Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Pehlivan, Erol , Ersoz, Mustafa , Yildiz, Salih and Duncan, Harry J.(1994) 'Sorption of Heavy Metal Ions on New Metal-Ligand Complexes Chemically Derived from *Lycopodium clavatum*', Separation Science and Technology, 29: 13, 1757 — 1768

To link to this Article: DOI: 10.1080/01496399408002170
URL: http://dx.doi.org/10.1080/01496399408002170

SEPARATION SCIENCE AND TECHNOLOGY, **29**(13), pp. 1757–1768, 1994

Sorption of Heavy Metal Ions on New Metal–Ligand Complexes Chemically Derived from *Lycopodium clavatum*

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ABSTRACT

Sorption of heavy metal ions from aqueous solution has been investigated as a function of pH using a novel exchanger system whereby *Lycopodium clavatum* is functionalized with carboxylate and glyoxime metal–ligand complexes. The new ligand exchangers were prepared using a reaction of diaminosporopollenin with various metal–ligand complexes of glyoxime and monocarboxylic acid. The sorptive behavior of these metal–ligand exchangers and the possibilities to remove and to recover selectively heavy metal cations using these systems are discussed on the basis of their chemical natures and their complexing properties.

INTRODUCTION

The sorption of heavy metal ions onto ion exchangers has been the subject of many studies over recent years (1–5). Only very low concentrations of heavy metals are permitted to be discharged in wastewaters in

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order to prevent public streams and water resources from becoming contamination. Heavy metals are often present in various industrial wastewaters together with complex-forming organic compounds. Under these conditions various metal–ligand complexes are formed and, consequently, the removal and the recovery of heavy metal cations from aqueous solutions and their separation from complexing compounds is very complicated because of the high stability constants of these complexes. Chelating resins have been used for the removal and recovery of heavy metals and also for the concentration and analysis of trace heavy metals (6). It is known that functional groups of standard cation exchangers (either strongly acidic or weakly acidic) are not able to compete successfully with many of these organic complexes with heavy metal cations.

Like the solvent extraction technique, chelating ion exchange is an effective and powerful unit operation for the separation/purification/concentration of metal ions from aqueous solutions, especially from very dilute solutions. A number of synthetic chelating resins containing various functional groups, such as iminodiacetic acid, aminophosphonic acid, and dithiocarbamic acid, have been developed to date (7), and some of them are now in everyday use on a commercial scale. However, the majority of these chelating resins have not shown satisfactorily high selectivity toward the specific metal ion to be separated, thus requiring the use of very large amounts of resin per unit volume of process solution.

Sporopollenin is a natural polymer (8–10) obtained from *Lycopodium clavatum* which is highly resistant to chemical attack, has a high capacity, is stable, has a constant chemical structure, and occurs naturally as a component of spore walls. Sporopollenin is produced by oxidative polymerization of carotenoids, which led to proposed monomer structures of macromolecular sporopollenin. In the experiments described here on the sorption of heavy metal ions, various metal–ligand complexes were prepared using the reaction of diaminosporopollenin with various complexes of carboxylate and glyoxime.

The aim of the present paper is to investigate the sorption capacity of metal–ligand complexes derived from *Lycopodium clavatum* with respect to aqueous solutions of some metal ions, specifically Cu(II), Co(II), Ni(II), Zn(II), Cd(II), and Al(III). This will permit the evaluation of modified new metal–ligand exchangers for utilization as sorbents in the elimination of these ions from wastewater and potable water. Because of the harmful effect of these ions on human health and other biological systems, their removal from wastewater has become an important problem from a sanitary point of view (11). There are reports that the health of a considerable number of people has been seriously endangered by the high concentration of heavy-metal ions in potable water (12). The objective is also to investigate the selectivity series in the sorption of various metal ions on a resin prepared from diaminosporopollenin with metal ion as a template by examining the pH dependence of the sorption of metal ions to obtain fundamental information for the hydrometallurgical and water treatment application of sporopollenin and to serve as an aid for the synthesis, choice, improvement, and effective use of such resins.

EXPERIMENTAL

Materials

The resin used was *Lycopodium clavatum*, 20 μm particle size mesh from BDH Chemicals. Reagents grades of $CuSO_4{\cdot}5H_2O$, $Al_2(SO_4)_3{\cdot}8H_2O$, and $CdSO_4{\cdot}8H_2O$ were used as the sulfate series, $CoCl_2{\cdot}7H_2O$ and $NiCl_2{\cdot}7H_2O$ as the chlorides, and reagent grade $Zn(NO_3)_2{\cdot}6H_2O$ as the nitrate of these metals. Solutions were prepared by dissolving appropriate weights of the chlorides, sulfates, or nitrates of the metals in deionized water, the pH of which was adjusted by adding a small amount of nitric acid or aqueous sodium hydroxide solution to maintain constant pH. Nitric acid 65%, hydrochloric acid 37%, and sodium hydroxide standard solutions were used.

Preparation of DAE Sporopollenin

A suspension of sporopollenin from *Lycopodium clavatum* in dry toluene containing 1,2-diaminoethane was aminated by refluxing for 9 hours. The reaction was as follows:

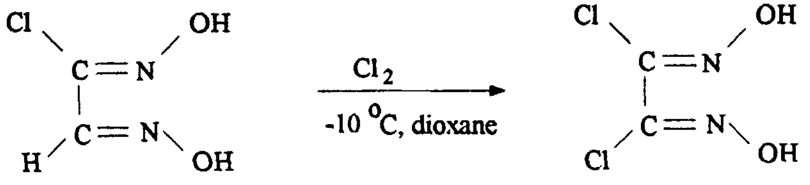
$$\textcircled{S} + NH_2(CH_2)_2NH_2 \longrightarrow \textcircled{S} - NH(CH_2)_2NH_2$$

(DAE-sporopollenin)

where Ⓢ indicates sporopollenin (*L. clavatum*).

Preparation of Dichloro-antiglyoxime

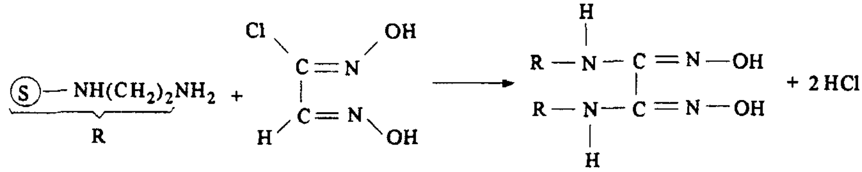
Chloro-antiglyoxime was passed through the solution in sunlight (13). The reaction is as follows:



(Dichloro-anti glyoxime)

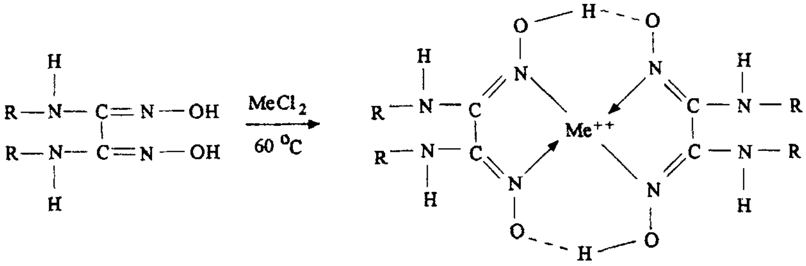
Preparation of Bis-diaminoethyl-glyoximated (bDAEG) and Carboxylated (DAEC)-Sporopollenin

Air-dried DAE-sporopollenin and a slurry of dichloro-antiglyoxime were placed in a two-part reaction vessel, and bromoacetic acid was added. These suspensions were stirred for 24 hours and washed with water and dilute acetic acid. bDAEG and DAEC-sporopollenin were obtained. The reaction is as follows:



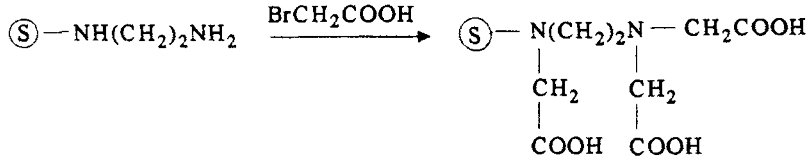
bis-diaminoethyl-glyoximated-sporopollenin
(bDAEG-sporopollenin)

The bDAEG-sporopollenin resin was treated with heavy metal ions which are fixed to the resin matrix. The structure of the metal–ligand complex is as follows:



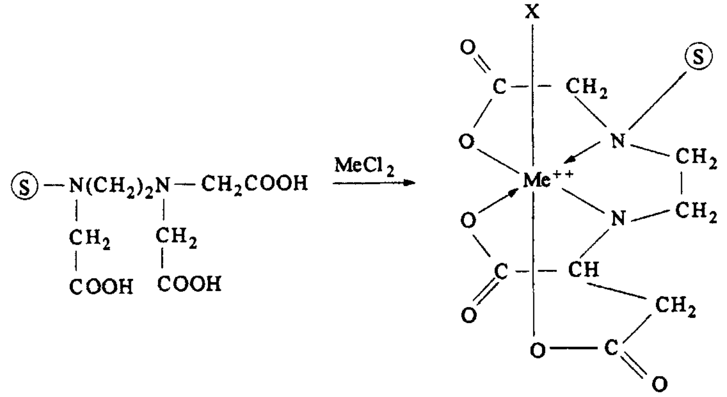
Me^{++} loaded bis diaminoethyl-glyoxime-sporopollenin
(Me^{++}-loaded bDAEG-sporopollenin)

The reaction of carboxylated diamino-sporopollenin is as follows:



Carboxylated diamino-sporopollenin (DAEC)

The DAEC-sporopollenin resin was treated with heavy metal ions which are fixed to the resin matrix. The structure of the metal–ligand complex is as follows:



Me^{++} loaded carboxylated-diaminoethyl-sporopollenin

Me^{++} loaded DAEC-sporopollenin

Sorption Experiment

About 0.2 g of the resin and 10 mL of aqueous solution containing metal ions were shaken in an incubator at 25°C for 24 hours to achieve equilibration. The shaker was set at 180 rpm. Initial and equilibrated metal concentrations in the aqueous solution were determined by AAS using a Perkin Elmer 1100 B atomic absorption spectrophotometer. The amount of sorbed metal ion was calculated from the change in the metal concentration in the aqueous solution before and after equilibrium and the weight of the dry resin used. The pH values at equilibrium were measured by using an Orion model 720 pH meter. Each resin was used after pretreatment by washing with hydrochloric acid and rinsing with distilled water to ensure that impurities did not remain in the resins.

RESULTS AND DISCUSSION

Metal–ligand complexes of sporopollenin were prepared from *Lycopodium clavatum*, diaminoethane, bromoacetic acid, and chloroglyoxime. Ethylenediamine complexes possess a very stable structure and have a very minor dissociation tendency, and they act as suitable functional groups for a ligand exchange matrix (14). Oxime functional groups resins are, in fact, solvent impregnated resins, and they differ from conventional chelating ion-exchange resins which contain chelating ligands covalently bonded to a polymeric matrix (7). Chelating ion-exchange resins incorporating oxime functionality form an interesting and useful class of polymeric ligands because of their strong chelating properties. Glyoxime complexes possess strong metal-binding properties, especially dichloro-antigloxime, have selectivity toward transition metals, and they are capable of undergoing incorporation in a resin matrix (15). The resins readily sorb various kinds of metal ions in a 10^{-3} mol/L aqueous solution with a pH range from 2 to 10. Percent sorption isotherms (showing the variation in sorption with pH) are presented in Figs. 1 and 2 for heavy metal ions. In each case the initial cation concentration was 10^{-3} M. At low pH values the sorption of metal ions was low. With an increase of pH, the sorption of metal ions increased considerably. At low pH values the electrostatic repulsion between the complex and the metal ions prevents their sorption.

Sorption isotherms of single heavy metal ions (Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Al^{3+}) in aqueous solutions on sporopollenin derivatives with glyoxime and carboxylic metal–ligand complexes were measured and are discussed as a function of pH. The uptake of heavy metals except aluminum was found to be 90% or more over a range which encompasses the pH of most natural water systems. The conventional separation factors for sorption on normal ion-exchange resins are incorporated for selective sorption of heavy metal ions against hydrogen ion on chelating ligand exchange resins.

Metal–ligand complexes of sporopollenin resins employed in this study were synthesized from *Lycopodium clavatum*. In the experiments reported here, the total amount of heavy metal was held strongly at higher pH, which was varied over a wide range. This is appropriate for testing models for the pH dependence of sorption. An alternative approach—the addition of heavy metal cations to a resin suspension at constant pH—allows the stoichiometric relationship between cation sorption and proton release to be determined. The increase in the stability of the chelating metal–ligand complexes can be attributed to a combination of such factors as the polymer entropy effect and a lower dielectric constant of the resin matrix.

The amount of the sorbed metal at pH 8–10 increases in the order $Cu \geq Ni > Co > Zn > Cd > Al$ for DAEC and $Ni \geq Cu > Co > Zn > Cd > Al$ for bDAEG. This order is determined by many factors, the most significant of which are the ionic potential q/r (q is the ionic charger, r is the ionic radius), chemical properties, ionic radius, and hydrolysis. Cu has higher ionic potentials (2.8) than Cd (1.9) and Zn (2.4). It is seen that, together with their hydrate shell, Cu has the smallest radius and so can penetrate into smaller pores and thus have larger access to the matrix.

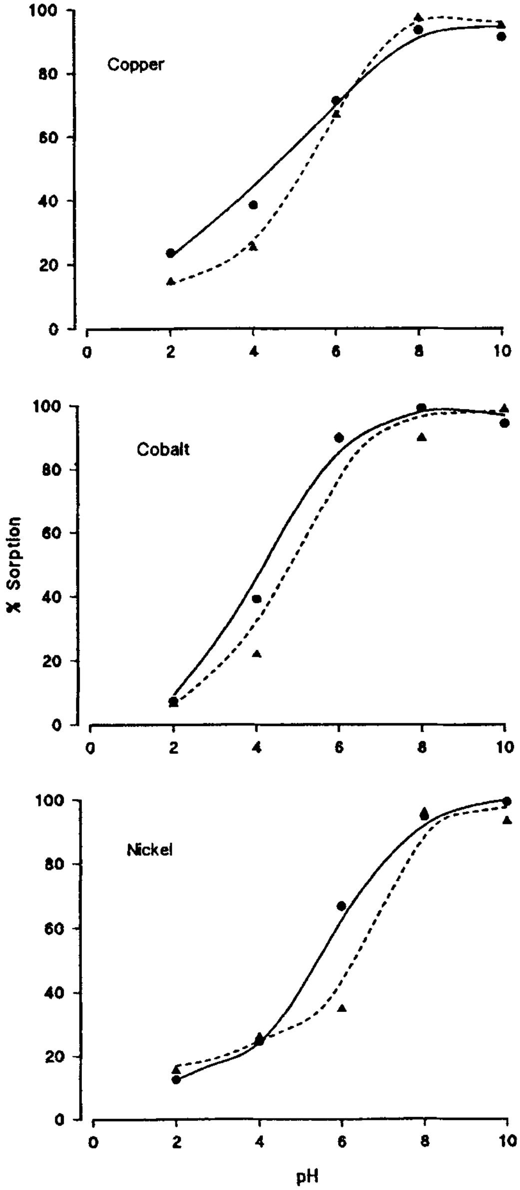


FIG. 1 Sorption of Cu^{2+}, Co^{2+}, and Ni^{2+} into DAEC-sporopollenin (●, ——) and bDAEG-sporopollenin (▲, ---) as a function of pH at a concentration of 10^{-3} M.

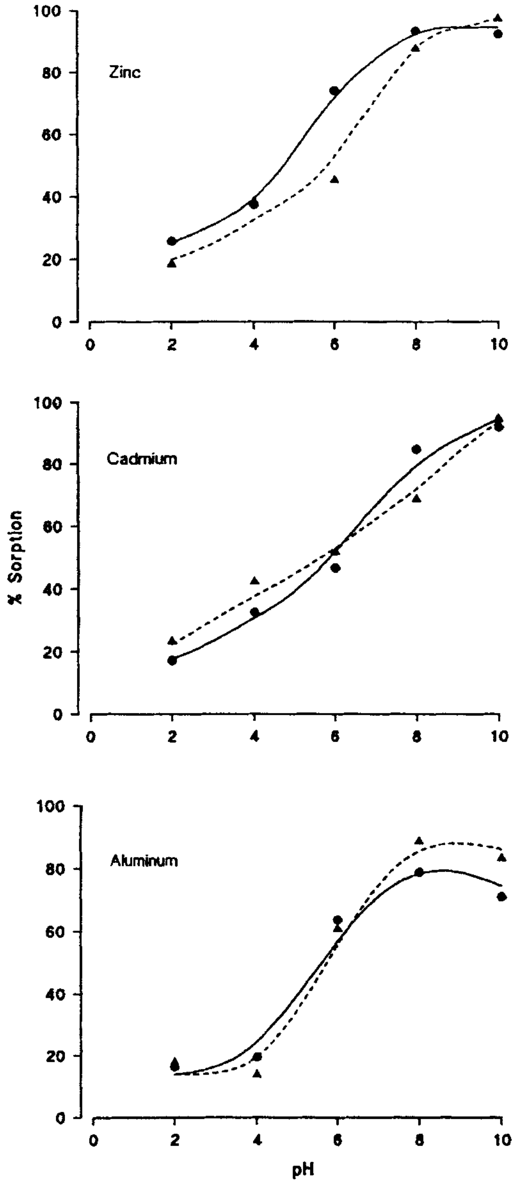


FIG. 2 Sorption of Zn^{2+}, Cd^{2+}, and Al^{3+} into DAEC-sporopollenin (●, ——) and bDAEG-sporopollenin (▲, ---) as a function of pH at a concentration of 10^{-3} M.

This determines the higher sorption capacity of Cu compared to Al or Cd, as corroborated by the experimental data.

The results presented here and analysis indicate that the metal–ligand complexes of sporopollenin show an ability to sorb metal ions from aqueous solution with increasing pH. It is noteworthy that the sorption of metallic ions increased considerably in the pH 6 to 10 range. This high sorption ability of the resin may be due to the formation of a metal chelate in the carboxyl groups through coordination of the nitrogen atoms in glyoxime and ethylene diamine. It is suggested that a natural polymer and its glyoximated and carboxylated derivatives can be useful for chromatographic separations of nucleosides, nucleic acid bases, and amines (15).

Compared with commercial chelating resins, especially iminodiacetic acid type chelating resins, the order of adsorption of each metal ion on these resins is very similar to that on the Chelex-100 resin. However, sorption with these resins takes place at a much higher pH for all metal ions, which may be attributed to the large difference between the acid dissociation constant of the alcoholic hydroxyl group of the carotenoid ester unit of sporopollenin and that of the carboxyl group. Glyoxime and carboxylic acid preferably form a multidentate ligand with a metal ion. From the results shown in Fig. 1 and 2, the following sorption behaviors of these resins are noted: Ni, Co, Cu, and Zn(II) are much more sorbed over the pH ranges studied than is Al(III). This enables selective sorption and effective separations of small amount of Ni, Cu, Co, and Zn(II) in the presence of Cd(II) or Al(III). These characteristic properties of these resins are expected to be applicable to the commercial separation, recovery, and purification of divalent metals from trivalent metals.

In this paper we studied the selective and effective uptake of heavy metal cations from aqueous solutions. Heavy metal cations are taken up by coordination to the donor nitrogen atoms of the functional group of the glyoxime to the nitrogen and oxygen donor atoms of the functional groups of the carboxylated resin, thus creating very strong coordination compounds in the resin phase. The stabilities of coordination complexes are very high, and glyoximated diamino-sporopollenin is very strong and selective for divalent metal ions in chromatographic applications, particularly the transition metals which are strongly bound to the complex. Metal leakage is also inhibited (15). Electrostatic attractive forces between metal and carboxyl or hydroxyl groups prevail in complex formation. In the case of glyoxime and bromoacetic acid, the coordination bonds between metal and N-donor atoms play a very important part in overall complex stability. Glyoxime gives stationary, strong complexes with Co cations on oxime nitrogens, as determined by elemental analysis (13). The precise determination of the coordination behavior of the functional group toward metal ions and the geometry around the metal ions are essential for the further development of metal–ion selective ion-exchange resins.

It was mentioned above that the metal–ligand complex resins contain carboxyl and phenolic groups. Metal ion sorption is unfavorable at a pH value of 3 since this is below the dissociation constant p*K* value of the functional groups of carboxyl and phenolic. At near-neutral and alkaline pH values, i.e., close to and above the p*K* of carboxyl and phenolic groups, the sorption of the metal is appreciable. Phenolic groups (p*K* about 9–10) contribute to the ion-exchange capacity in alkaline media (i.e., pH range 8–12).

From the above-mentioned cases the following conclusion can be drawn. The uptake efficiency of metal will depend preferentially on the type of forces (coordination of metal to the donor atom or electrostatic attraction) that prevail between ligand and metal in the complex compound. These resins show high stability toward concentrated acids and bases during regeneration and, in turn, retain their high capacity for heavy metals. They are cheaper and easier to prepare than many commercial resins. They possess higher selectivity, which makes them more versatile ion exchangers for industrial purposes.

In general, the range of stationary phases used in ligand exchange chromatography (LEC) can be substantially increased because most of the sorbents that are used for the selective sorption of transition metals are also suitable for LEC. Diamine complexes with Cu(II) ions are more stable than those with Zn(II) ions (16). Cation-exchange resins with carboxylic and phosphonic groups retain the metal sufficiently firmly and are being used advantageously at present as sorbents in LEC. Carboxylic cation exchangers bind the metal ions more strongly than the sulfonic type as carboxylate anions enter the coordinative metal sphere. Functional carboxyl groups retain Cu(II) and other metals more strongly than do sulfonate groups (17). Displacement of metal ions is minimized by choosing an exchanger whose functional groups form coordinate bonds with the metal ions, like carboxylate or iminodiacetate ions which are the functional groups of chelating ion-exchange resins.

LEC is most often performed with metal ions of the acid type, and primarily with Cu(II) which is the ion of choice because it forms very stable complexes. Earlier Tjusi (16) used metal–ligand complexing in chemical separations, and he reported that the strongest absorption was obtained with Cu(II) with the decreasing order of absorption strength of the other cations being Ni, Hg, Co, Cd, Zn, Fe, Pb, Mg, and Al. The Irving–Williams (17) series states that as one proceeds along the first transition series, the divalent ions form complexes, the stability of which rises in the order Mn $<$ Fe $<$ Co $<$ Ni $\ll$ Cu with a sharp peak at Cu, then falls in going from Cu to Zn. This stability order is the same for all soft-acid ligands. The results obtained here are in agreement with those mentioned above. The Cu(II) ion has a square planar distribution of coordinative valences, which sets it apart from the others; Ni(II) favors octahedral coordination and Zn(II) favors tetrahedral. Cu(II) complexes can also be octahedral, but the octahedron is a distorted one with its axial bonds much weaker than the square planar or equatorial bonds. The axial coordination of Cu(II) is vitally important in ligand exchange selectivity.

Metal ions are held much more strongly if the resin has other functional groups. Commonly used is the iminodiacetate chelating resin, Chelex-100, but diffusion in and out of this resin is slow and its chromatographic performance is poor. Further, the ligand binding capacity is limited by the coordination of the metal ion to the resin functional group. The most important use of these new ligand exchange resins, both in ligand exchange and in the exchange of inorganic ions, is the recovery and concentration of trace substances from large volumes of water.

CONCLUSION

The present work clearly demonstrates that sporopollenin derivatives containing glyoxime and bromoacetic acid ligand exchangers have large collective sorption. They were also found to have a strong chelating ability with various kinds of metal ions. The sorption of metal ions at trace level concentrations in aqueous solution is very important. The concentration of the contaminant metal onto metal–ligand complexes of sporopollenin could facilitate pollution control in nuclear, wastewater, and effluent treatment industries.

ACKNOWLEDGMENTS

The authors wish to thank Universities of Selcuk and Glasgow for research facilities.

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Received by editor January 21, 1994