

ZBIGNIEW HUBICKI*, LUCJAN PAWŁOWSKI**

POSSIBILITY OF COPPER RECOVERY FROM WASTEWATER CONTAINING COPPER-AMMINE COMPLEXES

The investigations dealt with sorption and desorption of copper present in ammonia wastewater on cation exchangers: polystyrenesulphonic resin of gelous and macroporous matrix, carboxylic resins based on acrylic, metacrylic and phenolcarboxylic acids, chelating resins as well as some anion exchangers.

Carboxylic resins showed the best properties for selective removal of copper from ammonia containing wastewater. The highest copper concentration, equal to 50–70 g $\text{Cu}^{+2}/\text{dm}^3$, was achieved with 2 M solution of sulphuric acid used for regeneration,

1. INTRODUCTION

Copper ions due to their toxicity disturb the operation of biological treatment plants and exert a negative effect on self-purification of water and on some organisms living in water reservoirs. Therefore these ions should be removed from wastewater by precipitation, electrolysis, electrodialysis, flotation, separation (by means of liquid membranes) and extraction (especially using oximes — LiX, derivatives of 8-hydroxyquinoline — Kelex, fatty acids, etc, as extraction solvents) [1], [2]. For selective copper removal from wastewater and in hydrometallurgy ion exchangers were also used [3]–[15].

Copper removal from solutions containing ammonium ions (e.g., nitrogen effluents) is one of the more complex and insufficiently studied processes. Therefore, the aim of the present paper was to study the processes of sorption and desorption of copper-amine complexes on various ion exchangers.

* Institute of Chemistry, Maria Skłodowska-Curie University, ul. Nowotki 12, 20-031 Lublin, Poland.

** Department of Water and Wastewater Technology, Technical University of Lublin.

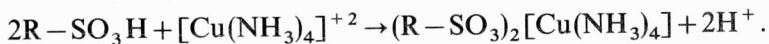
2. EXPERIMENTAL

Resins of particle-size distribution ranging within 0.3–0.8 mm were selected for our studies. Weak-base anion exchangers were used in the form of hydrated amine and cation exchangers being employed in H^+ or NH_4^+ forms. Synthetic wastewater solution contained 0.1 M Cu^{+2}/dm^3 and ammonia in the molar ratio 1:4. Sorption of copper from this solution was studied using glass columns filled with the resin (20–400 cm^3). The presence of Cu^{+2} ions in the effluent was assumed as breakthrough point. The exhausted ion exchanger bed was rinsed with distilled water (in volume 3 times greater than bed) and desorption of Cu^{+2} ions was carried out either with sulphuric acid, formic acid or a mixture of the latter with ammonium formate. The flow rate of reagent was 0.4 cm^3/cm^3 min. The 200 cm^3 effluent fractions were collected in both sorption and desorption processes. Copper contents in consecutive fractions were determined by polarographic method, while pH of effluent was controlled pH-metrically. Breakthrough capacities have been determined for copper–ammine complexes sorbed from model solutions on polystyrene–sulphonic resins of gelous and macroporous matrix, moreover, for all anion exchangers and some carboxylic resins based on acrylic and metacrylic acids, phenolcarboxylic and selective exchangers of amino acid, aminooxime, sulphohydril types, the working breakthrough capacity was determined with respect to 0.1 M solution of copper sulphate of $pH = 4.0$.

3. RESULTS AND DISCUSSION

3.1. SORPTION AND DESORPTION OF COPPER–AMMINE COMPLEXES ON POLYSTYRENESULPHONIC RESINS

Formation of coloured layers in the ion exchanger beds indicates sorption of different ionic forms. When synthetic solution was let through polystyrenesulphonic cation exchanger bed in H^+ form, 3 coloured zones were formed: green-brown zone — sorption of Cu^{+2} and NH_4^+ ions, green zone — sorption of Cu^{+2} ions and violet zone — sorption of $[Cu(NH_3)_4]^{+2}$ ions. Sorption of $[Cu(NH_3)_4]^{+2}$ ions on polystyrenesulphonic cation exchanger in H^+ form is described by the following reaction:



It was found that breakthrough capacity obtained for sorption of cupric ions from synthetic solution on polystyrenesulphonic resin in NH_4^+ form was twice lower than the resin capacity for H^+ form. It was chiefly caused by the fact that for

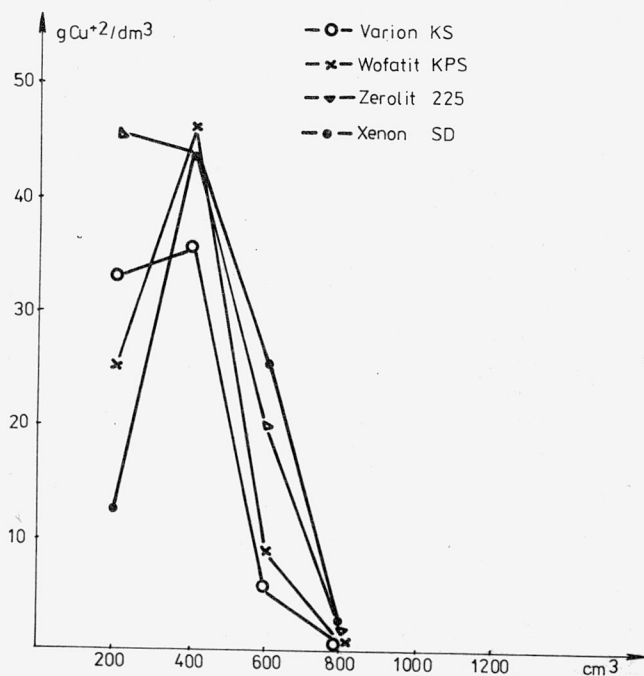


Fig. 1. Copper-amine complex desorption on polystyrenesulphonic resins of gelous matrix with 2 M solution of sulphuric acid

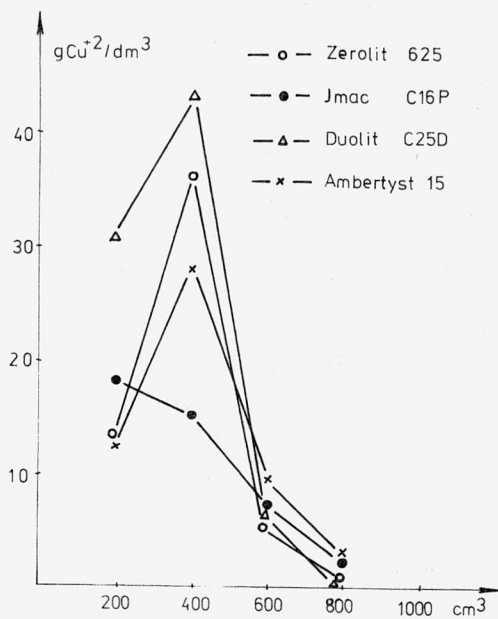


Fig. 2. Cooper-amine complex desorption on polystyrenesulphonic resins of macroporous matrix with 2 M solution of sulphuric acid

Table 1

Breakthrough ion exchange capacities for various resins

Trade name	Manufacturer	Matrix	Capacities given by manufacturers eq/dm ³	Capacities obtained eq/dm ³
Amberlite IR-120	Rohm and Haas, USA	(S+DVB) ¹	1.9	1.25
Amberhpt 15	Rohm and Haas, USA	(S+DVB) ^{1M}	1.9	1.05
Dudite C-250	Dia-Prosim, France	(S+DVB) ^{1M}	1.7	1.20
Imac C 16P	Imacti, Holland	(S+DVB) ^{1M}	2.1	0.86
Xenon SD	Xenon, Poland	(S+DVB) ¹	1.6	1.00
Wofatite KPS	Wolfen	(S+DVB) ¹	1.9	1.30
Varion KS	Chemolimpex, Hungary	(S+DVB) ¹	1.9	1.30
Zerolite 225	Permutit, England	(S+DVB) ¹	2.1	1.65
Zerolite 625	Permutit, England	(S+DVB) ^{1M}	1.9	1.15

¹ — copolymer of styrene with divinylbenzene.^{1M} — copolymer of styrene with divinylbenzene of macroporous matrix.

Cu⁺²-NH₄⁺ pair the difference of polystyrenesulphonic cation exchanger affinities is lower than that of Cu⁺²-H⁺ pair. Moreover, copper-ammine complexes, due to their size and polarization of charges, are sterically limited during their diffusion into resin matrix and are not destroyed on polystyrenesulphonic resin in NH₄⁺ form. It was also stated that in the case of desorption with 2 M sulphuric acid, the concentration of Cu⁺² ions in eluate for resins of gelous matrix was higher than that for macroporous resins (figs. 1, 2). In most cases the obtained breakthrough capacities were by more than 30% lower (see tab. 1) probably due to competitive sorption of ammonium ions.

3.2. SORPTION AND DESORPTION OF COPPER-AMMINE COMPLEXES ON CARBOXYLIC RESINS

In the case of copper sorption from synthetic solution on carboxylic cation exchanger beds, 3 zones of different colours were also formed: white zone (cation exchanger in H⁺ form), blue zone (cation exchanger with mixture of H⁺, NH₄⁺, Cu⁺² ions) and violet zone (cation exchanger in [Cu(NH₃)₄]⁺² form). From the analysis of the composition of violet zone it follows that acrylic cation exchangers sorb mostly [Cu(NH₄)₃]⁺² ions, while metacrylic resins — [Cu(NH₃)₂₋₃]⁺² ions.

In sorption of polyfunctional phenolcarboxylic resins there occurs also the process of reduction. Difference in behaviour of resins may be caused by the fact that the acidity of functional groups of acrylic resins (e.g., Kastel C-101 — pK = 4.5, Amberlite IRC-84 — pK = 5.3) is higher than that of metacrylic resins (Amberlite IRC 50, pK = 6.1).

Breakthrough ion exchange capacity for sorption of $[\text{Cu}(\text{NH}_3)_4]^{+2}$ ions on some carboxylic cation exchangers

Trade name	Manufacturer	Matrix	Ionic group	Capacity for copper waste-water eq $\text{Cu}^{+2}/\text{dm}^3$	Capacity for 0.1 M CuSO_4 eq $\text{Cu}^{+2}/\text{dm}^3$
Amberlite IRC-50	Rohm Haas, USA	(M+DVB) ¹	carboxylic	3.1	0.3
Kastel C-100	Montecatini, Italy	(A+DVB) ²	carboxylic	3.0	0.7
Permutit H	Permutit, USA	(P) ³	phenolcarboxylic	2.9	1.3
Permutit HC	Permutit, USA	(P) ³	phenolcarboxylic	2.8	0.8

¹ — carboxylic resin based on metacrylic acid (M).

² — carboxylic resin based on acrylic acid (A).

³ — phenolcarboxylic (P) condensation resin.

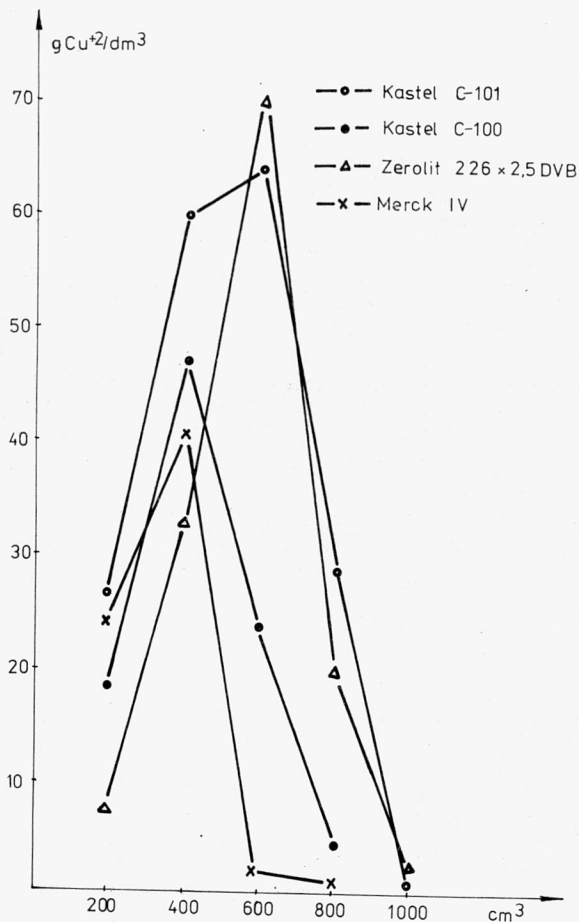


Fig. 3. Copper-ammine complex desorption on carboxylic resins of gelous matrix with 2 M solution of sulphuric acid

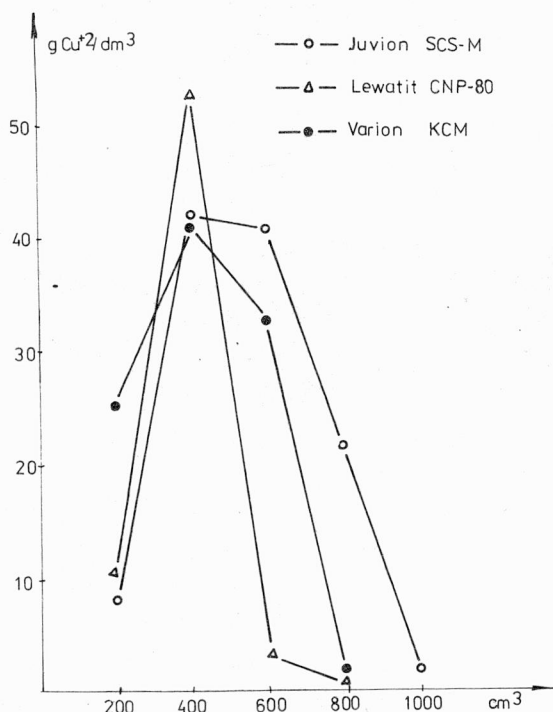


Fig. 4. Copper–ammine complex desorption on carboxylic resins of macroporous matrix with 2 M solution of sulphuric acid

For comparison, breakthrough capacities of carboxylic resins (Amberlite IRC-50 (metacrylic), Kastel C-100 (acrylic), Permutit H, Permutit HC (phenolcarboxylic)) have been determined for sorption of copper ions from synthetic solution and 0.1 M copper sulphate solution of pH = 4.

The results obtained (tab. 2) show that phenolcarboxylic resins (chelation) are characterized by the highest capacities for 0.1 M solution of copper sulphide, and that the capacity of metacrylic resin — Amberlite IRC-50 is the lowest one. It has been also found that when 2 M solution of sulphuric acid was used for desorption of copper–ammine complex from carboxylic resin of gelous matrix the highest concentration of copper ions in eluate was about 70 g/dm³ (fig. 3), whereas in eluate obtained from regeneration with 8 M solution of HCOOH this concentration amounted to about 77 g Cu²⁺/dm³ (fig. 4). The influence of HCOOH concentration and HCOOH/HCOONH₄ ratio on the efficiency of copper ion desorption for macroporous carboxylic resin was also studied (fig. 5).

Although desorption efficiency of copper ions was higher when HCOOH was used, the addition of HCOONH₄ is useful because such a mixture may be recycled directly to copper washing in gas synthesis during the process of ammonia production (removal of CO).

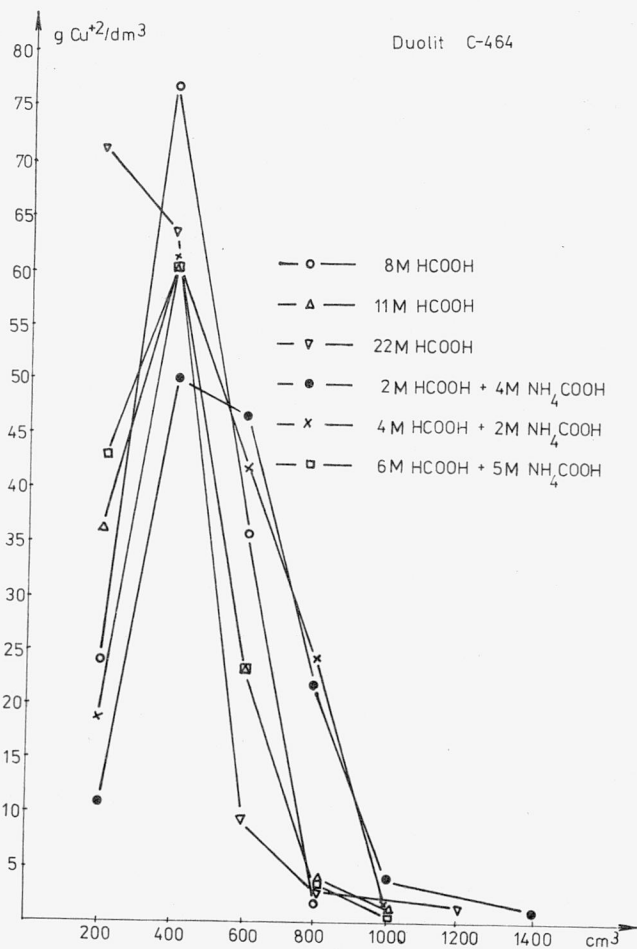


Fig. 5. Copper-amine complex desorption on macroporous carboxylic resin, Duolite C-464, with HCOOH and HCOOH-HCOONH₄

3.3. SORPTION AND DESORPTION OF COPPER-AMMINE IONS ON SELECTIVE RESINS

The investigations involved sorption of copper-amine complexes on chelating ion exchangers such as amino acid (gelous and macroporous matrix), amidooxime and sulphhydryl-type resins. For these ion exchangers breakthrough capacities and swelling degrees were determined (tab. 3). As it follows from tab. 3, Lewatit TP-207 is the best one of all selective resins being tested. Figure 6 presents the curve of copper-amine complex desorption from the ion exchanger by means of 2 M solution of sulphuric acid. The highest concentration of copper in eluate is equal to 60 g/dm³.

Breakthrough ion exchange capacity for sorption of $[\text{Cu}(\text{NH}_3)_4]^{+2}$ ions on some selective resins

Trade name	Manufacturer	Matrix	Ionic group	Capacity for copper wastewater eq $\text{Cu}^{+2}/\text{dm}^3$	Degree of swelling %
Duolite ES-346	Dia-Prosim, France	—	amidoxime	2.0	15.0
Duolite ES-466	Dia-Prosim, France	(S+DVB) ¹	imidodiacetic	1.2	2.5
Lewatit TP-207	Bayer, Germany (West)	(S+DVB) ^{1M}	imidodiacetic	2.1	30.0
Sulphohydryl Wofatit MC-50	WSE, Poland	—	thiol	0.3	5.0
	VEB Chemie Kombinat, Germany (East)	(S+DVB) ¹	imidodiacetic and aminodiacetic	1.6	42.0
Zerolit S-1006	Permutit, England	(S+DVB) ¹	EDTA type	0.4	2.5

¹ — copolymer of styrene with divinylbenzene.

^{1M} — copolymer of styrene with divinylbenzene of macroporous matrix structure.

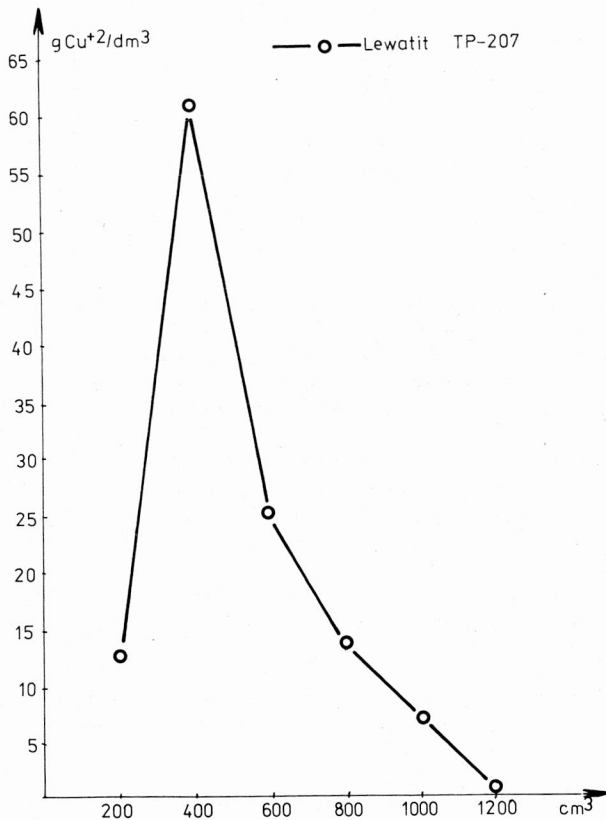


Fig. 6. Copper-amine complex desorption on macroporous chelating resin, Lewatit TP-207, with 2 M solution of sulphuric acid

Breakthrough ion exchange capacity for sorption of $[\text{Cu}(\text{NH}_3)_4]^{+2}$ and Cu^{+2} ions on some anion exchangers

Trade name	Manufacturer	Matrix	Ionic group	Capacity for CuSO_4 solution eq $\text{Cu}^{+2}/\text{dm}^3$	Capacity for ammoniacal copper wastewater eq $\text{Cu}^{+2}/\text{dm}^3$
1	2	3	4	5	6
Amberlite IRA-945	Rohm Haas, USA	(S + DVB) ¹	-N(R ₂)	0.95	—
Amberlite IRA-45	Rohm Haas, USA	(S + DVB) ¹	-NH ₂ , -NH(R), -N(R ₂)	0.65	0.07
Amberlite IRA-68	Rohm Haas, USA	(A + DVB) ²	-N(R ₂)	0.1	—
Amberlite IRA-93	Rohm Haas, USA	(S + DVB) ^{1M}	-N(R ₂)	1.4	0.08
Amberlite IRA-400	Rohm Haas, USA	(S + DVB) ¹	-N(R ₃)Cl	0	0
Amberlite IRA-410	Rohm Haas, USA	(S + DVB) ¹	-N $\begin{cases} (\text{CH}_3)_2\text{Cl} \\ \text{CH}_2\text{CH}_2\text{OH} \end{cases}$	0	0
Amberlite IRA-900	Rohm Haas, USA	(S + DVB) ^{1M}	-N(R ₃)Cl	0	0
Amberlite IRA-910	Rohm Haas, USA	(S + DVB) ^{1M}	-N $\begin{cases} (\text{CH}_3)_2\text{Cl} \\ \text{CH}_2\text{CH}_2\text{OH} \end{cases}$	0	0
Asmit 259N	Imacti, Holland	(S + DVB) ^{1M}	-N(R ₃)Cl	0.1	—
Diaion WA-10	Mitsubishi Chemical Industries, Japan	(A + DVB) ²	weakly basic	0.34	—
Diaion WA-11	as above	(A + DVB) ²	weakly basic	0.2	—
Diaion WA-20	as above	(S + DVB) ^{1M}	weakly basic	0.4	—
Diaion WA-21	as above	(S + DVB) ^{1M}	weakly basic	0.9	—
Diaion WA-30	as above	(S + DVB) ^{1M}	weakly basic	0.2	—
Diaion CR-20	as above	(S + DVB) ^{1M}	polyamine	0.15	0.30
Duolit A-6	Dia-Prosim, France	(F) ³	-N(R ₂)	0.49	0.30
Duolit A-7	Dia-Prosim, France	(F) ³	-NH ₂ , -NH(R), -N(R ₂)	0.2	—
Duolit A-308	Dia-Prosim, France	(F) ³	-N(R ₂)	0.14	—
Duolit A-368	Dia-Prosim, France	(S + DVB) ¹	-N(R ₂)	0.26	—
Duolit S-37	Dia-Prosim, France	(F) ³	-NH(R), -N(R ₂)	0.5	0.55

1	2	3	4	5	6
Imac A-27	Imacti, Holland	(F) ³	-NH ₂ , -NH(R), -N(R ₂), -N(R ₃)	0.12	—
Imac A-20S	Imacti, Holland	(S+DVB) ¹	-N(R ₂)	0.9	—
Imac A-20R	Imacti, Holland	(S+DVB) ¹	-N(R ₂)	0.8	—
Kastel A-101	Montecatini, Italy	(S+DVB) ^{1M}	-N(R ₂)	0.5	0.06
Lewatit MP-62	Bayer, Germany (West)	(S+DVB) ^{1M}	weakly basic	0.9	—
Lewatit 9247HL	Bayer, Germany (West)	(S+DVB) ^{1M}	weakly basic	0.5	—
Merck II	Merck, Germany (West)	(S+DVB) ¹	-NH ₂ , NH(R), -N(R ₂)	0.4	0.05
Ostion AMP	Chemppol, Czechoslovakia		weakly basic	0.46	—
Permutit EM-13	Bermutit, Germany (West)	(S+DVB) ¹	weakly basic	0.5	—
Permutit SK	as above	(S+DVB) ¹	pyridine	0.1	—
Relite MG-1	Resindion, Italy	(A+DVB) ²	weakly basic	0.44	—
Relite 4MS	Resindion, Italy	(S+DVB) ¹	-N(R ₂)	0.4	—
Warion AP	Chemolimpex, Hungary	(S+DVB) ¹	pyridine	0	0
Wofatit AD-41	VEB Chemie Kombinat, Germany (East)	(S+DVB) ^{1M}	-N(R ₂)	1.15	0.05
Zerolit E	Permutit, England	(F) ³	weakly basic	0.1	—

¹ — copolymer styrene with divinylbenzene.

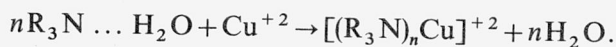
^{1M} — copolymer styrene with divinylbenzene of macroporous matrix.

² — acrylic matrix.

³ — condensation resin based on polyphenol.

3.4. SORPTION OF COPPER-AMMINE AND CUPRIC IONS ON ANION EXCHANGERS

Sorption of copper-amine ions and cupric ions on different types of anion exchangers was also studied. Breakthrough capacities for CuSO_4 and $[\text{Cu}(\text{NH}_3)_4]^{+2}$ ions were determined (tab. 4). The data presented in tab. 4 indicate that the capacity of macroporous weak base anion exchanger Amberlite IRA-93 for aquo-complex of copper is the highest. Sorption of Cu^{+2} ions on the anion exchanger follows the reaction:



Low capacity of this ion exchanger for copper-amine complex may be probably caused by the fact that ammonia molecules compete with ion exchange groups of chelating resins. In fact, it has been found that copper is not sorbed by anion exchangers either from solution of CuSO_4 or copper-amine ions. The highest breakthrough capacity for $[\text{Cu}(\text{NH}_3)_4]^{+2}$ ions stated for weak-base anion exchanger Duolite S-37 may be caused by the fact that some phenol groups can bind copper ions. It has been found that copper can be quickly and effectively eluted with 0.5–2.0 M solution of sulphuric acid. When using less than 2 bed volumes of sulphuric acid solution, 99.9% of copper ions was desorbed from the weakly basic anion exchanger.

4. CONCLUSIONS

Preliminary studies seem to confirm the usability of carboxylic cation exchanger use in removal of copper-amine complexes from wastewater. However, it should be noted that the presented interpretation of ionic equilibria is far from being fully explained. Therefore studies of ion equilibrium under static conditions are necessary for optimization of the process.

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MOŻLIWOŚĆ ODZYSKIWANIA MIEDZI ZE ŚCIEKÓW ZAWIERAJĄCYCH AMMINOKOMPLEKSY MIEDZI

Zbadano sorpcję i desorpcję miedzi ze ścieku amoniakalnego na następujących jonitach: polistyrenosulfonowych o strukturze matrycy żelowej i makroporowatej, karboksylowych na bazie kwasu akrylowego, metakrylowego i fenolokarboksylowego, jonitach chelatujących i na anionitach. Wymieniacze karboksylowe okazały się najlepsze do selektywnego usuwania miedzi ze ścieków zawierających amoniak. Stwierdzono, że prowadząc regenerację tych wymieniaczy 2 M roztworem kwasu siarkowego, uzyskuje się maksymalne stężenie miedzi 50–70 g Cu/dm³.

ВОЗМОЖНОСТЬ РЕКУПЕРАЦИИ МЕДИ ИЗ СТОКОВ СОДЕРЖАЩИХ АМИНОКОМПЛЕКСЫ МЕДИ

Исследована сорбция и десорбция меди аммиачного стока на следующих ионитах: полистиролосульфоновых со структурой гелевой и макропористой матрицы, карбоновых на основе акриловой, метакриловой и фенолокарбоновой кислоты, на внутрикомплексно соединенных ионитах и на анионитах. Карбонообменники оказались наилучшими для отборочной рекуперации меди из стоков содержащих аммиак. Доказано, что, проводя восстановление этих обменников 2м раствором серной кислоты, получается максимальная концентрация меди 50–70 гр Cu⁺²/дм³.