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ION EXCHANGE PURIFICATION OF COPPER CONTAINING RINSE WASTEWATERS FROM ELECTROPLATING PLANTS

Purification of copper containing rinse wastewaters from electroplating plant by means of a combination of different types of ion-exchange resins has been studied.

It has been found that there is no substantial difference in breakthrough capacities of H-, Na- and NH₄-forms of strong acid cation exchangers. The breakthrough capacities of Na- and NH₄-forms of weak acid cation exchangers are higher than the breakthrough capacity of strong acid cation exchangers.

The wastewater treated in ion exchange unit arranged as follows: strong acid cation exchanger-weak base anion exchanger-strong base anion exchanger is characterized by specific conductivity of 3-4 $\mu\text{s/cm}$ and concentrations of Cu²⁺ and SO₄²⁻ below 0.1 mg/dm³ and can be utilized in the process again.

1. INTRODUCTION

The development of the electroplating industry leads to increase in the consumption of water. However, wastewaters of different composition are formed during the process which causes serious environmental pollution. Therefore effective methods of wastewater treatment are of urgent need.

Different physico-chemical and chemical methods [1]-[10] can be applied to the treatment of electroplating industry wastewaters, particularly to copper containing rinse wastewaters.

Taking into account the possibilities of the ion exchange process, a few authors are involved in research on ion exchange purification of copper containing wastewaters [3]-[4]. Strong acid cation exchanges as well as weak acid cation exchangers or anion exchangers have been used for this purpose. It has been established that the application of a definite type of ion exchanger depends on the

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wastewater characteristics (ion concentration, pH, presence or absence of complex-forming ions, etc.). The choice of the proper ion exchanger is strongly dependent on the requirements for the characteristics of the purified water.

2. MATERIALS AND METHODS

Ion exchange purification of copper containing rinse wastewaters (concentration of Cu^{2+} — 50 mg/dm³, concentration of SO_4^{2-} — 125 mg/dm³, specific conductivity — 450 $\mu\text{s}/\text{cm}$) has been studied.

The wastewater has been treated either with strong acid cation exchangers (Amberlite 200 C, Duolite C-26, Wofatit KS-10, Lewatit S-100, Varion KSM) or with weak acid cation exchangers (Wofatit CA-20 and Varion KCO) in various ion forms (H-, Na- and NH_4 -forms for strong acid cation exchangers and Na- and NH_4 - forms for weak acid cation exchangers). The use of weak acid cation exchangers in H-form under given conditions proved to be senseless because at low pH values (below 4) the ion exchange process is obstructed.

Four series of experiments have been carried in the following systems:

Wofatit KS-10(R—H)—Wofatit AD-41(R—OH)—Wofatit SBW(R—OH), (I)

Amberlite 200 C(R—H)—Amberlite IRA-93(R—OH)—Amberlite IRA-900(R—OH), (II)

Wofatit CA-20(R—Na)—Wofatit AD-41(R—OH)—Wofatit SBW(R—OH), (III)

Varion KCO(R—H)—Varion ADAM(R—OH)—Varion ATM(R—OH). (IV)

The experiments have been carried out under dynamic conditions in ion exchange columns (22 mm diameter) charged with 200 cm³ of the proper ion exchanger converted to the suitable ion form. The copper containing wastewater passes downward through the columns at load of 15 dm³/dm³ · h. In the wastewater purified in such a way, Cu^{2+} and SO_4^{2-} concentrations are determined [12], [13] and its specific conductivity is measured.

The breakthrough capacities of the ion exchangers tested in the different ionic forms have been determined.

3. RESULTS AND DISCUSSION

The results of the experiments are shown in tables 1 and 2 and in figures 1–4.

It has been established that the breakthrough capacities of H-, Na- and NH_4 -forms of strong acid cation exchangers do not differ noticeably. The breakthrough capacities of Na- and NH_4 -forms of weak acid cation exchangers are higher than the breakthrough capacities of strong acid cation exchangers (table 1).

Taking into account the requirements established for recycle water quality (specific conductivity up to 50 $\mu\text{s}/\text{cm}$) and the limitations put on concentration of copper ions in open cycles of water consumption, it was possible to carry out

the experiments in the above mentioned systems (I–IV) consisting of cation and anion exchangers arranged in series.

Table 1

Ion exchangers	Breakthrough capacities [eq/dm ³]			
	Ionic form of ion exchangers			
	R—H	R—Na	R—NH ₄	R—OH
Amberlite 200 C	1.30	1.34	1.35	—
Duolite C-26	1.35	1.37	1.37	—
Wofatit KS-10	1.21	1.24	1.24	—
Lewatit S-100	1.40	1.42	1.44	—
Varion KSM	1.38	1.40	1.40	—
Wofatit CA-20	—	1.73	1.37	—
Varion KCO	—	1.81	1.42	—
Amberlite IRA-93	—	—	—	1.08
Wofatit AD-41	—	—	—	1.04
Amberlite IRA-900	—	—	—	0.50
Wofatit SBW	—	—	—	0.45

It has been established that use of systems I, II, III and IV allows purification of 870, 950, 1280 and 1300 bed volumes of wastewater, respectively. Moreover, Cu²⁺ concentration in the purified water is below 0.1 mg/dm³ (table 2). Thus, when the system operates basing on weak acid cation exchanger (systems III and IV), the quantity of purified wastewater is 1.5 times larger than in the system basing on strong acid cation exchangers (systems I and II, table 2, figures 1, 2).

Table 2

A quantity of the purified copper containing rinse wastewater by using the systems I–IV

No.	System	Bed volumes	
		Specific conductivity [$< 50\mu\text{s/cm}$]	Breakthrough point of Cu ²⁺ [$< 0.1 \text{ mg/dm}^3$]
I	Wofatit KS-10–Wofatit AD-41–Wofatit SBW	700	870
II	Amberlite 200 C–Amberlite IRA-93–Amberlite IRA-900	780	950
III	Wofatit CA-20–Wofatit AD-41–Wofatit SBW	—	1280
IV	Varion KCO–Varion ADAM–Varion ATM	—	1300

There is no doubt that the quantity of purified wastewater is larger when systems II and IV are in operation. Their application is recommended if presence of Na⁺ ions in the purified water is allowed (i.e. in open cycles of water consumption).

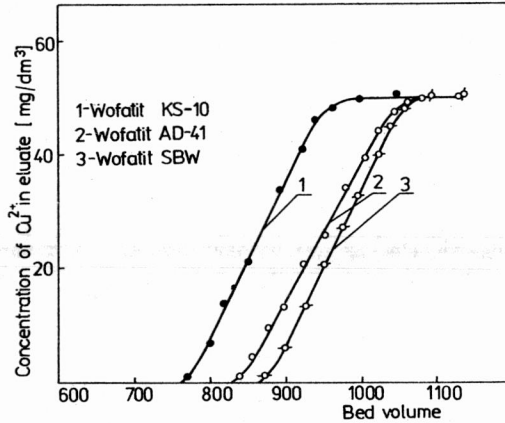


Fig. 1. Concentration of Cu^{2+} ions in eluate after wastewater passing through Wofatit KS-10 (1), Wofatit AD-41 (2), Wofatit SBW (3)

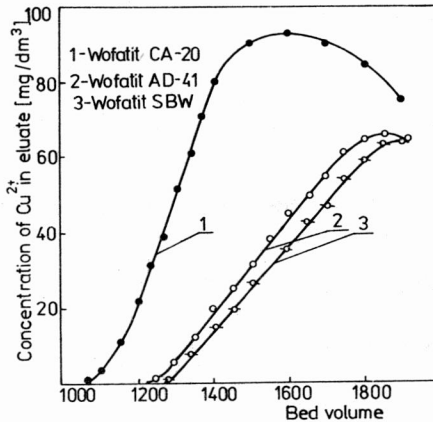


Fig. 2. Concentration of Cu^{2+} ions in eluate after wastewater passing through Wofatit CA-20 (1), Wofatit AD-41 (2), Wofatit SBW (3)

In the case of water recycle (specific conductivity below $50 \mu\text{s}/\text{cm}$) it is better to apply system I or II, thus obtaining desalinated water.

Figure 3 and table 2 show that by applying systems I and II it is possible to purify approximately 700 and 780 wastewater bed volumes, respectively. The purified water is characterized by specific conductivity (up to $50 \mu\text{s}/\text{cm}$). Moreover, the specific conductivity of the purified water during filtration cycle is ranging from 3 to $4 \mu\text{s}/\text{cm}$, and concentration of Cu^{2+} ions is below $0.1 \text{ mg}/\text{dm}^3$.

It has been established that increase in the value of specific conductivity of treated water is due to SO_4^{2-} breakthrough and can be observed only after purification of 870 and 950 bed volumes for systems I and II, respectively.

The SO_4^{2-} breakthrough capacities of the anion exchangers tested have been calculated basing on the results of the experiments. These values are as follows: 1040, 1080, 450 and 500 meq/dm³ (table 1) for Wofatit AD-41, Amberlite IRA-93, Wofatit SBW and Amberlite IRA-900, respectively.

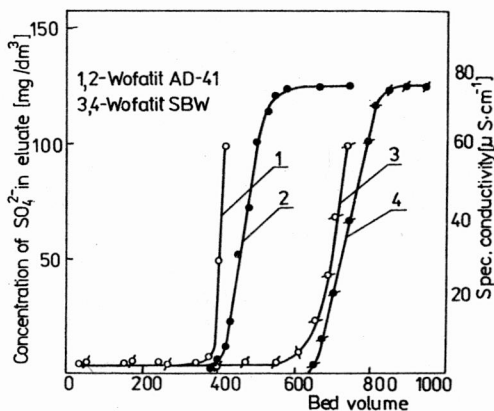


Fig. 3. Specific conductivity and concentration of Cu^{2+} ions in eluate after wastewater passing through Wofatit KS-10–Wofatit AD-41–Wofatit SBW system

1, 2 – conductivity and concentration of Cu^{2+} ions after Wofatit AD-41, 3, 4 – conductivity and concentration of Cu^{2+} ions after Wofatit SBW

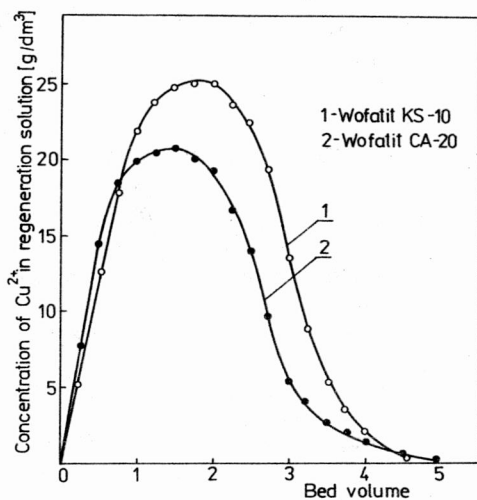


Fig. 4. Regeneration curves of Wofatit CA-20 (1) and Wofatit KS-10 (2)

A comparison of the results shown in figures 1 and 2 accentuates a certain difference in the saturation curves of the strong acid cation exchanger, Wofatit

KS-10, and the weak acid cation exchanger, Wofatit CA-20. This difference can be caused by partial regeneration of Na-form of Wofatit CA-20 due to the presence of sulphuric acid in the water treated.

Figures 1 and 2 show that a certain amount of Cu^{2+} ions is bonded by both anion exchangers, which is most probably possible due to a process of complex formation [14].

The cation exchangers tested have been regenerated by means of 10% H_2SO_4 (load $4 \text{ dm}^3/\text{dm}^3 \cdot \text{h}$). The regeneration curves (figure 4) show that concentration of Cu^{2+} ions in the first two bed volumes of the regeneration solution is about $20 \text{ g}/\text{dm}^3$.

The anion exchangers have been regenerated by means of 5% NaOH (load $4 \text{ dm}^3/\text{dm}^3 \cdot \text{h}$). The concentration of SO_4^{2-} ions in the regeneration solution ranged from 10 to $20 \text{ g}/\text{dm}^3$ and the concentration of Cu^{2+} ions, from 1 to $1.5 \text{ g}/\text{dm}^3$.

4. CONCLUSIONS

Basing on the experimental results, it can be concluded that Wofatit KS-10(R—H)—Wofatit AD-41(R—OH)—Wofatit SBW(R—OH) and Amberlite 200 C (R—H)—Amberlite IRA-93(R—OH)—Amberlite IRA-900(R—OH) systems can be applied to purification of copper containing rinse wastewaters when the water purified is recycled.

Wofatit CA-20(R—Na)—Wofatit AD-41(R—OH)—Wofatit SBW(R—OH) and Varion KCO(R—Na)—Varion ADAM(R—OH)—Varion ATM(R—OH) systems can be applied when the presence of Na^+ ions in the purified water is permissible (in open cycles of water consumption).

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OCZYSZCZANIE ZAWIERAJĄCYCH MIEDŹ WÓD POPLUCZNYCH Z GALWANIZERNI METODĄ WYMIANY JONOWEJ

Metodą wymiany jonowej zbadano proces oczyszczania wód poplucznych z galwanizerni zawierających miedź. Zastosowano połączenie różnych typów żywic jonowymiennych.

Stwierdzono, że nie ma istotnych różnic w wartościach pojemności jonowymiennych silnie kwaśnych kationitów o różnych formach jonowych (H, Na, NH₄). Pojemności jonowymiennie słabo kwaśnych kationitów w formie Na i NH₄ są większe od pojemności jonowymiennych silnie kwaśnych kationitów.

Ścieki oczyszczone w następującym układzie jonitów: silnie kwaśny kationit–słabo zasadowy anionit–silnie zasadowy anionit wykazywały przewodnictwo właściwe rzędu 3–4 μs/cm, stężenie jonów Cu²⁺ i SO₄²⁻ zaś było mniejsze niż 0,1 mg/dm³. Oczyszczone ścieki mogą być ponownie wykorzystane w procesie technologicznym.

ИОНООБМЕННАЯ ОЧИСТКА ПРОМЫВНЫХ СТОЧНЫХ ВОД ГАЛЬВАНИЧЕСКОЙ ПРОМЫШЛЕННОСТИ, СОДЕРЖАЩИХ ИОНЫ МЕДИ

Исследована возможность очистки промывных сточных вод из гальванической промышленности, содержащих медь, при их обработке комбинациями разных типов ионообменных смол.

Было установлено, что нет существенных различий в значениях ионообменных емкостей сильноокислых катионитов разных ионных форм (H, Na, NH₄). Ионообменные емкости слабоокислых катионитов Na- и NH₄-форм выше ионообменных емкостей сильноокислых катионитов.

Сточные воды, очищенные в следующей системе: сильноокислый катионит–слабощелочной анионит–сильнощелочной анионит, обнаруживали удельную проводность порядка 3–4 μs/cm, следовательно, концентрация ионов Cu²⁺ и SO₄²⁻ была меньше 0,1 мг/дм³. Очищенные сточные воды можно снова использовать в технологическом процессе.