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Removal of Selenium from Aqueous Solution Using Complexes of Iron(III)- and Copper(II)-Chelating Resins.

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Abstract. Poly(hydroxamic acid) (PHA) and Amberlite IRC-718 (AMB) loaded with either Fe(III) or Cu(II) were used as sorbent for selenium ion removal from aqueous solution. The results show that the Fe-PHA complex was the most effective for the selenite removal in the pH range between 2.0 and 4.7. The sorption of selenite by the complex followed a Langmuir model with a maximum capacity of 1.56 mmol/g. Kinetic of the sorption is fast and a column method for the removal of selenite is possible. The selenite sorbed can be eluted with 0.5 M NaOH solution.

Abstrak. Poli(asid hidroksamik) (PHA) dan Amberlite IRC-718 (AMB) yang di erapkan dengan Fe(III) atau Cu(II) telah digunakan sebagai bahan pengerap untuk menyingkir selenium dari larutan akueus. Keputusan menunjukkan bahawa kompleks Fe-PHA merupakan bahan yang berkesan untuk menyingkirkan ion selenite pada julat pH antara 2.0 dan 4.7. Erapan selenite oleh kompleks ini mematuhi model Langmuir dengan muatan erapan meksima 1.56 mmol/g. Kinetik erapan ini adalah cepat dan erapan ini boleh dilakukan dengan kaedah turus. Ion selenite yang telah dierap oleh resin ini dapat dinyaherapkan oleh larutan NaOH 0.5M.

Keywords: Selenite removal, Fe- and Cu- chelating resin complexes, poly(hydroxamic acid),amberlit.

Introduction

Selenium is one of the toxic elements to plant and animal. It enters the atmosphere and aquatic environment through a natural and an anthropogenic activity such as the burning of coal for electric power generation. Sorption process is one of the techniques used by many researchers for selenium removal from aqueous solution. One of the materials used were metal loaded ion exchange resin such as complex of copper-Dow-2N [1] and zirconium loaded activated charcoal [2]. Oxides of titanium [3] and iron [4] were also found to be effective for the selenite removal. This paper reports results of our investigation using Fe(III)- and Cu(II)-poly (hydroxamic acid) (Fe-PHA and Cu-PHA) and, Fe(III)- and Cu(II)-Amberlite (Fe-AMB and Cu-AMB) resin complexes for removal of selenium ion from aqueou solution. The Fe-PHA resin complex was found to be the most effective for selenium ion removal. Various factors such as pH, kinetic and the effect of initial selenium ion concentration as well as the mechanism of removal are discussed.

Experimental

Amberlite IRC-718 (AMB) was purchased from Aldrich Chemical Company and Poly(hydroxamic acid) chelating ion-exchange resin (PHA) was synthesized by poly(methyl - acrylate divinyl benzene) as described else where [5]. The resins were loaded with either Fe(III) and Cu(II) as shown in Table 1.

Removal of selenium ion by M-PHA and M-AMB Resin (M=Fe or Cu)

A 0.5 g of the M-PHA or M-AMB resin was added to a 25 ml of 5.0 mM selenium ion solution of which pH was adjusted. The mixture was shaken for 4 hours and filtered and analyzed for selenium and the metal ions using inductively coupled plasma –atomic emission spectophotometer (ICP-AES) (Perkin Elmer Plasma 1000).

The sorption rate was measured by shaking 0.5 g of the Fe-PHA resin in 25 ml of 5 mM selenite solution for different period of time. The sorption isotherm was measured by shaking 0.5 g of the resin in 25 ml of selenite solution of different concentrations. The selectivity of the resin for various anions was determined by equilibrating 0.5 g of the resin in 25 ml of 5 mM selenite solution containing either arsenate, floride or phosphate. A glass column (1.0 cm i.d) packed with the resin to 5 cm height was fed with arsenite solution of various concentrations at pH 3 with a flow rate of 0.5 mL/min. The effluent from the column was collected in fractions of 10 mL each and the concentration of selinium ion was determined by ICP-AES. Desorption of selenite from the resin was carried out using NaOH solutions.

Results and Discussion

Preparation of Metal-complexed Resins

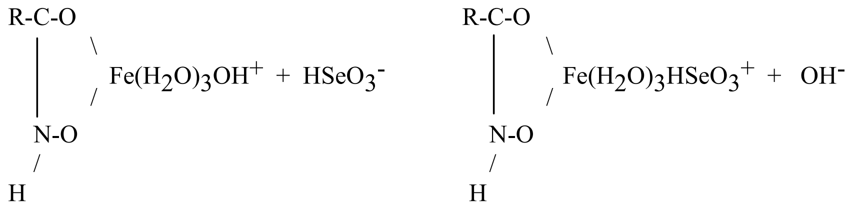
Table 1 shows the capacity of Fe and Cu in the resins at the optimum pH . The metal ions capacities of PHA resin were higher than those of the AMB. This is in parallel with the sodium exchange capacity of 1.46 mmol/g [6] and hydroxamic acid content of 2.71 mmol/g [5] for the AMB and PHA resins, respectively.

Sorption of Selenite by Metal-resin Complexes.

Fig. 1 shows the percentage of selenite removal by the metal-resin complexes at an optimum pH. The Fe-resin complexes have a higher percentage selenite removal compared to the Cu-resin. The characteristics of the Fe-PHA resin, which is the most effective for selenite removal was studied in detail and the results are discussed.

Removal of selenite by the Fe-PHA at various pH

Fig. 2 shows more than 90% of the selenite was removed by Fe-PHA in the pH range between 2.0 to 4.7 and the removal was sharply decreased at a lower pH. It was also found that the Fe(III) ion was significantly desorbed from the resin in the pH <2.0 and the decrease in selenite removal can be related to the desorption of the metal ion. The selenite sorption by the complex was followed by the increase in pH, indicating the released of hydroxide ions. It can be suggested that the sorption of selenite followed a ligand exchange mechanism as follow [7]:



$$\left.\begin{array}{l}\text{R-C-O}\\ \quad|\\ \text{N-O}\\ /\\ \text{H}\end{array}\right\rangle Fe(H_2O)_3OH^+ + HSeO_3^- \qquad \left.\begin{array}{l}\text{R-C-O}\\ \quad|\\ \text{N-O}\\ /\\ \text{H}\end{array}\right\rangle Fe(H_2O)_3HSeO_3^+ + OH^-$$

where R is the polymer matrix of PHA resin and $HSeO_3^-$ is the selenite ion species at modarate acidic pH.

Table 1 Conditions for preparation of metal-resin complexes

Resin Complex	Amount Resin (g)	Buffer concentration (M)	Initial pH	Initial metal concentration (mM)	Adsorption capacity (mmol/g)
Fe-PHA	14.8	3	5.2	218.3	3.69
Cu-PHA	14.6	1	5.2	241.7	3.89
Fe-Amb	14.4	3	5.2	237.2	2.64
Cu-Amb	11.5	1	5.2	241.7	2.38

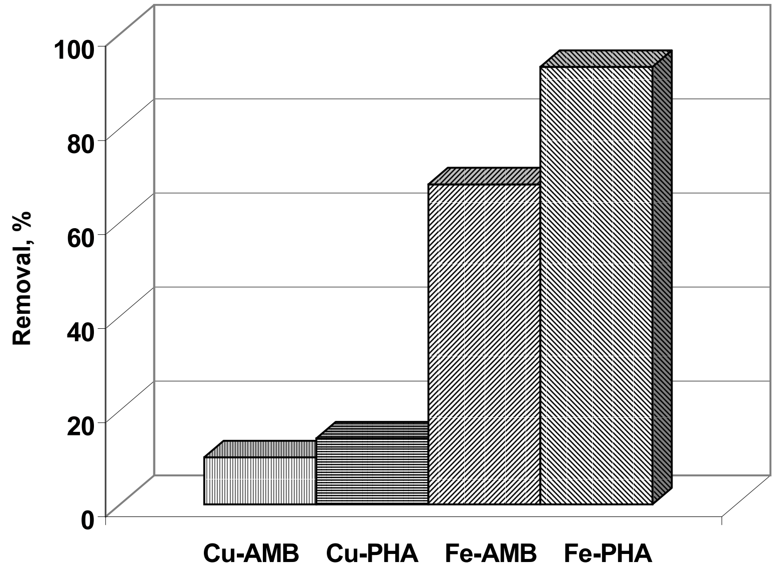


Figure 1. Removal of selenite by metal-resin complexes.

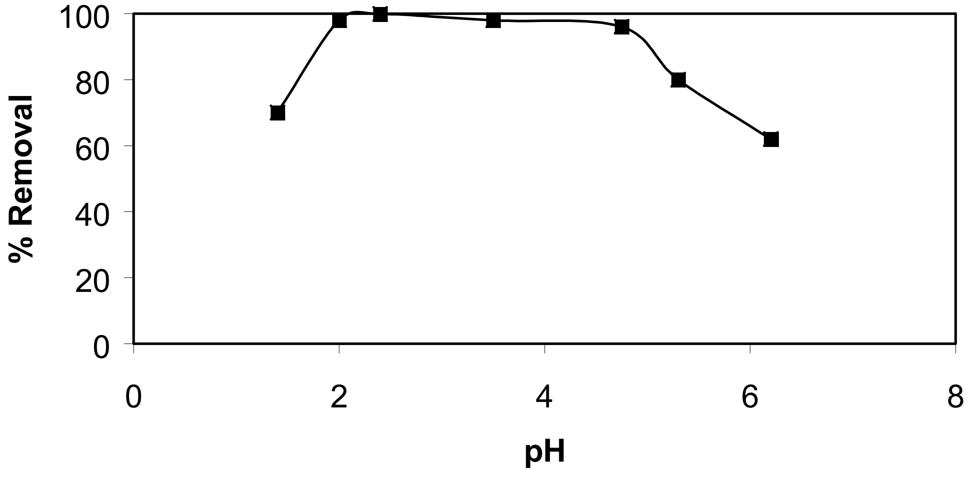


Fig. 2 Removal of Se(IV) by Fe-PHA at various pH

Rate of Selenite Sorption by Fe-PHA complex

Fig. 3. shows the sorption process was very rapid at the initial stage where, $t_{1/2}$, time taken to reach 50 % removal was about 5 min which indicates the resin is suitable to be used in a column method.

Sorption Isotherm

Fig. 4 shows the amount of selenite sorbed by the resin increased as initial selenite concentration increases and reached the maximum at 50 mM.

This implied that the resin has a limited site for the sorption. The sorption isotherm data was analyzed using Langmuir isotherm equation :

$$C_e/q_e = 1/Q°b + C_e/Q°$$

where C_e (mmol/L) and q_e (mmol/g) are the concentration of the selenite in the solution and in the resin, respectively, and Q° and b are the Langmuir constants. Fig. 5 shows that the plot of C_e/q_e vs. C_e is a straight line showing that the sorption follows the Langmuir model and the constants which are related to the sorption capacity and the sorption energy were 1.56 mmol/g and 0.36 L/mmol, respectively

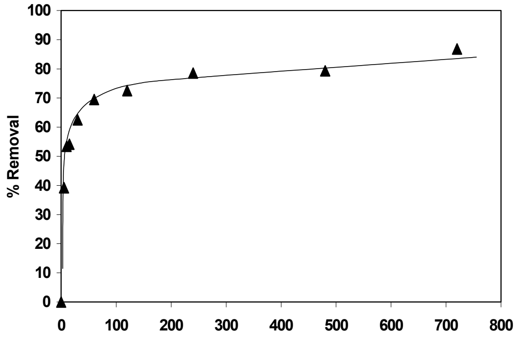


Fig. 3 Effect of equlibrium time on removal of selenite by Fe-PHA resin.

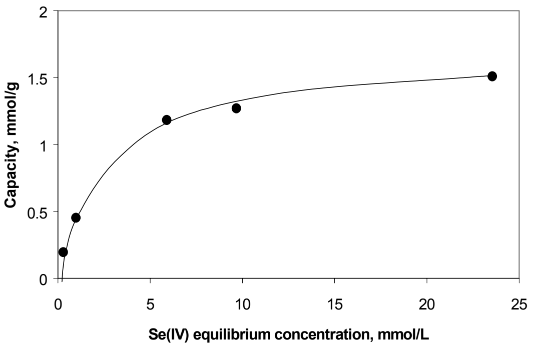
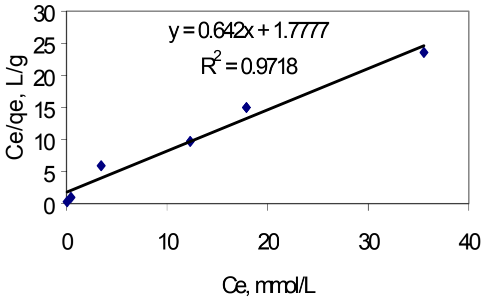


Fig. 4 Sorption capacity of Fe-PHA for selenite at different concentrations

Figure 5. Langmuir isotherm plot for sorption of selenite by Fe-PHA resi complex.



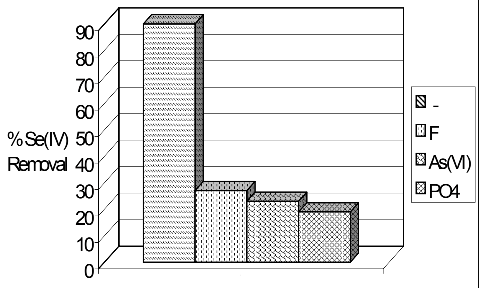


Fig. 6 Removal of Se(IV) by Fe-PHA in the presence of interfering anions

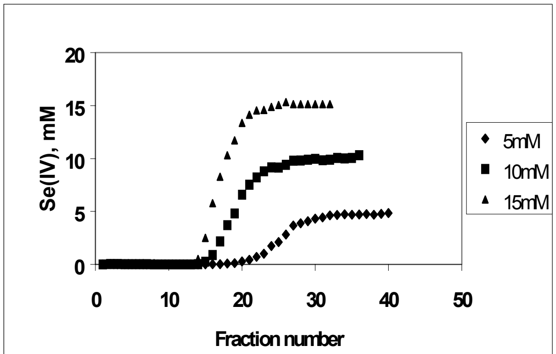


Fig. 7 Breakthrough curves for selenite at different initial concentrations with Fe-PHA resin column

Sorption Selectivity

Fig. 7 shows 90 % selenite removal was attained in the absence of the other anions. The percentage of selenite removal was decreased to 19, 23 and 27% in the presence of arsenate, phosphate and floride, respectively.

Column Studies

Fig. 7. shows the breakthrough volumes for 50 % removal of selenite were 170, 200 and 260 mL for initial selenite concentrations of 15, 10 and 5 mmol/L, respectively. The resin was regenerated by 0.5 M NaOH and the percentage of selenite desorbed was 77%.

Acknowledgements

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