Environmental Engineering and Management Journal, September 2006, Vol.5, No.3, 297-305
http://omicron.ch.tuiasi.ro/EEMJ/

"Gh. Asachi" Technical University of Iasi, Romania

COPPER (II) AND MERCURY (II) RETENTION PROPERTIES OF A POLYACRYLAMIDOXIME CHELATING FIBER

Doina Bilba[1], Gabriela Moroi[2], Nicolae Bilba[3*]

[1] Technical University of Iasi, Faculty of Chemical Engineering, 71 Mangeron Blvd., 700050 Iasi, Romania; [2] "Petru Poni" Institute of Macromolecular Chemistry, 41 A Grigore Ghica Vada Alley, 700487, Iasi, Romania; [3] "Al.I.Cuza" University of Iasi, Faculty of Chemistry, 11 Carol I Blvd., 700506 Iasi, Romania

Abstract

A polyacrylamidoxime chelating fiber containing amidoxime groups $-C(NH_2)=NOH$ was prepared through the reaction of Romanian commercial acrylonitrile-based fiber Melana with hydroxylamine in methanol and was used as sorbent to remove copper and mercury ions from aqueous solutions. The batch sorption experiments were conducted to establish the optimum retention conditions. The sorption behaviour of copper and mercury ions on the polyacrylamidoxime fiber is depended on the solution pH values, equilibration time, initial metal concentration and nature of anions. The infrared spectroscopy was employed to characterize the surface composition and the sorption mechanism.

Keywords: cooper, mercury removal, sorption, polyacrylonitrile fiber, amidoxime functional groups

1. Introduction

Chemical pollution of aquatic environment is a consequence of presence of certain inorganic and organic chemicals. Heavy metals may arise from natural sources (ores, rocks, volcanos) or anthropogenic sources (mining and metallurgical activities, petroleum processing, catalysts, fungicides, pharmaceuticals and urban emissions (Lin and Juang, 2002). The increase of industrial activities has intensified environmental pollution problems and the deterioration of several aquatic ecosystems. Although at low concentrations these metals are essential to live, at high concentrations may become hazardous; they tend to accumulate in organisms, causing numerous diseases and disorders (are toxic or carcinogenic) (Inglezakis et al., 2003). A large variety of

* Author to whom all correspondence should be addressed: Phone: 0040-232-201135, e-mail: nbilba@uaic.ro

environmental regulations require that the heavy metal content of the waste aqueous streams must be reduced to the ppm levels before discharge.

Many processes including precipitation, coagulation/coprecipitation, adsorption, ion exchange, reduction, and membrane separation are currently available for removing dissolved heavy metals (Liu, 1997). Adsorption is commonly used to remove heavy metal ions from aqueous solutions at trace concentrations. Various types of adsorbents such as activated carbon, mineral oxides, polymer fibres, resins and biosorbents may be employed to accumulate metal ions from the solutions onto its surfaces (Loyd-Jones et al, 2004). Also, the alternative low-cost materials, namely peat (Ho et al., 2000, Kicsi et al, 2006) or natural zeolites (Erdem et al., 2004) have been used as potential sorbents for the removal of heavy metals. Attachment of metal ions to the sorbent surfaces may be due to various physical or chemical interactions (ion exchange or chelation mechanism) between the metal ions and the surface functional groups of sorbent (Jin and Bai, 2002; Deng et al., 2003).

Recently, much attention has been paid to the synthesis and applications of ion exchangers and chelating sorbents based on natural and synthetic fibres in removal of harmful contaminants from aqueous media (Gulina et al., 2002, Deng et al., 2003). The major advantages of these materials over the granulated sorbents are determined by high specific surface area, elevated selectivity of sorption (in correlation with the chemical structure of the functional group) and significant adsorption rate, as well as the simplicity of handling in various forms (fibres, filters, fabrics) (Lin and Hsieh, 1997; Lacour et al., 2001). Many fibrous sorbents for selective removal and recovery of various metal ions have been prepared from polyacrylonitrile fiber, a common and cheap commercial product (Liu et all, 1999, 2002; Simanova et al., 2001).

In this research, the sorptive capacity of a polyacrylamidoxime chelating fiber synthesized from Romanian polyacrylonitrile Melana was evaluated for the removal of copper and mercury ions from aqueous solutions. Batch experiments were carried out involving process parameters such as solution pH, equilibration time, initial metal concentration and nature of anions.

2. Experimental

2.1. Materials

The polyacrylamidoxime chelating fiber (AOPAN) was obtained from Romanian commercially available polyacrylonitrile fibre (90.6% acrylonitrile, 6.2% vinyl acetate and 3.2% α-methylstyrene) (PAN) by the one-step reaction with hydroxylamine in methanol (3 wt.%) at 80^{o}C (Bilba et al., 2004) (the molar ratio PAN/hydroxylamine and the reaction time were 1.17 and 1.5 h respectively); its characteristics, i.e. concentrations of nitrile (CN), ester (COO) and amidoxime (AO) groups, percentage conversion (C) of nitrile groups into amidoxime groups, molar ratios of polar groups and repeating unit mass are presented in Table 1.

Table 1. Characteristics of AOPAN fiber

Sample	*Functional group concentration (10^3 mol/g)*			*C[a] (%)*	*Molar ratio of functional groups*			*Mass*
	AO	CN	COO		CN/AO	AO/COO	CN/COO	
AOPAN	2.43	3.29	0.66	5.46	5.47	3.68	20.14	86.48[b] 388.92[c]

[a] C = mol of AO 100/(mol of CN + mol of AO).
[b] Of AOPAN repeating unit.
[c] Of the shortest sequence of AOPAN chain with the molar ratio CN/AO 5.47.

In AOPAN, the anion-exchange capacity corresponding to the amount of introduced amidoxime groups (determined according to Egawa et all.,1987) is 2.43 mmol HCl/g and the molar ratio of the unreacted nitrile groups to those converted into amidoxime groups is 5.47 (Table 1).

The stock solutions 10^{-2} M of Cu^{2+} and Hg^{2+} were prepared from analytical grade salts: $CuSO_4$, $Cu(NO_3)_2$, $Hg(NO_3)_2$ and $HgCl_2$. The working solutions were prepared by diluting the stock solution with distilled water. The solution pH was adjusted with adequate amounts of either acid (HNO_3) or buffers (HCl-KCl, CH_3COOH-CH_3COONa, NH_3-NH_4Cl).

2.2. Methods

The retention capacity of AOPAN fiber toward heavy metal ions Cu^{2+} and Hg^{2+} from aqueous solutions was evaluated by batch experiments: samples of 0.1 g of AOPAN were contacted with 50 mL solutions of variable concentrations in Cu^{2+} or Hg^{2+} and pH, under intermittent stirring. After a prefixed time the phases were separated by filtration and the concentration of metallic ion in solution was determined by spectrophotometric methods.

The percent removal by sorption (% R) and amount of retained metal ion (q, mg/g) were calculated as (Eqs.1, 2):

$$R(\%) = \frac{c_0 - c}{c} \times 100 \quad (1)$$

$$q = \frac{(c_0 - c\ ).v}{m} \quad (2)$$

where c_0 and c are metal ion concentration (mg/L) in initial solution and at equilibrium, v is the volume of the solution (L) and m is the weight of the fibrous sorbent (g).

3. Results and discussion

The sorption of metal ions on polyacrylamidoxime chelating sorbent is dependent on the pH of the sample solution due to competitive reaction between amidoxime chelating group and protons in the solutions ($pK_a \sim 6$):

$$R{-}C(=NOH){-}NH_2 \quad \underset{\pm H^+}{\rightleftarrows} \quad R{-}C(=NOH){-}{}^{+}NH_3$$

In order to minimize the effect of solution pH, the sorption experiments were conducted in buffered media (Table 2). It is noted that the sorption of copper and of mercury ions slowly increases in the pH range 2-6, but the amount retained onto fibrous sorbent is higher for mercury in comparison with cooper; also, copper retention increase in ammoniacal media. The sorption from nonbuffered solutions, with a slightly acidic pH (4-5) due to hydrolysis, is somewhat lower as compared to that from the buffered solutions with similar pH.

Table 2. Influence of solution pH on retention of copper and mercury ions on AOPAN

pH	***q (mg metal /g of sorbent) for initial metal ion concentration***				
	508.3 mg/L $Cu(NO_3)_2$	127.08 mg/L ($CuSO_4$)	317.7 mg/L ($CuSO_4$)	200 mg/L ($Hg(NO_3)_2$)	200 mg/L ($HgCl_2$)
2.0 (HNO_3)	2.28	-	-	130.4	-
2.0 (HCl-KCl)	-	15.93	20.02	-	72.4
3.6 (CH_3COOH–CH_3COONa)	16.57	15.93	22.83	142.4	101.0
4.6 (CH_3COOH–CH_3COONa)	18.49	15.77	28.85	146.0	102.4
5.6 (CH_3COOH–CH_3COONa)	-	14.89	31.88	155.6	111.6
≈9 (NH_4OH–NH_4Cl)	-	23.78	58.85	-	-

In parentheses are provided the substances added to adjust the pH value and salts of copper and mercury, respectively.

Regarding the influence of contact time between AOPAN and salt solution on the metal ion sorption, it was noted that the equilibrium is reached rather slowly (Fig.1).

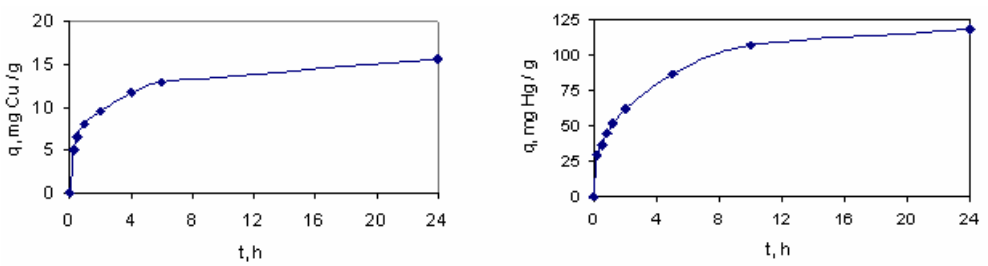

Fig. 1. Influence of phases contacting time on Cu^{2+} and Hg^{2+} sorption on AOPAN fiber
$CuSO_4$, c_0 = 50.8 mg/L, pH = 4.6; $Hg(NO_3)_2$, c_0 = 200 mg/L, pH = 2

Thus, the amount retained exhibits a more pronounced increase in the first

20 min, but afterwards the slope of the q *vs.* time curve gradually decreases with increasing time. Actually, the retention continues to increase during several days; for example, from a nonbuffered (pH = 4-5) solution with initial copper concentration 317.7 mg/L, the amounts retained after 24, 48 and 96 h are 22.85, 32.35 and 46.07 mg/g, respectively. The time necessary to attain the equilibrium is greatly diminished when the solution is heated.

The sorption (R, %) of Cu^{2+} and Hg^{2+} onto AOPAN fiber as a function of their concentrations was studied varying the metal concentration from 50 to 1200 mg/L (Fig.2).

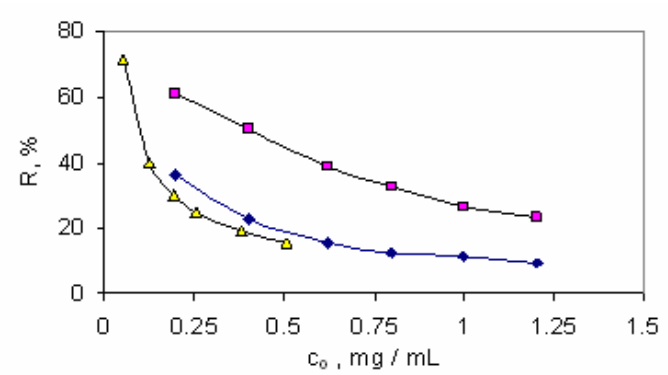

Fig.2. Sorption of metal ions on AOPAN fiber as a function of initial concentration
□ - $Hg(NO_3)_2$, pH = 2 ; ◆- $HgCl_2$, pH = 4.5 ; Δ- $CuSO_4$, pH = 4.6

A good retention takes place at low initial concentration but percentage sorption for Cu^{2+} and Hg^{2+} decreases with increasing initial metal concentration in aqueous solutions. These results indicate that energetically less favourable sites become involved with increasing metal concentrations in solutions.

The relationships between the concentration of the sorbed species in the solid phase and that in the solution phase are represented by the sorption isotherms (Fig. 3).

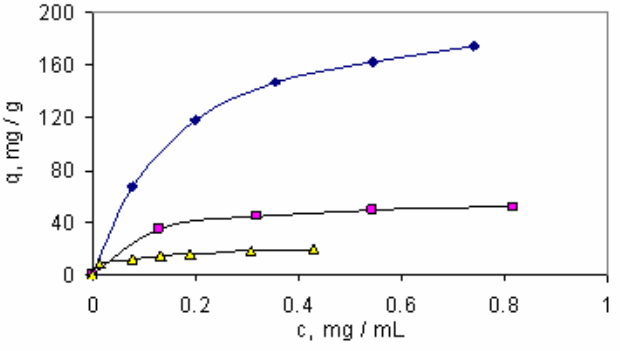

Fig.3. Sorption isotherms of metal ions on AOPAN fiber; (□ - $Hg(NO_3)_2$, pH = 2 ; ◆- $HgCl_2$, pH = 4.5 ; Δ - $CuSO_4$, pH = 4.6)

The equilibrium data for metal ions over the investigated concentration range have been correlated with the Langmuir isotherm:

$$\frac{c}{q} = \frac{c}{q_0} + \frac{1}{K_L . q_0} \tag{2}$$

where q_0 and K_L are Langmuir constants related to sorption capacity and sorption energy, respectively. The statistical fits of the sorption data to this equation, the Langmuir model parameters obtained from linear plots c/q *vs*. c and the values of free energy changes ($\Delta G = -RT \ln K_L$), characteristic to Cu^{2+} and Hg^{2+} sorption onto AOPAN are given in Table 3.

Table 3. The correlation coefficients and the characteristic parameters of Langmuir equation

Metal ion (salt)	R^2	q_o		K_L		***ΔG (kJ/mol)***
		(mg/g)	(mmol/g)	(L/g)	(L/mol)	
Cu^{2+} ($CuSO_4$)	0.993	21.79	0.343	17.13	1087.75	-18.834
Hg^{2+} ($Hg(NO_3)_2$)	0.997	222.27	1.108	5.195	1039.0	-17.200
Hg^{2+} ($HgCl_2$)	0.996	60.61	0.302	8.926	1785.2	-18.54

The values of the correlation coefficients are higher than 0.99 indicating that the experimental data are well fitted by the Langmuir model of monolayer coverage of sorbent with sorbate. According to q_o parameter, sorption onto AOPAN fiber is produced following the sequence $Hg^{2+} > Cu^{2+}$. The nature of the anion of salt is, also, very important; the sorption capacity is much lower for mercury chloride than for mercury nitrate, in accordance with the nature of chemical species present in solution (neutral stable chlorocomplexes $HgCl_2$). The high values of K_L which reflect the strength of sorbed ion-sorbent binding and the negative values of free energy changes suggest a strong interaction (covalent bond) between metal ions and functional group of chelating fiber.

The chelation mechanism of sorption at retention of heavy metals, cooper and mercury, from aqueous solutions onto fibrous sorbent AOPAN was confirmed by infrared spectroscopy (Fig.4 and Fig.5). The spectra of AOPAN exhibit the characteristic bands of amidoxime group, i.e. C=N (1670 cm^{-1}), N-H (1610 cm^{-1}), N-O (920-940 cm^{-1}) and C-N (1020-1230 cm^{-1} region), as well as of nitrile C≡N (2260 cm^{-1}), carbonyl C=O (1740-1750 cm^{-1}) and ether C-O-C (1250 and 1060-1150 cm^{-1} region) groups; the broad band located over 3000 cm^{-1} contains the absorptions of N-H and OH groups. As compared to AOPAN, for Cu-AOPAN and Hg-AOPAN the band at 2260 cm^{-1} remains unaltered, indicating that the nitrile groups are not involved in the interaction with metallic ions. The modifications taking place, revealing that the ions interact with the other functional groups, consist mainly of splitting and shifting towards different frequencies of the existing bands.

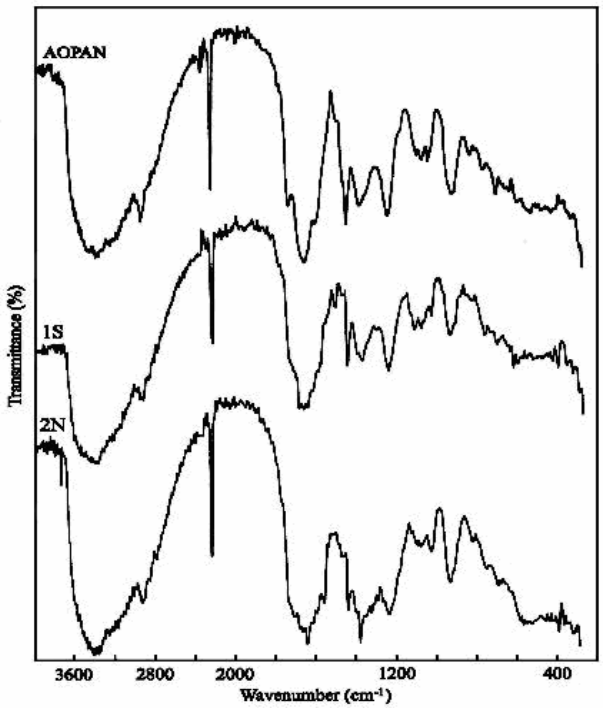

Fig. 4. Infrared spectra of AOPAN before and after Cu^{2+}sorption from sulphate (1S) and nitrate (2N) solutions

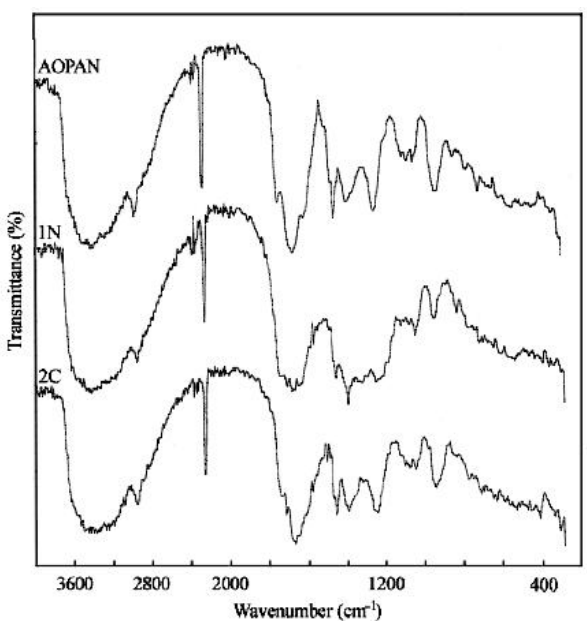

Fig. 5. Infrared spectra of AOPAN before and after Hg^{2+}sorption from nitrate (1N) and chloride (2C) solutions

Meantime, the appearance of new bands at frequencies characteristic to sulphate (1000-1150 cm^{-1} and 600-650 cm^{-1}) and nitrate (1280-1430 cm^{-1}, 1040 and around 830 cm^{-1}) groups occurs; the absorptions of metal-chlorine bonds are outside the frequency range of the IR spectrometer. As concerns the bands of the bonds formed by copper ions with the oxygen and nitrogen atoms, it is known that in complexes, this type of bands generally appear at low frequencies and, therefore, their recording and assignment are difficult.

Taking into consideration the characteristics of AOPAN and the information provided by equilibrium study of metal ions sorption and IR spectroscopy, the predominant structures of the complexes formed by the interaction of AOPAN with copper and mercury ions was proposed. The amidoxime groups act as bidentate ligands, coordinating to metallic ions through the nitrogen atoms of the amino groups and the oxygen atoms of the oxime groups; as a result, five-membered chelate rings are formed. A metallic ion is intermolecularly complexed, being coordinated by two amidoxime groups belonging to different polymeric chains. The intermolecular complexation of metallic ions generates the crosslinking of AOPAN chains.

4. Conclusions

The sorption of copper ions as sulphate and nitrate is favoured by increasing pH and decreasing initial concentration of the copper salt solution.

The sorption of mercury ions as nitrate and chloride increases with decreasing mercury ion concentration and increasing pH of the initial salt solution.

The time necessary to attain equilibrium is greatly diminished when the solutions are heated.

The experimental data for copper and mercury ions retention onto AOPAN fiber are well fitted by the Langmuir model.

The retention of metallic ions takes place prevalently by formation of chelate complexes at the amidoxime groups of chelating fiber.

References

Bilba N., Bilba D., Moroi G., (2004), Synthesis of an polyacrylamidoxime chelating fiber and its efficiency in retention of palladium ions, *Journal of Applied Polymer Science*, **92**, 3730-3735.

Deng S., Bai R., Chen J.P., (2003), Aminated polyacrylonitrile fibers for lead and copper removal, *Langmuir*, **19**, 5058-5064.

Deng S., Bai R., Chen J.P., (2003), Behaviors and mechanisms of copper adsorption on hydrolyzed polyacrylonitrile fibers, *Journal of Colloid and Interface Science*, **260,** 265-272.

Egawa H., Nakayama M., Nonaka T., Sugihara E., (1987), Recovery of uranium from sea water. IV. Influence of crosslinking reagent on the uranium adsorption of macroreticular chelating resin containing amidoxime groups, *Journal of Applied Polymer Science,* **33**, 1993.

Erdem E., Karapinar N., Donat R., (2004), The removal of heavy metal cations by

natural zeolites, *Journal of Colloid and Interface Science,* **280,** 309-314.

Gulina L.V., Grigoryan E.A., Gabrielyan G.A., Galbraikh L.S., (2002), Fibre chemisorbents based on modified graft copolymers of cellulose and polycaproamide, *Fibre Chemistry,* **34**, 440-447.

Ho Y.S., McKay G., Wase D.A.J., Forster C.F., (2000), Study of the sorption of divalent metal ions on to peat, *Adsorption Science and Technology,* **18**, 639-650.

Inglezakis V.J., Loizidou M.D., Grigoropoulou H.P., (2003), Ion exchange of Pb^{2+}, Cu^{2+}, $Fe^{3+}$and Cr^{3+} on natural clinoptilolite: selectivity and influence of acidity on metal uptake, *Journal of Colloid and Interface Science,* **261**, 49-54.

Jin L., Bai R.B., (2002), Mechanism of lead adsorption on chitosan/PVA hydrogel beads, *Langmuir,* **18**, 9765-9770.

Kicsi A., Bilba D., Macoveanu M., (2006), Batch copper(II) removal from aqueous solution by sphagnum moss peat, *Environmental Engineering and Management Journal,* **5**, 19-28.

Lacour S., BollingerJ-C., Serpaud B., Chantron P., Arcos R., (2001), Removal of heavy metals in industrial wastewaters by ion-exchanger grafted textiles, *Analitical Chimica Acta,* **428**, 121-123.

Lin W., Hsieh Y.L., (1997), Ionic adsorption of polypropylene functionalized by surface grafting and reactions, *Journal of Polymer Science: Part A: Polymer Chemistry,* **35**, 631-642.

Lin S.H., Juang R.S., (2002), Heavy metal removal from water by sorption using surfactant-modified montmorillonite, *Journal of Hazardous Materials,* **92**, 315-326.

Liu D.H., (1997), *Environmental Engineers Handbook,* Second Edition, CRC net Base Product, Lewis Publishers.

Liu R., Li Y., Tang H., (1999), Application of the modified polyacrylonitrile fiber with aminocarboxyl-tetrazine groups for the preconcentration of trace heavy metal ions, *Journal of Applied Polymer Science,* **74**, 2631-2636.

Liu R., Li Y., Tang H., (2002), Synthesis and characteristics of chelating fibers containing imidazoline group or thioamide group, *Journal of Applied Polymer Science***, 83**, 1608-1616.

Loyd-Jones P.J., Rangel_Mendez J.R., Streat M., (2004), Mercury sorption from aqueous solution by chelating ion exchange resin, activated carbon and a biosorbent, *Process Safety and Environmental Protection,* **82** (B4), 301-311.

Simanova S.A., Kuznetsova T.V., Demidov V.N., Knyazkov O.K., Konovalov L.V., (2001), Platinum complexation at sorption of hexachloroplatinate (IV) ion with fibrous N, S containing sorbents based on polyacrylonitrile (of TIOPAN type), *Russian Journal of Applied Chemistry,* **74**, 1439-1445.