➤ Current Research Paper

Removal Of Cd+2 By Starch As A Natural Polymer From Aqueous Solutions

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ABSTRACT

Attempts to solve the problem of heavy metals removal and recovery from waste waters and sewage have led to the development and application of several techniques. One of the most important techniques involves application of starch and starch derivatives containing amide groups as functional group. The heavy metal ions such as cadmium, copper, lead, cobalt, zinc, nickel and mercury are adsorbed quantitavely during passage of aqueous solutions through the starch and starch derivatives beads. After the separation and preconcentration stage, then the solution filtered and the analyte determines by flame atomic adsorption spectrometry (FAAS). There are different factors which affect the metal ion adsorption on starch adsorbent; such as pH of sample solution, metal ion concentration, type of starch and starch derivatives, contact time, ionic strength and temperature. In this work the effect of the important factors and also the effect of interference ions are studied on the removal of Cd+2 from aqueous solution.   © 2006 Trade Science Inc. - INDIA

INTRODUCTION

Removal of toxic heavy metal ions from industrial and mining waste waters has received much attention in recent years because they cause health problems in human beings and animals. Various methods, such as ion exchange, reverse osmosis, and electro dialysis technique, have been developed for the removal and recovery of heavy metal ions from sewage and industrial waste water. In spite of their

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effectiveness of these methods in the removal of ions, they are often quite expensive. Traditional chemical precipitation can be envisaged, but the generation of precipitated bulky hydroxides and colloidal particles are major disadvantage[1].

Synthetic ion exchangers are widely used in the removal of heavy metal ions from industrial water effluents. Many research's showed the ability of heavy metal removing from industrial waste water by using starch derivatives containing carboxyl[2,3], phosphate[4], sulphite, phosphate and/or carboxyl groups[5]. In addition, the removal of heavy metal ions was carried out via chelation by using cationic starches[6].

Accordingly, complexation of metal ions is an important technique for recovering metals from various sources (hydrometallurgy) and for their removal from streams in municipal and industrial wastes. As a consequence, complexation, separation, and removal of metal ions become increasingly attractive areas of research and have led to new technological developments. Metal-chelating and ion exchange polymers were used in hydrometallurgical such as recovery of rare metal ions from seawater and removal of traces of radioactive metal ions from wastes[7].

The development of high-performance adsorbents for removing heavy metal ions from wastewater is considered a research in the environmental field. Chelating resins have been successfully used for enriching some metal ions from aqueous solutions. They are very useful because they have a higher selectivity and larger adsorbing capacities than those of other adsorbents (e.g. activated carbons and metal oxides) and they are easily eluted and regenerated. Many researchers have prepared highly selective chelating resins for particular ions over the last two decades. For example, a new copper-selectivity chelating resin containing a salicylaldoxime group[8] was designed for the large-scale hydrometallurgical separation of copper ions from its ores.

The use of polymer-bonded ligands in selective mercury removal has been subject of several studies[10-13]. Because of high toxicity of all mercury compounds, the extraction of mercuric ions from aqueous wastes and drinking water are of special environmental importance. Two common ligand types,

sulfur and amide, are currently being used in the design of polymer sorbents for selective binding of mercuric ions. The amide group has less of a other metal ions under the same conditions because of the weak electron-donating nature of the amide group. As a result, the amide ligand is unique in its selective mercury uptake[9].

The solid phase extraction SPE and liquid-liquid extraction are widely applied for the separation and preconcentration of metals among a variety of methods. In the SPE, various sorbents such as activated carbon[14], polyurethane foam[15], silica gel[16], amberlite XAD resins[17], and others[18-24] have been used for the preconcentration of trace copper ions from various media such as drinking and river water samples. Silva and Ganzarolli[25] investigated adsorption properties of copper and cadmium on silica gel modified with niobium(v) oxide using an online preconcentration system. Granado-Castro et al.[26] developed a transport system for copper through a bulk liquid membrane containing pyridine-2-acetaldehyde benzoylhydrazone because of this metal from natural water. Ferreira et al.[27] described a procedure for separation and preconcentration of trace levels of copper in water samples. Matoso et al.[28] proposed an analytical method using silica gel chemically modified with zirconium(IV) phosphate for preconcentration of lead and copper in a column system, and their sequential determination by FAAS[29].

In spite of above methods and their power in separation of heavy metal ions starch is a natural low-cost polymer that can be highly cross-linked starch with epichlorohydrin or other agents to make it water insoluble. Chemical modification of the cross-linked starch with various reactive monomers yields products that can be used to remove heavy metal ions from wastewater[1].

The aim of this work is to investigate the use of the starch as solid-phase extractor for the separation and preconcentration of cadmium from aqueous solution. This natural polymer has been selected because of its durability and purity. This a simple and efficient solid-phase extractor for cadmium determination in waste water and other solution samples. The efficiency of the solid-phase extractor was checked by monitory of remaining of the Cd^{+2}

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in aqueous solution using flame atomic absorption spectrometry (FAAS).

EXPERIMENTAL

Apparatus

A flame atomic absorption spectrometer, FAAS, (Model: AA-6300, Shimadzu), equipped with a cadmium hollow cathode lamp, a deuterium lamp for background correction and air-acetylene as the atomizer, was used as the detector for the cadmium. The apparatus runs under the conditions suggested by the manufacturer, i.e., lamp current, 3.7 mA; wavelength, 324.8 nm; bandwidth of the slit, 0.5 nm; acetylene flow rate, 1.2 L/min. A pH-meter (Model: 726 Titroprocessor, Metrohm) and a rotary (Model: Laborotary 4000-efficient, Heidolph) were used to adapt the pH and temperature of solution, respectively.

Reagents

The metal salts (all from Merck, Germany) used are cadmium(II) nitrate octahydrated, zinc(II) sulphate heptahydrated, copper(II) sulphate pantahydrated, cobalt(II)nitrate hexahydrated, nickel(II) nitrate hexahydrated and iron(II) sulphate pentahydrated were of analytical grade and used without any further purification except for vacuum drying over P_2O_5 for 75 hr.

Solution

All chemicals used were of analytical reagent grade. Subboiling, distilled and organic free water was used throughout. A stock solution of cadmium (1000 ppm) was prepared by dissolving 2.28gm of $[3(CdSO_4)\cdot 8H_2O]$ in 1000ml of water. A working solution of cadmium(II), 50 ppm was also prepared from stock solution of cadmium (1000 ppm). The used starch was purchases from Fluka.

Sample preparation

We mixed 2.5gm of starch with 50 ml of cadmium solution (50 ppm), and then we adjusted the pH of solution at 8 by using of HCl and NaOH. After 15 minutes stirring with magnetic stirrer and

filtration with filter paper (Hardened ashless, 9.0 cm, 100 circles, Whatmann), we determined remained concentration of cadmium with FAAS. In the interference studies experiments the volume of solutions were 50 ml.

RESULTS AND DISCUSSION

Optimization of experimental factors

In order to investigate which would be the most adequate adsorption measurement of the analytical signals, taking into consideration the sensitivity and precision of the analysis, the optimization was carried out.

1. Optimization of pH

The first variable optimized was the pH of the sample solution. Because pH is one of the most important environmental factors influencing not only site dissociation, but also the solution chemistry of the heavy metals, hydrolysis, complex formation by organic and/or inorganic ligands, redox reactions, and precipitation are strongly influenced by it, and on the other side, it strongly influences the speciation and the biosorption availability of the heavy metals. The recovery was determined by applying the general sorption procedure, by changing the pH of sample solution in the range 1–8 by adding HCl or NaOH. According to the results shown in (Figure 1 and TABLE 1), quantitative recoveries (95%) were obtained for cadmium at pH range of 7-8.in used
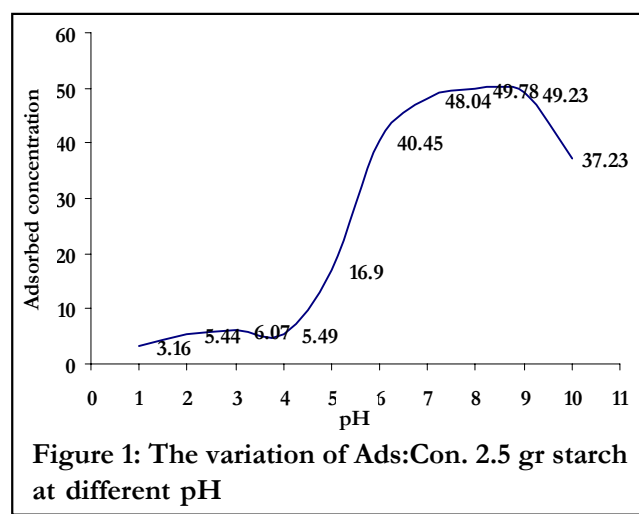

Figure 1: The variation of Ads:Con. 2.5 gr starch at different pH

TABLE 1: The effect of pH variation on the percentage of adsorption(2.5 gm starch/50ml of Cd(II))

pH	Remained concentration	Adsorbed concentration	Percentage of adsorption
1	46.84	3.16	6.32
2	44.56	5.44	10.88
3	43.93	6.07	12.14
4	44.51	5.49	10.98
5	33.10	16.90	33.80
6	9.55	40.45	80.99
7	1.96	49.04	98.08
8	0.22	49.78	99.56
9	0.77	49.23	98.46
10	12.77	37.23	74.46

TABLE 2: Effect of the ionic strength variation on the percentage of adsorption(2.5gm starch/50ml of Cd(II))

Ionic strength	Remained concentration	Adsorbed concentration	Percentage of adsorption
0.5	47.49	2.51	5.02
1.0	46.40	3.60	7.20
1.5	47.78	2.22	4.44
2	49.34	0.66	1.32

concentration (2.5 gr starch & 50 ml of Cd^{+2} 50 ppm) above pH 8, insoluble cadmium hydroxide starts precipitating from the solution, making true sorption studies impossible. Therefore, above pH 8, both adsorption and precipitation are the effective mechanisms to remove the cadmium (II) in aqueous solution. This type of behavior has also been observed for other hydrolysable metals[30].

2. Optimization of amount of starch (natural polymer), sample volume and contact time

The amount of starch, sample volume and contact time are another important parameters that affect the recovery. A quantitative retention is not obtained when the amount of resin is less. On the other hand, an excess amount of resin prevents the elution of the retained species by a small volume of eluent quantitatively. For this reason, the amounts

of resin were optimized. Quantitative recoveries of the cadmium were obtained 2.5 mg of starch. Therefore, this amount of starch has been used for subsequent experiments because of easy elution and sufficient recovery in experiments. In this manner, the sample volume was optimized and 50 ml of cadmium solution were obtained. In addition, contact time was 15 minute. This is verified by using figure 2. This figure shows the adsorbed concentration of cadmium versus contact time which does not show significant variation at time range of 15-24 hrs. therefore the starch sites occupied in primary times and this means optimized amount of starch, sample volume and contact time.

3. Optimization of ionic strength

For studying the effect of ionic strength on adsorption of Cd^{+2} on starch, the different concentrations of NaCl was selected and variation of adsorption were investigated in different ionic strengths. Effect of ionic strength on adsorption is probably due to of its effect on starch sites. The optimum ionic strength showed in figure 3 and TABLE 3. Na^+ occupies the starch sites which decreases the adsorp-
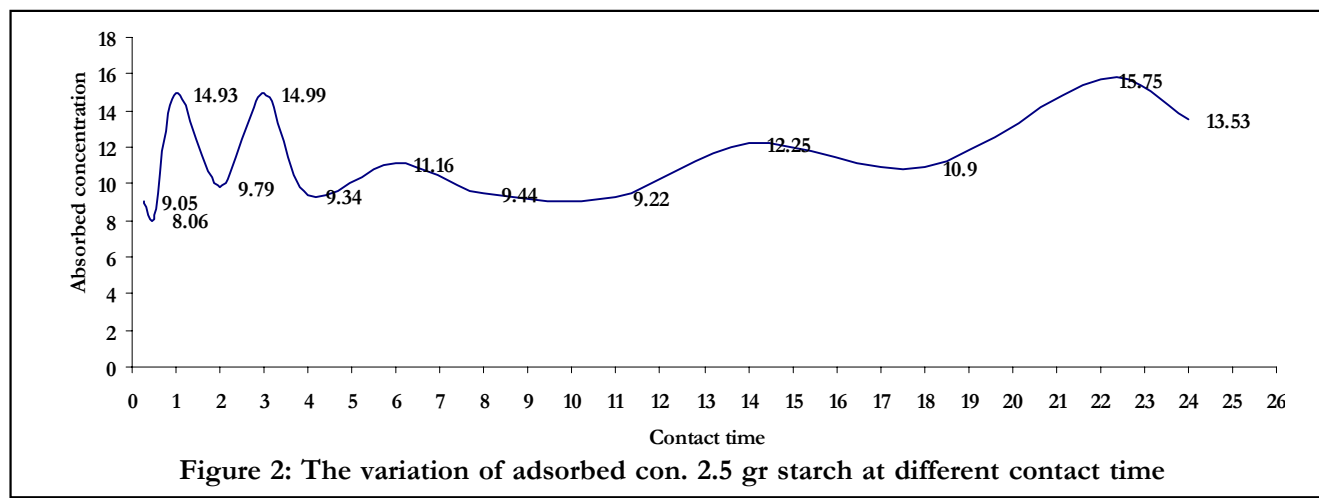

Figure 2: The variation of adsorbed con. 2.5 gr starch at different contact time

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TABLE 3: Effect of the temperature variation on the percentage of adsorption(2.5gm starch/50ml of Cd(II))

Temperature	Remained concentration	Absorbed concentration	Percentage of absorption
10	22.43	27.57	55.14
20	17.53	32.47	64.94
30	16.51	33.49	66.98
35	14.97	35.03	70.06
40	16.03	33.97	67.94
45	15.23	34.77	69.54
50	16.00	34.00	68.00
55	15.36	34.64	69.28
60	15.86	34.15	68.30
65	31.59	18.41	36.82

TABLE 4: Effect of Co²⁺ on Cd²⁺ adsorption

Ratio (conc. of Cd²⁺/ Conc. of Co²⁺)	Remained conc.	Adsorbed conc.	Percentage of adsorption
50/0	14.84	35.52	71.04
50/50	20.03	29.97	59.94
50/100	34.26	15.74	31.48
50/150	43.48	6.52	13.04
50/200	45.50	4.50	9.00
50/250	38.97	11.03	22.06
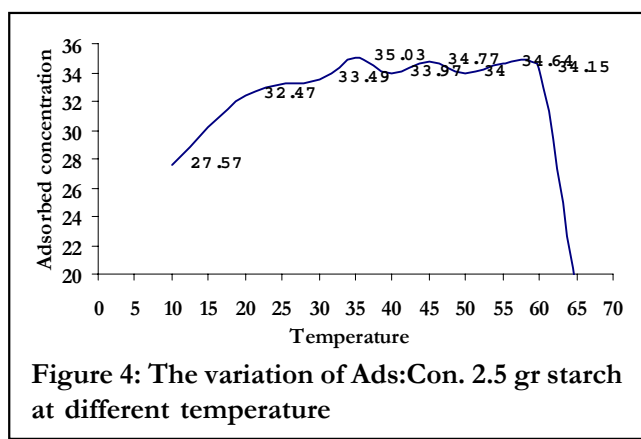
Figure 4: The variation of Ads:Con. 2.5 gr starch at different temperature

Figure 3: The variation of adsorbed concentration 2.5 gr starch at different ionic strength

their data were showed in figure 4 and TABLE 4. This figure and data shows a few variations in adsorption of Cd⁺² on starch by change in temperature at rang of 10-60ºC. Thus temperature variation is not suitable because increase of temperature need to more cost.

Effect of interference ions

The effects of foreign ions usually found in wastewater were examined using cadmium (II) and excess matrix ions. The ions were added to model
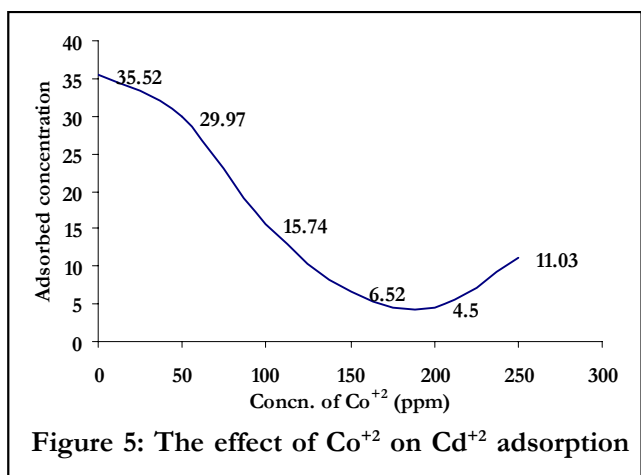
tion percentage of heavy metal ion such as Cd⁺².

The adsorption power of bonded Na⁺ is higher than bonded Cd⁺², therefore Na⁺ get Cd⁺² out of starch sites. Since decreasing effect of ionic strength on Cd⁺² adsorption, we performed the adsorption studies at zero ionic strength.

4. Optimization of temperature

The temperature has two major effects on the adsorption process. Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution. In addition, changing to temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate. Optimization of temperature and

Figure 5: The effect of Co⁺² on Cd⁺² adsorption

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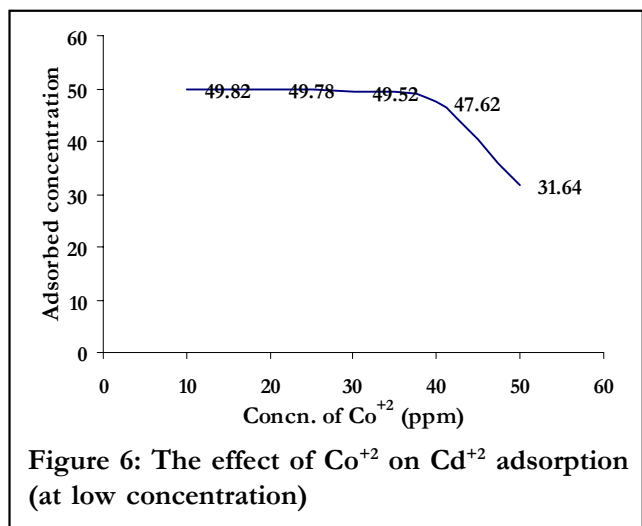**Figure 6: The effect of Co⁺² on Cd⁺² adsorption (at low concentration)**

TABLE 5: Effect of Co²⁺ on Cd²⁺ adsorption (at low concentration)

Ratio (conc. of Cd²⁺/ conc. of Co²⁺)	Ratio (conc. of Cd²⁺/ conc. of Co²⁺)	Adsorbed conc.	Percentage of adsorption
5/10	0.18	49.82	99.64
5/20	0.22	49.78	99.56
5/30	0.48	49.52	99.04
5/40	2.38	47.62	95.24
5/50	18.36	31.64	63.28

solution as their nitrate and sulphate salt. These ions were Ca⁺², Mg⁺², Zn⁺², Fe⁺², Cu⁺², Ni⁺², Co⁺², that Ca⁺² and Mg⁺² ions showed irregular variation. According to the K_{sp} of Zn⁺², Fe⁺², Cu⁺² ions hydroxides, their concentration (Max: 250 ppm) and used pH 8 these anions are in their hydroxide form and haven't interference. Ni⁺² in low concentration (25 ppm) is not hydroxide but in high concentration (up of 30 ppm) is a hydroxide and has not interference. Trouble of Co⁺² is a considerable because it isn't hydroxide in low and high concentration (Figures 5, 6 and TABLE 5).

Other cations not one had a serious interfering effect. Therefore, cadmium in wastewater can be recovered quantitatively and determined quantitatively by using the proposed procedure.

CONCLUSION

In this study we observed that starch is able to removal of Cd⁺² in aqueous solutions and we found the pH is an important experimental factor on Cd⁺² separations by starch. The ionic strength, temperature and contact time was not much effective on this separation process. Also we experimented removal ability of starch in presence of interference ions and saw that most of them are a hydroxide in my optimum pH. We suggest, others in next works investigate the effect of source of starch in separation of a specified ion.

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