

Assessment of Functional Characteristics of Some Metal Chelating Polymers

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Abstract: Lewatit mono plus S100H and purolite C100 are ion-exchange resins, which were selected for study. Polystyrene is the resin matrix cross linked with divinyl benzene for the studied resins. Heavy metal ions [Cd(II) and Pb(II)] and also Mn(II), Fe(II), Co(II), Ni(II), Bi(II) and Cu(II) were removed with these ion-exchange resins. The metal ion uptake efficiency, reusability of the resins, thermodynamic parameters, and effects of pH. Metal ion concentration, resin weight, sodium chloride concentration, temperature and stirring time on the metal removal were also studied. The amount of metal uptake by the studied resins was determined by atomic absorption spectrophotometry and inductively coupled plasma spectrophotometry. Both resins manifested reasonable removal efficiencies for the studied elements.

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1. Introduction

Heavy metals present numerous ecological and environmental concerns when their concentrations in soil for water exceed permissible limits^[1-5]. Examples of these pollutants are lead, mercury, manganese, silver, cadmium, barium and others.

Chemical precipitation, adsorption, solvent extraction, membrane processes (reverse osmosis) and ion exchange are the most important methods for removing the toxic heavy metal ions from the aqueous solutions^[6-10].

The selection of a particular process for the removal heavy metal ions (HMS) should depend on reliable technical, environmental removal.

One of the most practical methods for the removing of the toxic heavy metal is the adsorption of heavy metals by a variety of substances^[11]. Extensive efforts had been made to develop low-cost adsorbents, for removal of metals from aqueous solutions including natural and industrial wastewater^[12,13].

Using the exchange of ions as a method of treating, the adsorbents have to achieve the number of requirements to be active, stable, accessible, cheap, easy to regenerate^[14-16].

There are many factors that affect on the exchange of the dissolved elements with the ion exchangers including solution pH, time of contact, metal ion concentration, temperature, organic matter, the presence of competing ions, particle size and others^[17,18].

In this paper commercial resins for the removal of Cd(II) and Pb(II) from industrial effluents are: Lewatit mono plus S100H and Purolite C100, where they are

cationic exchange resins of gel resin type of polystyrene matrix, crosslinked with divinylbenzene.

2. Experimental

Materials

Hydrochloric acid (BDH) and sodium hydroxide (Merck) were used for adjusting pH metal ion solutions. Stock solutions of metal ions were prepared using lead acetate (Aldrich) and cadmium chloride (BDH) salts. The effect of sodium chloride (Aldrich) on the metal uptake was studied.

Physico-chemical measurements:

Metal uptake of Cd(II) ions and Pb(II) ions by using the studied resins were estimated by atomic absorption spectrophotometry (Varian SpectrAA-220) and inductively coupled plasma spectrophotometry (ICPS-7500).

Procedure for the sorption of metal ion at different pHs

Investigated metal ions [Cd(II) or Pb(II)] solutions (100 ml) pHs were adjusted by 0.1 M HCl and 0.1 M NaOH at a suitable weight of resin in a 100 ml beakers were stirred magnetically for 2h. The metal laden resin was filtered. The amounts of Pb (II) and Cd(II) present in the filtrate were determined by atomic absorption spectroscopy [Pb, 283.3 nm and Cd, 228.8 nm].

Sorption of metal ion at different resin weights:

Investigated metal ions [Cd(II) or Pb(II)] solutions (100 ml) at a certain pH value – according to the type of resin and metal ion- with a different resin weights were stirred magnetically for 2h. The metallated resin was filtered. The amounts of Pb (II)

and Cd(II) present in the filtrate were determined by atomic absorption spectrophotometry.

Sorption of metal ion at different sodium chloride concentrations:

Metal ion [Cd(II) or Pb(II)] solutions (100 ml) at a certain pH, suitable resin weight with different sodium chloride concentrations (1000, 5000, 10000, 15000 and 20000 mg /L) were stirred magnetically for 2h. The metallated resin was filtered. The amounts of Pb (II) and Cd(II) present in the filtrate were determined by atomic absorption spectrophotometry.

Sorption of metal ion at different stirring time:

Metal ion [Cd (II) or Pb(II)] solutions (100 ml) at a certain pH, suitable resin weight were stirred magnetically for different periods of time [15, 30, 45, 60 and 120 minutes]. The metallated resin was filtered. The amounts of Pb (II) and Cd(II) present in the filtrate were determined by atomic absorption spectrophotometry.

Sorption of metal ion at different temperature:

Metal ion [Cd (II) or Pb (II)] solutions (100 ml) at certain pH and resin weight are studied at different temperature degrees (25, 30, 35 and 40 °C). The mixture were placed and stirred magnetically for 2h. The metallated resin was filtered. The amounts of Pb (II) and Cd(II) present in the filtrate were determined by atomic absorption spectrophotometry.

Sorption of metal ion at different metal ion concentration:

Metal ion [Cd(II) or Pb(II)] solutions (100 ml) at certain pH, resin weight and temperature of 25 °C in a 100-ml beakers were stirred magnetically for 2h. The metallated resin was filtered and washed several times by distilled water. The amounts of Pb (II) and Cd(II) present in the filtrate were determined by atomic absorption spectrophotometry.

Metal uptake:

Metal uptake was carried out by the batch technique at room temperature by stirring the resin with Cd(II) or Pb(II) solutions, the metal uptake percentage (M%) was calculated as the following.

$$M \% = \frac{(C_o - C_e) \times 100}{C_o}$$

Where:

C_o , the initial concentration of the metal ion.

C_e , the final concentration of the metal ion.

3. Results and Discussion

Effect of pH on removal of metal ions:

The effect of pH on the metal uptake by the studied resins is shown in Figure (1). Lewatit mono plus S100H shows almost stable performance at the investigated operational range. Further Purolite C100 manifests decreasing uptake in the alkaline range. The

observed decrease in sorption at higher pH is due to the formation of insoluble hydroxy complexes of the metal ions [19].

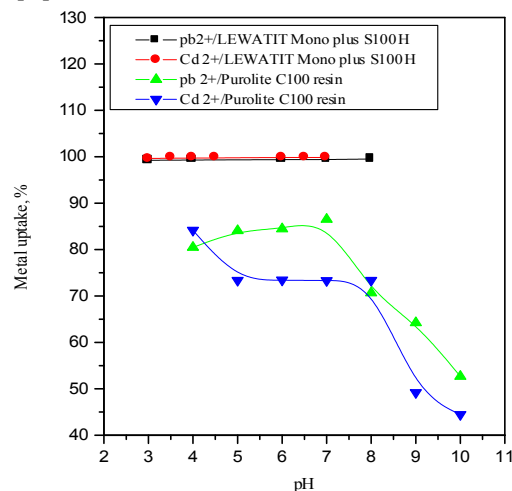


Fig. (1): Effect of pH on the sorption of Cd (II) and Pb (II) at 20 ± 2 °C, stirring time 2 hr and 500 rpm by the two studied resins.

Effect of resin weights on removal of metal ions:

The effect of resin weight on the metal ion uptake by the resins in shown in Figure (2). It is evident that metal ion uptake by the resins depended strongly on the resin weight. In general, as resin weight increases, the uptake of metal ion by resin also increased. This may be due to the increasing of the resin weight increase the active sites of the resin. This result is essential to the determination of the specific resin weight to remove the existing metal ion.

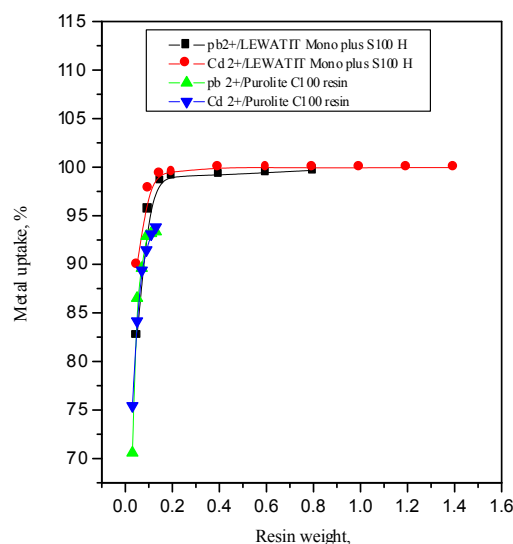


Fig. (2): Effect of resin weight on the sorption of Cd (II) and Pb (II) at 20 ± 2 °C, stirring time 2 hr and 500 rpm by the two studied resins.

Effect of presence of sodium chloride on the metal ion removal:

The effect of sodium chloride concentration on the metal ion uptake by the resins is shown in Figure (3). It is evident that increasing sodium chloride concentration, the uptake of metal ion by resin decreases^[20]. This may be due to the higher activity for Na(I) ion than Cd(II) or Pb(II) towards the adsorption on the functional group of ion-exchange resin.

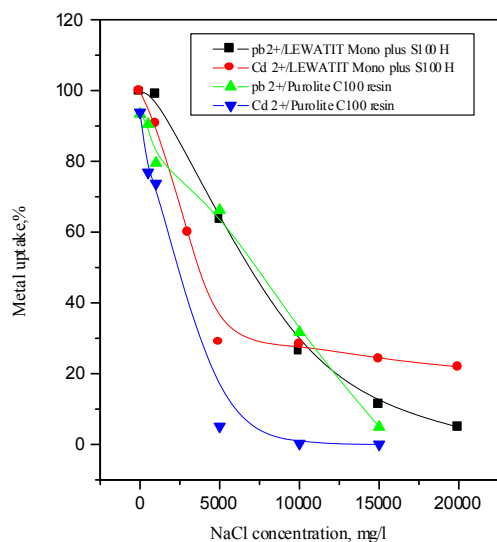


Fig. (3): Effect of sodium chloride concentration on the sorption of Cd (II) and Pb (II) at 20 ± 2 C°, stirring time 2 hr and 500 rpm by the two studied resins.

Effect of stirring time on removal of metal ions:

The effect of stirring time on metal ion uptake by the resins is shown in Figure (4). It is evident that metal ion uptake by the resins depended on the stirring time. In general, stirring time increases, the uptake of metal ion by resin also increased. This may be due to the time of stirring increases the chances of collision with the unoccupied resin functional sites and consequently enhanced metal ion uptake^[21-22].

Effect of temperature on removal of metal ion:

The effect of temperature on metal ion uptake by the resins is shown in Figure (5). It is evident that metal ion uptake by the resins depended on the stirring time. In general, temperature increases the uptake of metal ion by both resins^[20, 23]. This may be due to, the increasing of the mobility of metal ions with increase of temperature. Lewatit mono plus S100H shows better response for temperature increase in the case of Pb^{2+} . The minimum comparative response is manifested by Pb^{2+} removal using purolite C100 resin.

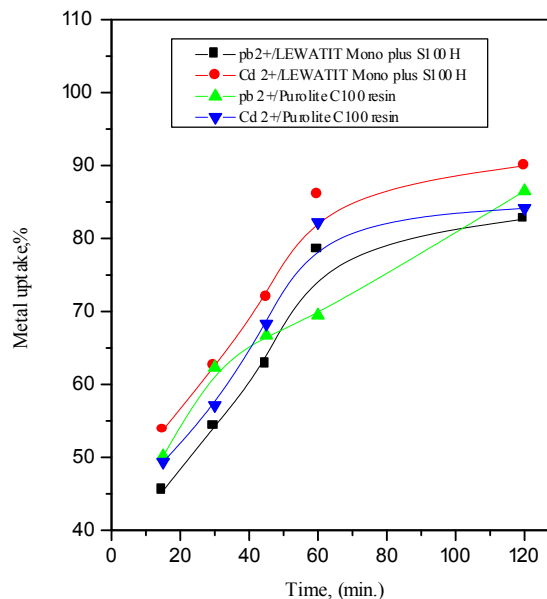


Fig. (4): Effect of stirring time on the sorption of Cd (II) and Pb (II) at 20 ± 2 C° and 500 rpm by the two studied resins.

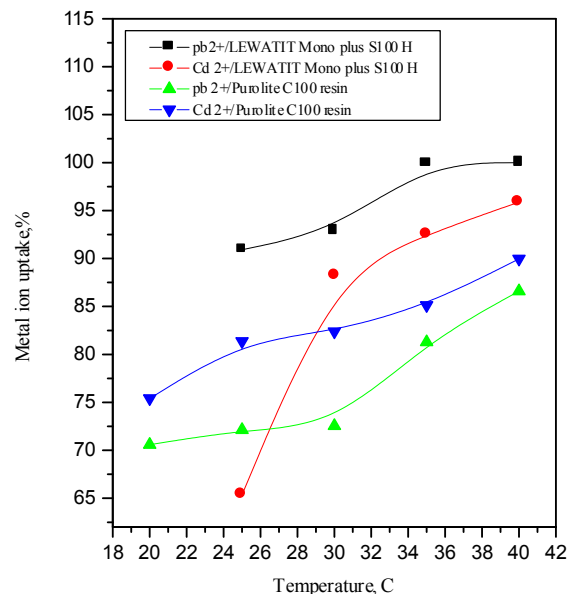


Fig. (5): Effect of temperature on the sorption of Cd (II) and Pb (II) at stirring time 2 hr and 500 rpm by the two studied resins.

Effect of metal ion concentration on removal of metal ions:

The effect of metal ion concentration on metal uptake by the resins is shown in Figure (6). The results indicate that the two different resin responses. Lewatit mono plus S100H manifests slight increase of metal uptake as concentration increases and subsequent relative uptake stability up to about 50 mg / liter. The initial metal uptake increase probably due to increased

chances of collision with active sites on the resin^[24,25] till at a certain metal ion concentration, by increases the metal ion concentration The metal ion uptake decreases, this may be due to increased probability of collision between the metal ions and the resins particles even all the active sites participated in the adsorption of metal ions. On the other hand purolite C100 resin manifest decreasing metal uptake with increasing concentration which may be related to the lower resin weight used (resin weight is 0.4 gm / 100 ml for lewatit mono plus S100H and 0.3 gm / 100 ml for purolite C100).

Reuse of the ion-exchange resin:

A most important property of resins is its capability for reuse. The resins could be brought into their original state by desorbing the metals from the metallated resins with 1.0 M HCl and 1.0 M NaCl. The metal free resins could be reused after in neutralization. In acidic medium, the metallated resins are protonated which releases the metal into the solution. Metal ion uptake was almost same, even after 4 cycles, the percent metal ion desorption and uptake were estimated the data are given in Table (1).

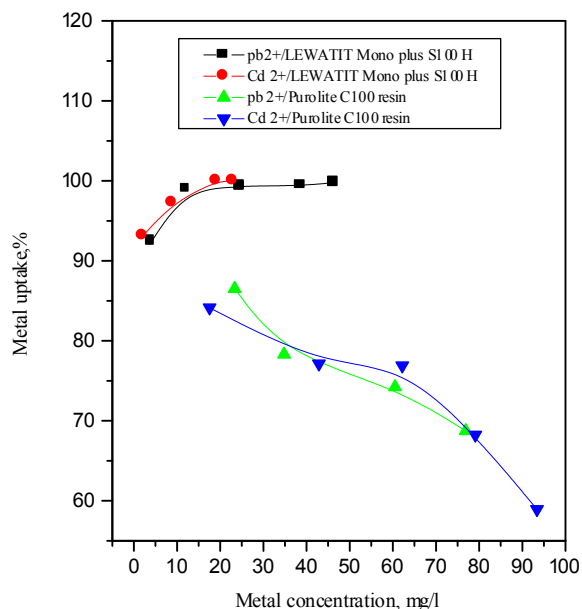


Fig. (6): Effect of metal ion concentration on the sorption of Cd (II) and Pb (II) by the two studied resins.

Table (1): Reuse of the resins on filtered pH = 7.0 of all metals solution except pH = 4.0 for Cd²⁺ solution with Purolite C₁₀₀ resin.

Recycle no.	Resin	Cd ²⁺			Pb ²⁺		
		Initial metal ion solution (µg ml ⁻¹)	metal uptake (µg ml ⁻¹)	Capacity (%)	Initial metal ion solution (µg ml ⁻¹)	metal uptake (µg ml ⁻¹)	Capacity (%)
0	LEWATIT® Plus S ₁₀₀ H		18.962	100*		24.4	100*
1			18.937	99.87		15.08	61.8
2		18.97	18.2	96.0	24.6	16.93	69.4
3			18.77	99.0		14.49	59.4
4			18.962	100		13.13	53.8
0	Purolite C ₁₀₀		14.75	100*		20.2	100*
1			14.66	99.4		19.88	98.4
2		17.53	14.75	100	23.35	20.2	100
3			14.75	100		20.2	100
4			13.73	93.1		20.2	100

Thermodynamic parameters:

The thermodynamic parameters can be calculated from the results obtained of the effect of temperature on the sorption of Cd(II) and Pb (II) ions by the two studied resins:

The equilibrium constant "K" can be calculated from:

$$K = \frac{C_i - C_f}{C_f}$$

where:

C_i: the initial metal ion concentration.

C_f: the find metal ion concentration.

The thermodynamic parameters of change in the entropy ΔS, change of the free energy ΔG and the change in enthalpy ΔH for the sorption of Cd (II) and Pb (II) on the two studied resins are recorded in Table (2).

Table (2): Thermodynamic parameters for the sorption of Cd²⁺ and Pb²⁺ by S₁₀₀H Resin and C₁₀₀ Resin.

Type of resin	M ²⁺	ΔG KJ/mol	ΔH KJ/mol	ΔS J/mol
LEWATIT Mono Plus S ₁₀₀ resin	Cd ²⁺	-15.86 x 10 ⁻³	83.2	279
	Pb ²⁺	-5.7	257.7	884
Purolite C ₁₀₀ resin	Cd ²⁺	-3.64	33.26	124
	Pb ²⁺	-2.35	37.41	133

* Note: ΔG, ΔH and ΔS are calculated at T = 298 K (absolute temperature).

Applications:

The two studied resins are applied in the treatment process of a different metal ions like: Pb, Cd, Fe, Mn, Bi, Ni, Cu and Co from waste water of some plating companies and Batteries manufacturing

companies were located in 10th of Ramadan City, Egypt. The results showed that the studied resins have the ability to decrease the initial metals concentration by 75%. As shown in Tables (3a and 3b).

Table (3a): Detection of the heavy metal ions in the waste water of Cairo Company for metal painting, 10th of Ramadan City, Egypt by using ICPS- 7500 before and after ion exchange with Purolite C100 resin at pH = 7.0 and T = 25 °C.

Metal	Initial metal concentration (ppm)	Final metal concentration (ppm)	Metal uptake		BDL mg / l
			(ppm)	(%)	
Fe	1.37	0.05	1.32	96.4	0.03
Pb	0.07	*	-	> 40	0.03
Cu	1.14	0.11	1.03	90.4	0.03
Mn	0.48	*	-	> 99.0	0.002
Cd	*	*	-	-	0.03
Co	5.09	1.04	5.17	79.6	0.02
Ni	3.65	0.07	3.58	98.1	0.01
Bi	0.16	*	-	> 98.6	0.002

*: BDL: Below detection limit.

- Total adsorbed metal ions by Purolite C100 resin = 10.69 mg/g of resin.

Table (3b): Detection of the heavy metal ions in the waste water of Cairo Company for metal painting, 10th of Ramadan City, Egypt by using ICPS-7500 before and after ion exchange with Lewatit mono plus S100 H Resin at pH = 4.0 and t = 25 °C.

Metal	Initial metal concentration (ppm)	Final metal concentration (ppm)	Metal uptake		BDL mg / l
			(ppm)	(%)	
Fe	1.37	0.28	1.09	79.6	0.03
Pb	0.07	*	-	> 40	0.03
Cu	1.14	0.06	1.08	94.7	0.03
Mn	0.48	*	-	> 99.0	0.002
Cd	*	*	-	-	0.03
Co	5.09	1.37	3.72	73.1	0.02
Ni	3.65	0.13	3.52	96.4	0.01
Bi	0.16	*	-	> 98.6	0.002

*: BDL: Below detection limit.

- Total adsorbed metal ions by Lewatit mono plus S100 H resin = 10.12 mg/g of resin.

Conclusion:

Heavy metal ions of Pb(II) and Cd(II) are known inorganic pollutants and their presence in aquatic systems pose as heavy risk to human health. Therefore, removal of such metal ion from water bodies is an important research activity. The studied resins are highly stable as evidenced by kinetic data and may be used for the removal of metal ions at room temperature. The metal uptake efficiency of the resins increases with increasing in pH, resin weight, stirring time and temperature, and at higher metal ion concentration the metal uptake decreases. The increasing of sodium chloride concentration decreases the metal uptake by resin. The metal ion uptake efficiency of the resin is not altered much, even after five cycles. Thermodynamic parameters are calculated and the application of the studied resins on the sorption of some metal like (Pb, Cd, Fe, Mn, Bi, Ni, Cu and Co) from waste water give a reduction in the initial metal concentration by 75% and the two types of resins shows a good resins for removing the heavy metals from wastewater .

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