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Removal of Cu Copper (II) Ions from Water Solutions by Complex Formation–Ultrafiltration Method

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Abstract

A process of ultrafiltration purification of water solutions from copper ions with addition of polymer chelating agents of various chemical nature (polyethyleneimine, poly(diallyl dimethylammonium chloride), dextrane, humic acids) has been explored. A possibility to perform a recovery of Cu^{2+} polyethyleneimine complex with the aim to re-use the chelating agent has been demonstrated.

INTRODUCTION

Accumulation of heavy metals (HM) in the environment, including that in natural waters, represents a serious danger in view of their biological activity and toxic properties. The main part of HM enters natural waters with sewage from various industrial productions (metallurgy, engineering, and power industries) [1].

To remove HM from sewage, reagent treatment [2], ion exchange [2, 3], adsorption [3], and membranous methods [4] are used traditionally.

Reagent sewage treatment is performed by HM precipitation in the form of sparingly soluble substances (hydroxides, sulphates, carbonates, and sulphides). However, the precipitation process takes a long time and occurs incompletely in certain cases owing to the formation of colloidal solutions. In this relation, there is a necessity of salvaging the formed slimes [2].

When ion exchange and adsorption method is used to clear sewage from HM, it is necessary to solve the problem of treatment of the reclamation solutions [3].

Membranous methods to remove HM ions from water solutions, such as reverse osmosis and electrodialysis, do not offer high selectivity and they require higher than usual energy consumption [2, 4–6].

Thus a search for new ways to remove HM from water solutions is of actual importance.

One of promising approaches the researchers give recently great attention to is a method of complex formation–ultrafiltration (CFUF) [4, 7–10].

The purpose of this work is to study the process of removal of copper ions from water solutions by the CFUF method on adding chelating agents of a variable chemical nature, including organic matters of natural waters (humic acids), as well as to study in more details the conditions of the formation and destruction of a metal–polymer complex with the aim to re-use the chelating agent.

EXPERIMENTAL

Water solutions with the copper ion concentration of 10 mg/ dm^3 have been chosen as the research objects, and water-soluble polymers of various chemical nature manufactured in Sigma-Aldrich Corp. (USA), namely, poly(diallyldimethylammonium chloride) with the molecular mass of 10 000 ($PDADMAC_{10\,000}$), polyethyleneimine with the molecular mass of 10 000 ($PEI_{10\,000}$), dextrane with molecular mass of 10 000 and 70 000 ($DE_{10\,000}$ and $DE_{70\,000}$, respectively), and humic acids (HA) have been chosen as chelating agents.

A one-side open type membranous cell with the internal volume of 0.2 dm^3 was used to carry out ultrafiltration experiments. The cell was equipped with UPM-20 ultrafiltration membrane (Vladipor Co., Russia), 24.6 cm^2 in area. The working pressure comprised 0.05–0.3 MPa. The first 2 cm^3 of the permeate were rejected, and then the samples were taken for the analysis. The permeate bleeding degree during the determination of the retention coefficients of copper ions and the productivity of the process comprised 20 %.

A residual concentration of copper ions in samples was defined by the atomic absorption spectroscopy with an S-115-M spectrophotometer, and the concentration of PEI, by means of ITR-2 interferometer.

The retention coefficient of copper ions by the membrane was calculated with the formula

$$R = (C_0 - C_{per}/C_0) \cdot 100\ \%$$

where C_0, C_{per} are the concentrations of Cu^{2+} in the initial solution and in the permeate.

The productivity of a membrane was determined with the formula

$$J_v = \Delta V/(S\Delta\tau)$$

where ΔV is the permeate volume, dm^3; S is the area of a membrane, through which the permeate passed, m^2; $\Delta\tau$ is the time to pass the permeate, h [4].

RESULTS AND DISCUSSION

It is evident from Fig. 1 that as the working pressure (P) increases, the retention coefficient of copper ions decreases. This is brought about by the fact that with an increase in working pressure, when the flow through the membrane is increased, transport of copper ions to its surface becomes more intensive, and as a consequence, the effect of the concentration polarization rises. Meanwhile, the most effective removal of copper ions (45 %) is achieved at the working pressure of 0.05 MPa. The productivity of the UPM-20 membrane increases practically proportionately with the applied working pressure.

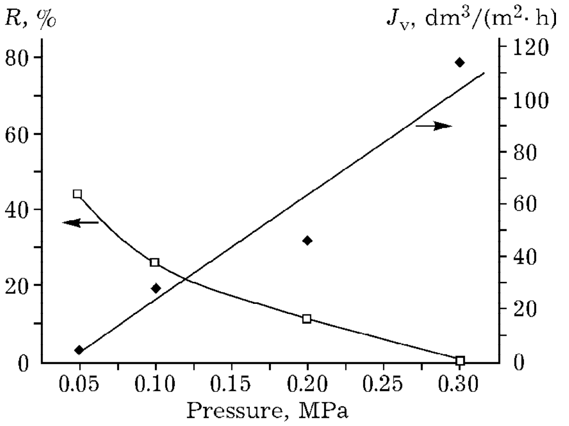

Fig. 1. Dependence of retention coefficient (R) of copper ions and of the productivity (J_v) of a UPM-20 membrane on the working pressure when filtering the solution with ion concentration of copper of 10 mg/dm^3 (pH 5.1).

With the aim of determination of an optimum copper ions chelator, polymers of different chemical nature were introduced in the solution. It is evident from Fig. 2 that the retention coefficient of copper ions in the presence of the applied chelating agents decreases in the following succession: $PEI_{10\ 000}$ > HA > $DE_{70\ 000}$ > $DE_{10\ 000}$. It appears that the high copper retention coefficient (97.7 %) with the use of $PEI_{10\ 000}$ is caused by the high complexation capacity of PEI with copper ions and by the stability of the formed complexes. According to [11], the stability constant of Cu^{2+}–$PEI_{10\ 000}$ complex comprises 10^{16}–10^{17}. Complex formation of Cu^{2+} with $PEI_{10\ 000}$ occurs due to the interaction of copper ions with PEI amino groups and due to the formation of inner complex compounds. Figure 3 presents an idealized structure of Cu^{2+}–$PEI_{10\ 000}$ complex that is formed in the solution.

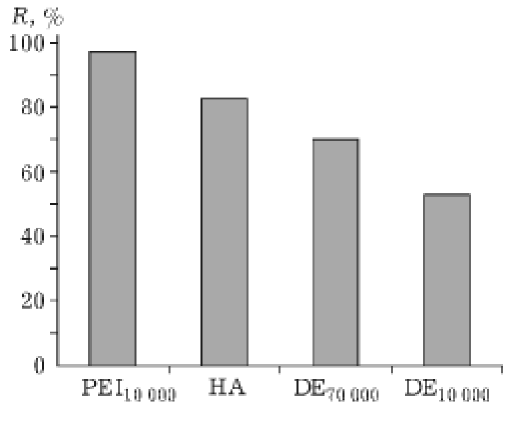

Fig. 2. Dependence of retention coefficient (R) of copper ions on chemical nature of the chelating agent when filtering solutions through a UPM-20 membrane. The ratio Cu^{2+}/chelating agent is equal to 1 : 2 (10 : 20 mg/dm^3), P = 0.1 MPa, pH 5.1.

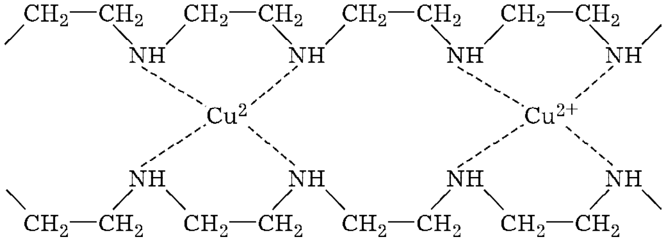

Fig. 3. Idealized structure of Cu^{2+}–PEI complex [8].

In the presence of HA, the copper retention coefficient comprises 82.8 % (see Fig. 2), which is caused apparently by the formation of HA–Cu^{2+} complex during the interaction of ions of metal with carboxylic groups of HA. A high molecular mass of the used HAs (on evidence of [12], the molecular mass of more than 94 % of the macromolecules exceed 50 000) is responsible for a rather high retention coefficient of copper, although the constant of stability of HA–Cu^{2+} complex is relatively low ($\log K = 7.53$ [13]).

Complex formation of DE with Cu^{2+} is realized due to the interaction of copper with hydroxyl groups of monomer units of the polymer [14]. The process occurs preferentially under the alkaline condition and it is characterized by the constant of stability of the complex in the range 10^{15}–10^{16} [15]. It appears that the realization of the process of complex formation in the neutral and sub-acidic media is related to the acceleration of deprotonization of the DE hydroxyl groups in the presence of ions of metal [16].

It is evident from Fig. 2 that the use of DE of high molecular mass (with the molecular mass of 70 000) is favourable to a more effective removal of ions Cu^{2+} when compared to $DE_{10\,000}$. It appears that this is determined by a large size of the formed complexes of DE with copper ions at the increased molecular weight of the polymer and, as a consequence, by their more active retention on the membrane.

It follows from the analysis of the acquired data that the pH of the solution has a tangible influence on the efficiency of the removal of Cu^{2+} ions by the CFUF method. Meanwhile, the retention coefficient of copper ions for the membrane (with no chelating agents introduced) is rather low in acidic medium (Fig. 4, curve *1*). To take an illustration, at pH 3.7, the retention coefficient of Cu^{2+} comprises only 5.3 %. However, with an increase in pH and with a shift into alkaline region, the efficiency of retention of ions Cu^{2+} with the membrane increases. Accordingly, the retention coefficient of Cu^{2+} comprises 79.6 % at pH 7.0. It appears that a significant part of copper ions under these conditions is in the form of slightly soluble $Cu(OH)_2$ hydroxide that is held back by the UPM-20 membrane.

When polymeric chelating agents are introduced (see Fig. 4, curves *2*–*5*), an appreciable change in the retention coefficient of Cu^{2+} also occurs in an interval of the pH values being investigated. Cu^{2+} ions are most effectively removed from the solutions when $PEI_{10\,000}$ is used, and the retention coefficient increases with the increase in pH (see Fig. 4, curve *3*). This is brought about by the fact that conceivably, PEI as a weak-basic polymer gives rise for the following reactions in water solution:

$$PEI + nH_2O = PEIH_n^{n+} + nOH^-$$

$$PEI + aCu^{2+} = PEICu_a^{2a+}$$

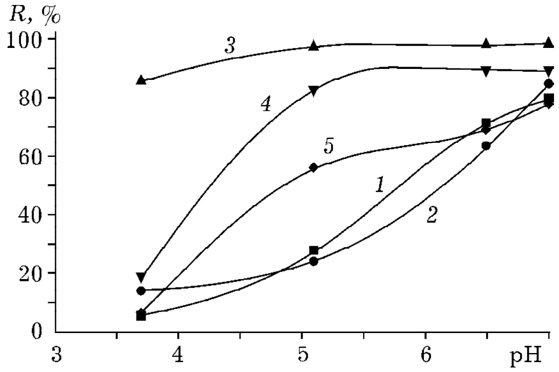

Fig. 4. Dependence of retention coefficient (*R*) of copper ions on the pH when filtering solutions of Cu^{2+} (*1*), $Cu^{2+}/PDADMAC_{10\,000}$ (*2*), $Cu^{2+}/PEI_{10\,000}$ (*3*), Cu^{2+}/HA (*4*), $Cu^{2+}/DE_{10\,000}$ (*5*) through a UPM-20 membrane. The ratio Cu^{2+}/chelating agent is equal to 10 : 20 mg/dm^3, $P = 0.1$ MPa.

It is evident that $PEI_{10\ 000}$ in the protonated form is not capable to complex formation with copper ions. The degree of protonation of $PEI_{10\ 000}$ essentially depends on the pH of the solution. Accordingly, with an increase in pH, the number of the protonated amino groups in a PEI macromolecule decreases [17], which causes the interaction of polymer chains with Cu^{2+} to strengthen and thus to enhance the retention coefficient of metal.

A degree of removal of copper ions in the presence of HA also depends essentially on the pH of the solution. It is evident from Fig. 4 (curve *4*) that a retention coefficient of Cu^{2+} in the range of 5.1–6.5 pH values comprises 82.8–89.6 %. This fact is attributable to the formation of a stable HA–Cu^{2+} complex owing to an interaction of copper ions with dissociated carboxylic groups of HA. At a decreased pH of the solution, the retention coefficient of copper ions is lowered, which is related to a reduced dissociation degree of carboxylic groups of HA [18]. Thus, in general, during the ultrafiltration treatment of natural waters containing copper ions, we should expect the increased removal degree for Cu^{2+} ions in view of their complex formation with a soluble natural organic matter.

When carrying out the CFUF process with the use of $DE_{10\ 000}$ (see Fig. 4, the curve *5*), copper retention coefficient rises with an increase in pH, which is caused, as it is specified previously, by strengthening of the process of complex formation [15].

As opposed to $PEI_{10\ 000}$, HA, and $DE_{10\ 000}$, there is no complex formation with Cu^{2+} ions upon the introduction of $PDADMAC_{10\ 000}$ in the solution, as demonstrated by virtually identical dependences of retention coefficient of copper ions that have been obtained without the use of a polymer and upon its adding to the solution (see Fig. 4, curves *1, 2*). This is caused by the fact that the $PDADMAC_{10\ 000}$ molecules are charged positively in the investigated interval of pH values and consequently they have no capacity to interact with copper ions.

The process of complex formation of Cu^{2+} with $PEI_{10\ 000}$ has been studied in greater detail by means of a spectrophotometric method. It is common knowledge that the Cu^{2+}–$PEI_{10\ 000}$ complex is characterized by the maximum light absorption at $\lambda = 590–620$ nm [8]. By virtue of the fact that light absorption of Cu^{2+} solution is practically unavailable in this range, it is possible to estimate a completeness of the process using a dependence of optical density on the pH of complex formation. It is evident from Fig. 5 that optical density in the system Cu^{2+}–$PEI_{10\ 000}$ hardly varies at pH 5, which bears witness to a practically complete complex formation.

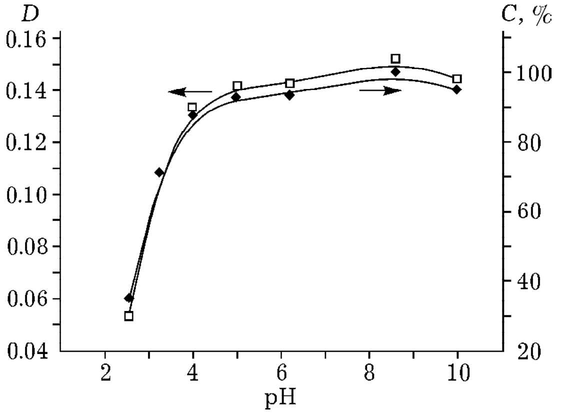

Fig. 5. Complex formation in the system Cu^{2+}–$PEI_{10\ 000}$ depending on the pH. The ratio $Cu^{2+}/PEI_{10\ 000}$ = 1 : 2 (10 : 20 mg/ dm^3). *D* is an optical density of the solution; *C* is a fraction of the formed complex.

Provided that the maximum value of optical density *D* corresponds to the maximum complex formation (100 %), it is possible to estimate the process of complex formation in terms of percentage ratio (see Fig. 5, the curve *2*). With this end in view we shall present graphically the dependence of magnitude *C* on the pH ($C = D_{max}/D) \cdot 100$ %, where D_{max} is an optical density under condition of the complete complex formation). It is evident from Fig. 5 that no more than about 35 % of copper is fixed in the complex with $PEI_{10\ 000}$ at pH 2.5, whereas more than 93 % of copper exists in the complex with $PEI_{10\ 000}$ at pH ≥ 5.

To determine a capacity of complex formation of $PEI_{10\ 000}$, *i.e.* the maximum quantity of copper that can be fixed by a given quantity of polymer, a variable quantity of copper ions was added to the polymer solution with a constant concentration at a fixed pH value. The maximum quantity of copper (in terms of mass ratio) that can be linked with 20 mg of $PEI_{10\ 000}$ comprises 15 mg, which corresponds to $2.34 \cdot 10^{-10}$ of copper ions for $2 \cdot 10^{-6}$ mol of $PEI_{10\ 000}$ (Fig. 6). It should be remarked that the functional fragment (FF) of the $PEI_{10\ 000}$ molecule

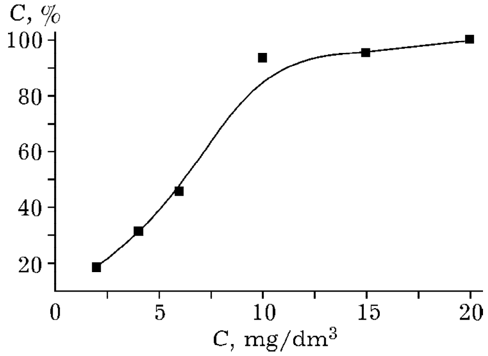

Fig. 6. Dependence of the formation of the Cu^{2+}–$PEI_{10\ 000}$ complex on the concentration of copper ions. The concentration of $PEI_{10\ 000}$ is 20 mg/ dm^3, pH 6.

that is involved in complex formation with copper ions is a ($-CH_2-CH_2-NH-$) unit, and a $PEI_{10\ 000}$ macromolecule contains 233 fragments of this kind. Thus it is simple to calculate that in this case, for one copper ion there are two FFs. For the complex of copper with a linear $PEI_{10\ 000}$ that contains secondary amino groups, this ratio comprises 1 : 4 (see Fig. 3). It appears that the difference is associated with the fact that the used $PEI_{10\ 000}$ represents a branched polymer that contains a mixture of primary, secondary, and tertiary amino groups in the ratio 1 : 2 : 1 [17]. Various types of amino groups that are involved in complex formation with copper ions, as well as the branched nature of $PEI_{10\ 000}$ macromolecules that gives rise to steric restrictions, result apparently in that the Cu^{2+}/FF ratio is less as compared with the idealized scheme.

The economy of the CFUF process is controlled in many respects by the possibility of the repeated use of the chelating agent. With the aim of a re-use of polymer, we have studied the recovery of Cu^{2+}–$PEI_{10\ 000}$ complex that was conducted by acidifying the solution that contained Cu^{2+} : $PEI_{10\ 000}$ with the mass ratio 1 : 2 (500 : 1000 mg/ dm^3) up to the pH 2.0 and by the subsequent membrane separation with the UPM-20 membrane at the working pressure of 0.2 MPa. The permeate was collected and analysed for the content of copper ions and $PEI_{10\ 000}$. With the permeate bleeding degree that was equal to 30 %, it was found that practically all copper passes through the membrane, and the retention coefficient of $PEI_{10\ 000}$ comprises 93.1 %. The incomplete retention of $PEI_{10\ 000}$ is related obviously to the polydispersity of the polymer and it is attributable to its low-polymeric fractions passing through the membrane. In general however, the use of the method of chemical destruction of Cu^{2+}–$PEI_{10\ 000}$ complex with the subsequent separation of the ingredients with the UF membrane allows one to recycle most part of the polymer during the CFUF process. Figure 7 presents a conceptual sketch to realize the CFUF process for purification of water solutions from copper ions with the stage of chelating agent recovery.

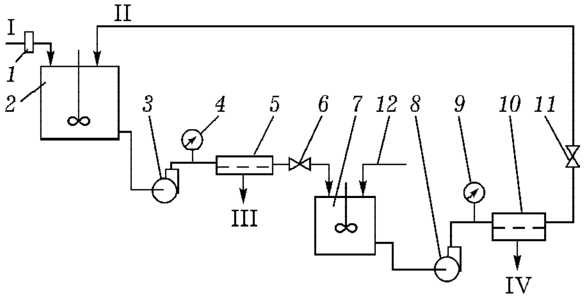

Fig. 7. Conceptual sketch to realize a process of complex formation–ultrafiltration to remove copper ions from water solutions: *1* – filter of preliminary purification; *2* – reactor for complex formation; *3*, *8* – pumps; *4*, *9* – manometers; *5*, *10* – ultrafiltration devices; *6*, *11* – gates-regulators; *7* – reactor for the regeneration of the chelator polymer, *12* – acid to acidify the Cu^{2+}–$PEI_{10\ 000}$ solution; I – solution containing copper ions; II – recovered polymer; III – treated water; IV – filtrate that is enriched by copper ions.

SUMMARY

1. This paper examines the process of ultrafiltration purification of water solutions from copper ions on addition of polymer chelating agents of a variable chemical nature. It was found that the efficiency of fixing and removal of copper essentially depends on the nature of the chelating agent, on its molecular mass, and on the pH of the solution.

2. The best results in the removal of copper ions from water solutions by the CFUF method have been received when PEI and humic acids were used as the chelating agent.

3. A possibility of chemical destruction of the formed Cu^{2+}–$PEI_{10\ 000}$ complex with the aim to re-use a chelating agent has been demonstrated.

4. It was found that the use of the CFUF method enhances significantly the efficiency of removal of copper ions from water solutions

owing to high performance ultrafiltration membranes applied.

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