



Removal and recovery of copper from wastewater by a complexation–ultrafiltration process

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Abstract

Carboxyl methyl cellulose (CMC) as a water-soluble metal-binding polymer in combination with ultrafiltration (UF) was used in a hybrid approach for selective removal and recovery of copper from water. In the complexation–UF process the cationic forms of heavy metals were first complexed by a macro ligand in order to increase their molecular weight to having a size larger than the pores of the selected membrane that can be retained and flow out in the retentate whereas permeate water was purified to a certain extent from heavy metals. The complexation of Cu^{2+} , Pb^{2+} , Fe^{2+} and Mn^{2+} by CMC from synthetic solutions and real wastewater followed by UF filtration used as a complex separation step was studied. The aim was to recover water-soluble polymers and to obtain a heavy metal concentrate; attempts were also made to destroy the Me:CMC complexes by a pH decrease. The decomplexation procedure was followed by a second step of UF. The results obtained show that a low mole Cu:CMC ratio favors both ultrafiltrate permeability during the first stage of the process and the separation following the next step of complex destruction at a lower pH. The comparative experiments with (1) synthetic water containing copper as a single heavy metal; (2) copper containing a solution with addition of ferrous iron, manganese and lead; and (3) drainage mine water contaminated with copper, ferrous iron, manganese and lead show a selectivity for Cu during the first stage of UF approaching 99% in these three cases. However, the destruction of complexes of heavy metals from the real wastewater was limited — up to 80%.

Keywords: Copper removal; Copper recovery; Complexation; UF

1. Introduction

Among the various processes used for heavy metal removal from water, the technique of

complexation–ultrafiltration proved to be a promising alternative to technologies based on precipitation and ion exchange. The use of water-soluble metal-binding polymers in combination with ultrafiltration (UF) is a hybrid approach to

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concentrate selectively and to recover valuable elements as heavy metals. In the complexation–UF process cationic forms of heavy metals are first complexed by a macroligand in order to increase their molecular weight with a size larger than the pores of the selected membrane that can be retained and which flow out in the retentate; permeate water is then purified from the heavy metals.

Recently numerous studies on this subject have been described in the literature [1–4]. However, the choice of water-soluble oligomers remains important for developing this technology. Several experiments have been done using biopolymer macroligands such as sodium alginate and polysaccharide extracted from brown seaweed [2] able to complex heavy metal cations and cell aggregates [1]. The other group of macroligands is that of the synthetic macroligands such as carboxyl methyl-cellulose, polyvinylethylenimin, polyvinyl alcohol, etc.).

Our previous studies [5] have shown that CMC possesses a good complexation ability towards Cu^{2+} , Cd^{2+} , Co^{2+} , Zn^{2+} , Ni^{2+} and Pb^{2+} . As was reported, membrane selectivity for the heavy metals under investigation increases continuously within a pH range of pH 2–8, with an optimal value of around 8. Based on these results, the value of pH 8 is accepted as the optimal pH of complex formation in our current investigations. The studies of the complexation activities of CMC show that it has a high specific affinity towards certain cations, specifically Cu^{2+} . The sequence with regard to complexing abilities of CMC is $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$. These results show that the affinity found from CMC towards Cu^{2+} is suited to the Irving–Williams series [6], but zinc complexation is surprisingly low. The high affinity of CMC towards copper is the rational point to study the processes of copper removal and especially its recovery from effluents containing a high level of this metal. Based on the results of the non-acceptable effect of complexation at lower pH, attempts were made

to destroy the metal:CMC complexes at lower pH. The present work, part of a large screening experiment (EU funded project, FP5, METASEP) aimed to study the complexation abilities of CMC in removing Cu^{2+} , Zn^{2+} , Pb^{2+} , Ni^{2+} , Fe^{2+} and Mn^{2+} by and by the complexation–UF technique from synthetic and real wastewater containing these metals. In addition, the work focused on investigating metal recovery from the UF retentate.

2. Experimental

The experimental apparatus consisted of a flow circuit in which a 5 l suspension containing CMC and the corresponding metal(s) were fed. The feed suspension was pumped continuously through the UF unit. As the first step in membrane separation, a laboratory-scale UF instrument, a Mini Lab 10-DDS (Denmark) was used. The membrane, UF-10-PAN, was an acryl-nitril copolymer with a molecular cut-off of 10,000 Da. The membrane was efficient within the pH range of 2–11, maximum pressure of 1 MPa and temperature of 20–80°C. Its permeability for distilled water was in the range of 200–240 L/m².h. “Ekofilter” – Bourgas (Bulgaria) manufactured the membrane used. Its effective area is 0.1 m². The process was carried out in a recirculation mode at transmembrane pressure of 0.3 MPa. The desired filtration conditions were maintained by manually operating valves. The schematic of the UF laboratory equipment and experimental details are given elsewhere [5]. Following the first step of separation, named herein UF-1, the pH of the retentate was lowered to the required level, aiming to destroy the CMC–Me complexes. Following a pH adjustment to a pre-requested level, the retentate suspension was treated in batch conditions in a Sartorius SM-165 cell, named herein UF-2. Experiments on decomplexation were carried out at pH 2 and pH 5. The UF units sequence is given in Fig. 1. The cell has a volume of 1000 ml and works at transmembrane

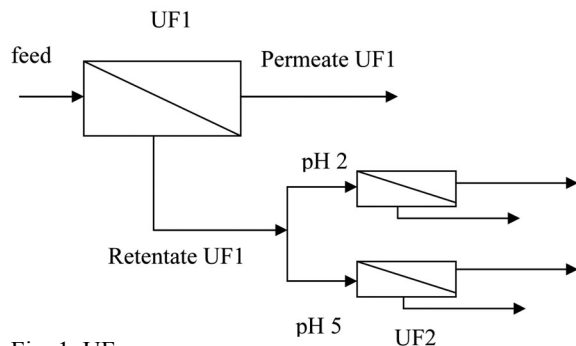


Fig. 1. UF sequence.

pressure of 0.7 MPa. The diameter of the membrane used (UF-10-PAN) is 30 mm.

Part of the experiments was carried out with different synthetic wastewater containing:

- Cu^{2+} , Zn^{2+} , Pb^{2+} and Ni^{2+} (single ion) with a concentration of 10 mg/L at low ion strength of the water solution
- Cu^{2+} , Zn^{2+} , Pb^{2+} and Ni^{2+} (single ion) with a concentration of 10 mg/L at high ion strength of the water solution (besides the heavy metals, the water contains 500 mg/L of both Na^+ and Ca^{2+} added as nitrates)
- Cu^{2+} with a concentration of 200 mg/L at low ion strength of the water solution
- Cu^{2+} , 200 mg/L; Mn^{2+} , 20 mg/L; Fe^{2+} , 20 mg/L; Pb^{2+} , 0.2 mg/L.

Another group of experiments with real wastewater was carried out with:

- mine drainage water with Cu^{2+} , 231.01 mg/L; Mn^{2+} , 21.12 mg/L; Fe^{2+} , 17.47 mg/L; Pb^{2+} , 0.12 mg/L;
- mine drainage water with Cu^{2+} , 741 mg/L; Mn^{2+} , 18.21 mg/L; Fe^{2+} , 21.33 mg/L; Pb^{2+} , 0.25 mg/L.

The model solutions were prepared based on corresponding metal nitrates produced by Merck. The water-soluble macroligand was CMC supplied by Sviloza. The complexing agent was added into the feed tank and the recirculation was starting. The recirculation was continuous for 10 min; then, at the end of the recirculation

period, the pH was adjusted according to the plan of the experiment.

Heavy metal concentrations were analyzed by atomic absorption (AAS-3 spectrometer, Germany). The membrane retention (R , %) was calculated based on the following equation:

$$R = \frac{Me_0 - Me_{\text{per}}}{Me_0} \cdot 100\%$$

where Me_0 is the initial metal concentration and Me_{per} is the metal concentration in permeate.

3. Results and discussion

3.1. Single metal, low and high ion-strength experiment

The single metal ion experiment, both in low and high ion-strength conditions, was performed at the optimal Me:CMC ratio of 1:6 and pH 8. The behavior of permeate flux decay was similar for all single metal ions studied, both at low and high ion-strength conditions. The values of the transient flux varied within the narrow range of 20 to 22 L/m².h. Typically, in all the cases studied, an obvious decay of the transient permeate flux was observed. An example of copper transient flux decay is given in Fig. 2.

Regarding metal retention (Table 1), considerable differences in metal retention were found. The retention observed for Pb and Cu was much higher than the corresponding values for Ni and Zn. The order of metal rejection was $\text{Cu} > \text{Pb} > \text{Ni} > \text{Zn}$. According to the Irving–Williams series [6], which ranks the divalent metal ions in their tendency to complexity, regardless of the nature of the complexing agent, the cations were ranked as follows: $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+}$. Current results confirm our previous data [5], which indicated a low complexation ability of CMC towards zinc. On the other hand, the data show that the ion strength practically does not influence metal retention.

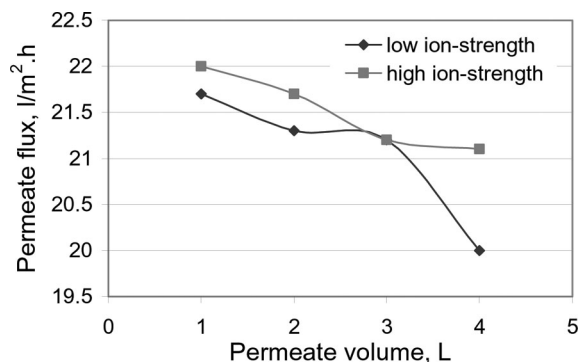


Fig. 2. Single metal experiment, UF1 step (Cu:CMC = 1:6; pH 8; initial copper concentration: 10 mg/L).

Table 1

Retention (R_{UF-1}) at the different stages of membrane separation^a

Metal	R_{UF-1} (low ion strength experiment)	R_{UF-1} (high ion strength experiment)
Cu	96.5	97.1
Zn	72.3	72.0
Pb	95.4	95.4
Ni	91.6	92.1

^aRetention was calculated on permeate metal concentration of the last 100 ml permeate produced. The entire permeate volume was 4 L; initial volume treated: 5 L.

Table 2

Retention (R_{UF-2}) following pH decrease of retentate

Metal	Low ion strength		High ion strength
	pH 5	pH 2	pH 2
Cu	22.9	0.7	0.7
Zn	2.8	0.6	0.4
Pb	7.8	0.4	0.3
Ni	56.4	0.7	0.6

The results related to the effect of metal decomplexation at lower pH are given in Table 2. The data obtained at low ion strength show that at pH 5 (pH of UF-1 retentate following the pH

adjustment), the extent of decomplexation compared to the corresponding data at pH 2 is much lower; even for Zn and Pb, quite a large effect of separation is observed. Evidently, these data indicate a strong pH influence on the decomplexation phenomena. The pH influence can be explained by the pK_a values of binding organic material. According to Niu [7], many organic molecules such as CMC have a pK_a greater than 2, and therefore, at a pH below 2, the metal bonding is expected to be low; at this or close to this pH, a metal decomplexation can occur.

Based on these results our further experiments were carried out at pH 2 (pH of UF-1 retentate). A comparison of the results of metal separation obtained at the same pH (pH 2) and at different ion strengths of the solutions treated indicated that the decomplexation effect appears to be independent of ion strength (Table 2).

The retention through the UF-2 step of separation was calculated by the following equation:

$$R_{UF-2} = \frac{C_{ret\ UF-1} - C_{perm\ UF-2}}{C_{ret\ UF-1}} \cdot 100\%$$

where $C_{ret\ UF-1}$ is the UF-1 retentate metal concentration and $C_{perm\ UF-2}$ is the UF-2 permeate metal concentration.

Practically no differences of permeate flux registered through the UF2 step for both the low and high strength experiments were found. The flux values observed during this step of the experiment were close to 21–22 L/m².h. The comparatively low flux value during the UF2 separation step can be attributed to the high CMC:Me ratio.

Our previous studies [5] have shown that an increase of the CMC:Me ratio to 6:1 increases higher metal retention for systems in which the metal is in comparatively low concentration. The present study emphasized investigations at high initial metal concentration. Furthermore, as the current study focused to a certain extent on solving the specific problem of copper recovery

from copper-rich effluents (drainage water from copper mining industry), experiments with synthetic water containing copper as the sole heavy metal were performed.

3.2. Experiment with synthetic water containing 200 mg/L Cu^{2+}

The data obtained for the first step of separation at different Cu:CMC ratios are shown in Tables 3 and 4.

Table 3
UF-1 retention at different Cu:CMC ratio

Cu:CMC ratio	Initial volume, L	Final volume, L	R^* (UF-1)
1:6	5	1	99.2
1:6	10	1	99.3
1:2	7	2	96.1
1:1	10	4	95.0

Note: R^* measured at the final stage of UF-1 (sample taken from the last 10% of the permeate produced).

Table 4
UF-2 retention at different Cu:CMC ratio

Cu:CMC ratio	Initial volume, L	Final volume, L	R^* (UF-2)	UF-2 permeate copper conc., mg/L
1:6	1	0.5	—	—
1:6	1	0.5	—	—
1:2	1	0.5	6.1	330
1:1	1	0.5	6.7	235

Regarding the values of copper retention through the first separation step, the results are acceptable with a certain advantage at higher CMC:Cu ratios. However, attempts to perform the second step of separation, following the pH adjustment of the UF-1 retentate obtained at the Cu:CMC ratio of 1:6 failed because of the very

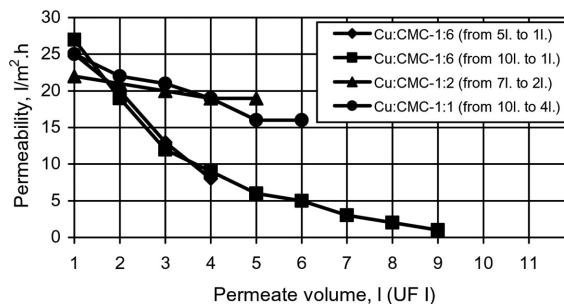


Fig. 3. UF-1 permeability at different Cu:CMC ratios.

low permeate flux registered (below 5 L/m².h.). The decay of the transient permeate flux is shown in Fig. 3. In contrast, the permeate flux decay for the lower Cu:CMC ratio (1:2 and 1:1) drifted as well towards smaller fluxes with filtration time but in a slower way. This is an indication that the effect of Cu adsorption on the CMC matrix is of negligible importance [1].

Regarding the effect of separation during the UF-2 step, 6.1% and 6.7% retention at the corresponding mole ratio was obtained. It follows to a UF-2 permeate copper concentration of 330 and 235 mg/L, respectively.

3.3. Experiments with synthetic water containing Cu, Mn, Fe and Pb

Because of non-satisfactory results obtained at a Cu:CMC ratio of 1:6 in applying the method for a highly concentrated copper solution, further experiments were carried out at Cu:CMC ratios of 1:1 and 1:2. The results obtained with water of similar real mine drainage water quality are given in Table 5. The content of the synthetic water is as follows: Cu^{2+} , 200 mg/L; Mn^{2+} , 20 mg/L; Fe^{2+} , 20 mg/L; Pb^{2+} , 0.2 mg/L.

The copper retention through the UF-1 step was 97.5% and 96% for Cu:CMC mole ratios 1:2 and 1:1, respectively (the samples for metal analysis were taken from the last 10% of the permeate produced). The values of copper in retentate meet material balance for copper in the

Table 5
Results obtained from mine drainage water

UF step	Cu–CMC ratio	Initial/final volume of the model solution treated	Retention, %	Retentate, mg/L Cu
UF-1 (pH 8)	1:2	7 L → 2 L	97.5	667.22
	1:1	10 L → 3 L	96.0	641.67

UF-1 permeate (Cu:CMC =1:1): Fe <0.01 mg/L; Mn = 0.51 mg/L; Pb <0.01 mg/L.

UF step	Cu–CMC ratio	Initial/final volume of the model solution treated	Retention, %
UF-2 (pH 2)	1:2	1 L → 0.5 L	2.8
	1:1	1 L → 0.5 L	2.5

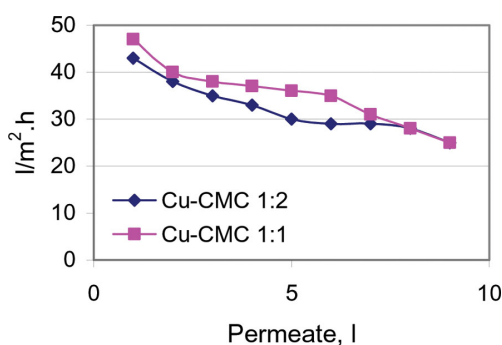


Fig. 4. Membrane permeability during the UF-2 step.

system. The metal separation (UF-2 step) that followed the pH decrease was quite high; the copper retention was below 3%, i.e., over 97% of the copper was transferred into the permeate.

Regarding the membrane permeability, an obvious transient flux decay was registered through the UF-1 step of treatment (Fig. 4) for both Cu–CMC ratios studied. The permeability during the UF-2 step (measured only once through the run) was close to 20 L/m².h (19.5 and 20.3 for Cu:CMC ratio 1:2 and 1:1, respectively).

3.4. Experiment with real wastewater

The real wastewater contained: Cu²⁺, 231.01 mg/L; Mn²⁺, 21.12 mg/L; Fe²⁺,

17.47 mg/L; and Pb²⁺, 0.12 mg/L. The results of the UF-1 and UF-2 step implementation are shown in Table 6. Surprisingly, a better separation effect was found during the UF-1 step compared to the experiments with synthetic water. In the case of real wastewater treatment, copper retention was over 99%. These results were confirmed with experiments at higher initial volumes of metal complexation/metal mixtures (Table 7a). The increased effect of metal retention might be due to micropollutants of an organic nature which are available in the mine drainage effluents.

The separation effects that followed the pH adjustment of UF-1 retentate to pH 3.5 and pH 2 are shown in Tables 6a and 7b. In the case of the test performed at pH 3.5, a considerable part of copper remained bonded with the complexing agent, resulting in a comparatively high retention factor (28%). The decomplexation procedure carried out at pH 2 caused almost complete separation of copper ($R < 0.01\%$, i.e., around 99% of copper was liberated).

The membrane permeability through the second run of the experiment with real wastewater (UF-1) is shown in Fig. 5. The values of the transient flux are much higher compared to the results obtained in the treatment of synthetic

Table 6a

Permeate and retentate parameters through the UF-1 step performed at pH 8 (first run)

Cu–CMC ratio	Initial/final volume of the model solution treated	Permeate, mg/L		Retentate, mg/L	
1:1	10 L → 6 L	Cu	0.05	Cu	641.00
		Fe	0.03		
		Mn	0.18		
		Pb	<0.01		

Table 6b

Permeate and retentate parameters through the UF-2 step performed at pH 3.5

Retentate conc., mg/L copper	Initial/final volume of the retentate treated	Permeate conc., mg/L copper		Retentate, mg/L	
641	2 L → 1 L	Cu	340.12	Cu	650.33
		Fe	12.5		
		Mn	16.8		
		Pb	0.10		

Table 7a

Permeate and retentate parameters through the UF-1 step performed at pH 8 (second run)

Cu–CMC ratio	Initial/final volume of the model solution treated	Permeate, mg/L		Retentate, mg/L	
1:1	15 L → 5 L	Cu	0.03	Cu	670.29
		Fe	0.01		
		Mn	0.15		
		Pb	<0.01		

Table 7b

Permeate and retentate parameters through the UF-2 step performed at pH 2

Retentate conc., mg/L copper	Initial/final volume of the retentate treated	Permeate conc., mg/L copper		Retentate, mg/L	
670	5 L → 2.5 L	Cu	644.02	Cu	648.30
		Fe	16.5		
		Mn	20.3		
		Pb	0.11		

solutions. In addition, the UF-2 step membrane permeability is also over 50 L/m².h. Typically, the flux decay observed is negligible.

Experiments were carried out with the same type of mine drainage water sampled at a different period of time. This wastewater contained

Table 8a
Treatment of mine drainage water with high copper content, UF-1 step

Parameter	Initial value	UF-1 sample number						Retentate
		1	2	3	4	5	6	
Permeate flux, (J_N) , l/m ² .h	89.1	90.0	89.1	81.7	45.6	32.7	32.3	—
Permeate volume, L	—	5	10	15	20	25	30	20
Cu ²⁺ , mg/L	741	0.12	0.49	0.54	0.49	0.49	0.49	1760

Table 8b
Treatment of mine drainage water with high copper content, UF-2 step

Parameter	Initial value	UF-2 sample number					Retentate
		1	2	3	4	5	
J_N , l/m ² .h	—	20.4	16.3	12.8	13.6	13.0	—
Permeate volume, L	—	1	2	3	4	5	5
Cu ²⁺ , mg/L	1760	1760	1758	1720	1700	1680	2160

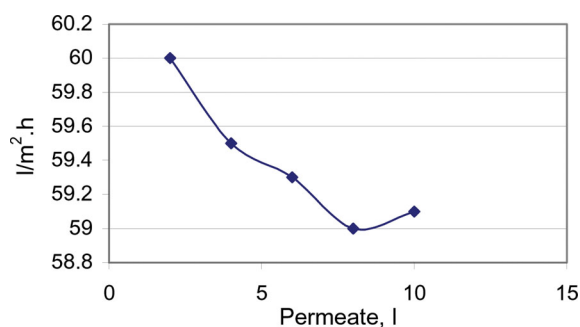


Fig. 5. UF-1 membrane permeability in treatment of real wastewater at a Cu:CMC ratio of 1:1 and pH 8.

four major metals: Cu²⁺, 741 mg/L; Mn²⁺, 18.21 mg/L; Fe²⁺, 21.33 mg/L; and Pb²⁺, 0.25 mg/L. The results of membrane separation following the processes of complexation and decomplexation are given in Table 8.

Specific features of this run are the higher metal concentration, in particular for copper, and

the aim to show the effects of separation of the treatment of larger amounts of water (in this run 50 L of drainage mine water were treated with the UF-1 step of membrane separation). The results obtained show a high retention for copper. The residual copper concentration within the release of 30 L permeate is steadily close to 0.5 mg/L. The separation in the UF-2 stage was not that high compared to the real wastewater of lower copper content. However, a considerable part of copper, around 80%, was decomposed and was available for separation during the UF-2 step. The high amount of copper liberated opens an opportunity for its economical recovery.

The results show as well that in the treatment of highly polluted water with heavy metals (in this specific case, copper), the transient permeate flux dropped significantly, both during the UF-1 and UF-2 step (see Table 8). Visual inspection of the metal-complexing agent suspension shows

that many flocks were formed. The latter could, to a certain extent, block the membrane surfaces. This observation of coagulation at a high concentration of organic bonding agents, leading to reducing the effective surface area for metal binding, have been reported [1].

4. Conclusions

- It has been shown that UF assisted by complexation can be successfully applied for removal of heavy metals using CMC as a complexation agent.
- Regarding the transient permeate flux during the membrane separation of complexes, some of the data obtained indicate that, while at low heavy metal concentration, the optimal metal:CMC mole ratio is 1:6; at higher metal concentrations (over 200 mg/L), a lower mole ratio, 1:2 or 1:1, is preferable.
- Several experimental results show that the rejection of metal–CMC complexes is improved in treatment of drainage mine water compared to synthetic water with the same heavy metal concentration.
- The high effect of decomplexation of metal:CMC complexes was proved at pH 2. Almost complete separation of metal (Cu) from the mixture was performed at this pH using a second UF unit. However, a rapid permeate flux decay at high metal concentration has to be considered.
- The overall results related to the two-step process of metal (copper) complexation/UF separation — decomplexation/UF separation could be of technological interest as an opportunity for metal (copper) recovery.

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