ANNA JÓŹWIAK*, ZBIGNIEW GORZKA*

APPLICATION OF WOFATIT KPS AND KS-10 IN SORPTION OF CU(II) AND NI(II) IONS FROM BINARY SOLUTIONS

Results of the treatment of binary solutions showed that there exists the possibility of application of gelous Wofatit KPS and macroporous Wofatit KS-10 in the removal of metal ions from plating effluents. The possibility of selective sorption of those ions from binary solutions by the ion exchangers was also investigated. Partition coefficients for Cu(II) and Ni(II) ions were found to be in the range from 25 to about 700. These coefficients depended on the concentrations of Cu(II), Ni(II) and H⁺ ions in the solutions treated. It was also found that exchange capacity of the exchanger depends on the ratio of Cu(II) concentration to Ni(II) concentration in a solution in the case of both ion exchangers.

1. INTRODUCTION

Wastewaters from electroplating plants are one of the most hazardous wastes to environment [1], [2]. Application of ion-exchange method in their treatment makes possible the recovery of heavy-metal ions and regeneration of electroplating baths. In order to check the possibility of ion-exchange application in the removal of Cu(II) and Ni(II) from washery effluents, the investigations of the kinetics of ion-exchange H^+/Cu^{2+} and H^+/Ni^{2+} and of equilibrium in binary systems were carried out [3], [4]. The results of experiments proved that gelous Wofatit KPS and macroporous Wofatit KS-10 are applicable in removal of the above-mentioned heavy-metal ions from washery effluents. Due to the fact that ions of heavy metals seldom occur separately, but often in a mixture, the investigations of ion-exchange H^+/Cu^{2+} and H^+/Ni^{2+} were carried out in binary solutions.

The aim of this work was to determine the selectivity of Cu(II) and Ni(II) ions in the ion exchangers tested.

2. EXPERIMENTAL

Experiments were carried out under equilibrium conditions. Solutions were kept in glass flasks in a thermostat at a temperature of 293 K. They were periodically stirred

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* Institute of General and Ecological Chemistry, Technical University of Łódź, 90-924 Łódź, ul. Żwirki 36, Poland.

during experiments. The solutions contained a mixture of metal ions at the concentration of 1 meq/dm^3. The concentration ratio of Cu(II) to Ni(II) ranged from about 0.08 to 10. Sulphuric acid at the concentration up to 5 eq/dm^3 was added to each solution.

Two types of ion exchangers: gelous KPS and macroporous KS-10 were used in the experiments. Small samples of these ion exchangers (with a known humidity) were kept in distilled water for 24 hours in order to swell them. Next, the samples of exchangers were placed in the solutions tested and were periodically stirred for 24 hours. This time was sufficient to attain the equilibrium state which had been proved previously [4]. After this time the solutions were decanted and concentrations of Ni(II), Cu(II) and H$^+$ ions were determined using the procedures described in [6].

3. RESULTS AND DISCUSSION

Partition of ions between two phases can be characterized by the partition coefficient λ:

$$\lambda = \frac{C_j^{Me}}{C_r^{Me}}, \tag{1}$$

where:

C_j^{Me} – concentration of metal ions in ion-exchanger phase in equilibrium,

C_r^{Me} – concentration of metal ions in aqueous phase in equilibrium.

The partition coefficients of Cu(II) or Ni(II) ions are not constant. They depend on a ratio of the Cu(II) ion amount to the Ni(II) ion amount in a solution. Thus, the aim of this work was to determine the partition coefficients λ for the exchange of H$^+$/Cu^{2+} and H$^+$/Ni^{2+} in binary systems at various concentrations of sulphuric acid. The partition coefficients for Cu(II) and Ni(II) ions were calculated according to the following equations:

$$C_{kw}^{r-j} = C_{kw}^r - C_{kw}^0, \tag{2}$$

$$Me^{r-j} = Me^{0-r} - Me^{r-r}, \tag{3}$$

$$X^{Me-j} = \frac{Me^{r-j}}{V_w}, \tag{4}$$

$$X^{Me-r} = \frac{Me^{r-r}}{V_j}, \tag{5}$$

$$\lambda = \frac{X^{Me-j}}{Me^{Me-r}}, \tag{6}$$

where:

C_{kw}^0 – concentration of sulphuric acid in the solution before contact with ion exchanger [meq/dm^3],

C_{kw}^r – concentration of sulphuric acid in the solution being in equilibrium [meq/dm^3],

C_{kw}^{r-j} – concentration of H$^+$ ions released from the ion exchanger to the solution [meq/dm^3],

Me^{0-r} – content of metal ions in the solution before contact with ion exchanger [meq],

Me^{r-r} – content of metal ions in the solution in equilibrium [meq],

Me^{r-j} – content of metal ions in equilibrium state in the ion-exchanger phase [meq],

X^{Me-j} – equivalent fraction of metal ions in equilibrium state in the ion-exchanger phase [meq/dm^3],

X^{Me-r} – equivalent fraction of metal ions in equilibrium state in the solution [meq/dm^3],

V_w – volume of water in the ion exchanger in equilibrium state [dm^3],

V_j – volume of the solution in a cylinder [dm^3].
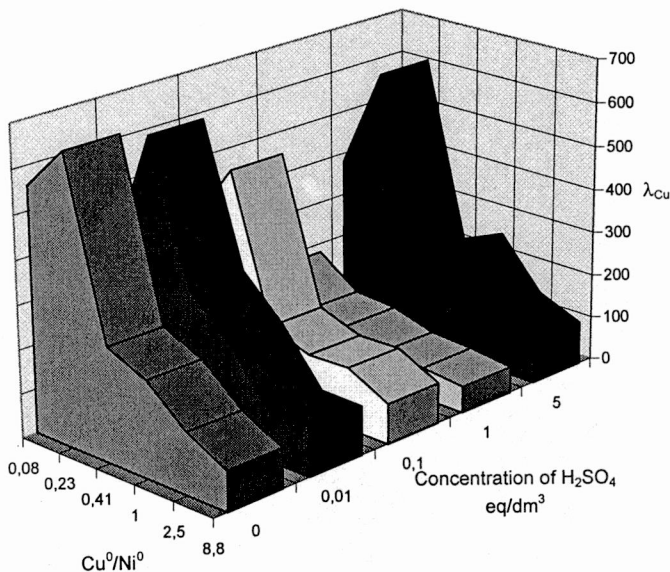
The results obtained are presented in figures 1–4.

Fig. 1. Values of the partition coefficients of copper between ion exchanger
and solution phases at the presence of nickel for Wofatit KPS

Values of the the partition coefficients for Cu(II) ions are in the range from 71 to 657 for Wofatit KPS and from 58 to 573 for Wofatit KS-10. In the case of Ni(II) ions these values range from 42 to 560 and from 25 to 505 for Wofatit KPS and KS-10,

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respectively. In the case of both ion exchangers, these coefficients crucially depend on the concentration of H^+ ions present in a solution during ion exchange. They decrease with the increase in acid concentration in such a way that the higher H^+ ion concentration in a solution, the smaller the amount of exchanged ions.
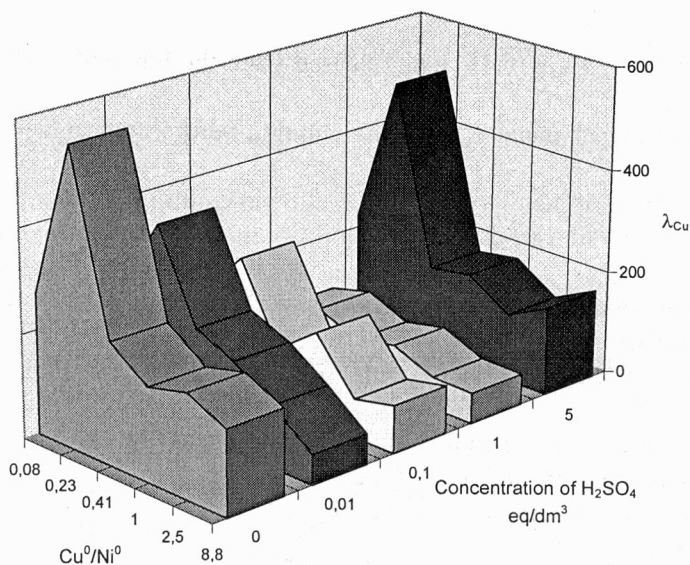

Fig. 2. Values of the partition coefficients of copper between ion exchanger and solution phases at the presence of nickel for Wofatit KS-10
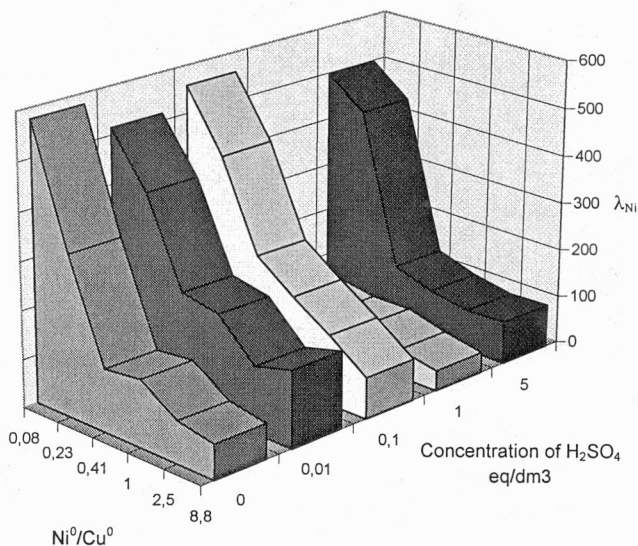

Fig. 3. Values of the partition coefficients of nickel between ion exchanger and solution phases at the presence of copper for Wofatit KPS
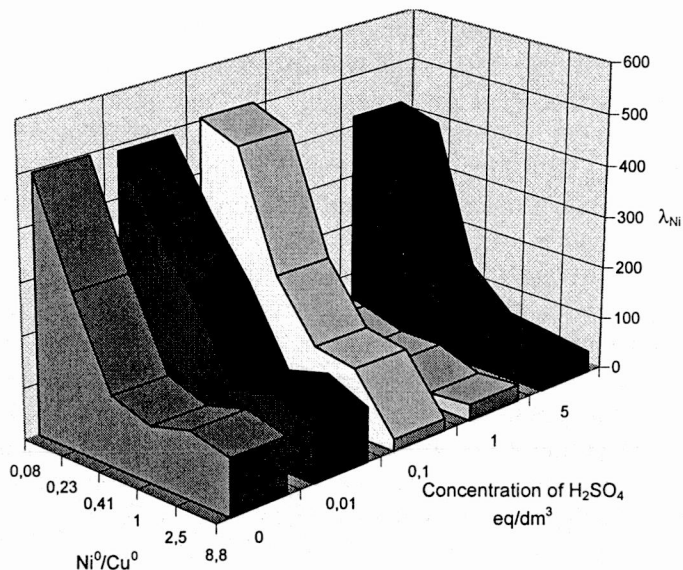
Fig. 4. Values of the partition coefficients of nickel between ion exchanger
and solution phases at the presence of copper for Wofatit KS-10

T a b l e

Effect of Cu(II) and Ni(II) concentrations in the solution with various sulphuric acid concentrations
on the partition of these ions between aqueous and ion-exchanger phases

$c_{H_2SO_4}^0$ (val/dm^3)	Wofatit KPS		Wofatit KS-10		$c_{H_2SO_4}^0$ (val/dm^3)	Wofatit KPS		Wofatit KS-10	
	Cu_r^0/Ni_r^0 (val/val)	Cu_j^r/Ni_j^r (val/val)	Cu_r^0/Ni_r^0 (val/val)	Cu_j^r/Ni_j^r (val/val)		Cu_r^0/Ni_r^0 (val/val)	Cu_j^r/Ni_j^r (val/val)	Cu_r^0/Ni_r^0 (val/val)	Cu_j^r/Ni_j^r (val/val)
	0.078	0.085	0.092	0.176		0.608	0.342	0.702	0.329
	0.235	0.507	0.226	0.603	0.10	2.422	1.301	2.321	1.195
0.0	0.410	0.579	0.425	0.587		6.366	2.582	6.001	1.788
	0.997	1.741	0.976	1.479		0.077	0.093	0.090	0.197
	2.525	1.359	2.762	1.929		0.170	0.336	0.190	0.716
	8.794	6.610	8.020	5.115	1.00	0.440	0.984	0.481	0.682
	0.076	0.099	0.079	0.119		0.780	0.783	0.958	1.070
	0.191	0.367	0.232	0.457		2.994	2.253	3.184	3.755
0.01	0.495	0.920	0.473	0.821		9.809	9.113	9.599	6.291
	0.907	1.219	0.838	0.719		0.096	0.282	0.096	0.403
	2.156	0.852	2.250	1.007		0.254	0.873	0.271	1.504
	6.744	2.324	6.042	1.218	5.00	0.425	0.468	0.472	0.505
	0.099	0.292	0.091	0.519		0.964	1.426	0.939	1.184
0.10	0.190	0.347	0.219	0.371		2.384	1.066	2.427	1.085
	0.405	0.362	0.441	0.357		7.879	5.228	7.248	4.011

Similarly as it was observed in unary solutions, the lowest values of the partition coefficients for Cu(II) and Ni(II) ions in binary solutions were obtained at sulphuric acid concentration of 1 eq/dm³ in the case of both ion exchangers. This concentration of sulphuric acid is the most effective when both ion exchangers are subjected to re-generation. Analyses of results enabled determination of the partition coefficient val-ues for ions tested in a stock solution and solution in an equilibrium state. The data obtained are presented in the table.

A relative ratio of Cu(II) to Ni(II) amounts in ion exchanger was found to be not the same as that in a stock solution. It depends on experimental conditions and above all on initial concentration of copper and nickel ions in a stock solution. The results obtained in the case of both tested ion exchangers show that partition of ions in an exchanger phase changes to the advantage of that ion which is present in a stock solu-tion at lower concentration. However, this change is not relatively high which does not allow us to make use of it in practice during selective removal of Cu(II) or Ni(II) ions in such ion exchangers as Wofatit KPS and KS-10. In the case of both ion ex-changers, no difference in partition of Cu(II) and Ni(II) ions kept in these exchangers was observed with the change in H⁺ ion concentration.

3. CONCLUSIONS

The values of the partition coefficient obtained for binary solutions prove that there exists the possibility of applying the ion exchangers tested in simultaneous re-moval of Cu(II) and Ni(II) ions from aqueous solutions. The values of those coeffi-cients depend on the conditions under which experiments were carried out, above all on the concentration of Cu(II) and Ni(II) ions in a stock solution – their values in-crease with dilution of a solution. They also depend on H⁺ ion concentration in a stock solution. The higher the H⁺ ion concentration, the smaller amounts of the copper and nickel ions are exchanged. The most effective concentration of sulphuric acid used for ion-exchanger regeneration totals 1.0 eq/dm³. At this concentration of acid, the small-est partition coefficients for both Cu(II) and Ni(II) ions in the exchanger phase are reached. Their values depend on partition of these ions in a stock solution. Partition of ions in ion-exchanger phase changes to the advantage of that ion, which occurs in a stock solution at lower concentration. Thus, such ion exchangers as Wofatit KPS and Wofatit KS-10 select that metal ion whose amount is smaller in a stock binary solution. Independently of H⁺ ion concentration this selectivity is too slight to make use of it in practice during removal of Cu(II) and Ni(II) ions from aqueous solutions.

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ZASTOSOWANIE WOFATITÓW KPS I KS-10 DO SORPCJI JONÓW CU(II) I NI(II)
Z ROZTWORÓW DWUSKŁADNIKOWYCH

Badając wymianę jonową H^+/Cu^{2+} i H^+/Ni^{2+} między roztworami dwuskładnikowymi a silnie kwaśnymi jonitami: żelowym Wolfatitem KPS i makroporowatym Wolfatitem KS-10, wyznaczono współczynniki podziału jonów Cu(II) i Ni(II). Stwierdzono, że są one zawarte w zakresie od ok. 25 do ok. 700 i zależą zarówno od stężenia badanych jonów, jak i stężenia jonów H^+ w roztworze wyjściowym. Ilości zaadsorbowanych jonów Cu(II) i Ni(II) w fazie obu jonitów zależą od stosunku stężeń tych jonów w roztworze wyjściowym.