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8-Hydroxyquinoline-5-sulfonic Acid (HQS) Impregnated on Lewatit MP 600 for Cadmium Complexation: Implication of Solvent Impregnated Resins for Water Remediation

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ABSTRACT

The impregnation of 8-hydroxyquinoline-5-sulfonic acid (HQS) onto an anionic strong base resin Lewatit MP 600 is described. The procedure was carried out by mixing HQS with Lewatit MP 600 in water, instead of in organic solvents generally used in solvent impregnated resins (SIRs). The maximum impregnation is 0.95 mmol of HQS/g of Lewatit MP 600. The HQS-impregnated resin was used in a flow injection system incorporating a mini-column for cadmium chelation. Measured cadmium breakthrough curves were used to study the influence of various impregnated HQS,

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the influent concentration of cadmium, and the packed HQS-Lewatit MP 600, on cadmium binding. By increasing the impregnated HQS from 0.098 to 0.830 mmol/g of Lewatit MP 600, column capacity increased from 11.29 to 52.57 mmol Cd/L of HQS-Lewatit MP 600. Increasing the influent concentration of Cd reduced the column capacity due to a concurrent increase of competing anion (ClO_4^-). This in turn reduced the stability of cadmium complex in the resin phase. Varying the amounts of HQS-Lewatit MP 600 packed in a mini-column caused variations in Cd binding. A 450 mg quantity of 0.95 mmol HQS/g of Lewatit MP 600 can remove cadmium from an initial value of 1 ppm to 30 ppb (detection limit of our instrument). Cadmium and partially impregnated HQS can be eluted by 2 mol/L HNO_3 and the resin can be regenerated to impregnate HQS for further cadmium complexation.

Key Words: Ion exchange resins; Permeable reactive barriers; Water quality.

INTRODUCTION

There is a growing need in the area of water remediation to pursue effective materials to remove or preconcentrate toxic heavy and transition metal ions. The materials currently in use involve, generally, inorganic ion exchangers[1] or some biological sources.[2] Ion-exchange resins are well known to be effective in recovery and separation of toxic heavy and transition metal ions from contaminated water[3] and in tap water treatment.[4] Such resins might therefore also be effective in remediation of groundwater contaminated by heavy and transition metals, by emplacing them in permeable reactive barriers (PRBs). Indeed, in a recent paper, we present the feasibility of in situ groundwater remediation using PRBs containing various resins.[5] Four resins were considered: two commercially available resins, Duolite GT-73 (Rohm and Haas; a macroporous polystyrene-di-vinyl-benzene copolymer with thiolic functionality) and Amberlite IRC-748 (Rohm and Haas; a macroporous polystyrene-di-vinyl-benzene copolymer with iminodiacetic functionality), and two solvent impregnated resins (SIRs). The SIRs were prepared by impregnation of two different thiophosphoric extractants onto Amberlite IRA-96 (Rohm and Haas; a macroporous polystyrene-di-vinyl-benzene copolymer with tertiary amine functionality), respectively. The practicality of using such SIRs for in situ groundwater remediation is that they combine the advantages of ion-exchange resins and solid–liquid extraction technology with solvent extraction chemistry.[6]

The use of impregnated resins or solvent impregnated resins in extraction and recovery processes dates back to the pioneering work of the early 1970s by Warshawsky,[7] Grinstead,[8] and Kroebel,[9] and the topic has been thoroughly dealt with in several papers and reviews. The common method for preparing SIRs is to choose hydrophobic organic molecules that have a high metal extraction capability, as well as binding properties to the polymer in an organic solvent; once impregnated, the solvent is removed using a dry or wet method. Acidic organophosphorus or thiophosphorous reagents are common impregnated extractants. In the current study, HQS is chosen as an impregnating extractant for several reasons: (i) it incorporates a sulfonic acid group; (ii) as a chelating agent, HQS is second in importance after EDTA; (iii) HQS is odorless compared to thiophosphoric acid extractants; and (iv) there is a difference in photochemical properties between HQS and its metal complexes.[10] Preliminary work has described the use of HQS-loaded Dowex 1-X8 for selective absorption of metal ions.[11] Furthermore, anionic complexes of 8-hydroxyquinoline derivatives with metals can be functionalized on anion exchangers.[12–14] The quaternary ammonium groups of diverse anion exchange resins and anionic reagents, such as sulfonated ligands, can form rather stable metal complexes even in salt solutions, for instance in sea water.[15] However, prior to metal complexation, impregnation of HQS onto an anion exchange resin Lewatit MP 600, and then use of a mini-column packed with only milligrams of HQS-Lewatit MP 600 resin (in conjunction with flow injection) to chelate metal, has not been reported.

The HQS-Lewatit MP 600 resin was prepared by mixing HQS with Lewatit MP 600 in water. This principle is based on electrostatic interaction between quaternary ammonium groups bearing on Lewatit MP 600 and sulfonate groups present on the anionic extractant HQS. This method facilitates the introduction of an accurate, yet variable, amount of the extractant, reaching the maximum capacity of ion-exchange resin. Consequently, such a resin allows the highest metal loadings and complexation. The resin can be easily regenerated in acidic conditions, such as HNO_3. Furthermore, the easy recovery of metal complexes accumulated on the ion-exchange resin may overcome analytical limitations of analyzing samples directly, especially if these samples contain interference or metals having inadequate sensitivity to available analytical methods.

In this paper, we describe a simple pathway to impregnate HQS on a strong-base anion-exchange resin, Lewatit MP 600. The most effective impregnation procedure was found by using neutral water, reaching 0.95 mmol of HQS/g of Lewatit MP 600. Cadmium adsorption and elution properties from the HQS-Lewatit MP 600 mini-column are then presented. The effect of the packed resin amounts and the influent metal concentration on cadmium uptake were studied. Strong metal complexation, as exhibited, for example, by a 450 mg quantity of 0.95 mmol HQS/g of Lewatit MP 600 removing 1 ppm cadmium to below 30 ppb, suggests the possible use of the HQS-Lewatit MP 600 resin as an effective material for water remediation.

EXPERIMENTAL PROCEDURES

Materials and Reagents

Prior to impregnation, Lewatit MP 600 was washed extensively with distilled deionized water (Milli-Q system, Millipore), 1:1 methanol/H_2O, methanol, 1:1 methanol/CH_2Cl_2, and CH_2Cl_2, successively. The purified Lewatit MP 600 was dried under vacuum at room temperature to constant weight. Analytical grade reagents were used throughout. The solution of HQS (Aldrich Chemical Company) was freshly prepared for impregnation. Stock solution of cadmium was obtained by dissolving cadmium perchlorate hydrate (Aldrich Chemical Company) in water and concentration was detected by AAS measurements. All solutions were stored in plastic bottles and all glassware was soaked overnight in 5% nitric acid prior to use.

Apparatus

Solution fluorescence was detected on a SLM 8100 spectrofluorometer. Cadmium in the solutions was analyzed by a Perkin–Elmer 5100 Atomic Absorption Spectrophotometer (AAS).

Impregnation of HQS on Lewatit MP 600

Approximately 200 mg Lewatit MP 600 was mixed thoroughly with water containing the required amounts of dissolved HQS. The mixtures were allowed to shake for 24 hours at 180 rpm, to reach equilibrium. The resin was filtered. The supernatant was analyzed by the addition of cadmium to form a fluorescent complex. The filtered resin was then shaken with 30 ml of water at 180 rpm for 5 hours. To ensure the lowest leakage of the impregnated HQS from Lewatit MP 600, the water-washing procedure was repeated seven times. Although HQS was found in the aqueous phases during each time, the leakage was small and could be ignored in calculating the impregnated amount of HQS; this calculation was made only from the differences between the impregnated and residual HQS concentrations in the supernatant.

Mini-column Experiment

The impregnated HQS-Lewatit MP 600 resin was slurry-packed into a mini-column (1.0 ml of sterile single-use plastipak syringe) fitted with 25-μm polyethylene frits as bed supports. Solutions were delivered by a Masterflex L/S digital drive (Cole–Parmer model 7523-40) and an easy-load pump head II. Before the cadmium binding experiment was performed, a 0.05 mol/l ammonium acetate buffer (pH 7.0) was passed through the mini-column for 30 min at a flow rate of 1 ml/min. The uptake of cadmium was studied at pH 7.0, in order to simulate many natural waters. The effluent was collected continuously and then analyzed by AAS measurements. After the effluent concentration had mostly reached the influent concentration, the sample flow was stopped. The mini-column was then disconnected from the line tubing, the cadmium in the line tubing was removed by changing the motor direction of the pump, and the tubing was washed by a buffer solution. The column was reconnected to the line tubing and the motor direction changed again. The cadmium in the dead volume of the column was then removed by a buffer solution, followed by 2 mol/l HNO_3 for elution. Cadmium in the buffer and HNO_3 solutions was analyzed by AAS measurements.

RESULTS AND DISCUSSION

HQS Impregnation

Because the impregnation was carried out in aqueous solution, pH is one of the most important factors that can influence the impregnation process. Basic conditions are favored with the deprotonation of SO_3H and —OH groups present on an HQS molecule. Consequently, the base increases the mol fractions of HQS anions and in turn strengthen the interactions with quaternary ammonium cations bearing on Lewatit MP 600. However, the base also acts to reduce the impregnated HQS due to competitive binding of both OH^- and HQS anions with quaternary ammonium cations.[10] Therefore, the best impregnation procedure was carried out in neutral HQS aqueous solutions. As shown in Fig. 1, the impregnated HQS increases with increasing HQS in the aqueous phases. In principle, the maximum amount of the impregnated HQS should reach a saturation value of the chloride counter-ions in the resin (4.1 meq/g of Lewatit MP 600), but the solubility of HQS in water is a limiting step in the impregnation process.

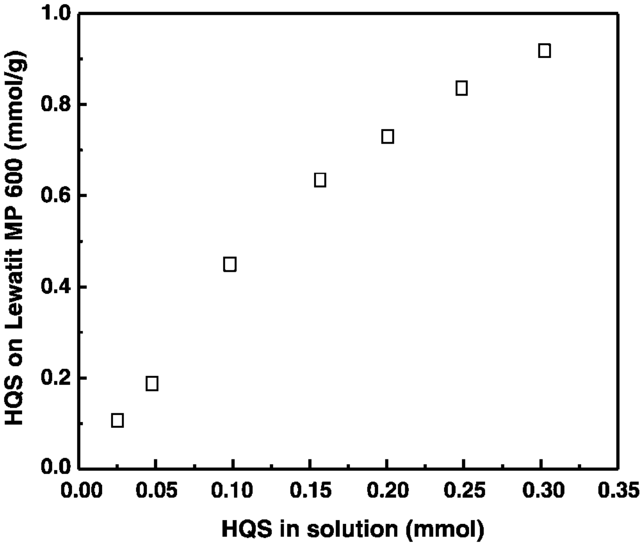

Figure 1. The variation of impregnated HQS on Lewatit MP 600 with the initial HQS in solution.

Effect of Impregnated HQS on Cadmium Binding

Conditioning the column by a 0.05 mol/l ammonium acetate buffer causes slight leakage of HQS from the resin. The leakage can be easily detected by the addition of cadmium into the solution to form a fluorescent Cd-HQS complex. After passing 30 ml of the buffer solution through the columns, the leakage was sufficiently small to be ignored, indicating these columns were ready for cadmium complexation. The final impregnated HQS was calculated by determining the difference before and after the column conditioning. Table 1 shows the calculated results.

The effect of impregnated HQS on cadmium binding was determined for 0.098, 0.188, 0.623, and 0.830 mmol of HQS/g of Lewatit MP 600, using 10.0 ppm cadmium influent solution pumped through these columns loaded with 0.72 ml of various HQS-Lewatit MP 600 resins at a flow rate of 1 ml/min. The breakthrough curves (cadmium effluent concentration vs. bed volume) are presented in Fig. 2. Depending on the amount of the impregnating HQS, the breakthrough curves show differences in shape. The two curves for impregnated 0.098 and 0.188 mmol of HQS/g of Lewatit MP 600 rise quickly

Table 1. Impregnated HQS and the column capacity.

Weight of Lewatit MP 600 (mg)	HQS on Lewatit MP 600 (mmol/g)	Column conditioned by 0.05 mol/NH_4Ac, HQS on Lewatit MP 600 (mmol/g)	HQS-Lewatit MP 600 in column (ml)	Cadmium found on HQS-Lewatit MP 600 resin (mmol/l)	Theoretically calculated cadmium on HQS-Lewatit MP 600 resin[a] (mmol/l)
221.81	0.1068	0.098	0.72	11.29	68.05
219.32	0.188	0.1879	0.72	25.34	130.48
201.67	0.635	0.623	0.70	46.00	445.00
207.31	0.8364	0.830	0.70	52.57	576.39

[a] The calculation is based on the assumption of a 1:2 complex between cadmium and HQS.

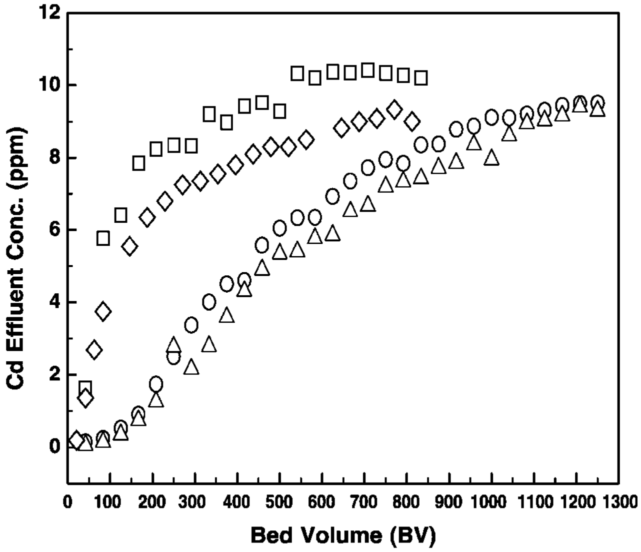

Figure 2. Breakthrough curves of cadmium binding to various amounts of impregnated HQS on Lewatit MP 600 upon 10.0 ppm cadmium perchlorate solution (in a buffer of pH 7.0) pumping through these columns. (□) 0.098 mmol HQS/g of Lewatit MP 600,(◇) 0.188 mmol HQS/g of Lewatit MP 600, (○) 0.623 mmol HQS/g of Lewatit MP 600, (Δ) 0.830 mmol HQS/g of Lewatit MP 600.

during 40 ~ 140 BV (bed volume [BV] = volume of solution/volume of column) of cadmium pumped, while the other two curves for impregnated 0.623 and 0.830 mmol of HQS/g of Lewatit MP 600 rise slowly with an early time baseline region, suggesting that the strong binding of HQS with cadmium takes place. It can also be seen from Fig. 2 that the lowest impregnated HQS-Lewatit MP 600 column reaches equilibrium after 555 BV of 10.0 ppm cadmium. Namely, the column containing impregnated 0.098 mmol HQS/g of Lewatit MP 600 reaches equilibrium, with the effluent concentration becoming equal to the influent concentration.

In the breakthrough curves for cadmium binding columns containing 0.188, 0.623, and 0.830 mmol of HQS/g of Lewatit MP 600, the cadmium effluent concentrations do not reach the influent concentration of 10.0 ppm after 833 BV (600 ml of cadmium passed, or 10 hours), for the column impregnated with 0.188 mmol of HQS/g of Lewatit MP 600, and after 1250 BV (900 ml of cadmium passed, or 15 hours), for both columns impregnated with 0.623 and 0.830 mmol of HQS/g of Lewatit MP 600. This means that more HQS binding sites remain available for cadmium complexation. Based on these breakthrough curves, the total amount of cadmium bound per mmol/l of HQS-Lewatit MP 600 was calculated according to Ref.[16]. Namely, the bound cadmium per liter of HQS-Lewatit MP 600 can be calculated following the equation:

$$C_s = \frac{(C_m^0 V - \int_0^V C_m dV)}{V'} \tag{1}$$

where C_s is the cadmium bound to the column material (mmol/l) after V ml of cadmium passed through the column, C_m^0 is the molar influent concentration, C_m is the column effluent concentration, and V' is the volume of HQS-Lewatit MP 600 used in the mini-column.

Table 1 also lists column capacity and the related information used in the calculation and discussion. Regardless of assuming 1:1 or 1:2 Cd-HQS complexes, the actual amount of bound cadmium (mmol/l) is in all cases smaller than that of calculated cadmium binding (see Table 1). This result indicates that there are a significant number of sites on the resin that are unavailable for cadmium complexation. Furthermore, with increasing HQS on Lewatit MP 600, the column capacity increases, but without significant differences between columns containing 0.623 and 0.830 mmol of HQS/g of Lewatit MP 600 (Table 1). This result suggests that higher HQS impregnation does not necessarily lead to the highest degree of complexation, because some impregnated HQS molecules may be sterically hindered either by the backbone of the polymer itself or by other HQS molecules.

Effect of Influent Cadmium Concentration on Column Capacity

The uptake of cadmium by HQS-Lewatit MP 600 resin was studied in order to determine the effect of influent cadmium concentration on column capacity. Figure 3 shows breakthrough curves for 10.188 and 19.625 ppm cadmium perchlorate solutions buffered with pH 7.0 on the column containing 0.95 mmol of HQS/g of Lewatit MP 600. After 972 BV (700 ml) of Cd, the column reached equilibrium for 10.188 ppm influent cadmium, but not for the column-pumped 19.625 ppm cadmium perchlorate solution. This phenomenon may be related to the stability of the ternary system (strong base resin/anionic HQS/cationic Cd) in the presence of ClO_4^-. Burba[12] suggests that a 100-fold increase of the electrolyte concentration ($ClO_4^-, NO_3^-, WO_4^{2-}$) causes the distribution coefficient, K_d, to decrease by one-to-two orders of magnitude (K_d was defined as the distribution of

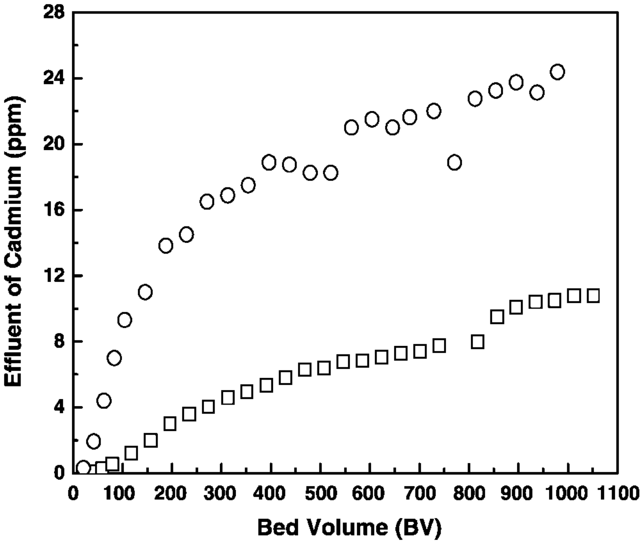

Figure 3. Breakthrough curves of cadmium binding on column containing 0.95 mmol of HQS/g of Lewatit MP 600, (□) 10.188 ppm and (○) 19.625 ppm cadmium perchlorate solutions in the buffer of pH 7.0.

sulfonated chelator between the anion exchanger and the solution phase), but not in the case of Cl^- and SO_4^{2-}. Therefore, the increase of cadmium concurrent with the increase of competing anion (ClO_4^-) concentration, causes the decrease in stability of the anionic complex (HQS-Cd). As a result, HQS-Cd complex was released from the resin into the solution phases. Thus, we observed a larger effluent of cadmium (~24 ppm) in comparison to cadmium influent (19.625 ppm). In other words, nonequilibrium breakthrough curves expressed by increased Cd concentrations were observed for the 19.625 ppm cadmium influent.

By use of Eq. (1), the total amounts of cadmium absorbed on the columns were determined by measuring the difference between the influent amounts of cadmium and the integration of the breakthrough curves. The cadmium retention on the column is 0.0647 mmol of Cd/g of wet HQS-resin for 10.188 ppm influent and 0.031 mmol of Cd/g of wet HQS-resin for 19.625 ppm influent. Again, the values as shown here provide evidence that the lower column capacity is a result of the increase of competing anion (ClO_4^-) concentration along with the increase of cadmium.

Effect of Packed HQS-Lewatit MP 600 Amount on Cadmium Binding

One of the aims of the present study was to seek improved materials for water remediation. Since the ion pair complexes among quaternary ammonium groups of diverse anion exchanges and anionic (e.g., sulfonated) reagents are stable in the presence of high salts, including sea water,[15] the possibility to use HQS-Lewatit MP 600 for water remediation was studied. Figure 4 shows the breakthrough curves of 1 ppm cadmium buffered with pH 7.0 ammonium acetate, on various amounts of 0.95 mmol of HQS/g of Lewatit MP 600 in the mini-column. It is obvious that the uptake of cadmium depends on the used amounts of HQS-Lewatit MP 600. A 450 mg of HQS-Lewatit MP 600 resin can uptake cadmium from 1 ppm and reduce it to 30 ppb (the detection limit of our instrument). The strong complexation suggests that HQS-Lewatit MP 600 is a promising material for removal of low concentration of cadmium from water, even possibly in the presence of high salt solutions.

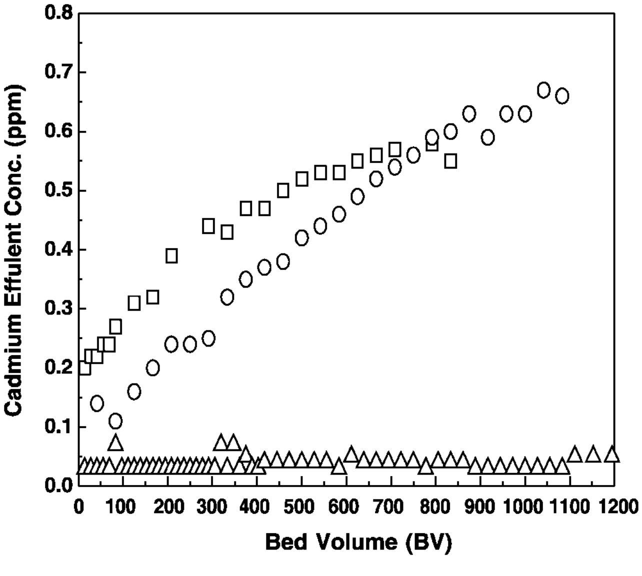

Figure 4. Breakthrough curves on various amounts of 0.95 mmol of HQS/g of Lewatit MP 600 for 1 ppm cadmium perchlorate solution buffered with pH 7.0. (□) 49 mg of 0.95 mmol HQS/g of Lewatit MP 600, (○) 92 mg of 0.95 mmol HQS/g of Lewatit MP 600, (Δ) 450 mg of 0.95 mmol HQS/g of Lewatit MP 600.

Removal of Cadmium from the Interstitial Volume of the Column

Prior to evaluation of elution efficiency by 2 mol/l HNO_3, it is essential to remove cadmium from the interstitial volume of the column. A 0.05 M ammonium acetate buffer was pumped through four different columns, which has various cadmium binding and impregnated HQS. The effluent was collected in five fractions containing 10 ml of solution. Cadmium was detected from these fractions by AAS measurements. The result is shown in Fig. 5. As can be seen, cadmium in the dead volume of four columns can be depleted after 50 ml of buffer passed through these columns.

2 mol/l Nitric Acid Efficiency in Elution of Cadmium

The elution efficiency of 2 mol/l HNO_3 in removing cadmium was evaluated from three columns. The first fraction containing 5 ml solution was

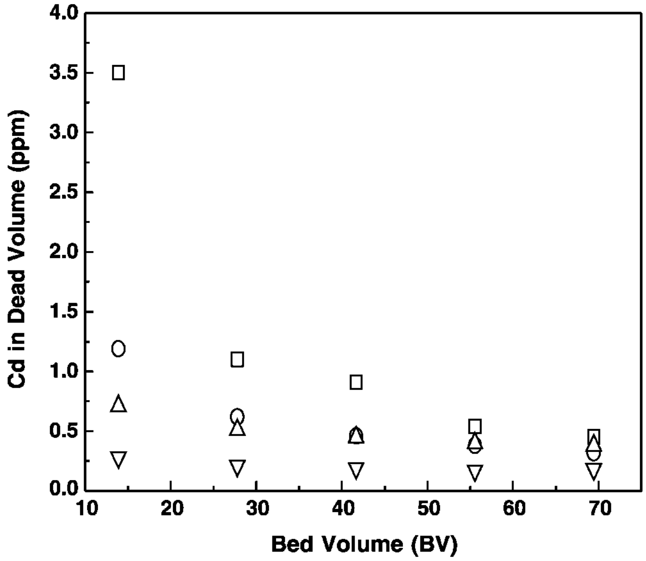

Figure 5. The residual cadmium in the dead volume of column, exited by pumping through 0.05 M NH_4Ac buffer. (□) 11.29 mmol of Cd/l of 0.098 mmol HQS-Lewatit MP 600 column, (○) 25.34 mmol of Cd/l of 0.188 mmol HQS-Lewatit MP 600 column, (Δ) 46.00 mmol of Cd/l of 0.623 mmol HQS-Lewatit MP 600 column, (▽) 52.57 mmol of Cd/l of 0.830 mmol HQS-Lewatit MP 600 column.

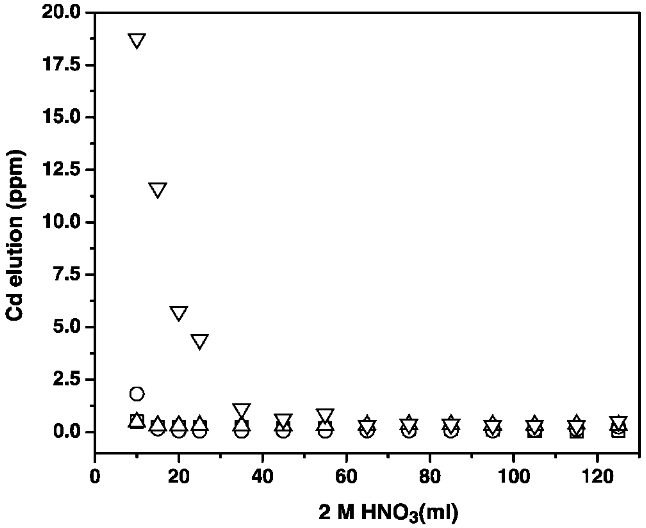

Figure 6. The eluted cadmium from four columns after the first fraction was collected. The meaning of different symbols representing experimental points is the same as in Fig. 5.

diluted for cadmium measurements. The other 5 or 10 ml solutions were collected continuously and then analyzed for cadmium. The analysis shows most of the cadmium was eluted from the column in the first 5 ml of nitric acid. The analysis of other fractions for cadmium is shown in Fig. 6. It is seen that following the pumping of 2 mol/l HNO_3 through the columns, the concentration of cadmium is lowered, finally approaching the detection limit of the instrument. This means that cadmium can be completely washed off the column by 2 mol/l HNO_3. It was also found that HQS was bleached

Table 2. Cadmium recoveries from three columns.

Column	mmol of Cd/l of resin	Cadmium found in the first fraction containing 5 ml solution (mmol)	mmol of recovered Cd/l of resin	Cd recovery (%)
1	25.34	0.01413	20.19	70.68
2	46.00	0.03269	45.40	98.69
3	52.57	0.031	43.10	81.98

from the column, evidenced by a color change of column from yellow to white. Table 2 shows the recovery of cadmium from three columns analyzed only from the first 5 ml solution. As can be seen from this table, the recovered cadmium is mostly in good agreement with the calculated cadmium from breakthrough curves.

CONCLUSIONS

A simple procedure for preparing HQS-Lewatit MP 600 for cadmium complexation in mini-columns, in conjunction with a flow injection system, is presented. The HQS-Lewatit MP 600 has sufficient capacity to chelate cadmium from dilute solutions, showing potential for use in water remediation. The bound cadmium and partially impregnated HQS can be eluted by 2 mol/l HNO_3 and the resin can be regenerated for impregnation of HQS, and subsequent complexation with cadmium.

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