Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.989635

57 (2016) 1436–1442
January

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UV spectrophotometric studies of Cu(II) ions separation by ultrafiltration enhanced with poly(sodium acrylate)

Irena Korus*, Marta Rumińska

Institute of Water and Wastewater Engineering, Silesian University of Technology, Konarskiego 18, 44-100 Gliwice, Poland, Tel. +48 32 2371978; Fax: +48 32 2371047; email: irena.korus@polsl.pl (I. Korus)

Received 2 July 2014; Accepted 7 November 2014

ABSTRACT

Polymer-enhanced ultrafiltration is an effective separation technique which enables heavy metal ions removal from aqueous solutions. In this work, a water soluble polymer containing carboxylic groups and poly(sodium acrylate) (PSA), was used to enhance the separation of Cu(II) ions during ultrafiltration. The UV spectrophotometric analysis of the solutions containing PSA and Cu(II) ions revealed an absorption band with its maximum at a wavelength of 255 nm. The methods of continuous variations (Job's method) and molar ratio were employed to assess the stoichiometry of PSA–Cu(II) complexes formed. The molar ratio of PSA repeat unit to Cu(II) ion was evaluated to be ca. 2.8–2.9. The effect of the polymer—metal concentration ratio, solution pH, and the presence of anions: Cl^-, SO_4^{2-}, CO_3^{2-}, PO_4^{3-}, as well as a complexing agent (EDTA) on copper ions separation was investigated. The study revealed a good compatibility of spectrophotometric analysis and the ultrafiltration results.

Keywords: Polymer-enhanced ultrafiltration (PEUF); Cu(II)–poly(sodium acrylate) complexes; UV spectrophotometric analysis

1. Introduction

Polymer-enhanced ultrafiltration (PEUF) is a relatively new and effective technique for heavy metal separation from solutions. It employs dissolved polymers whose functional groups are capable of binding metal ions. The macromolecular complexes produced are then separated using an ultrafiltration membrane. The polymers enhancing ultrafiltration should be selective toward separated ions and have good solubility and sufficient molecular weight so that they can be retained on an ultrafiltration membrane. The polymers used in PEUF include chelating compounds and polyelectrolytes which contain amino, amide, hydroxyl, carboxyl, and sulfo groups. The synthetic polymers mostly used to enhance ultrafiltration of heavy metal separation includes polyethyleneimine (PEI) and partially ethoxylated polyethyleneimine (PEPEI) [1–7], carboxylic polymers (poly(acrylic acid) (PAA), its salts and copolymers of acrylic acid and maleic acid (PAC-MA)) [6–10], polymers with strong ion exchange groups such as poly(sodium 4-styrenesulfonate) (PSS) [11,12], and polymers containing quaternary ammo-

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*Corresponding author.

Presented at the 12th Scientific Conference on Microcontaminants in Human Environment
25–27 September 2014, Czestochowa, Poland

nium groups used to separate the anionic forms of metals and metalloids [1,13,14]. Besides the synthetic polymers, PEUF employs natural macromolecular compounds, such as chitosan and humic substances [1,15]. A lot of heavy metals and metalloids, such as: Cu(II), Zn(II), Ni(II), Cd(II), Co(II), Pb(II), Hg(II), Cr(III), Cr(VI), As(III), and As(V) can be separated from solutions by PEUF [1–15]. The effectiveness of the process depends on a number of factors e.g. concentration of metal ions, the type and amount of added polymer, pH, the presence of other ions, and ultrafiltration mode (a dilution method, a concentration method).

This study employed the UV spectrophotometric analysis to investigate the complexation of Cu(II) ions with poly(sodium acrylate) (PSA) and the results were verified by PEUF. The use of two spectrophotometric methods i.e. the continuous variations method and the molar ratio method enabled the assessment of the stoichiometry of PSA–Cu complexes, and the effect of the amount of polymer, pH, and the presence of selected ions on the effectiveness of copper separation during ultrafiltration.

2. Materials and methods

2.1. Reagents

The solutions containing Cu(II) ions were prepared using $Cu(NO_3)_2 \times 3H_2O$ (POCH SA). PSA with an average molar weight of 35 kDa was purchased as a 40% aqueous solution (Sigma-Aldrich). Suitable sodium salts (POCH SA) used to prepare stock solutions (concentrations of 100 and 2 mmol/dm^3) constituted a source of Cl^-, SO_4^{2-}, CO_3^{2-}, and PO_4^{3-} ions. From analytical weighed amount (POCH SA), 50 and 1 mmol/dm^3 EDTA solutions were prepared. pH was adjusted using 1 mol/dm^3 NaOH and HNO_3 solutions.

2.2. Ultrafiltration

Ultrafiltration was carried out in a Amicon 8050 stirred cell (Millipore) (capacity 50 cm^3, membrane area 13.4 cm^2) at a transmembrane pressure of 0.2 MPa. A polysulfone ultrafiltration membrane denoted as EW was supplied by GE Osmonics. In order to avoid solution concentration, the permeate recovered did not exceed 10% of the feed volume.

2.3. Analysis

The concentrations of copper ions in the feeds and permeates were analyzed and the results were used to determine the retention coefficient of copper ions: $R_{Cu} = 1 - C_P/C_F$ where C_P and C_F denoted copper concentrations in the permeate and feed, respectively.

The solutions were analyzed with a Cary 50 Scan UV–Vis spectrophotometer (Varian), recording absorptions spectra at a wavelength range of 400–190 nm. The same spectrophotometer measured solution absorbance using the method of continuous variations—the measurements were taken at a wavelength of 255 nm.

2.4. Methods

The method of continuous variations (Job's method) was employed to determine the stoichiometry of Cu(II)–PSA complexes. The procedure involved preparation of a series of 24 solutions containing Cu(II) ions and PSA polymer with the total concentration of both reagents of 1.05 mmol/dm^3 and variable Cu(II), and PSA concentrations over the range of 0.05–1 mmol/dm^3 (PSA concentration was determined per mer unit. In the solutions prepared in that way, the PSA molar fractions fell within 0.048–0.952 and the ratio of molar concentrations C_{PSA}/C_{Cu} changed over the range of 0.05–20. The solution absorbance was measured at a wavelength of 255 nm. The molar ratio method was used to analyze the stoichiometry of Cu(II)–PSA complexes as well as to assess the effect of polymer's amount on the effectiveness of copper separation by PSA enhanced ultrafiltration. This method involved a series of 14 solutions characterized by a constant Cu(II) concentration of 0.25 mmol/dm^3 and variable PSA concentration of 0–2.5 mmol/dm^3 (C_{PSA}/C_{Cu} concentration ratio changed over a range of 0–10). The solutions were analyzed spectrophotometrically at a wavelength of 190–400 nm, but the reference solutions used had analogous PSA concentrations without Cu(II) ions. The solutions of variable C_{PSA}/C_{Cu} concentration ratio were subjected to ultrafiltration, analyzing copper concentration in the feeds and permeates, and thus, determining the retention coefficient R_{Cu}.

In order to determine, the effect of pH on the formation of Cu(II)–PSA complexes and the effectiveness of Cu(II) separation, a series of solutions were prepared and characterized by: Cu(II) concentrations of 0.25 mmol/dm^3, PSA concentration of 0.75 mmol/dm^3, and changeable pH of 1–10. The solution spectra were registered at the wavelength range of 190–400 nm and the solutions underwent ultrafiltration, determining Cu(II) concentration in the feeds and permeates and the retention coefficient of Cu(II) ions (R_{Cu}).

The research also evaluated the effect of selected anions (Cl^-, SO_4^{2-}, CO_3^{2-}, and PO_4^{3-}) and a complexing agent (EDTA, versene ion) on the complexation of

Cu(II) ions with PSA and effectiveness of Cu(II) ions separation during PEUF. The series of solutions prepared had Cu(II) and PSA concentrations of 0.25 and 0.75 mmol/dm^3, respectively, with additions of the following concentrations of selected ions: 0, 0.025, 0.25, 2.5, and 25 mmol/dm^3 which corresponded to the C_{ion}/C_{Cu} concentration ratios of 0, 0.1, 1, 10, and 100. The solutions underwent spectrophotometric and ultrafiltration tests to determine separation coefficients of Cu(II) ions.

3. Results

The preliminary spectrophotometric analyses of the solutions containing Cu(II) ions and PSA revealed the presence of an absorption band in their spectra falling within a wavelength of 240–320, the maximum being found at $\lambda = 255$ nm. The band did not occur in the solutions which contained a single component (Cu(II) ions or PSA) and served as a basis for the spectrophotometric analyses.

Fig. 1 shows the absorbance values at a wavelength of 255 nm (A_{255nm}) found in the solutions with Cu(II) and PSA which differed in the molar fractions of the components (X_{PSA} and X_{Cu}) at a constant total concentration of both components (in accordance with the method of continuous variations).

The absorbance A_{255} changed with changing molar fractions of PSA and Cu(II) in their mixture. The intersection of the trend's lines determined from the initial and final correlation of $A_{255} = f(X_{PSA})$ indicated the formation of Cu(II)–PSA complexes in which X_{PSA} molar fraction reached 0.74, while X_{Cu} molar fraction equaled 0.26. Those molar fractions corresponded to the C_{PSA}/C_{Cu} molar ratio of 2.85 in the complex formed. The value was similar to the one obtained in similar studies of Pb(II)-PSA complexes which revealed the formation of Pb(II)-PSA complexes with a C_{PSA}/C_{Pb} molar ratio of three [16].

Fig. 2 depicts the UV spectra of the solutions containing a constant concentration of Cu(II) ions (0.25 mmol/dm^3) and variable PSA concentration over a range of 0–2.5 mmol/dm^3.

The solutions containing Cu(II) ions and polymer PSA revealed an absorption band over a wavelength range of 240–320 nm, with maximum at $\lambda = 255$ nm. The initial increase in PSA concentration (at constant Cu(II) concentration) brought an increase in the intensity of absorption band related to an increase in the concentration of Cu(II)–PSA complex formed. At a certain value of PSA concentration, an increase in the intensity of the band stopped, which resulted from the maximum concentration of the complex (at a given Cu (II) concentration) that remained unchanged with a further increase in PSA concentration in the solution.

Fig. 3 demonstrates the effect of the C_{PSA}/C_{Cu} molar ratio in the solution on the effectiveness of A_{255nm} absorbance and the retention coefficients of Cu (II) ions (R_{Cu}) found during ultrafiltration of the solution with constant Cu(II) and variable PSA concentrations.

Both correlations presented in Fig. 3 were of similar nature. An increase in the C_{PSA}/C_{Cu} molar ratio up to three brought both an increase in absorbance at a wavelength of 255 nm and a rise in the retention coefficient of copper ions during ultrafiltration. Those phenomena resulted from increasing concentration of Cu (II)–PSA complex in the solution (with increasing C_{PSA}/C_{Cu}). An analysis of the intersection of the trend's lines plotted in Fig. 3 showed that the C_{PSA}/C_{Cu} molar ratios in the complexes formed were 2.8

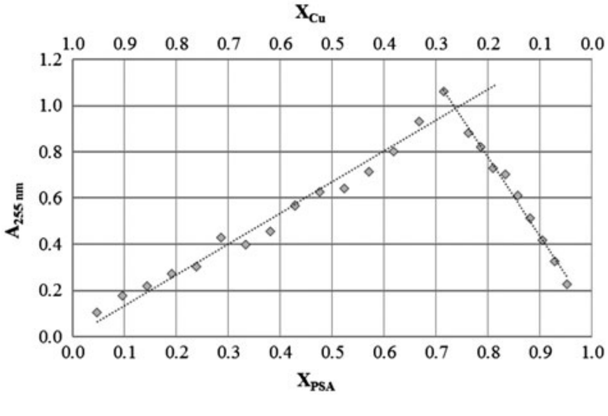

Fig. 1. The absorbance at $\lambda = 255$ nm (A_{255nm}) in the solutions containing Cu(II) and PSA at various polymer (X_{PSA}) and metal (X_{Cu}) molar fractions.

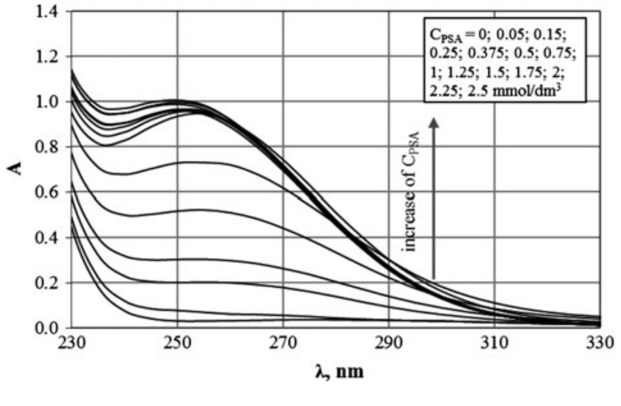

Fig. 2. UV spectra of solutions with a constant Cu(II) concentration and variable PSA concentration. $C_{Cu} = 0.25$ mmol/dm^3, $C_{PSA} = 0–2.5$ mmol/dm^3.

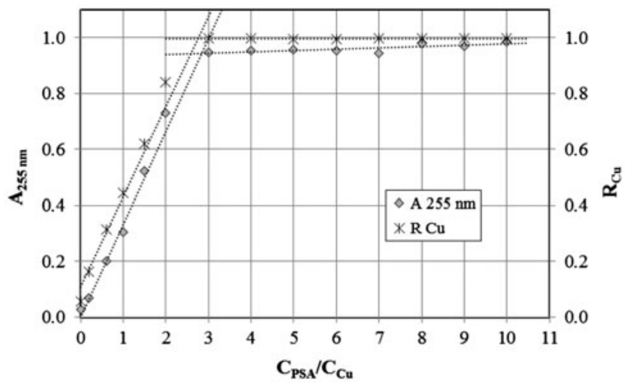

Fig. 3. The effect of polymer/metal molar ratio C_{PSA}/C_{Cu} on A_{255nm} absorbance and Cu(II) retention coefficient R_{Cu}. ($C_{Cu} = 0.25$ mmol/dm^3, $C_{PSA} = 0$–2.5 mmol/dm^3).

($R_{Cu} = f(C_{PSA}/C_{Cu})$ and 2.9 ($A_{255nm} = f(C_{PSA}/C_{Cu})$. The values were consistent with those produced by the method of continuous variations.

Fig. 4 depicts the spectra of solutions containing Cu(II) ions and PSA with concentrations of 0.25 and 0.75 mmol/dm^3, respectively, and variable pH of 1–10.

The spectra of the solutions with low pH (1–3) revealed an absorption band with the maximum at a wavelength of 300 nm whose intensity decreased with an increase in pH. The band disappeared at pH 3 and did not occur in a solution of lower acidity. The occurrence of the band was probably related to the presence of nitrate ions in the acidic environment. The spectra of the solutions with pH of 1–3 did not show an absorption band with its maximum at a wavelength of 255 nm, which indicated the lack of possibility regarding forming Cu(II)–PSA complexes in such acidic environment, and was connected to the protonation of the carboxyl groups of the polymer essential to Cu(II) ion binding. The A_{255nm} absorbance values and Cu(II) retention coefficients at different pH are given in Fig. 5.

The A_{255nm} absorbance decreased at a pH of 1–3, which was associated with the presence of a peak with its maximum at 300 nm in UV spectra. The peak is not connected to the formation of Cu–PSA complexes indicated by low retention coefficients of Cu(II) ions (R_{Cu}) of 0.03–0.04 at that pH range. At pH above 2.5–3, there was an increase in retention coefficients consistent with an increase in A_{255nm} absorbance, which indicated the formation of Cu–PSA complexes. The maximum values of R_{Cu}, exceeding 0.99, and the highest A_{255nm} were found at pH of 4.5–8. The more basic environment ($pH > 8$) brought a slight decrease in R_{Cu} and A_{255nm}, proving that those are less favorable conditions for the complexation of copper(II) ions with PSA.

Fig. 6 shows the UV spectra of solutions which had constant $C_{Cu(II)}$ and C_{PSA} concentrations of 0.25 and 0.75 mmol/dm^3, respectively, and variable concentrations of Cl^-, SO_4^{2-}, CO_3^{2-}, PO_4^{3-} ions and versene ion (EDTA) over the range of 0–25 mmol/dm^3. The values corresponded to the C_{ion}/C_{Cu} concentration ratio of 0–100. Fig. 7 depicts A_{255nm} absorbance and the retention coefficient R_{Cu} obtained during ultrafiltration of those solutions.

The study has not found any significant effects of chloride and sulfate ions (at the concentration range used) on A_{255nm} absorbance, and the shape of UV spectra recorded in the solutions containing Cu(II) ions and PSA. Elevated concentrations of Cl^- and SO_4^{2-} ions revealed a negligible increase in the intensity of absorption bands and A_{255nm} absorbance (which could have resulted from an increase in pH

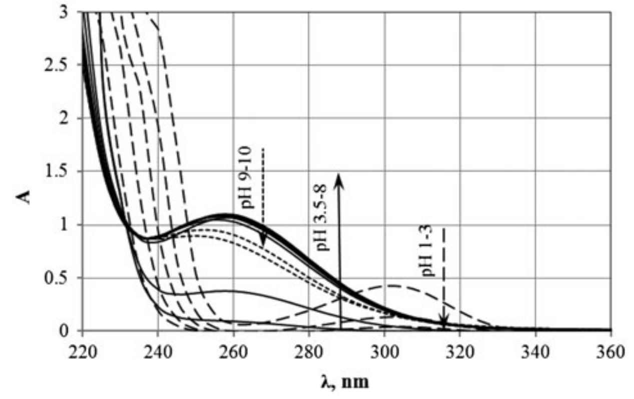

Fig. 4. Spectra of the solutions with constant Cu(II) and PSA concentrations and variable pH. $C_{Cu} = 0.25$ mmol/dm^3, $C_{PSA} = 0.75$ mmol/dm^3, pH 1–10.

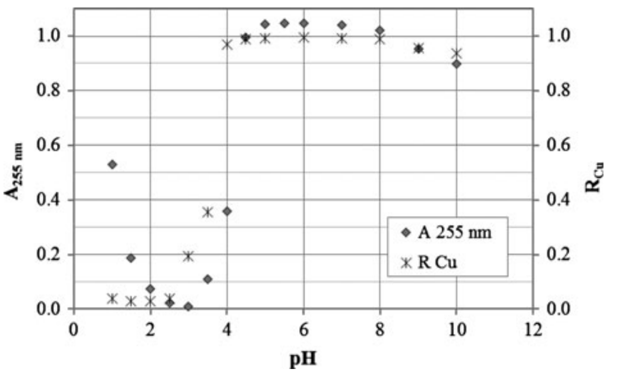

Fig. 5. Effect of pH on the A_{255nm} absorbance and Cu(II) retention coefficient. $C_{Cu} = 0.25$ mmol/dm^3, $C_{PSA} = 0.75$ mmol/dm^3, pH 1–10.

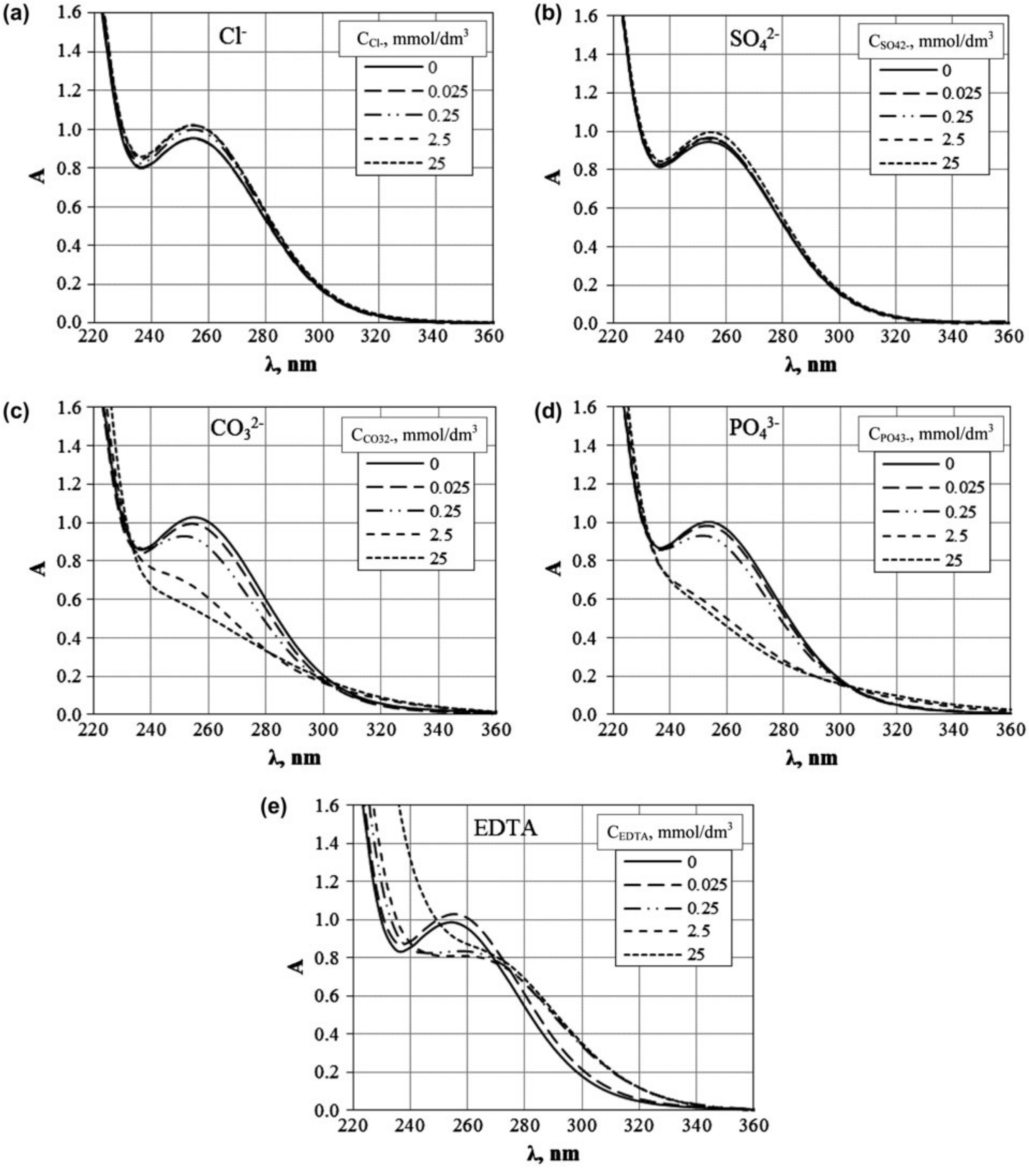

Fig. 6. Spectra of the solutions with constant Cu(II) and PSA concentrations and variable concentrations of (a) Cl^-, (b) SO_4^{2-}, (c) CO_3^{2-}, (d) PO_4^{3-} ions and (e) EDTA. $C_{Cu} = 0.25$ mmol/dm^3, $C_{PSA} = 0.75$ mmol/dm^3, $C_{ion} = 0$–25 mmol/dm^3.

over a range of 5.1–6.7), but Cu(II) retention coefficients remained high.

An addition of CO_3^{2-} and PO_4^{3-} ions whose concentrations exceeded those for Cu(II) concentrations by a factor of 10 and 100 caused a considerable decline in A_{255nm} absorbance, and some significant changes in the optical properties of the solutions observed in the UV spectra. Nevertheless, the high retention coefficients

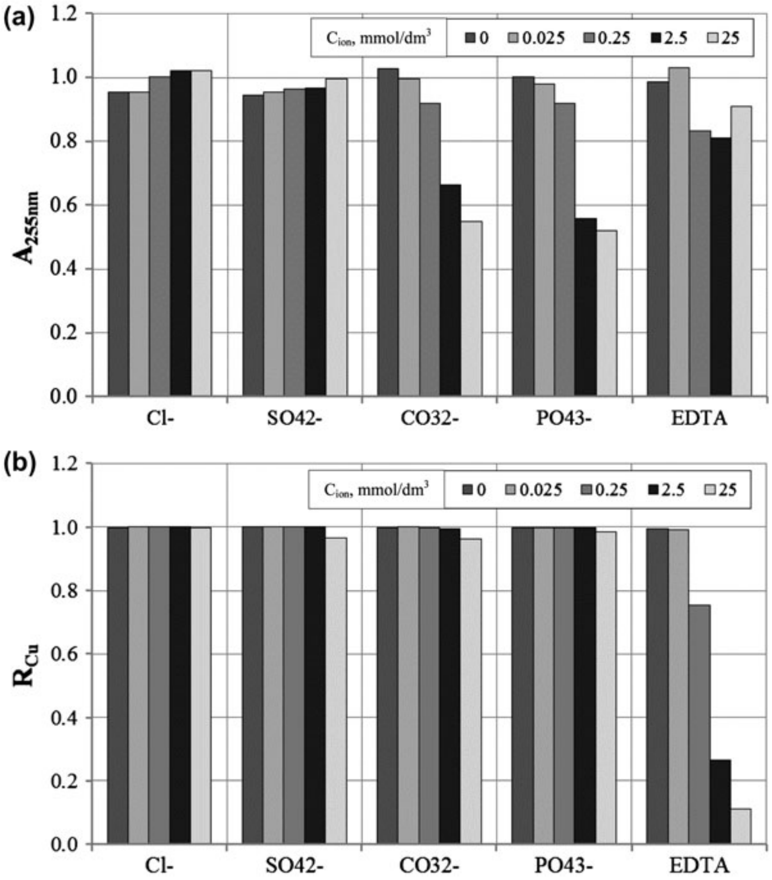

Fig. 7. The effect of the addition of Cl^-, SO_4^{2-}, CO_3^{2-}, and PO_4^{3-} ions and EDTA on absorbance A_{255nm} (a) and retention coefficient R_{Cu} (b). $C_{Cu} = 0.25$ mmol/dm^3, $C_{PSA} = 0.75$ mmol/dm^3, $C_{ion} = 0–25$ mmol/dm^3.

R_{Cu} observed under those conditions indicated the presence of macromolecular copper(II) compounds which were retained on an ultrafiltration membrane.

A marked decrease in PEUF effectiveness was found for the solutions which contained an addition of versene ions (EDTA) whose concentrations were equal or higher than Cu(II) concentration. A change in the UV spectra and a decrease in A_{255nm} absorbance indicate the formation of complexes of other type (Cu–EDTA complexes) and the relatively low retention coefficients R_{Cu} point to its low-molecular nature. Versene ligands of strong complexing properties compete with PSA functional groups and decrease the effectiveness of PEUF by binding copper ions.

4. Conclusions

Spectrophotometric methods can be used as an efficient tool for evaluating the PEUF process. UV spectrophotometry enables the examination of copper (II) complexes with PSA. In the solutions containing both Cu(II) ions and PSA, the UV absorbance band with the maximum at 255 nm was observed, which did not appear during the analyses of solutions containing only metal ions or polymer.

The analyses of UV spectra and effectiveness of ultrafiltration enhanced with that polymer revealed the formation of complexes in which C_{PSA}/C_{Cu} concentration molar ratio was 2.8–2.9.

The intensity of UV spectra and the value of the absorbance at 255 nm as well as the effectiveness of Cu(II) separation were dependent on the solution pH. High Cu(II)–PSA complex concentration and Cu(II) retention coefficients were ensured by a pH range of 4.5–8.

In this study, an addition of Cl^-, SO_4^{2-}, CO_3^{2-}, and PO_4^{3-} at a C_{ion}/C_{Cu} concentration ratio of 0.1–100 did not affect significantly the effectiveness of copper separation, but the presence of EDTA whose concentration was equal or higher than that of Cu(II) significantly decreased the retention coefficient R_{Cu}.

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