HUNGARIAN JOURNAL
OF INDUSTRIAL CHEMISTRY
VESZPRÉM
Vol. 36(1-2) pp. 17-22 (2008)

NICKEL AND ZINC REMOVAL BY COMPLEXATION-ULTRAFILTRATION METHOD

G. BORBÉLY, E. NAGY✉

University of Pannonia, FIT, Research Institute of Chemical and Process Engineering
H-8201 Veszprém, P. O. Box 158., HUNGARY
✉E-mail: nagy@mukki.richem.hu, nagye@mik.vein.hu

There are a lot of toxic materials in several industrial wastewater streams, for example heavy metals (i.e. Zn^{2+} and Ni^{2+}) in the wastes of electroplating industries, which should be removed before recycling or discharging these aqueous solutions into surface water. One of the methods for removing toxic metals is the complexation enhanced ultrafiltration process that might be an effective membrane technique. This method was tested 2 types of polyether-sulphone – PES – membranes with different cut-off and several complexation agents (polyethylene-imine – PEI –, polyethylene-glycol – PEG –, and 2 types of polyamido-amin dendrimers – PAMAM) for removal these heavy metals from model solutions by a membrane filtration method, which worked in cross-flow mode.

Keywords: heavy metal removal, complexation, ultrafiltration, membrane separation

Introduction

In the 21st century, water has been rising into a key position for many industries and also of course for many peoples because of the global environmental trends and problems that started in last few decades of the 20th century. The main parts of heavy metals, which are going out to the environment caused by human activity, are or will be in aqueous solution. There are a lot of heavy metals (i.e. Zn^{2+} and Ni^{2+}, etc.) or their oxyanions in up to few hundred mg/dm^3 concentration in many industrial wastewaters, for example in the wastes of electroplating industries, which should be removed before recycling or discharging them into a surface water. These metal ions are also toxic, similarly to several other heavy metals. Impact of nickel can be manifested in allergic reactions, chronic toxicity (dermatitis nausea, chronic asthma, coughing, abdominal cramps, diarrhea, vertigo and lassitude), but acute toxicity is not typical. It is known that nickel is human carcinogen. Zinc is biological essential, but the overdose can lead to depression, lethargy, neurological signs such as seizures and ataxia, and increased thirst [Schäfer et al, 1999; Kurniawan et al., 2006]. Both metals can inhibit or kill the microorganisms in a biological wastewater treatment plant [Illés et al., 1983].

The conventional processes to treat this kind of wastewater are e.g. chemical precipitation, ion exchange, adsorption or biosorption – and nowadays membrane separations, like electrodialysis (ED), and pressure-driven methods (nanofiltration (NF) and reverse osmosis (RO)) [Kurniawan et al., 2006]. The main disadvantages of these processes are e.g. inadequate selectivity, high residual metal concentration, not high enough concentrated metal concentrates for its reuse, periodical batch processes, etc.

One of the pressure driven membrane separation method is the ultrafiltration (UF) that is not suitable directly to remove dissolved metal ions because of the pore size of these membranes are too large (about 20-1000 Å). But in some hybrid processes, i.e. micellar [Yurlova et al., 2002] or complexation enhanced UF [Smith et al, 1995], metal ions could be removed more than 90% efficiency. Theoretically, this process does not have any by-products that could not be reused in industries due to the re-winning of complexation agent and the more quintessential metal solution. The regeneration of the complexation agent can be carried out e.g. by electrodialysis with bipolar membrane system [Schlichter et al., 2004].

A lot of parameters influence this separation process, the most important are the following:

- properties of the complexation agent [Smith et al., 1995],
- pH of the metal solution [Smith et al., 1995; Rether & Schuster, 2003],
- complexation agent/metal ratio [Korus et al., 1999],
- properties of membrane [Lee & Walker, 2006].

One of the most important problems is to find a near-optimal bounding agent. There are some requirements for which it should be managed. The most important ones are the following [Frenay, 2003]:

- high metal fixation capacity,
- fast reaction rate of metal fixation,

- possibility of regeneration,
- desired chemical and physical stabilities.

Materials and methods

In this paper, complexation- or polymer-enhanced ultrafiltration (PEUF) of Zn^{2+} and Ni^{2+} was studied, where the tested complexation agents are water soluble polymers. In the first step, a high molecular weight polymer compounds as complexation or bounding agent is added to the metal solution. The produced bounding agent/metal complex by a reversible reaction is removed from the solution by ultrafiltration. In the last step of the process, as it can be seen in *Fig. 1,* the concentrated polymer-metal complex in the retentate phase should be split for its regeneration and the two components should be separated from each other, e.g. by means of conventional membrane process as electrodialysis by bipolar membranes. An important aim of the process is that at the end of this separation step, the metal concentration of the outlet stream needs to be concentrated at about 10-fold higher than in the inlet stream for the economical operation.

The applied polymers for the complexation were polyethylene-imine – PEI, polyethylene-glycol – PEG, and 2 types of polyamido-amin dendrimers – PAMAM. The main parameters of the polymers were listed in *Table 1.* PEIs are the most currently applied polymers for complexation-UF, i. e. according to Smith & Robinson [1998]. It could not be found any data in the literature where metals were removed by pure PEG, only when PEG is in aggregates with sodium dodecyl sulphate [Xiarchos et al., 2008]. PAMAM dendrimers are a relative new group of polymers. These polymers could be applied in a very wide range of bio- and nanochemistry [Klajnert & Bryszewska, 2001], but they are also excellent for example in this kind of wastewater treatment [Diallo et al., 2005].

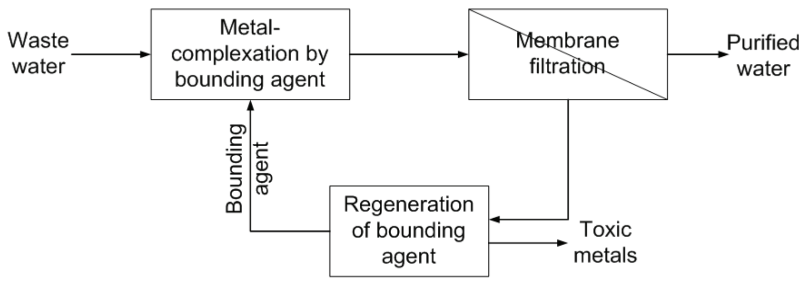


Figure 1: The flowchart of the process

Table 1: The main parameters of the applied polymers

Sign	*Function group*	*Molecular weight [g/mol]*	*Made by*
PEI-25	$-NH_2$	25000	Aldrich
PEI-70	$-NH_2$	70000	Polysciences Inc.
PEG	-OH	10000	Sigma-Aldrich
PAMAM G4.5	-COOH	23441	Res. Inst. of Chem. and Proc. Eng., Univ. of Pannonia
PAMAM G5.0	$-NH_2$	28825	Res. Inst. of Chem. and Proc. Eng., Univ. of Pannonia

It was tested 2 types of membranes, both of them were in poly(ether-sulphone), but they had different cut-off, namely 10 and 20 kDa, PES-10 and PES-20, respectively. Both of them were provided by Alfa-Laval.

Results were expressed in retention (R [%]) that means the following:

$$R\,[\%] = \left(1 - \frac{c_p}{c_0}\right) * 100$$

Where c_p is the metal concentration of the permeate, and c_0 is the metal concentration of the feedstock at $t_0 = 0$ time. (c_0 can be changed during separation, but it could be negligible.)

Tests with PEIs and PEG were carried out in laboratory scale equipment made by Beroplan. Tests with PAMAMs were carried out only in small scale equipment. The main parameters of the applied membrane filtration equipments showed in the *Table 2.*

Based on Schlichter et al. [11], the regeneration of complexation agents were tested by electrodialysis with bipolar membrane system (EDBM). The construction of the module showed in *Fig. 2.* The areas of membranes are 100 cm^2 one by one, the applied current was constant 36 V. The applied electrolyte solution was 0.05 M Na_2SO_4 and there was in the base cycle 2 g/l NaCl.

Results and discussion

It was investigated of the effect of pH, MWCO of membrane, polymer/metal molar ratio, feed concentration, temperature and pressure. It was experienced that the membrane with 10 kDa pore size was more favourable than with 20 kDa. The retention was similar but the flux was higher so the process was faster. Thus, majority of the measurements were carried out by membrane with cut-off of 10 kDa. Temperature in the range investigated (Table 2) does not affect significantly the separation. (It can cause only a few percent differences). Thus, we could work at room temperature without thermostating the solution. There was a slight increase of temperature during the measurement, because the pump and pipes are heating due to the stream (and the higher viscosity of the feed solution due to the presence of the polymer).

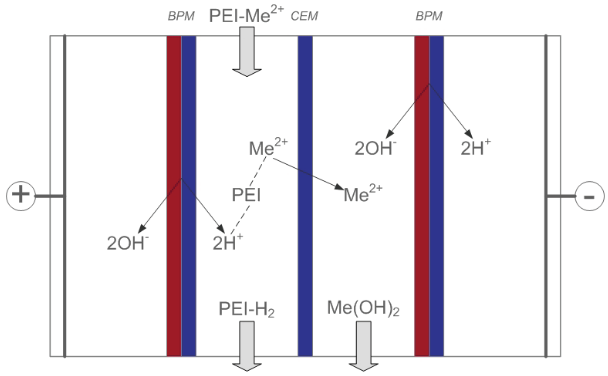


Figure 2: Construction of the module of electrodialysis with bipolar membrane system

Table 2: The main parameters of the membrane filtration equipments

	PEG	***PEIs***	***PAMAMs***
Type of membrane	PES-10	PES-10 PES-20	PES-10
Method of filtration	cross-flow	cross-flow	dead-end
$A_{membrane}$ [cm^2]	63.62	63.62	19.63
V_{feed} [cm^3]	1000	1000	50
p [bar]	0.5-5	0.5-5	5
T [°C]	15-25	15-25	~ 20 (room temp.)
pH of polymer	~5	>11	~11
pH of metal solution	2.1 (Zn^{2+})* 5.5 (Ni^{2+})*	2-9	2; 7; 9
Polymer/metal [mol/mol]	0.1; 1	0.001-5 (PEI-25) 0.001-0.1 (PEI-70)	0.1; 1

*: pH of 0.01 M $ZnCl_2$ and $NiCl_2$

According to some researchers [i.e. Korus et al. 1999], pH has a significant effect on the retention. In our measurements, these results could not be obviously reproduced in case of PEI, but could be it in case of PAMAM, as it can be seen in *Fig. 3* and *4*. The pH of feed solution is determined by that of polymer solution and not by the pH of the metal solution, because of polymer solution had a very high buffer capacity.

Retention was calculated from our measered data. An example for the calculation is the following:

$$V_{Feedstock} = 500 \text{ mL}$$
$$(=250 \text{ ml } 0.001 \text{ M } NiCl_2 + 250 \text{ ml } 0.001 \text{ M PEI-25})$$

S_o, c_0 = 0.0005 M = 29.345 mg/L, and PEI/Me^{2+} = 1. The pH was 7, temperature was about 20 °C. Permeatum volume was 40 mL/h, what is an average quantity from 3 measurements.

Flux can be described by the following equation:

$$\Phi = \frac{V_{Permeate}}{A_{Membrane} * t_{Permeate}} = \frac{40 \text{ ml}/1000}{6.36173 * 10^{-3} \text{ m}^2 * 1 \text{ h}} = 6.29 \frac{1}{\text{m}^2\text{h}}.$$

Retention was calculated about the equation what could be seen above:

$$R = \left(1 - \frac{c_p}{c_0}\right) * 100 = \left(1 - \frac{0.4 \text{ mg}/1}{29.345 \text{ mg}/1}\right) * 100 = 98.64\%,$$

where c_p was determined by atomic absorption spectrophotometry.

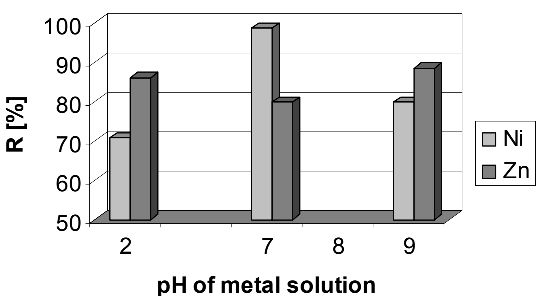


Figure 3: Retention of Ni^{2+} and Zn^{2+} binding by PEI-25 versus pH of metal solution
PEI/Me^{2+} = 1 mol/mol, PES-10 membrane

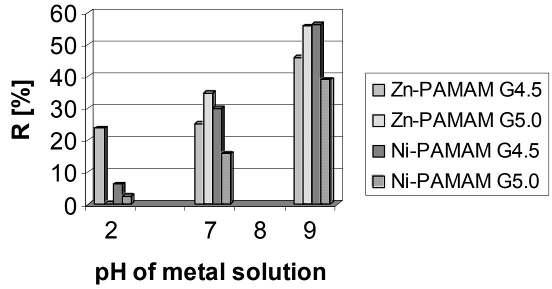


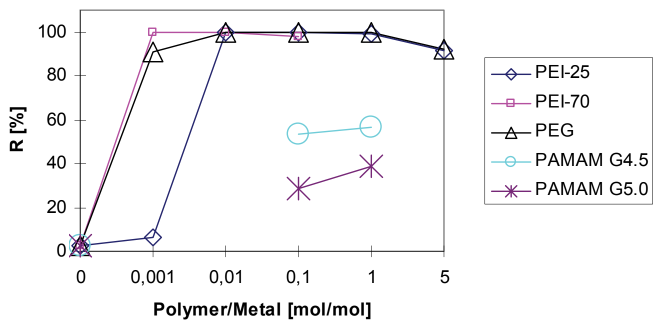
Figure 4: Capacity of metal bounding of PAMAM dendrimers versus pH of metal solution PAMAM/Me^{2+} = 1 mol/mol, PES-10 membrane

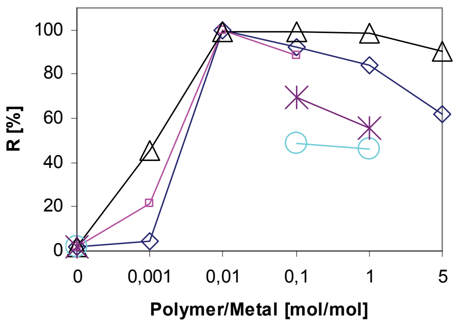
According to Müslehiddinoğlu et. al. [8], the complexation is affected more by the ratio of complexation agent/metal ion than by the initial concentration of metal or complexation agent polymer. This statement was supported also by our measurements. The effect of the molar ratio of the polymer and metal is plotted in *Fig. 5* and *6*. Let us look at first the Ni^{2+} separation (Fig. 5). Retention obtained more than 90 % (in some cases close up to 100 %). It is surprising that retention is high at very low value of the molar ratio of polymer and metal ion, even in the case when it is far below 1. This behaviour needs explanation. Further measurements should be carried out for it.

The change of retention has similar tendency in the case of Zn^{2+}. E.g. at molar ratio of 0.01, the zinc retention reaches about 100 %. Increasing the molar ratio upto 5, slight decrease of retention could be observed in both cases.

Retention is somewhat lower in the case of the PAMAM dendrimer. It should be known that only in cases of PAMAMs were pH adjusted, in the other cases it was kept at pH of metal solution. (See for it Fig. 3 and 4.)

The effect of the feed metal ion concentration was investigated at few concentrations. The results are listed in *Table 3*. Its effect is not significant on retention.





Membrane: PES-10; c_{feed} of polymers: 0.001 M; p: 5 bar

Figure 5: Effect of the complexation agent for the metal removal in case of Ni^{2+}

Figure 6: Effect of the complexation agent for the metal removal in case of Zn^{2+}

Table 3: The effect of the metal ion concentration in the feed solution for the retention (T = 20 °C, without pH adjustment)

Me^{2+}	***Polymer***	***Membrane***	***Polymer/Me^{2+} [mol/mol]***	***p [bar]***	***c_{feed} [M]***	***R [%]***
Ni^{2+}	PEI-25	PES-20	1	3	0.01	93.35
				5		81.77
				3	0.001	93.18
				5		95.47
Zn^{2+}	PEI-25	PES-20	1	3	0.01	59.00
				5		60.23
				3	0.001	82.10
				5		83.79
Zn^{2+}	PEI-70	PES-10	0.01	3	0.01	99.97
				5		
				3	0.001	99.69
				5		

The effect of pressure was dual: first, it is well known that on higher pressure the flux is also higher. However, the process will be faster, but it will expectedly be less effective. In our cases, it is difficult to explain the effect of pressure. There is a minimum point in all the pressure-retention curves, as it can be seen in case of Ni^{2+} with PEI-25 in *Fig. 7*. This could mean that the separation equipment could be operated at lower pressure range. But it should also be taken into account, that the permeation rate will be higher at higher pressure range. The achieved maximal enrichment in cases of polymers with the necessary operating parameters showed in *Table 4.*

Regeneration of complexation agents is the basic problem of these kinds of systems. There are only a few data about this step of the process in the literature, i.e. one of the work of Schlichter et. al. [11]. We have carried out preliminary experiments in this respect, but results obtained *(Table 5)* should improved by further experiments.

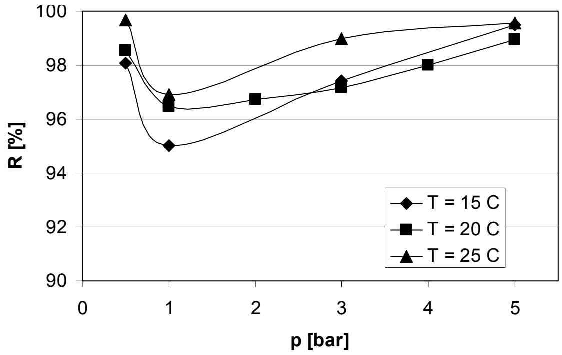


Figure 7: Effect of transmembrane pressure on removal of Ni^{2+} with PES-10 membrane at different temperature. PEI-25/Ni^{2+} = 1 mol/mol

Table 4: The achieved maximal retention by complexation polymers

	Membrane	***t [°C]***	***p [bar]***	***Polymer/Me^{2+} [mol/mol]***	c_{feed} ***[M]***	***R [%]***	***pH of Me^{2+*}***
Ni^{2+}							
PEI-25	PES-20	20	1	0.01	0.1	99.87	
PEI-70	PES-10	20	0.5	0.001	0.001	99.66	
PEG	PES-10	20	0.5	0.01	0.001	99.78	
PAMAM G4.5	PES-10	20	5	1	0.001	56.38	9
PAMAM G5.0	PES-10	20	5	1	0.001	39.00	9
Zn^{2+}							
PEI-25	PES-10	20	0.5	0.001	0.1	99.96	
PEI-70	PES-10	20	0.5	0.01	0.01	99.97	
PEG	PES-10	20	1	0.01	0.01	99.53	
PAMAM G4.5	PES-10	20	5	0.1	0.001	48.61	9
PAMAM G5.0	PES-10	20	5	0.1	0.001	69.81	9

*: Free cell means there was not pH adjustment

Table 5: Regenerated portion of bounding agent polymers from metal complex by electrodialysis

	PEI-25	***PEI-70***	***PEG***	***PAMAM G.4.5***	***PAMAM G5.0***
Ni^{2+}	21.4 %	23.7 %	47.4 %	69.0 %	19.4 %
Zn^{2+}	19.5 %	30.3 %	45.5 %	33.6 %	75.3 %

Conclusions

The complexation-ultrafiltration method can applied appropriate for heavy metal removal. In this paper, there are different types of water soluble polymer with high molecular weight, which could be applied for this kind of separation process, well. As it was shown, for removal of nickel and zinc ion with complexation-ultrafiltration method, both of the bounding agents with hydroxyl, carboxyl and amin groups were quiet effective. Temperature, pH, feed concentration of metals did not affect the process significantly, but pressure and polymer/metal ratio could be very important operating parameters, which should be the highest priority in this type of metal removal.

By the integration of the complexation-ultrafiltration and the electrodialysis steps, it gave a semi-continuous process for the removal. The bottle-neck of the process is the regeneration of the complexation agents. This problem should be solved in order to obtain economic and environmentally friendly separation process.

ACKNOWLEDGEMENTS

We kindly acknowledge Pál Halmos (Dept. of the Analytical Chemistry, Univ. of Pannonia) for the analytical measurements and the Hungarian Scientific Research Fund under Grants OTKA 63615/2006 for supported this work.

REFERENCES

1. Diallo, M. S., Christie, S., Swaminathan, P., Johnson, J. H. Jr., Goddard, W. A.: Dendrimer enhanced ulrafiltration. 1. Recovery of Cu(II) from aqueous solutions using PAMAM dendrimers with ethylene diamine core and terminal NH_2 groups, Environmental Science & Technology 39 (2005) 1366-1377
2. Frenay, J.: PERMEA 2003 Proceedings of the Membrane Science and Technology Conference of the Visegrad Countries with Wider International

Participation, Tatranské Matliare, Slovakia, 7-11 September, 2003, p. 38

3. ILLÉS, I., KELEMEN, L., ÖLLŐS, G.: Industrial water management, VÍZDOK, Budapest, 1983, pp. 231 (In Hungarian)
4. KLAJNERT, B., BRYSZEWSKA, M.: Dendrimers: properties and applications, Acta Biochimica Polonica 48 (2001) 199-208
5. KORUS, I., BODZEK, M., LOSKA, K.: Removal of zinc and nickel ions from aqueous solutions by means of the hybrid complexation–ultrafiltration process, Separation and Purification Technology 17 (1999) 111-116.
6. KURNIAWAN, T. A., CHAN, G. Y. S., LO, W. H., BABEL, S.: Physico–chemical treatment techniques for wastewater laden with heavy metals, Chemical Engineering Journal 118 (2006) 83-98.
7. LEE, J., WALKER H. W.: Effect of process variables and natural organic matter on removal of Microcystin-LR by PAC – UF, Environmental Science & Technology 40 (2006) 7336-7342
8. MÜSLEHIDDINOĞLU, J., ULUDAĞ, Y., ÖZBELGE, H. Ö., YILMAZ, L.: Determination of heavy metal concentration in feed and permeate streams of polymer enhanced ultrafiltration process, Talanta 46 (1998) 1557-1565
9. RETHER, A., SCHUSTER, M.: Selective separation and recovery of heavy metal ions using water-soluble N-benzoylthiourea modified PAMAM polymers, Reactive & Functional Polymers 57 (2003) 13-21.
10. SCHÄFER, S. G., DAWES, R. L. F., ELSENHANS, B., FORTH, W.: Metals, In: Marquardt, H., Schäfer, S. G., McClellan, R. O., Welsch, F. (Eds.): Toxicology, Academic Press, 1999, pp. 755-804.
11. SCHLICHTER, B., MAVROV, V., ERWE, T., CHMIEL, H.: Regeneration of bonding agents loaded with heavy metals by electrodialysis with bipolar membranes, Journal of Membrane Science 232 (2004) 99-105
12. SMITH, B. F., ROBISON, T. W., COURNOYER, M. E., WILSON, K. V., SAUER, N. N., MULLEN, K. I., LU, M. T., JARVIEN, J. J.: Polymer Filtration: A new technology for selective metals recovery, SUR/FIN ’95: American Electroplaters and Surface Finishers Society meeting and exhibition, Baltimore, MD (United States), 25-28 Jun 1995
13. SMITH, B. F., ROBISON, T. W.: Water-soluble polymers for recovery of metal ions from aqueous streams, United States Patent, Patent Number: 5766478, 1998
14. XIARCHOS, I., JAWORSKA, A., ZAKRZEWSKA-TRZNADEL, G.: Response surface methodology for the modelling of copper removal from aqueous solutions using micellar-enhanced ultrafiltration, Journal of Membrane Science (2008), *Article in press*
15. YURLOVA, L., KRYVORUCHKO, A., KORNILOVICH, B.: Removal of Ni(II) ions from wastewater by micellar-enhanced ultrafiltration, Desalination 144 (2002) 255-260