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Zinc removal from wastewater by a complexation–microfiltration process

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Abstract: Due to its wide industrial applications, zinc has become an important contaminant in aquatic environments since it is a toxic heavy metal and some of its compounds, such as zinc arsenate and zinc cyanide, may be extremely hazardous. Therefore, there is a growing need to develop simple methods capable of separating and recovering trace zinc from environmental waters. Nowadays, ultra- and microfiltration methods for trace metals removal from waters by the addition of a water-soluble polymer into the aqueous solutions have become a significant area of research. The choice of water-soluble macroligands remains important for the development of this technology. Sodium carboxymethyl cellulose (Na-CMC) was selected as the complexing agent. The microfiltration experiments were performed in a stirred dead-end cell. Versapor membranes were used to separate the formed polymer–metal complex. The concentration of heavy metal ions after microfiltration in aqueous solution was determined using atomic absorption spectroscopy (AAS). The effects of the amount of complexing agent, pH value, type of anion, ionic strength and operating pressure on the flux (J) and rejection coefficient (R) were investigated. Experimental results indicate a considerable influence of the pH, ionic strength and type of anion on the rejection coefficient, while the effect of the amount of the complexing agent was relatively insignificant. The Na-CMC used in the research proved very effective, which is supported by the high rejection coefficients obtained (99 %).

Keywords: microfiltration; complexation; heavy metal ions; wastewater treatment.

INTRODUCTION

Zinc is an essential heavy metal for biological functions; however in high concentrations, it can be harmful to people and animals. The toxicity of heavy metal contamination, however, is highly dependent on the chemical form of the

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metal in question. Dissolved free ions are more toxic than metals that are bound in particles or to organic compounds. Zinc is naturally present in water. Industrial wastewaters containing zinc stem from galvanic industries, battery production, *etc.* Zinc compounds are applied for many different purposes. Zinc chloride is applied for parchment production, zinc oxide is a constituent of salves, paints and catalysts, and zinc vitriol is applied as a fertilizer. Zinc leaks from zinc pipes and rain pipes, consequential to the circulation of carbon-rich water. Car tires containing zinc and motor oil from zinc tanks release zinc compounds on roads. Zinc compounds are present in fungicides and insecticides, and consequently end up in water. When inadequate safety measures are taken, zinc may be emitted from chemical waste dumps and landfills, or from dredge mortar.

Zinc may be removed from water by different methods. To achieve a level that meets legal standards, techniques such as coagulation, ion exchange, sand filtration and active carbon may be applied.¹

The continuous increase of world needs for most of the known metals, the decrease in the grade of the available ores and strict environmental regulations make it of interest to find effective and efficient methods for processing waste solutions containing metal ions, even at very low concentrations. The efficient and selective separation of heavy metal ions can be achieved by using water-soluble macroligands in combination with membrane filtration.² The use of membrane separation processes in the treatment of wastewater containing toxic metal ions is today an attractive and suitable technique, and is easily included in the whole process. For this reason, membrane separations are being employed more and more frequently. Moreover, the separation can be performed at room temperature; the modular membrane surface can be easily adjusted to the wastewater flow and various industrial membranes are now available. In order to retain metallic ions, reverse osmosis (or at least nanofiltration) can be used due to the size of the ions in aqueous solutions. However, the usual permeate fluxes of reverse osmosis membranes are limited and require high transmembrane pressure, which makes the process expensive.³ There are two widely used separation techniques among the membrane methods for the removal of heavy metal ions from aqueous solutions: micellar enhanced ultrafiltration (MEUF) and polyelectrolyte ultrafiltration (PEUF). MEUF⁴⁻⁷ and PEUF⁸⁻²⁶ combine ultrafiltration with the presence of water-soluble surfactants and polymers, respectively. The enhanced ultrafiltration processes have the advantages of operation at relatively low pressures and temperatures, resulting in excellent rejection of multivalent metals and organics. PEUF is the combination of two phenomena, the binding of metal ions to a water-soluble natural or synthetic polyelectrolyte, and ultrafiltration. Since the pore size of ultrafiltration membranes are not suitable to separate heavy metal ions, water-soluble polymers are used to bind the metals to form macromolecular complexes rejected by ultrafiltration.

THEORY AND EXPERIMENTAL

The removal and rejection of heavy metal ions from aqueous solutions has been traditionally carried out by chemical precipitation, ion exchange, adsorption, *etc.* Nowadays, ultra- and microfiltration methods for trace metals removal from waters by the addition of a water-soluble polymer into the aqueous solutions have become a significant research area. This method is based on the principles that polymers with a large molecular weight could bind heavy metal ions to form macromolecular complexes. Their metal complexes could then be retained and concentrated by a microfiltration membrane, whereas unbound metal ions would pass through the membrane. Up to now, many polymers, such as poly(vinyl alcohol) and sulfonated poly(vinyl alcohol),^{8,9} poly(ammonium acrylate),¹⁰ poly(acrylic acid),¹¹⁻¹³ poly-ethylenimine,¹³⁻¹⁷ diethylaminoethyl cellulose,¹⁸ poly(4-vinylpyridine) and poly(diallyl dimethylammonium) chloride,²¹ poly(vinyl sulfonic acid),²² partially ethoxylated polyethylenimine^{23,24} and chitosan and pectin^{15,25} have been used for metal removal from wastewaters.

Sodium carboxymethyl cellulose (Na-CMC) is a derivative of cellulose that is colorless, odorless and tasteless, physiologically inert, chemically stable, not dangerous for health or the environment and is water-soluble. It also possesses good complexation ability for some metal ions and was chosen as the macromolecular complexing agent for the selective removal and rejection of copper from water in a complexation–microfiltration process.²⁰

The aim of the present research was to evaluate the efficiency of Na-CMS in the removal of zinc ions from water. The experiments were conducted on two model solutions, ZnCl_2 (solution 1) and $\text{Zn}(\text{CH}_3\text{COO})_2$ (solution 2) in order that the influence of the anion be investigated. The initial concentration of zinc ions in both solutions was 50.00 mg dm^{-3} . The microfiltration experiments were performed in a stirred dead-end cell Millipore 8050. The influence of different experimental parameters, *i.e.*, the amount of complexing agent, ionic strength, pH value and operating pressure, on the flux and rejection coefficient were investigated. Versapor polyacrylic membrane 200 filters (Gelman Sciences Inc., USA) were used to separate the formed polymer–metal complex. A feed volume of 25.0 cm^3 of concentration $50.0 \text{ mg Zn dm}^{-3}$ and the desired Na-CMC concentration were prepared and stirred for 1 h at room temperature before filtration. Experiments with longer mixing time demonstrated that 1 h was sufficient to reach the complexation equilibrium. The pH was adjusted with HCl and NaOH solutions. The concentration of heavy metal ions in aqueous solution after microfiltration was determined using atomic absorption spectroscopy (Pye Unicam SP9, Philips) at 213.9 nm.

RESULTS AND DISCUSSION

The effects of the amount of complexing agent, ionic strength, pH value and operating pressure on the flux and rejection coefficient were investigated.

The flux, J , of solution containing Zn(II)-ions was calculated from equation:

$$J = \frac{V}{A\tau} \quad (1)$$

where V is the volume of the permeate, A is the effective membrane area and τ is time.

The rejection, R , of Zn-ions was calculated from equation:

$$R = 100 \left(1 - \frac{c_p}{c_f} \right) \quad (2)$$

where c_p and c_f are the concentrations of zinc ions in the permeate and feed, respectively.

Effect of pressure

The effect of applied pressure was investigated at a fixed initial concentration of zinc ions of 50.0 mol dm^{-3} , pH 9.0 and pressure of nitrogen in the range 100–400 kPa.

The flux of the solute was lower than that of pure water. From the shape of the curve in Fig. 1, it could be concluded that no sharp change in the curve of flux vs. pressure was found, although the flux was still a slight function of pressure at higher pressure. This indicates that a concentration polarization exists but no plateau was reached; hence, the gel-polarization effect was not dominant for the polymer in the pressure range studied.

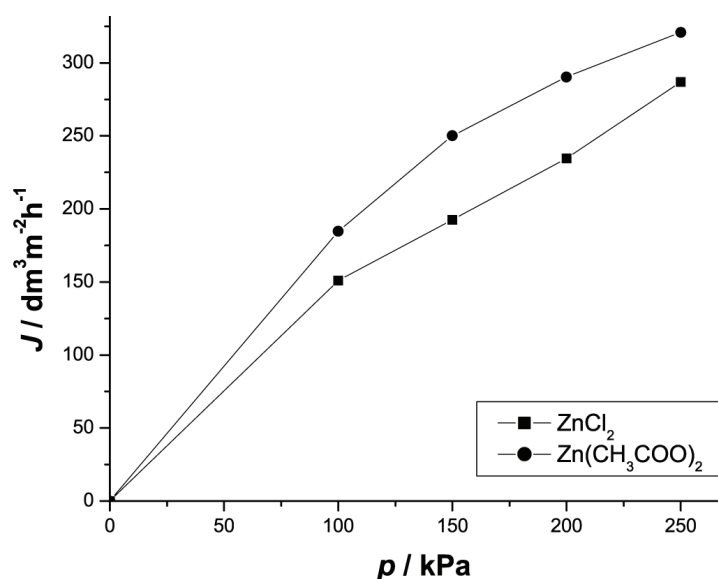


Fig. 1. Effect of pressure on the flux. Versapor membrane, $c_{\text{zn}} = 50.0 \text{ mg dm}^{-3}$, $c_{\text{Na-CMC}} = 75.0 \text{ mg dm}^{-3}$.

Effect of sample pH on the rejection of zinc

The effects of the solution pH in the range 2.0–9.0, at a fixed concentration of zinc ions of 50.0 mg dm^{-3} and pressure of 100 kPa were evaluated.

A strong influence of the pH of the solution on the retention was observed in complexation-microfiltration process. Increasing the pH leads to an increase in

the concentration of deprotonated carboxylic groups, which favors the formation of macromolecular polymer–metal complexes and subsequently increases in the metal rejection coefficients. As can be seen in Fig. 2, the rejection of zinc was increased with increasing pH value until the rejection reached its maximum (99 %) at pH 8.0 and then a flat profile was maintained when the pH was changed to 10.0. With increasing pH, more and more carboxymethyl groups dissociate gradually and complex with zinc ions. At low pH values, a large number of the H_3O^+ groups occupy the positions, which prevent the target zinc ions from form complexes with Na-CMC.

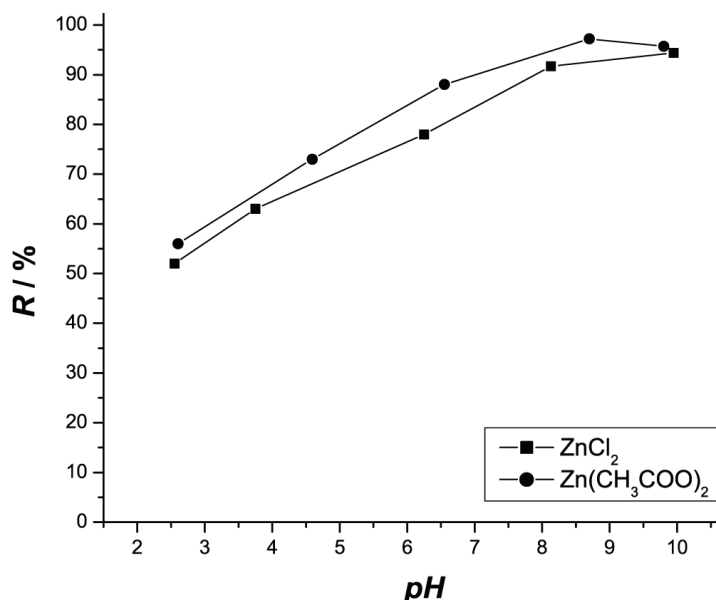


Fig. 2. Effect of pH on the retention. Versapor membrane, $c_{\text{Zn}} = 50.0 \text{ mg dm}^{-3}$, $p = 100 \text{ kPa}$, $c_{\text{Na-CMC}} = 75.0 \text{ mg dm}^{-3}$.

Effect of polymer concentration on zinc ion retention

The effect of the Na-CMC concentration on zinc removal was studied at pH 6.8 and 8.3 using solutions 1 and 2 containing 50.0 mol dm^{-3} of Zn and the concentration of Na-CMC was varied in range of $35.0\text{--}300.0 \text{ mg dm}^{-3}$.

The retention values of Zn(II) at different Na-CMC concentrations at pH 6.3 for both solutions are plotted in Fig. 3, from which it could be seen that the retention of Zn(II) remained almost constant at a value of around 89 % for all employed Na-CMC concentrations. It was also shown that the rejection of Zn(II), was not significantly affected by the Na-CMC concentration. Moreover, it was found that Na-CMC even at a very low concentration has the capability to bind with the metal to form macromolecular complexes as an effective complexing

agent. The explanation of this behavior is that equilibrium existed between free zinc ions, Na-CMC molecules and the formed complexes, and indicates that Na-CMC could be employed as a very effective water-soluble polymer for the removal of zinc(II).

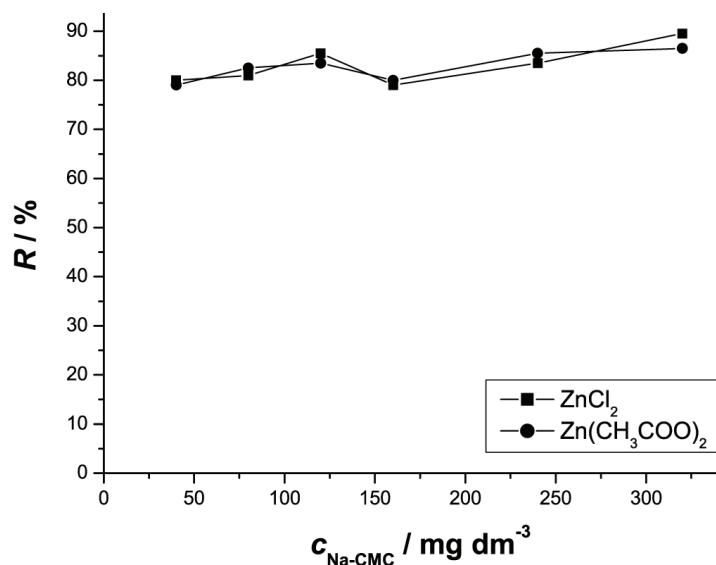


Fig. 3. Effect of different concentrations of Na-CMC on the retention at pH 6.8. Versapor membrane, $c_{\text{zn}} = 50.0 \text{ mg dm}^{-3}$, $p = 100 \text{ kPa}$.

A similar behavior was observed at pH 8.3 (Fig. 4). The retention remained almost constant at a value of around 85 % for solution 1 and 97 % for solution 2. Besides the influence of pH, the presence of the carboxyl anion in solution 2 affects the stability of the formed complexes and thus increases the retention of this solution.

Effects of ionic strength on the retention

The ionic strength of an aqueous stream may greatly affect the effectiveness of polymer-assisted microfiltration processes. Increasing the salt concentration leads to compression of the electrical double layer and thus to a reduction in the electrostatic attraction between ions and charged polymers. As a result, the unbound metals in the solution pass through the membrane leading to lower retention.²⁵

The effect of ionic strength on Zn(II) retention was examined at pH 6.8 and 8.3 by adding increasing amount of NaNO_3 into the solution. The effect of ionic strength on Zn(II) retention was observed to be more pronounced at pH 6.8 than at pH 8.3, especially at high salt concentrations.

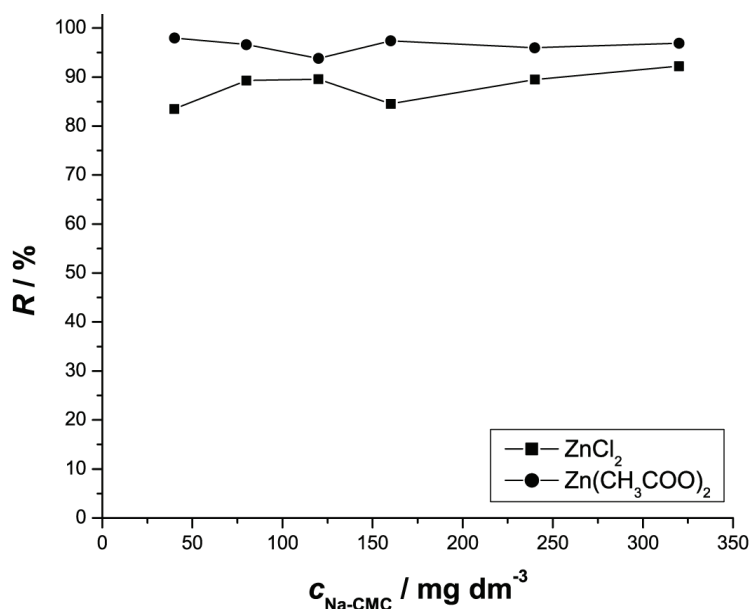


Fig. 4. Effect of different concentrations of Na-CMC on the retention at pH 8.3. Versapor membrane, $c_{\text{Zn}} = 50.0 \text{ mg dm}^{-3}$, $p = 100 \text{ kPa}$.

As shown in Fig. 5, at pH 6.8, the rejection decreased sharply in the presence of 0.05 mol dm^{-3} with a reduction of 40 and 50% for solutions 1 and 2, respectively. On increasing the salt concentration (up to $0.5 \text{ mol dm}^{-3} \text{ NaNO}_3$), no further decline of the retention was observed. These results can be explained by a conformational change of the polymer chains, a competitive adsorption between Na and Zn ions on the negatively charged polymer and an attenuation of the electrostatic repulsion. It is well known that negatively charged polyelectrolytes interact with positively charged divalent metal ions stronger than with monovalent ions.²⁶ Nevertheless, the filtration of metal ions and their subsequent release from the polymer induces an increase of the net negative charge on the polymer surface and then an expansion of the chains in order to increase the total surface, thereby minimizing the electrostatic repulsions. Related with this, the decrease on the surface charge density of the polymer induces a decrease in the strength of the interactions with the metal ions and, consequently, their easier release to the solution from the polymer domain during filtration.

At pH 8.3, the effect of salt addition was observed over a wider concentration range, *i.e.*, between 0.05 and $1.0 \text{ mol dm}^{-3} \text{ NaNO}_3$. As shown in Fig. 6, at pH 8.3, the addition of 0.05 – $0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$ caused only a 1–3 % decrease in the retention values. Since Zn(II)–Na-CMC complexation is more favorable at pH 8.3 and the bond is probably stronger than the one formed at pH 6.8, it can withstand changes in ionic strength. On increasing the salt concentration to 0.5

mol dm⁻³ NaNO₃, the retention dropped by around 28 % for both solutions. On the increasing the salt concentration further to 1.0 mol dm⁻³ NaNO₃, the slight increase in the rejection by 2–5 % is relatively insignificant.

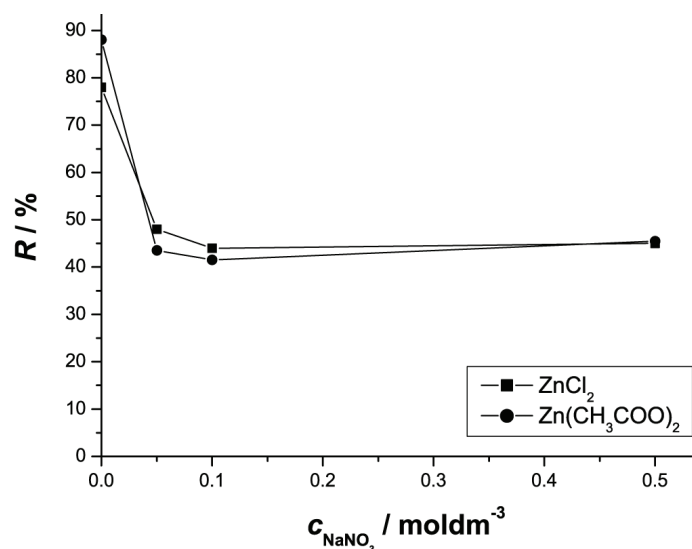


Fig. 5. Effect of ionic strength on the retention at pH 6.8. Versapor membrane, $c_{\text{Zn}} = 50.0 \text{ mg dm}^{-3}$, $p = 100 \text{ kPa}$, $c_{\text{Na-CMC}} = 75.0 \text{ mg dm}^{-3}$.

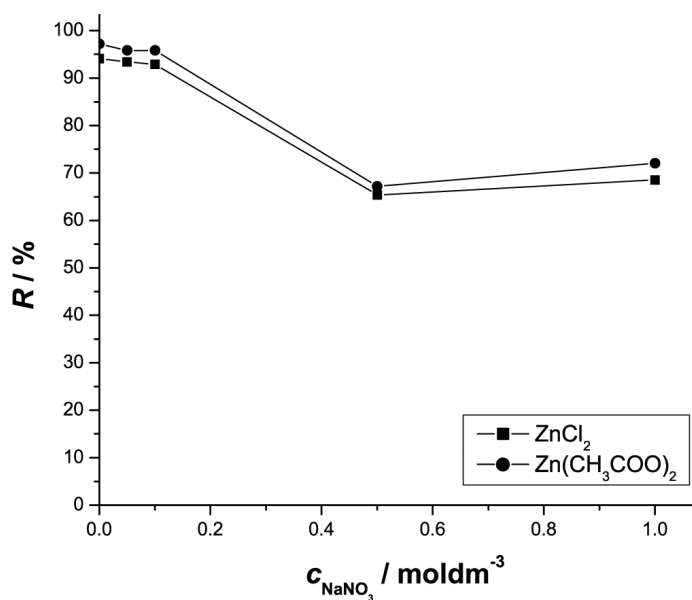


Fig. 6. Effect of ionic strength on the retention at pH 8.3. Versapor membrane, $c_{\text{Zn}} = 50.0 \text{ mg dm}^{-3}$, $p = 100 \text{ kPa}$, $c_{\text{Na-CMC}} = 75.0 \text{ mg dm}^{-3}$.

CONCLUSIONS

A complexation–microfiltration process was successfully applied for removal of Zn(II) ions from synthetic wastewater solutions. A polyacrylic membrane was used for filtration process, while sodium carboxymethyl cellulose was used as the metal complexing agent. It was shown that the complexation and filtration processes were pH dependent, the metal rejection was more efficient at neutral and alkaline conditions than at acidic ones. The Na-CMC used in the research proved to be very effective, which is evidenced by the high retention coefficients obtained. It was found that even at very low concentrations, Na-CMC has the capability to bind with zinc ions to form macromolecular complexes and is thus an effective complexing agent. The effect of ionic strength on Zn(II) retention was observed to be more pronounced at pH 6.8 than at pH 8.3, especially at high salt concentrations. Influence of anions proved to be very important for complexation process and stability of formed complexes.

The process is characterized by low-energy requirements involved in the microfiltration, very fast reaction kinetics and high selectivity for the metal ion separation. For developing a practical process, other important factors and operational parameters, such as different concentration of metal ions, mixture of metal ions, different anions, other membranes, *etc.*, must be studied.

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ИЗВОД

УКЛАЊАЊЕ ЦИНКА ИЗ ОТПАДНИХ ВОДА КОМПЛЕКСИРАЈУЋЕ-
МИКРОФИЛТРАЦИОНИМ ПРОЦЕСОМ

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Као резултат његове широке индустријске примене, цинк и његова једињења су постали значајне загађујуће материје водених ресурса. Због тога је постало неопходно развијати нове методе за њихово уклањање, које би биле ефикасне, једноставне и нешкодљиве по животну средину. Међу њима, метода мембранске филтрације се показала као веома успешна за уклањање различитих загађујућих материја, посебно у комбинацији са макромолекулима. Велики број истраживања усмерен је на избор селективног и специфичног макромолекула. У раду је проучаван комплексирајуће-филтрациони процес за уклањање јона цинка помоћу натријум-карбоксиметил целулозе. Микрофилтрација је вршена у ћелији са мешањем. Сепарација формираних комплекса је вршена на Версапор микрофилтрационим мембранама. Концентрација јона метала после микрофилтрације је одређена атомском апсорпционом спектроскопијом. Испитани су утицаји количине комплексирајућег средства, рН вредности раствора, радног притиска, јонске јачине и анјона на флуks и коефицијент задржавања. Експериментални резултати су показали значајан утицај рН, јонске јачине и анјона на коефицијент задржавања, док концентра-

ција комплексирајућег средства није имала значајан утицај на процес. Натријум карбоксиметил целулоза се показала као успешно средство за уклањање јона цинка што се може закључити на основу постигнутог веома високог коефицијента задржавања јона цинка од 99 %.

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