

## SELECTIVE RETENTION OF Hg<sup>2+</sup> IONS FROM AQUEOUS SOLUTIONS BY VARIOUS AMIDE GROUPS-FUNCTIONALIZED COPOLYMERS

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The study presents the synthesis of some copolymers with amide functional groups and their behaviour in selective mercury retention from aqueous solutions. The functionalized copolymers synthesis were performed by nucleophilic substitution reactions of pyridine, acrylic and styrene matrices with 2-chloroacetamide. The Hg<sup>2+</sup> retention from aqueous solutions on the performed copolymers takes place by chemo sorption processes leading to the formation of monoamido or diamido mercury compounds. The comparative studies of Hg<sup>2+</sup> ions retention on the synthesized functional copolymers were performed by batch experiments in mono- and binary heavy metal cations systems. The retention capacity of the functionalized copolymers toward Hg<sup>2+</sup> ions depends on the pH values of the aqueous solution, increasing with the increase of pH value in the range of 2 – 6 pH unities. The studied functional copolymers present high retention selectivity for the Hg<sup>2+</sup> ions during competitive sorption experiments in Hg<sup>2+</sup>/Cu<sup>2+</sup>, Hg<sup>2+</sup>/Zn<sup>2+</sup> and Hg<sup>2+</sup>/Fe<sup>3+</sup> aqueous systems.

### INTRODUCTION

Mercury is widely used for different industrial applications (paper industry, paints, cosmetics, thermometers, manometers, mercury batteries) and its presence in water represents a serious environmental problem due to its extreme toxicity towards the aquatic life and humans.<sup>1</sup> Among the different reported methods for the mercury removal from wastewaters, chemical precipitation, ion exchange, adsorption, solvent extraction, membrane filtration, coagulation and complexing are some of the most commonly used processes, but each has its own merits and demerits.<sup>2-6</sup> The chelating and ligand exchangers have received attention due to their specific selectivity toward certain ions. Many papers cover a vast number of different chelating groups immobilized on various synthetic and natural polymeric networks. The selective retention of the Hg<sup>2+</sup> is based on its great affinity towards some functional groups containing active hydrogen, such as thiol, thioether, amine and amide groups.<sup>7-9</sup>

The well-known reactivity of thiol and thioether compounds toward mercuric ions is the main

principle of selective mercury uptake for laboratory or industrial levels of applications. In fact, mercury-thiol interaction is not specific because thiol and thioether functions react also with other metal ions. The mercury-amide interaction is an exception, the amide compounds acting as selective reagents for mercury binding. In ordinary conditions the amide group is not capable of coordinative bonds forming with other transition metal ions, as a result of the reduced electron-donating character of the amide nitrogen.<sup>4</sup>

In fact, mercuric ions react with amides by covalent linkage to form mono or diamido mercury compounds. Nevertheless, the amide groups ensure a high selectivity for mercury binding. The reaction is fast even at low temperatures. Generally, the amide nitrogen atom lacks sufficient electron withdrawing carbonyl groups and cannot normally form coordination bounds with the transition metal ions. Therefore, the mercury salts can be removed from the amide group by the interaction of active hydrogen atoms. Some papers present the amide groups performances during the retention of Hg<sup>2+</sup> ions.<sup>10-14</sup> The amide group provides better selectivity in mercury binding by

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covalent bounds but not with other metal ions while the thiol and thioether groups retain the  $\text{Hg}^{2+}$  only by the complexing process.<sup>15</sup>

In the present study we report the synthesis of some crosslinked copolymers with amide functional groups based on pyridine, acrylic and styrene matrices, their mercury retention capacity and selectivity towards mercury ions from mono- and binary heavy metal cations aqueous solution systems ( $\text{Hg}^{2+}/\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}/\text{Zn}^{2+}$  and  $\text{Hg}^{2+}/\text{Fe}^{3+}$ ) at different pH values.

## RESULTS AND DISCUSSION

### Mercury sorption isotherms

Fig. 1 presents the sorption isotherms at  $20.0 \pm 0.5^\circ\text{C}$  for the mercury ions by the functionalized copolymers, respectively: PN1 sample

(pyridine-type matrix) as reference sample,<sup>16</sup> PN2 sample (acrylic-type matrix) and PN3 sample (styrene-type matrix), under noncompetitive conditions. The solid phase-retained mercury quantities increase with the initial liquid phase concentration until a saturation value is reached. At lower  $\text{Hg}^{2+}$  concentration values the maximal retention capacity belongs to PN1 sample whereas at higher concentrations, the order of the mercury retention capacities is:  $a_{\text{PN3}} > a_{\text{PN2}} > a_{\text{PN1}}$ .

The mercury retention values are not in agreement with the theoretical retention ones. This remark led to the conclusion that the amide groups reactivity towards  $\text{Hg}^{2+}$  depends on the chemical structures of the matrices. The Table 2 presents the molar ratio (MR) of the  $\text{Hg}^{2+}$  ions in the solid phase calculated as a function of mercury retention value ( $a$ , mmol Hg/g) and amide functional groups (Eq, mmol R-CONH<sub>2</sub>/g).

Table 1

Structural units of the performed functionalized copolymers

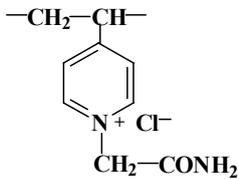
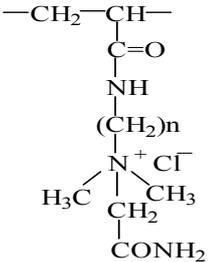
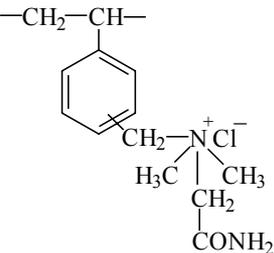
Polymer matrix	Pyridine	Acrylic	Styrene
Polymer structural units			
Code samples	PN1	PN2	PN3

Table 2

Molar ratio (MR) values for the studied functionalized copolymers

Sample code	Polymer matrix	Eq [mmol g <sup>-1</sup> ]	MR [mol Hg/mol R-CONH <sub>2</sub> ]
PN1	pyridine	3.70	0.750
PN2	acrylic	3.07	1.156
PN3	styrene	3.00	1.238

The order of the MR values for the synthesized compounds is the following PN3 > PN2 > PN1. Mercury binding via amide groups can occur in principle either by formation of monoamido or diamido mercury structures which provide  $\text{Hg}^{2+}$  retention from the aqueous solution. In the presented experimental conditions the interaction



of the amide groups with mercury ions in PN1 sample takes place by a non-complete monoamido bond according to the reaction (1) whilst the PN2 and PN3 functionalized copolymers have different behaviors, the mercury binding taking place both as monoamido (1) and diamido linkages (2).

Despite of the highest content of functional amide groups, the copolymer based on pyridine matrix present the lowest Hg<sup>2+</sup> retention capacity. This result can be explained by the lowest basic character of the functionalized copolymer based on pyridine matrix, due to the fact that its amide and aromatic amine groups are very weak bases. The

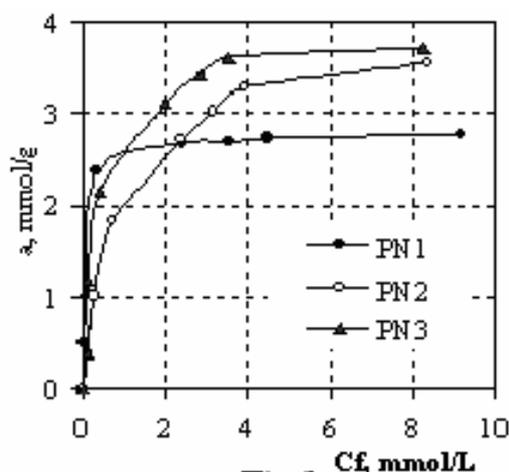


Fig. 1 – Hg<sup>2+</sup> sorption isotherms (pH 5.2±0.02).

#### Effect of pH on Hg<sup>2+</sup> sorption

Fig. 2 presents the experimental data for the mercury ion sorption on the functionalized copolymers - practically linear dependences of the Hg<sup>2+</sup> retention capacities on pH values. It can be seen that the Hg<sup>2+</sup> retention is highly sensitive to the pH changes, the retained mercury ions amount increasing with the increase of the solution pH value. This bearing is assigned by the interaction type between the amide group and the mercury ions which represents a chemical reversible reaction by covalent binding. The increase of the solution pH leads to the equilibrium modification in order to perform more mono- and diamido mercury linkages. The highest retention capacity values were registered for the PN2 and PN3 samples comparative to PN1 sample<sup>16</sup> and this finding is in agreement with the molar ratio (MR) data from Table 2.

#### Selectivity of the functionalized copolymers towards the mercury ions

In order to characterize the possible interferences from foreign ions on the mercury retention, we first treated the polymeric sorbent with each of the heavy metal ions, Hg<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and Fe<sup>3+</sup>, separately. Fig. 3 presents the retained metal amount – pH plots for all the unary studied systems. The high selectivity of the functionalized polymer samples towards Hg<sup>2+</sup> retention is obvious.

aromatic ring strongly decreases the basicity of the amine by its mesomeric effect (+M) which delocalizes the lone pair electron into the ring. Compared to PN1 sample, PN2 and PN3 samples present a higher basicity due to the inductive effect (+I) induced by the alkyl substituent groups to the nitrogen atom.

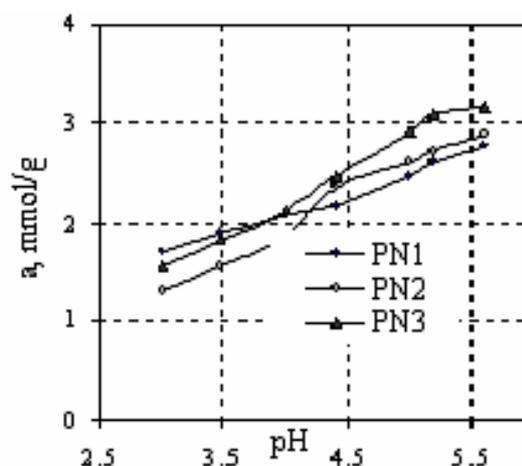


Fig. 2 – Hg<sup>2+</sup> sorption capacity dependence on solution pH.

The mercury ions are the only capable of coordinative bonding towards the amide group and as consequence the retention is highly selective. In ordinary conditions, the amide group is not capable of coordinative bonds forming with other heavy metals as a result of the reduced electron-donating character of the amide nitrogen. Nevertheless, small amounts (0.1 – 0.6 mmol g<sup>-1</sup>) of retained Cu<sup>2+</sup>, Zn<sup>2+</sup> or Fe<sup>3+</sup> ions were detected. This result is a consequence of different retention processes and mechanisms for mercury ions (chemisorptions processes) and other heavy metals ions (physical sorption processes). The different copolymer samples present similar behavior towards the heavy metals, the retention capacities following the order:  $a_{\text{Hg}} \gg a_{\text{Fe}} > a_{\text{Zn}} > a_{\text{Cu}}$ .

The increase of the solution pH value induces a strong increase of the mercury ions retention compared to the other heavy metal ions (Cu<sup>2+</sup>, Zn<sup>2+</sup> and Fe<sup>3+</sup>). This represents another proof of the existence of two different retention mechanisms, the amide group being strictly selective for mercury ions. The sorption experiments in the binary systems showed that the PN1, PN2 and PN3 functionalized copolymers are highly selective for Hg<sup>2+</sup> ions in the presence of the studied heavy metals (Figs. 4, 5 and 6). All the investigated binary sorption experiments showed a negative effect on the retention capacities due to the presence of the second metal cation.

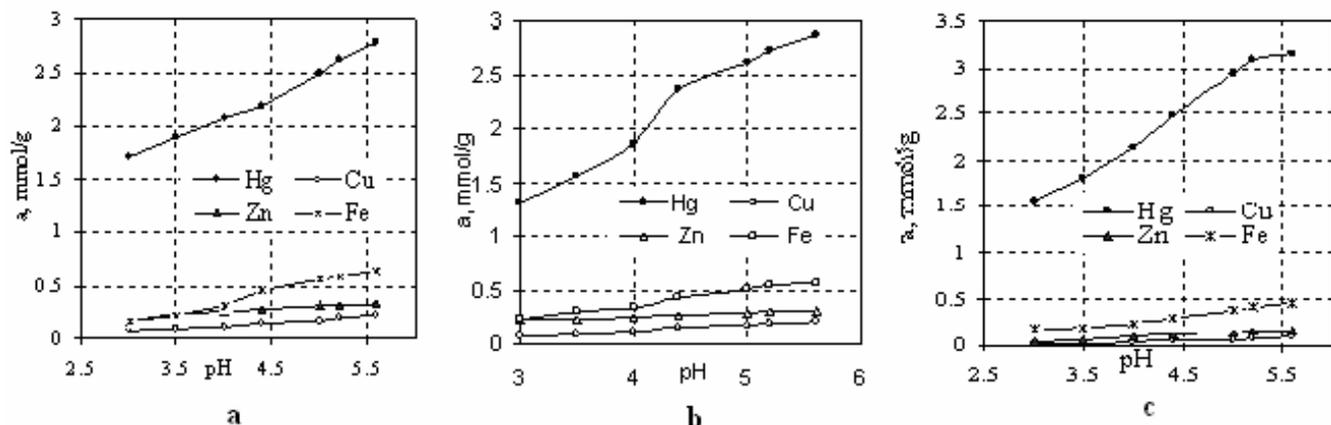


Fig. 3 – The influence of the solution pH on the heavy metal retention capacities for mono component systems (a - PN1 sample, b - PN2 sample, c - PN3 sample).

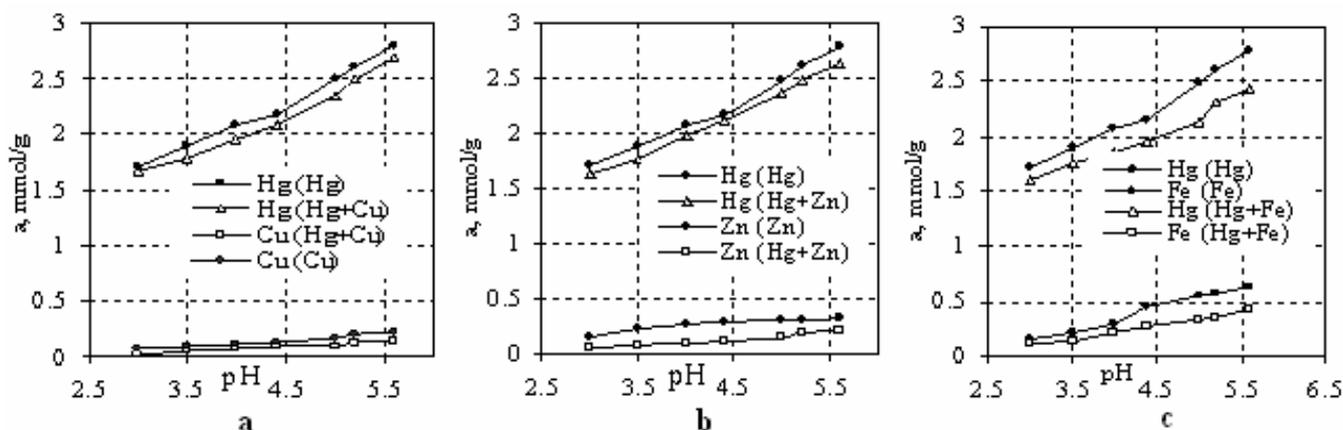


Fig. 4 – PN1 retention experiments on mono and binary systems- sorption capacity dependence on solution pH (a -  $\text{Hg}^{2+}$  and  $\text{Cu}^{2+}$ ; b -  $\text{Hg}^{2+}$  and  $\text{Zn}^{2+}$ ; c -  $\text{Hg}^{2+}$  and  $\text{Fe}^{3+}$ ).

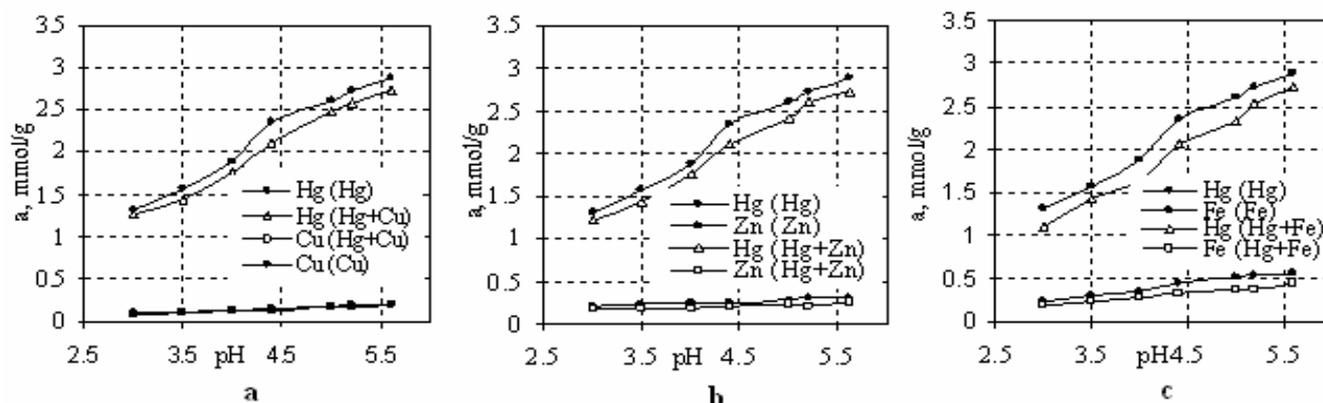


Fig. 5 – PN2 retention experiments on mono and binary systems- sorption capacity dependence on solution pH (a -  $\text{Hg}^{2+}$  and  $\text{Cu}^{2+}$ ; b -  $\text{Hg}^{2+}$  and  $\text{Zn}^{2+}$ ; c -  $\text{Hg}^{2+}$  and  $\text{Fe}^{3+}$ ).

This influence of the second heavy metal ion is more pronounced for the polymeric sorbents with acrylic and styrene matrices. It was also observed that the retention capacities for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  or  $\text{Fe}^{3+}$

ions decrease in the binary experiments compared to those of the mono experiments which could be explained by the hindrance of the metal cations in the retention processes.

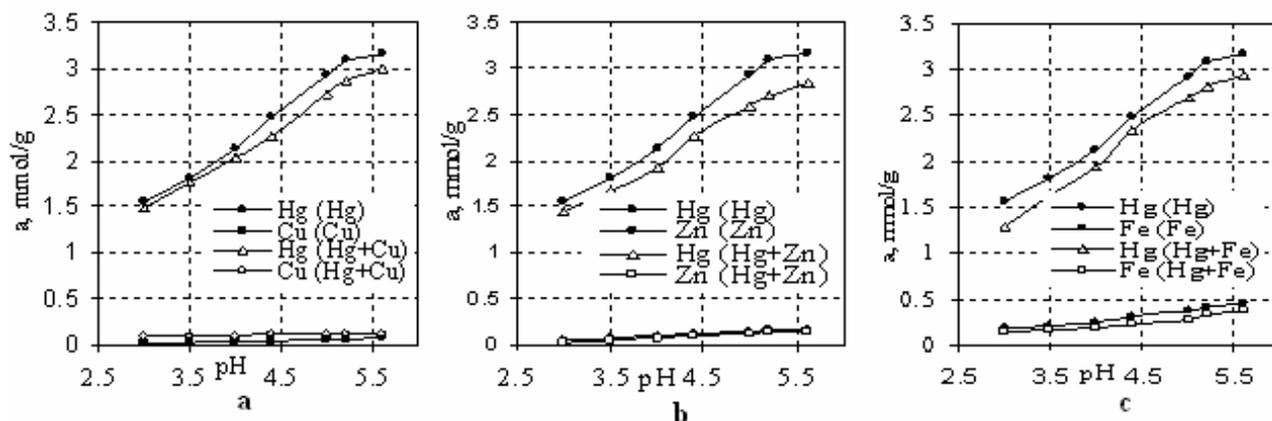


Fig. 6 – PN3 retention experiments on mono and binary systems- sorption capacity dependence on solution pH (a - Hg<sup>2+</sup> and Cu<sup>2+</sup>; b - Hg<sup>2+</sup> and Zn<sup>2+</sup>; c - Hg<sup>2+</sup> and Fe<sup>3+</sup>).

## EXPERIMENTAL

2-chloroacetamide, acrylamide as well as the other chemicals used for the synthesis of pyridine crosslinked copolymer were analytical-grade commercial products (Fluka). Commercially weak base anion exchange resins with acrylic matrix (Duolite A 375) and styrene matrix (Duolite A 378) in the amino form, 0.3 – 0.8 mm diameter size were obtained from Rohm and Haas Co. (USA).

The copolymer based on 4-vinylpyridine:divinylbenzene (4-VP:DVB) with 8 % crosslinking degree and gel-type morphological structure was synthesized according to [Luca et al (1995)]. The alkylation reaction of pyridine, acrylic or styrene matrices with 2-chloroacetamide was performed as a following: every type of copolymer beads (15 g) of 0.3 – 0.8 mm diameter size, was soaked into a solution of 2-chloroacetamide (1.5 ml) in 200 mL N,N-dimethylformamide. The mixture was shaken in a glass flask equipped with stirrer, cooler and thermometer at 60 °C for 48 h. The yielded compounds were filtered and washed with methanol and water, then dried at room temperature and finally, regenerated with NaCl 5mol dm<sup>-3</sup> concentration (Table 1).

The quaternized compounds were characterized by their strong base exchange capacities determined by the ion exchange of Cl<sup>-</sup> for SO<sub>4</sub><sup>2-</sup> anions, a means of the amide groups amount. Synthetic aqueous solutions containing the ions Hg<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup> and Fe<sup>3+</sup> were prepared from the chloride salts of the metals, HgCl<sub>2</sub>, ZnCl<sub>2</sub>·2H<sub>2</sub>O, CuCl<sub>2</sub>, FeCl<sub>3</sub>, (analytical grade products from Fluka).

In all the sorption experiments the solid/liquid ratio was 1g dm<sup>-3</sup>. Mercury salt in the chloride form was used in this study in order to avoid the competition of the anions during the mercury retention and because in most wastewater the frequency of Cl<sup>-</sup> anions is higher than another anions, such as NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>.

### Mercury sorption isotherms

The sorption experiments of Hg<sup>2+</sup> on the functionalized copolymers were performed by the batch method at 20.0 ± 0.5 °C. Fifty milligrams of polymer were contacted for 48 h (till the equilibrium was attained) with 50 mL HgCl<sub>2</sub> aqueous solutions with Hg<sup>2+</sup> concentrations ranging from 0 to 12 mmol dm<sup>-3</sup>. The solutions pH was maintained at 5.20 ± 0.02 using buffer solutions (Titrisol, Merck) and monitored by a pH electrode connected to a Jenway 370 pH-meter. Vigorous stirring of the solid and liquid phases was ensured by a

rotating magnetic bar. The amount, *a*, of retained mercury ions was calculated from the mass balance equation:

$$a = (C_i - C_f)V/m \quad (1)$$

Where: *a* - sorption capacity at equilibrium, mmol g<sup>-1</sup>, *C<sub>i</sub>* - concentration of solute in aqueous phase at initial, mmol dm<sup>-3</sup>, *C<sub>f</sub>* - concentration of solute in aqueous phase at equilibrium, mmol dm<sup>-3</sup>, *m* - mass of the sorbent, g; *V* - volume of solution, dm<sup>3</sup>.

### Effect of pH on Hg<sup>2+</sup> sorption

The sorption experiments under controlled pH were carried out using an initial metal concentration of 4.93mmol dm<sup>-3</sup>. The solutions pH was varied in the range of 3 – 6. The lower limit of the pH value for Hg<sup>2+</sup> sorption was imposed by the dissolution of the resins at pH < 2 and the upper pH limit was selected in order to avoid the precipitation of pure or mixed Hg carbonates or hydroxides. The pH was maintained at the desired value using appropriate buffer solution. The solid/liquid ratio was 1g dm<sup>-3</sup>.

### Selectivity of the functionalized copolymers towards mercury ions

The selectivity of the functionalized copolymers towards the mercury ions was studied by competitive sorption experiments in the binary heavy metal ions systems (Hg<sup>2+</sup>/Cu<sup>2+</sup>, Hg<sup>2+</sup>/Zn<sup>2+</sup> and Hg<sup>2+</sup>/Fe<sup>3+</sup>) with the initial concentration of 5.5mmol dm<sup>-3</sup> for each heavy metal. Thus, the two metals ratio in the binary systems was 1:1. Fifty milligrams of polymer were contacted for 48 hours with 50 10<sup>-3</sup> dm<sup>3</sup> mixed metal cations aqueous solutions. The solution pH varied in the range of 3 – 6 units.

The amounts of retained metal were calculated as difference between the initial and the final solution metal contents. The concentration was determined using a UV/VIS spectrophotometer Jenway 6405 (dithyzone colorimetric method). All measurements were made in duplicate and the reported values represent the averages values.

## CONCLUSIONS

The quaternization reactions performed on the pyridine, acrylic and styrene copolymers with

2-chloroacetamide led to functionalized quaternary compounds with amide groups. All the synthesized copolymers exhibit high  $\text{Hg}^{2+}$  retention capacity values, the binding of mercury ions being performed by interaction of mercury ions with the functional groups containing active hydrogen atoms.

The sorption isotherms reveal an increase of  $\text{Hg}^{2+}$  retention with the increase of the initial liquid phase concentration until a saturation value is reached. The retention capacities for mercury ions respect the following order:  $a_{\text{PN3}} > a_{\text{PN2}} > a_{\text{PN1}}$ .

The molar ratios of the mercury ions retained inside the solid phase show that the reactivity degree of the amide group depends on the basic character of the crosslinked copolymers. Despite the highest amide groups content, the PN1 sample present the lowest basicity compared to PN2 and PN3 ones. Therefore, the reactivity of the functionalized pyridine copolymer PN1 is the lowest, as the mercury binding via amide group occurred only by the formation of monoamido-mercury structures.

The solution pH has a strong influence on the mercury retention capacity - practically linear dependent on the pH value. During the competitive sorption experiments, all the functionalized polymers present a high selectivity for the mercury ions compared to the other heavy metals ions ( $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$ ).

This selectivity is explained by the retention of  $\text{Hg}^{2+}$  ions by the covalent bonding with amide group which possesses an active hydrogen atom. These results allow us to affirm that the synthesized functional copolymers with amide groups are very selective towards  $\text{Hg}^{2+}$  retention

and therefore, could have a great potential for wastewater treatment applications.

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