of definite mesh size [50–100 Mesh, (ASTM)] was used to evaluate various kinetic parameters. pH of the solution was adjusted to the value at which maximum sorption of respective metal ion takes place. Metal ion solution (50 mg/l), was shaken with 1.5 g of exchanger in stoppered conical flasks at constant temperature and predetermined time intervals with increments of 10 min (10, 20, 30, … 120). The supernatant was removed immediately after each prescribed time interval and the metal concentration was evaluated. Results so obtained from this study are described in the Fig 4. Maximum removal was attained after 60 min. (100% for Cd (II) and 81% for Ni (II). After 60 min very less or no removal was observed.

3.4. Effect of stirring speed

A proper stirring is required for the proper contact of the metal laden synthetic solutions with resin. To see the effect of stirring speed on the sequestering capacity of Chelex 100, mechanical shaking was given to the resin mixed with solution from 50 rpm to 250 rpm. As shown in the Fig. 5 maximum removal was observed at 250 rpm for the three heavy metals, reason being the density of the resins is more so they generally do not come in contact with the aqueous solution at low stirring speed in batch scale experiments.

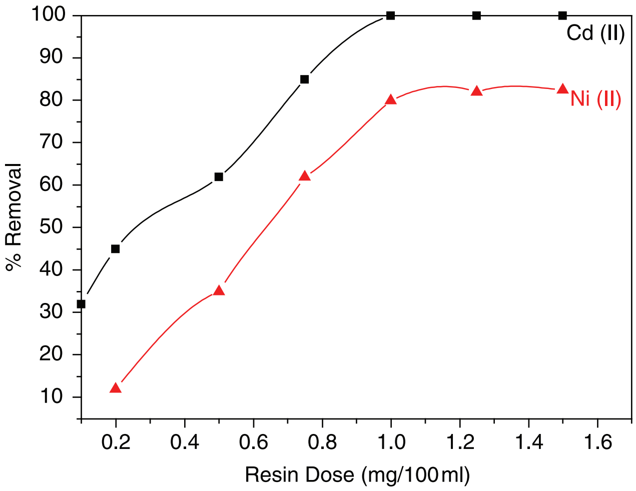

Fig. 3. Effect of resin dose on the amount of metal ions exchanged with chelex 100 resin.

Table 2
Removal capacities (mgg^{-1}) of different metal ions at different resin doses of chelex 100

Resin dose (g/l)	Cd (II) (mg/g)	Ni (II) (mg/g)
0.5	62	45
0.75	56.6	41
1.0	50	40
1.25	40	32.8
1.5	33.3	27.8

Table 3
Removal capacities (mgg^{-1}) of different metal ions at different metal ion concentrations

Metal ion concentration (mg/l)	Cd (II)	Ni (II)
50	33.3	27.8
75	43	32.5
100	45.33	34.67
150	53	38
200	64	40
250	66.67	43.3
500	83.3	50

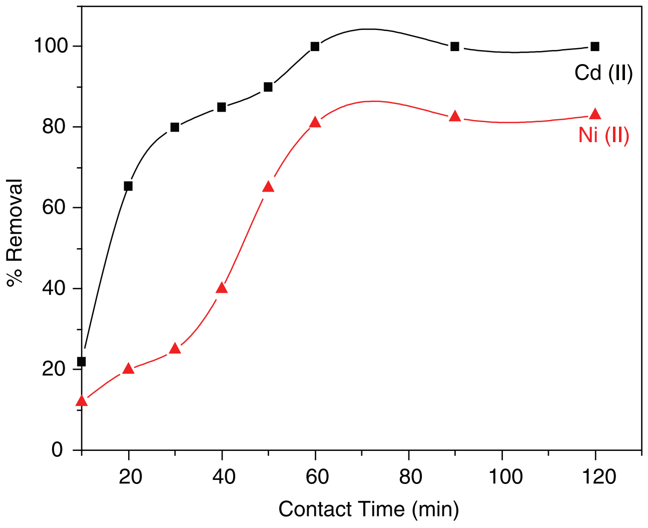

Fig. 4. Effect of contact time on the amount of metal ions exchanged with chelex 100 resin.

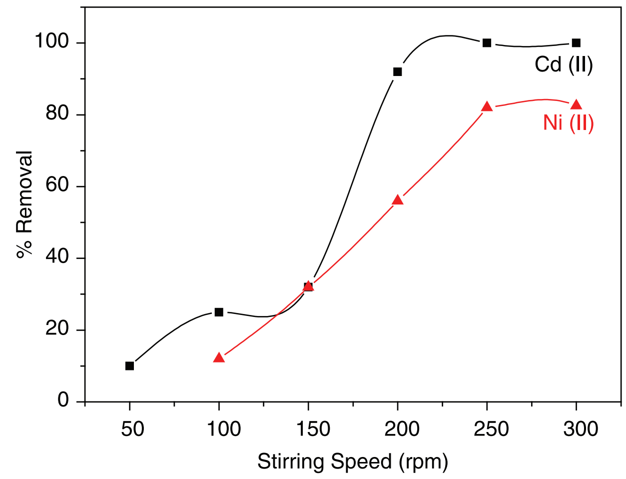

Fig. 5. Effect of stirring speed on the amount of metal ions exchanged with chelex 100 resin.

3.5. *Effect of initial metal ion concentration:*

Solutions of desired concentration (10–500 mg/g) from the standardized NI (II) and Cd (II) stock solutions were prepared using double distilled deionized water. Fig. 6 shows the effect of varying metal concentrations on the removal under the optimized conditions of 60 min contact time and 1.5 g of resin dose in aqueous medium. It was found that the metal amounts retained were almost stable in this concentration range for all three metals. The maximum removal efficiency was obtained as 100%, and 82.5% for cadmium (II) and nickel (II) respectively with optimum concentration of 50 mg/l.

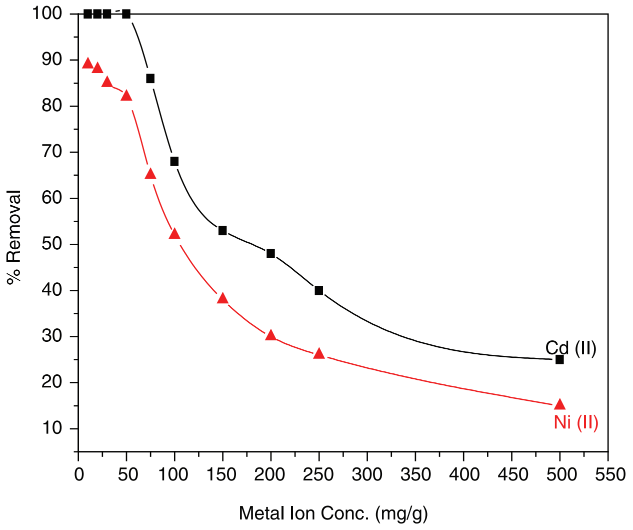

Fig. 6. Effect of metal ion concentration on the amount of metal ions exchanged with chelex 100 resin.

4. Conclusion

A commercial cation exchange resin, Chelex 100, was used in adsorption experiments to investigate removal behaviors of the heavy metals Cd (II) and Ni (II) in aqueous solutions. The optimum dosage of the resin for the removal of dissolved metal ions was 15 g/l with a metal concentration of 50 mg/l.

1. Each metal ion was almost totally exchanged onto the resin, approaching equilibrium, within an hour from the start of reaction. Additionally, the pH of the solution decreased as the reaction proceeded due to deprotonation of the imino-diacetate group of the resin.
2. The maximum amounts (%) of metals removed by the resin were 100% for Cd (II) and 82.5% for NI (II).
3. The sorption properties of heavy metals onto Chelex 100 were strongly influenced by the presence of competing cations in the solution. Cd (II) and Ni (II) which have an equivalent electrovalence were adsorbed onto the resin to similar degrees under similar experimental conditions in the solution.
4. The metal selectivity of the resin was in the order of Cd (II) > Ni (II).

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