International Journal of Biology and Chemistry 5, №1, 44 (2013)

UDC 541.64+678-9

E.E.Ergozhin, B.R.Tausarova,
R.K.Ashkeeva, L.M.Tugelbaeva*

Faculty of Chemistry and Chemical Technology, al -Farabi Kazakh National University,
Almaty, Kazakhstan
*E-mail: tugelbaeva-leila@mail.ru

Complex formation of polyelectrolytes with different groups of heavy and transition metal ions

The new copolymer based on styrene and divinylbenzene with groups of nicotinamide and copolymers based on isomers metakriloilaminobenzoic acids with 2-methyl-5-vinylpyridine are obtained by chemical modification and radical copolymerization. The optimal conditions of synthesis were found. Structure and properties of initial compounds and copolymers based on them have been studied by IR spectroscopy, elemental analysis. The sorption properties of the synthesized polymers with respect to the ions of heavy and transition metals were investigated.

Keywords: sorbent, chemical modification, radical copolymerization, complex creating ability, heavy and transitional metals, static exchange capacity.

Introduction

Treatment of waste water, liquids and gases, as an important part of a set of measures in reducting the scale and speed of the negative impacts of human economic activity on the environment, is a promising area of application of ion exchange. The synthesis, research and the use of chelating ion-exchange materials-polymer compounds with functional groups capable for forming chelate compounds with metal ions is one of the research areas.

In a special interest are the new cost-waste or low-waste and combined ion exchange purification methods based on the use of promising ion exchangers and ion exchange units [1-2].

The main pollutants of waste water are the heavy metals [3].

Heavy metals, especially cadmium, mercury, lead, zinc accumulates in plants. Consumption of plants, fish, water contaminated with heavy metals are the main sources of these pollutants penetrate into the humans body.

Therefore, the purification of waste-and industrial water from toxic ions is an urgent task [4-6]. In this regard growing interest in complexing sorbents.

The range of products made of ion exchangers is very broad, but the practical use of sorbents requires that they had a high exchange capacity for metal ions, satisfactory kinetics and dynamics of adsorption and were mechanically and chemically stable.

The most perspective are chelating polymers, ionic groups of which are able to form chelate compounds with metal cations [7].

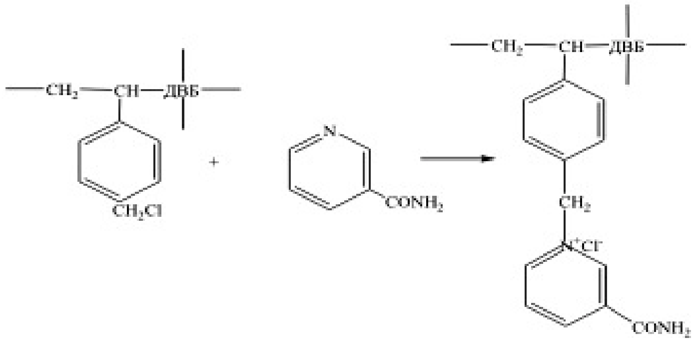
The purpose of this work – is getting of new chelating ion exchanges and study of their sorption properties on ions of certain heavy metals.

Materials and methods

By the chemical modification of chloromethylatedstyrene-divinylbenzene with known analytical reagent – nicotinamide, are obtained a spatial structured ion exchangers.

The high mechanical strength, chemical and thermal stability and resistance to oxidative degradation, combined with sufficient activity in the substitution reactions of the hydrogen atoms of the styrene phenylnucleus with divinylbenzene (DVB) allows to obtain a chelating ion exchangers

Printed in Kazakhstan



As an initial product was used the industrial samples of chloromethylated copolymers of styrene with 2, 4, 8, 10% DVB gel and macroporous structure with a chlorine content 17 – 21%.

To find the conditions for the maximal introduction number of nicotinamide groups in the polymer structure, the solvents' natural effect, the ratio of chloromethyl groups and analytical reagent, duration and temperature of the process was investigated. The degree of chloromethylated copolymer conversion was studied by elemental analysis. Among the used solvents, dimethylformamide was the most suitable: by using it was obtained the polymer with the highest content of nicotinamide groups. The ratio study of a reactive components showed, that the highest degree of conversion is achieved in the presence of a threefold excess of analytical reagent, for one basis –molechloromethylated copolymer of styrene and DVB.

The study of ambient temperature (Fig. 1a) and heating time effects (Fig. 1b) showed that the highest degree of conversion is achieved at 1000C (nitrogen content – 5.7%), the reaction is sufficient to conduct 7 hours.

Copolymers of o-, m- and p-MABK with 2-methyl-5-vinylpyridine (2M5VP), obtained by radical copolymerization MABK with 2M5VP at equimolar ratios of the initial monomer mixture (50:50 mol %), initiator concentration dimethylazoizooildacids (DAK) 5·10-3 and monomer 1.4 mol/L at 333K in

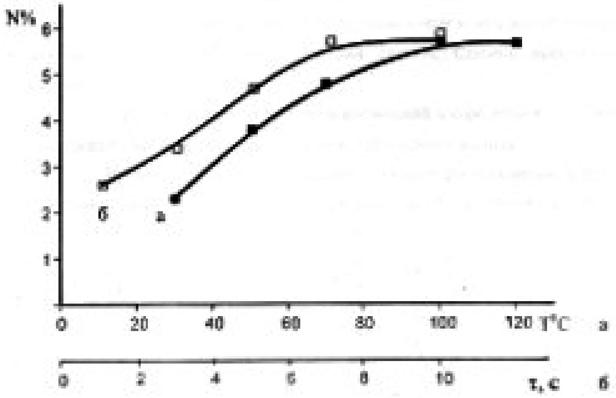
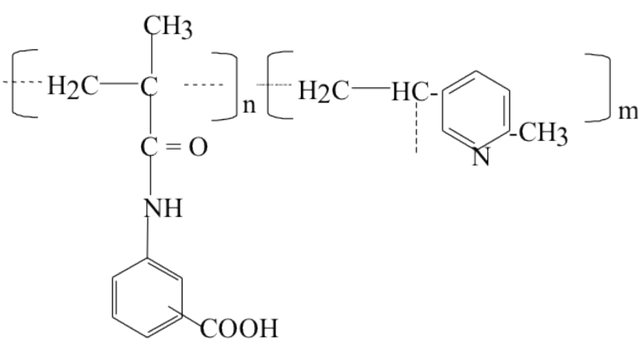


Figure 1 – Dependence of the placed nicotinamide groups quantity from the temperature (a) and process duration (b)



ethanol and dimethylformamide (DMF) were purified from unreacted monomers by two fold reprecipitation of DMF solution in ethyl acetate, followed by washing with several portions of acetone, and then dried under vacuum to constant weight. The obtained copolymers are brown, soluble in DMF, ethanol, acetone and aqueous alkali solution.

The structure of metakriloilaminobenzoic acids copolymer with 2-methyl-5-vinylpyridine can be schematically represented as:

Sorbent	COE (meq/ g)			
	Cd^{2+} Pb^{2+} Zn^{2+} Hg^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
The macroporous structured sorbent with nicotinamide group	1,8 1,8 1,1	3	1,4	1,5 1,65

Results and discussion

Using chelating ion exchangers the most favorable conditions for the formation of complexes are created [7]. For this, dependence of the metal ions exchange capacity from acid solutions were studied. pH of the metal salt solutions was changed from 3 to 8. A further increase of pH leads to the formation of the corresponding metal hydroxide precipitation. Figure 2 shows the dependence of the synthesized by the cadmium, lead, and zinc ions sorbent exchange capacity on the pH of solution. The figure shows that with the grows of pH the static exchange capacity (SEC) (meq/g) increases and reaches of maximum degrees for the Cd^{2+} ions at pH 5.9 (2.6 meq/g); for Zn^{2+} ions at pH 5.7 (1.29 meq /g) and Pb^{2+} ions at pH 4.7 (2.17meq/ g).

From these datas follows that polymer with nicotinamide groups shows selectivity for cadmium ions.

An ion-exchange property of obtained polyampholytes was studied by cations of copper, zinc, nickel, cobalt, cadmium, and manganese at different values of environment pH and concentration of metal ions in static conditions. Exchange capacity of the polyelectrolyte by metal ions was determined by the difference in the concentrations of metal ions in the equilibrium solution before and after the trilonometric contact with the ionite. For determining the equilibrium exchange capacity of investigated copolymers was used the 0.05 N solution of nitrate salts of appropriate metals in

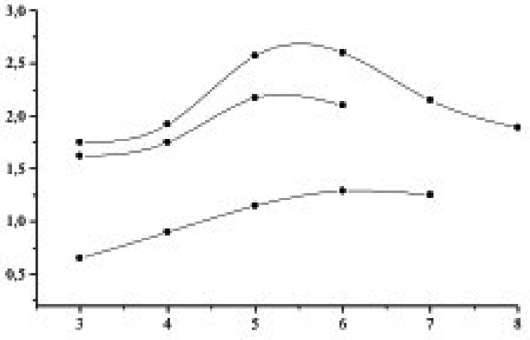


Figure 2 – The dependence of the sorbent static exchange capacity with nicotinamide groups at Cd^{2+}; Pb^{2+}; Zn^{2+} ions on the pH of solution.
Note: 1 – Cd^{2+}; 2 – Pb^{2+}; 3 – Zn^{2+}

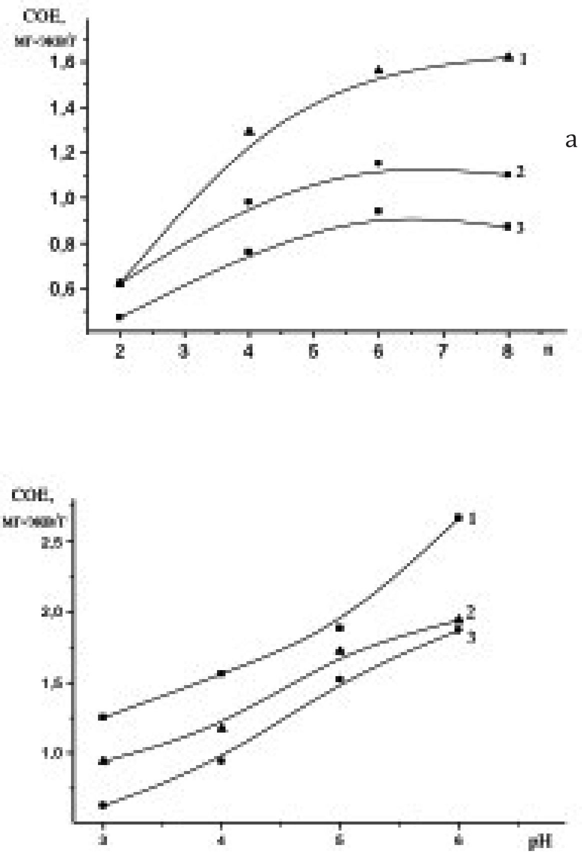


Figure 3 – The dependence of the MABK-2M5VP polyampholytes sorption capacity on the concentration of copper ions and the pH of the medium.
Note: п-МАВК (1); м-МАВК (2);
о-МАБК (3); Me^{2+} – Cu^{2+};
the concentration of copper ions (a); environ pH (б).

ammonium-acetate buffer solution with the pH range from 4to 7.Ion contention the solution before and after sorption was determined by complex metric method with use of appropriate indicators. A significant impact on the adsorption capacity of the polymer renders the location of the active group in the phenyl ring of the copolymer. The poliamfolit based on MABK para-isomer has a higher COE than the ortho-isomer. This is quite understandable, since the access to the COOH-group in the para position is maximally facilitated. Experimentally proved that they are responsible for formation of coordination relations with transition metal ions (Fig. 3).

Determined that when concentrations of the extracted substrate increasing along with the ion exchange the process of complexes formation occurs, which results in compression of the macromolecule. In this case the sorption goes only on the surface of the macromolecular coil, and the diffusion of the growing component in the inner layers of the copolymer due to steric factors becomes difficult.

Datas about changes in SEC copolymers of metakriloilaminobenzoic acids with 2-methyl-5-vinylpyridine depending on solution pH, showed that at low pH the binding degree of metal ions is low (SOE Cu = 0.5-2 meq/g at pH 2 and 3) then with the pH the capacity rises sharply (to 2 – 2.6 meq/g) followed by slowing down. The maximal extraction of metal ions from solution is achieved at pH 5-6. A further increase in pH contributes the formation of hydroxide precipitations and basic salts, therefore studies at pH 7 are not performed.

Table 2 shows the SEC of MABK homopolymer and copolymer polyelectrolytes determined in optimal sorption conditions.

MABK copolymers with 2-methyl-5-vinylpyridine have a higher sorption characteristics than homopolymers. Exchange capacity of copolymers in 1,1-3,5 times higher than that of homopolymers. This is due to the additional participation of pyridine nitrogen 2-methyl-5-vinylpyridine in formation of complexes with metal ions. The high values of SOE polyampholytes by metal ions, evidently due to the fact that because of the flowing side effects, such as insoluble coordination-bounded forms of metal ions with functional macromolecule groups formation during the extraction process, the accumulation of metal ions on the polymer surface occures.

Copolymers have a high rate of ion exchange and high sorption ability to Cu^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}, Cd^{2+} ions, so can be used for extraction, concentration and selective isolation from solutions of transition metals ions. That is due to the fact that obtained polymers have a greater macromolecules mobility, which creates less steric hindrance in metal ions sorption and complexing. Determined that optimal conditions for the process is the next ligand – ratio : metal ion = 1:6 and pH = 5-6. SOE by indicated ions are 1,5 – 8,0 meq/g.

Conclusion

Thus new copolymer of styrene and divinylbenzene with nicotinamide groups and copolymers of methacryloilaminobenzoic acid isomers with 2-methyl-5-vinylpyridine are obtained. The optimal synthesis conditions are defined. The structure and properties of initial compounds and copolymers are studied by IR spectroscopy and elemental analysis. The possibility of their

Table 2 – Chelating properties of polyampholytes with transition metal ions (pH = 5, C_{Me+} = 0.08 mol/ L).

Polyelectrolyte	SEC, мг-экв./г					
	Cu^{2+}	Zn^{2+}	Ni^{2+}	Mn^{2+}	Co^{2+}	Cd^{2+}
п- MABK-2M5VP	8,08	6,33	3,37	2,43	2,27	4,28
м- MABK-2M5VP	5,92	3,37	3,46	2,86	3,35	2,35
о- MABK-2M5VP	4,32	3,54	2,70	1,84	1,67	1,53
Poly-*п*- MABK	3,65	4,50	1,15	3,37	2,20	2,25

application for sorption of heavy and transition metals is investigated.

References

1 Ashirov A. Ionoobmennaya ochistka stochnikh vod, rastvorov i gazov. – L: Khimiya, 1993. – P. 291.

2 Senyavin M.M. Ionnyy obmen v tekhnologiy i analize neorganicheskikh veshchestv. – M.: Khimiya, 2000. – P. 202.

3 Bokris O.M. Khimiya okruzhayushchei sredy. – M.: Khimiya, 1982. – P. 670.

4 Ergozhin E.E., Tausarova B.R. Rastvorimye polielektrolity. – Alma-Ata: Gylym, 1991. – P.222.

5 Myasoedova G.B., Savvin S.B. Khelatoobrazuyushchie sorbenty – M.: Nauka, 1994. – P. 58-62.

6 Skurlatov Yu.I., Duka G.G., Miziti A. Vvedenie v ekologicheskuyu khimiyu. – M.: Vysshaya shkola, 2004. – P. 400.

7 Umland F., Yansen A. Kompleksnye soedineniya v analiticheskoi khimiy. – M.: Mir, 1995. – P. 256.