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Abstract: A fibrous sorbent containing chelating amidoxime groups $-C(NH_2)=NOH$ prepared from the Romanian commercial polyacrylonitrile -based fiber Melana was used for the removal of Hg^{2+} from aqueous solutions. The optimum conditions for the Hg^{2+} uptake were developed with respect to initial pH of solution, nature of anions, equilibration time, concentration of Hg^{2+}, and temperature. The sorption was described quantitatively by fitting the equilibrium data to the Langmuir isotherm. The Langmuir parameters and thermodynamic quantities (ΔG, ΔH, ΔS) were calculated. The chelation mechanism of Hg^{2+} uptake on polyacrylamidoxime fiber was confirmed by IR spectroscopy. The experimental results point out the possibility of polyacrylamidoxime fiber to reversibly bind Hg^{2+} from wastewaters.

Keywords: Polyacrylamidoxime fiber, sorption, mercury (II), isotherms, thermodynamic quantities

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INTRODUCTION

The discharge of heavy metal ions from many industries into the aqueous effluents has created serious problems for human health and aquatic ecosystems. If mobilized, metal ions may reach the groundwater—an important source for drinking water, or due to their bioavailability they can be toxic for groundwater fauna and flora. Removal of the heavy metal ions, particularly mercury (Hg^{2+}), from the environment is a main question of waste treatment and clean-up efforts. The microscopic organisms from water and soil in the presence of mercury and organic compounds form methylmercury which is readily absorbed by biota and can be passed up the aquatic food chain. Methylmercury is slowly metabolized to ionic mercury in the brain. Due to the high toxicity, persistency, mobility, and bioaccumulation of mercury (II) in the environment, the treatment of wastewaters containing this element has received a considerable attention. The U.S. Environmental Protection Agency recommends a maximal value of 1 μg Hg^{2+}/L in drinking water (1). A number of methods including chemical precipitation, coagulation/coprecipitation, activated carbon fiber adsorption, membrane separation, solvent or complexing extraction and ion exchange are currently available for the removal of mercury (II) from aqueous systems (2–8). The effectiveness of each method is determined by the chemical nature and initial concentration of mercury and, also, by the presence of interfering constituents in the wastewater. Many of these treatment processes are expensive or have some disadvantages such as incomplete removal of mercury ions, moderate or no ion selectivity, amount of toxic sludge, or concentrated brine solution produced.

A promising alternative to conventional techniques used for the heavy metal ions' removal from solutions of relatively low concentrations has proven to be utilization of chelating sorbents, which are functionalized materials prepared by the attachment of various chelating groups onto solid supports (natural or synthetic polymers and mineral oxides) (9–15). Depending on the nature of an immobilized functional group, these materials exhibit a high selectivity for some toxic metal ions.

In recent years the emphasis has been focused on chemically modified fibers as sorbents for removal of heavy metal ions from aqueous solutions (16–20). The main advantages of these functionalized fibrous polymers in comparison with those of powder types are the large external specific surface areas of polymeric support determining high rate of sorption and a good sorption capacity and, also, the easy handling in a variety of forms (fibers, fabrics, filters). Many fibrous chelating sorbents for selective removal and recovery of various metal ions have been prepared from polyacrylonitrile fiber, a common and cheap commercial product (21–25).

In our previous study, we have reported the synthesis of a polyacrylamidoxime fiber (AOPAN) and its employment as sorbent for palladium (II) recovery from aqueous solutions (26). AOPAN fiber is a specific sorbent

because amidoxime groups have no affinity for the common metallic cations which are usually in water (Na^+, K^+, Ca^{2+}, and Mg^{2+}). AOPAN fiber has affinity for the transition metal ions which are capable of chelation.

The present study's aim was to investigate the performance of the polyacrylamidoxime fiber in mercury ion sorption from synthetic aqueous solutions under the influence of experimental parameters such as pH, concentration, temperature, and time. The equilibrium and kinetic of the sorption process were evaluated. In order to investigate the mechanism of sorption, IR spectrometry was used.

EXPERIMENTAL

Materials

The polyacrylamidoxime fiber (AOPAN) was prepared in our laboratory from the Romanian polyacrylonitrile fiber Melana (PAN) (90.6 wt.% acrylonitrile, 6.2 wt.% vinyl acetate, 3.2 wt.% α-methylstyrene) by the one-step reaction with hydroxylamine in methanol (3 wt.%) at 80°C (26). The molar ratio between the two reactants was 1.17 and the reaction time was 1.5 h. The anion-exchange capacity of the reaction product (AOPAN), corresponding to the amount of introduced amidoxime groups (nitrile groups converted into amidoxime groups) is 2.43 mmol HCl/g.

The stock solutions 10^{-2} M of Hg^{2+} were prepared from analytical grade mercury nitrate (in 0.1 N HNO_3) and mercury chloride (aqueous), respectively.

Apparatus

A VSU-2P spectrophotometer was employed for the determination of Hg^{2+} concentrations (spectrophotometric method using diphenyl carbazide). The infrared spectra of samples pressed into pellets with KBr were recorded with a BioRad IR spectrophotometer. A pH-meter equipped with a combined glass electrode was used for pH measurement. The solution temperature was held constant during the experiment with a thermostatic bath. A magnetic stirrer was used for vigorous shaking of the samples.

Sorption Experiments

Batch sorption experiments were performed by equilibrating 0.1 g of dry AOPAN fiber with 50 mL solution with different initial concentrations of mercury, pH and temperature, under intermittent stirring. After a prefixed

time (usually 24 h), the mercury content in solutions was determined complexonometrically and/or spectrophotometrically.

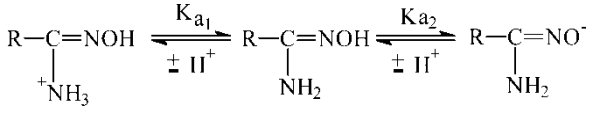
The sorption efficiency was calculated as percent of mercury removal, $R = [(c_0 - c)/(c_0)] \cdot 100$ (%) or as amount of mercury sorbed (retained on AOPAN), $q = [(c_0 - c)/(m)] \cdot V$ (mg/g), where c_0 and c are Hg^{2+} concentrations (mg/L) in the aqueous phase before and after equilibration respectively, V is the volume of aqueous solution (L) used for equilibration and m is the weight of AOPAN sample (g).

RESULTS AND DISCUSSION

Amidoxime sorbents are amphoteric exchangers with mixed weakly basic and weakly acid functionalities ($pK_{a1} \simeq 6$, $pK_{a2} \simeq 12-13$) (27), therefore their metal ion uptake properties must be affected by solution pH (Scheme 1).

In our experiments, the initial pH of solutions (mercury nitrate and mercury chloride, $c_0 = 10^{-3}$ M) was adjusted with nitric acid ($pH < 3.0$) and acetic acid-sodium acetate buffers ($3.0 < pH < 6$). The sorption efficiency of Hg^{2+} on AOPAN fiber as a function of solution pH is shown in Fig. 1.

It was found that the sorption efficiency, R, gradually increases with increasing pH, the values being lower for mercury chloride than for mercury nitrate. This behavior is consistent with the nature of various mercury chemical species present in acidic solution. Thus, in the pH range 2–5, a solution of mercury nitrate contain predominantly Hg^{2+} cations and only little $HgNO_3^+$ and $HgOH^+$, while in a mercury chloride solution, the neutral stable chlorocomplexes $HgCl_2$ predominate. At $pH > 5$ formation of hydroxy complex $Hg(OH)_2$ increases for both chloride and nitrate solutions (13, 28). The correlation between mercury speciation in solution and the sorption capacity of AOPAN fiber is confirmed by the following data. From a non-buffered mercury chloride solution ($pH \sim 4.5$) with $c_0 = 1$ mmol/L, percent of mercury removal is ~36%. In the presence of a potassium chloride solution (10^{-2} M), due to anionic chlorocomplexes $[HgCl_3]^-$ and $[HgCl_4]^{2-}$, R decreases at 28%. Further, in buffer acetate medium ($pH \sim 4.5$) R increases at 51.2% and this is due to the formation of acetate complexes $[Hg(OAc)]^+$ and $[Hg(OAc)_2]$. At the same time, the incomplete mercury sorption from solutions at $pH \leq 6$ is correlated with the protonation



Scheme 1.

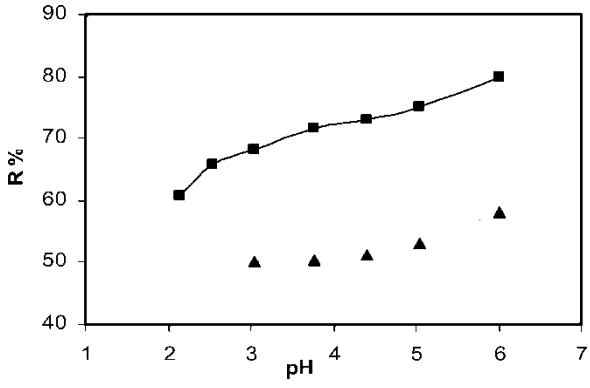


Figure 1. Variation of percentage sorption efficiency of Hg^{2+} onto AOPAN fiber with pH: ■, $Hg(NO_3)_2$; ▲, $HgCl_2$; T = 298 K; t = 24 h.

of amidoxime chelating group; the competition between hydrogen and mercury ions on the sorption sites diminishes the access of metal ions.

The effect of equilibration time between amidoximated fiber and a mercury nitrate solution of initial concentration $2 \cdot 10^{-3}$ M and pH = 2 at 25°C on Hg^{2+} removal is illustrated in Fig. 2.

The amount of Hg^{2+} sorbed after 24 h is of $q_e = 118$ mg/g. It is observed that initially sorption increases rapidly (the mercury ions accumulate at the surface functional groups) but after that the rate becomes slower (the sorption half-time is of ~ 100 minutes). This behavior is due to both the hydrophobicity of the polyacrylonitrile fiber and the complexation mechanism of sorption.

The sorption process of Hg(II) ions from an aqueous solution onto AOPAN fibers can be considered as a liquid-solid phase reaction, which includes the transport through diffusion or convection to the fiber surface

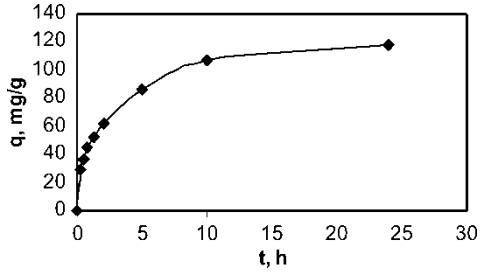


Figure 2. Dependence of Hg^{2+} sorption on AOPAN fiber on the time of sorption: $Hg(NO_3)_2$ $2 \cdot 10^{-}3$ M, pH = 2, T = 298 K.

and then the chemical reaction between Hg(II) ions and the surface functional groups of the sorbent. The presence of $-NH_2$, $-NH-$, and $-OH$ in amidoxime groups may result in the formation of metal-organic complexes through chelation. These groups are responsible for the sorption capacity of AOPAN fiber. It has been reported that adsorbents containing nitrogen on the surface facilitate metal ion adsorption through the chelating mechanism (25).

In recent years, the kinetic models based on the capacity of the sorbent in solid/liquid systems used to adjust the experimental data include the Lagergren's pseudo-first order equation, the Ho's pseudo-second order equation and the Zeldowitsch's equation (29–32).

In order to analyze the sorption kinetics of Hg^{2+} on AOPAN fiber the pseudo-first order Lagergren and the pseudo-second order models were applied to the experimental data. The linear forms of the rate expression for these two models are expressed by the equations:

$$\lg(q_e - q_t) = \lg q_e - k_1 \cdot t; \quad \frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \tag{1}$$

where q_e and q_t are the sorption capacity at equilibrium (24 h) and at time t, respectively (mg/g), t is the reaction time (min), k_1 is the rate constant of pseudo-first order sorption (1/min), k_2 is the rate constant of pseudo-second order sorption (g/mg · min), and $k_2 \cdot q_e^2 = h$ is the initial sorption rate as q_t/t approaches zero (mg/g · min). The rate constant k_1 obtained from the slope of $\lg(q_e - q_t)$ against t corresponds to a calculated sorption capacity at equilibrium of 85.43 mg Hg/g and rate constant k_2 obtained from the slope of the plot t/q_t against t to a calculated sorption capacity at equilibrium of 116.28 mg Hg/g which fits well the measured sorption capacity at equilibrium of 118 mg/g (Fig. 3, Table 1). The high correlation coefficient $R^2 = 0.99$ and the very good correspondence between the calculated and the experimental

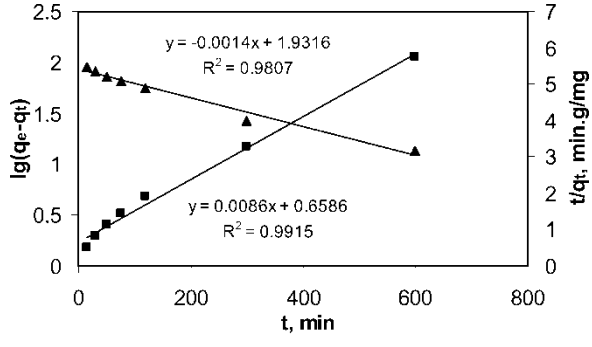


Figure 3. Pseudo-first order ($\lg(q_0\text{-}q_t)$ vs. t) (▲) and pseudo-second-order (t/q_t vs. t) (■) kinetics of Hg^{2+} sorption on AOPAN fiber: $Hg(NO_3)_2$ $2 \cdot 10^{-}3$ M, pH = 2, T = 298 K.

Table 1. Comparison between sorption rate constants, q_e calculated and coefficients of correlation, R^2, associated to the pseudo-first order and to the pseudo-second order kinetic models in the case of Hg^{2+} sorption on AOPAN fiber

Pseudo-first order			Pseudo-second order			
R^2	q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	h (mg/g · min)	k_2 (g/mg · min)
0.9807	85.43	3.22×10^{-3}	0.9915	116.28	1.518	1.123×10^{-4}

q_e measured: 118 mg/g.

values of sorption capacity show that the experimental kinetic data are in agreement with the pseudo-second order rate equation.

The pseudo-second order equation has been successfully applied to the sorption of metal ions, dyes, herbicides, and some organic substances from aqueous solution (32).

Figure 4 illustrates the effect of initial concentration of mercury, c_0 (mmol/L) from aqueous solution of nitrate and chloride, respectively, on the sorption q (mg/g), and on the sorption efficiency R, onto AOPAN fiber.

The amount of Hg^{2+} retained by the AOPAN fiber increases with increasing initial metal ion concentration in aqueous solution reaching a plateau, this trend being much more pronounced for mercury nitrate in comparison with mercury chloride. At the same time, the percentage of mercury removal decreases; this opposite trend is determined by occupation (at high concentrations) of available surface amidoxime groups, which inhibits diffusion of Hg^{2+} to the unreacted functional groups.

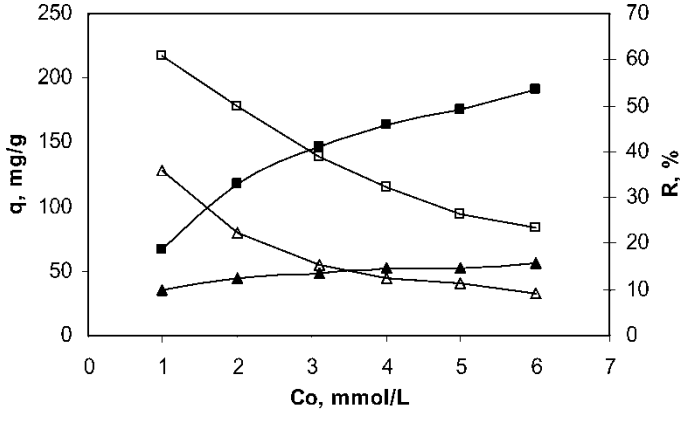


Figure 4. Influence of initial concentration of $Hg(NO_3)_2$ (pH = 2) (■, □) and $HgCl_2$ (pH = 4.5) (▲, △) on the amount of Hg^{2+} retained (■, ▲) and on the percent of mercury removal (□, △); T = 298 K; t = 24 h.

The Hg^{2+} sorption abilities on AOPAN fiber were evaluated from the equilibrium distributions of ions between the phases of sorbent and solution, respectively the functional dependences $q = f(c)$. The sorption isotherms of Hg^{2+} on AOPAN from nitrate solutions (pH = 2) and chloride solutions (pH = 4.5) at different temperatures are given in Figs. 5 and 6.

The equilibrium sorption data were fitted to the Freundlich and Langmuir sorption isotherms models, expressed by the following linear equations (29, 30):

Freundlich isotherm

$$\lg q = \frac{1}{n}\lg c + \lg K_F \tag{2}$$

Langmuir isotherm:

$$\frac{c}{q} = \frac{c}{q_e} + \frac{1}{K_L \cdot q_e} \tag{3}$$

where K_F and n are the Freundlich constants indicating the sorption capacity and sorption intensity, respectively, and q_e and K_L are the Langmuir constants, related to saturation sorption capacity and equilibrium binding constant, respectively. The sorption isotherm constants obtained from intercepts and slopes of linear plots for Hg^{2+} sorption on AOPAN at three temperatures, together with their correlation coefficients (R^2) are shown in Table 2.

The values of correlation coefficients show that the sorption isotherm data of mercury ions from both nitrate and chloride solutions can be better described by the Langmuir model of monolayer coverage.

The high values of K_L which reflect the strength of sorbed ion–sorbent binding suggest a strong interaction (covalent bond) between chelating fiber AOPAN and metal ions. The q_e values related to accessibility of functional groups are much lower for Hg^{2+} ions from mercury chloride in comparison

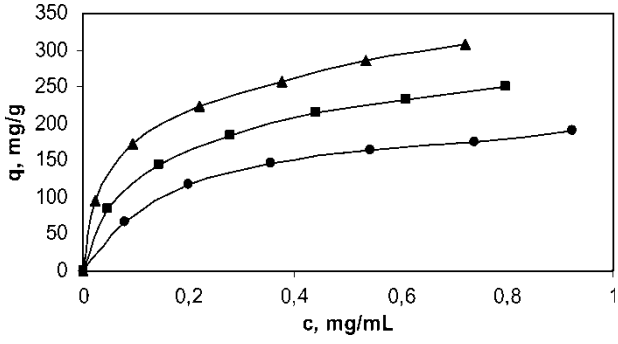


Figure 5. Sorption isotherms of Hg^{2+} (mercury nitrate) on AOPAN fiber at different temperatures: ● – 298 K, ■ – 318 K, ▲– 348 K; pH = 2; t = 24 h.

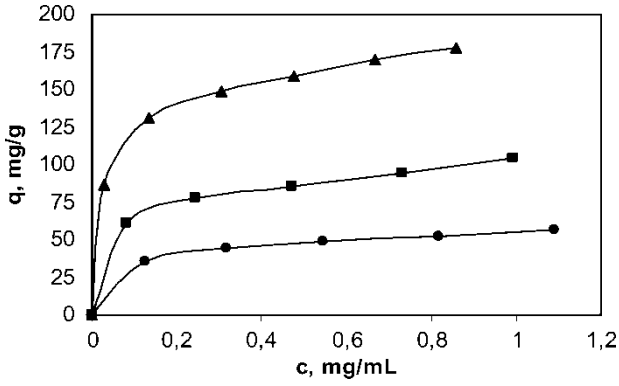


Figure 6. Sorption isotherms of Hg^{2+} (mercury chloride) on AOPAN fiber at different temperatures: ● – 298 K, ■ – 318 K, ▲ – 348 K; pH = 4.5; t = 24 h.

with those from mercury nitrate. Both q_e and K_L increases with increasing temperature showing the enhancement of Hg^{2+} diffusion at the hydrophobic surface of polyacrylonitrile-based fiber and, also, endothermic nature of sorption.

If the mercury sorption capacity is calculated based on the mole number, it is observed that the ratio of exchange capacity of AOPAN fiber (2.43 mmol/g) and q_e (mmol/g) is near to 2 for mercury nitrate at temperature of 298 K and for mercury chloride at increased temperature, suggesting that one mercury reacts with two groups of amidoxime. In the case of mercury nitrate at higher temperatures this ratio is lower than 2, indicating a possible formation of 1 : 1 complex between mercury and amidoxime functional group in the sorbent phase.

Table 2. Parameter values of Freundlich and Langmuir equations at Hg^{2+} sorption on AOPAN fiber

		Freundlich model			Langmuir model		
Mercury salt	T (K)	K_F (mg/g) $(L/mg)^{1/n}$	n	R^2	q_e (mg/g)	K_L (L/g)	R^2
$Hg(NO_3)_2$	298	12.25	2.44	0.963	222.27	5.195	0.997
	318	19.73	2.57	0.987	285.70	7.186	0.996
	348	34.76	2.97	0.988	333.33	11.25	0.992
$HgCl_2$	298	12.98	4.77	0.989	60.61	8.926	0.996
	318	25.25	4.94	0.987	107.53	11.44	0.995
	348	44.78	4.83	0.984	185.19	17.893	0.996

Table 3. Thermodynamic quantities at Hg^{2+} sorption on AOPAN fiber

Mercury salt	T (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol · K)
$Hg(NO_3)_2$	298	−17.216	13.341	102.54
	318	−19.229		102.42
	348	−22.340		102.53
$HgCl_2$	298	−18.558	12.064	102.76
	318	−20.459		102.27
	348	−23.683		102.72

The apparent thermodynamic functions characteristic to mercury sorption on AOPAN fiber were calculated from the temperature dependence of Langmuir binding constant by means of usual relations and are presented in Table 3.

$$\Delta G = -RT\ \ln K_L; \quad -\frac{d\ln K_L}{d(1/T)} = \frac{\Delta H}{R}; \quad \Delta S = \frac{\Delta H - \Delta G}{T} \qquad (4)$$

where R is the constant of gases (8.31 J/K·mol) and T is the Kelvin temperature.

The negative values of free energy changes (ΔG) for all temperatures and both nitrate and chloride salts show a strong binding between Hg^{2+} and functional groups of AOPAN fiber (spontaneous sorption). The variation of sorption enthalpy (ΔH) is positive indicating an endothermic process, facilitated by the increase of temperature. The positive entropy changes (ΔS) are characteristic to the increase of the system disorder at the Hg^{2+} sorption on AOPAN fiber (probably due to displacement of ligands—hydration water molecules or chloride anions—for the formation of the complex in the sorbent phase).

In order to clarify the sorption mechanism, polyacrylamidoxime fiber, before and after mercury sorption, was analyzed by IR spectrometry (Fig. 7).

The broad bands around 3100–3400 cm^{-1} assigned to the NH and OH stretching vibrations in amidoxime groups are almost invariable (show no significant changes). Also, the narrow band at 2243.2 cm^{-1} assigned to –C≡N is unaffected, this group being not involved in reaction with mercury ions. At the same time, the absorption bands attributed to amidoxime groups change the apparent intensity and a certain shift takes place in the spectra of Hg-AOPAN fibers (33–36). The band at wavenumber 1639 cm^{-1} associated with both C=N stretching and $-NH_2$ bending vibrations is shifted to lower frequency (1620.2 cm^{-1}) after sorption of mercury ions on AOPAN, indicating the existence of interactions between metal ions and amidoxime groups (nitrogen atoms). Also, the decrease of frequency from 1251 cm^{-1} to 1226.7 cm^{-1} and 1236.37 cm^{-1}, and from 1035.77 cm^{-1} to 1029.99 cm^{-1} and 1031.9 cm^{-1}, respectively, for the bands assigned to C–N stretching vibrations may be correlated with the attachment of the mercury ions at

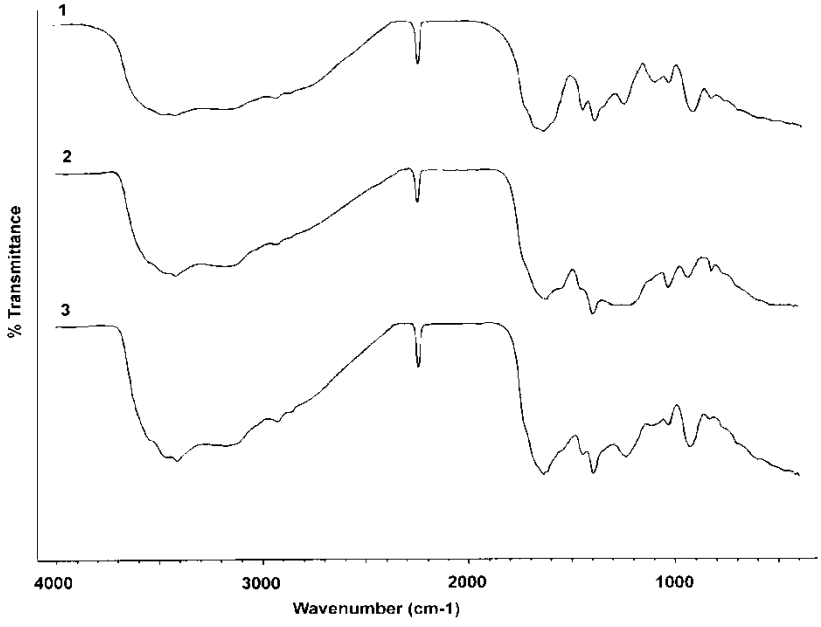


Figure 7. IR spectra of AOPAN fiber before (1) and after sorption Hg^{2+} from nitrate (2) and chloride (3) solutions.

NH_2 groups. Similarly, the band around 1100 cm^{-1} attributed to N–C–N bending decreases in the Hg-AOPAN spectra, as a result of bonded Hg^{2+} ions. Finally, the absorption band at 921.97 cm^{-1} assigned to N–O stretching vibrations in AO groups is shifted to higher frequency (935.47 cm^{-1} and 925.83 cm^{-1}, respectively) after complexation, indicating the formation of a mercury-oxygen bond.

The quantitative desorption of mercury ions from AOPAN fibers by elution with a hydrochloric solution of thiourea (0.5% in 0.1 M HCl) was performed. After six adsorption-desorption cycles the AOPAN fibers exhibit no considerable change in adsorption capacity. In the regenerant solution mercury is present as $Hg(CH_4N_2S)Cl_2$ and/or $Hg(CH_4N_2S)_2Cl_2$. From this solution mercury is precipitated as HgS by heating at 80°C in presence of NH_4OH, when by thiourea hydrolysis free sulphide ions (S^{2-}) are formed. This method offers the possibility of reutilization for many times of the regenerated fiber.

CONCLUSIONS

The polyacrylamidoxime fiber behaves as an efficient sorbent for mercury ions at low ionic concentrations in aqueous solutions. The retention of Hg^{2+} ions

from nitrate solutions is preferred as compared with that from of chloride solutions. The chelating fiber affinity for Hg^{2+} increases with the pH and temperature of solution. The kinetics of the mercury sorption is rather slow at room temperature. The sorption isotherms of Hg^{2+}on AOPAN fiber give excellent fits to the Langmuir equation. The values of Langmuir constants (the saturated sorption capacity and equilibrium binding constant) and also the characteristic thermodynamic quantities suggest a chelation mechanism of mercury sorption on AOPAN fiber. This sorption mechanism is confirmed by infrared spectra data. The data are important for the recovery of mercury ions from aqueous solutions.

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