

ENVIRONMENTAL PROBLEMS
OF CHEMISTRY AND TECHNOLOGY

Ways to Develop Low-Waste Technology for Purification of Wastewater Containing Heavy Metal Compounds

N. E. Manvelova, I. V. Vol'f, and M. A. Sinyakova

Maikop State Technological Institute, Maikop, Russia

St. Petersburg State University of Plant Polymers, St. Petersburg, Russia

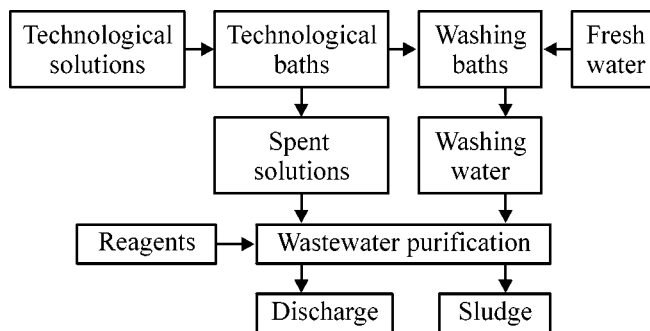
Received February 6, 2001

Abstract—A scheme is proposed for purification of wastewater of galvanic and printed circuit board shops. The scheme using reverse osmosis, ion exchange, and electrolysis techniques involves recycling of purified water and recovered metals.

Contamination of natural water with sewage water of galvanic industries is an ecological challenge. Discharge of this wastewater, containing highly toxic salts of heavy and non-ferrous metals, has a severe impact on the environment and leads to irretrievable loss of valuable metals in amounts of tens of thousands of tons.

The discharge of metals into water bodies of St. Petersburg was 3310.53 tons in 1999 [1]. The decline in galvanic manufacture in the succeeding years did not result in a proportional decrease in the environment contamination.

Most of domestic galvanic enterprises make use of outdated wastewater treatment facilities of 30–40-years-old conventional design. These bulky and cost-inefficient facilities fail to meet modern requirements to water recycling and heavy metal recovery. An essential drawback of such systems is the formation of a common wastewater flow including waste electrolytes, acidic and basic wastes, and rinsing water (see scheme). Mixing of wastes containing different ions in various concentrations hampers extraction of pollutants, and the mixed flow cannot be recycled even after reagent purification [2]. Purified wastewater is discharged into a sewer system or directly into a water body. Sediments formed in wastewater purification, i.e., sludges containing a combination of various heavy metal compounds, are transported to sludge stores, wherefrom these compounds are gradually washed out by ground waters and, all the same, find their way into the environment. Sludge processing is technologically complicated and economically inefficient.



Scheme of water use in degrading, etching, and electroplating.

Owing to the absence of water recycling, most of domestic galvanic plants consume fresh water in amounts of 2 m³ and more per 1 m² of treated surface area, whereas in Sweden the same parameter is 0.05 m³ m⁻². A promising engineering solution of the problem under discussion consists in passing at galvanic shops to local purification systems recycling purified wastewater and recovering heavy metals. Local systems are intended for purification of wastewater with relatively invariable composition, produced by a certain technological line or separate installation, which allows use of compact purifying systems based on more effective and expensive purification techniques. The recoument of such systems can be ensured by reduction of charges for the intake of pure water and disposal of wastewater and sludges. Moreover, wastewater produced by a particular technological line or separate installation usually contains ions of a single metal, rather than a mixture of metal ions, which significantly simplifies

its purification and creates new possibilities for further use of the recovered metals.

There are several efficient methods of purification, namely: adsorption and ion exchange [2–4], isolation of impurities by changing their aggregative state (distillation and freezing) [1, 2], and membrane techniques (electrodialysis, ultrafiltration, and reverse osmosis) [2, 5–9]. Comparative data [1] on capital investments and degree of nickel(II) removal from washing water are given in Table 1. The consumption of washing water was $0.2 \text{ m}^3 \text{ h}^{-1}$, and the initial concentrations of Ni(II) and organic compounds, 32 and 54 mg l^{-1} , respectively. The cost of wastewater purification by ion exchange was conditionally taken to be unity.

Naturally, the relative costs and residual concentrations may vary with discharge parameters.

EXPERIMENTAL

The aim of this work was to study the possibility of, and conditions for creation of a low-waste technology for purification of wastewater produced by galvanic industry and printed circuit board manufacture.

The proposed purification scheme involves use of reverse osmosis for washing water purification, ion exchange for concentrating metal ion solutions, and electrochemical methods for metal recovery from concentrates of washing water and spent technological solutions.

The advantages of reverse osmosis consist in that no chemical reagents are required, the installations are compact, and water can be purified to remove impurities of varied nature.

Membranes used for reverse-osmosis purification retain any particles larger than $0.001 \text{ }\mu\text{m}$: inorganic ions, molecules of organic substances, and colloid particles. This leads to a high degree of purification and water becomes suitable for recycling.

Among disadvantages of reverse osmosis are the possibility of precipitate formation on membranes owing to the concentration polarization and the resulting necessity for periodic regeneration of the membranes.

We determined the most favorable conditions of reverse-osmosis purification of washing water of galvanic shop on a pilot installation comprising filters for rough and fine mechanical pre-purification and a reverse-osmosis apparatus with roll elements (see figure).

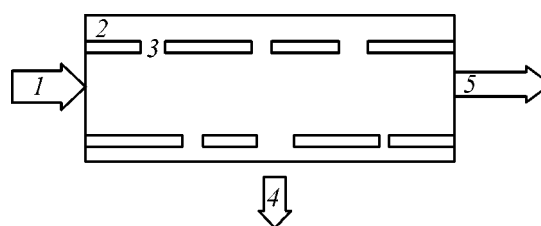
Table 1. Relative costs of purification of nickel-containing the washing waters by various methods and the attained degree of purification

Method	Relative cost	Residual concentration, mg l^{-1}	
		Ni(II)	organic substances
Ion exchange	1	0.008	–
Reverse osmosis	2–3	0.05	1.2
Electrolysis	3–4	0.3	–
Electrodialysis	5–10	0.55	6.7
Evaporation	8–12	0.1	4.1

Table 2. Reverse-osmosis purification of local washing water discharges

Source of washing water	Metal ion	$C_{M^{n+}}$, mg l^{-1}		Selectivity, %	pH
		initial solution	filtrate		
Acid etching line	Cu(II)	14.0	0.22	98.4	7.8
Nickel plating line	Ni(II)	10.2	0.44	95.7	7.05
Chromium plating line	Cr(VI)	18.0	1.6	91.1	5.6
Zinc plating line	Zn(II)	13.0	0.1	99.2	7.0

Comparative tests of the most widespread cellulose acetate membranes MGA-70, MGA-80, MGA-90, and MGA-100 demonstrated that MGA-100 membranes are the most effective under the test conditions, and these membranes were used in further studies. The possibility was established of purifying washing water containing various metal ions (Table 2). In all the experiments, the selectivity of a membrane, characterizing its separating ability, exceeded 90%, and the low residual content of metal ions in filtrates allowed their recycling as washing water.



Schematic of a reverse-osmosis element: (1) wastewater input, (2) reverse-osmosis apparatus, (3) membrane, (4) purified filtrate, (5) concentrate.

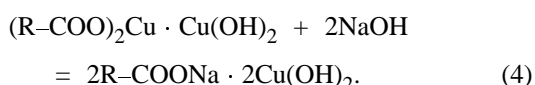
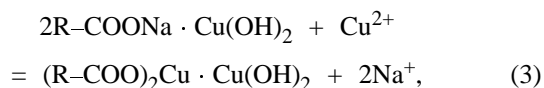
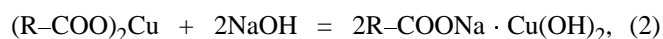
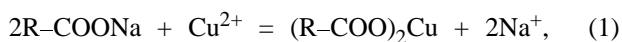
The experiments demonstrated that the residual content of metal ion in the filtrate, $C_{M^{n+}}$, is in inverse relationship with the effluent concentrate fraction—the ratio of the concentrate volume to the volume of washing water to be purified. In most cases, this fraction was maintained at a level of 10–15%.

Our study of the efficiency and selectivity of membranes in relation to reverse-osmosis purification determined the following optimal parameters: pressure 2.0–2.5 MPa, velocity of purified water flow along membrane 0.8–1.2 m s⁻¹, water temperature 12–27°C. In this case the degree of purification to remove salts of heavy metals is no less than 90%, and the extent of recycling of purified water, no less than 90%.

Comparative tests of the efficiency of membrane regeneration with solutions of oxalic, citric, and malic acids allow us to recommend a 2% solution of oxalic acid for practical use. A complete restoration of the initial properties of membranes can be achieved if regeneration with this solution is carried out once a month.

In most cases, more effective isolation of metals from concentrates obtained in reverse-osmosis purification can be performed if the concentration of metal ions is no less than 4–10 g l⁻¹. In this case, concentration can be carried out in the second stage of a reverse-osmosis installation or on an ion-exchange installation.

Heavy metal ions can be recovered from primary concentrates using various types of ion-exchange resins. We have shown previously [10] that carboxylic cation-exchange resins in Na form are extremely selective in sorption of copper(II) and other metal ions forming sparingly soluble hydroxides in hydrolysis. If hydroxides or basic salts of the metals being extracted are poorly soluble in alkalis, they can be accumulated in a cationite phase in amounts exceeding severalfold the exchange capacity in a single sorption by treating a cationite alternately with primary concentrates containing ions of a metal to be extracted and with alkali solutions.



For example, a triple sorption of copper(II) ions on a KB-4P-2 cationite, following equations (1)–(4), allowed us to raise the copper(II) concentration in the cationite matrix to 10 mg-equiv g⁻¹ or 320 mg g⁻¹ (in terms of dry cationite) [10].

At a comparatively small (in terms of volume or weight) required of amount ionites, it may be expedient to use relatively expensive new-generation ion-exchange resins. These resins have high exchange capacity, good kinetic characteristics, and granules of uniform size; the last factor ensures low hydraulic resistance of an ionite layer in filtration.

To recover metal ions from concentrates formed in purification by reverse osmosis and ion-exchange and containing about 4–4.5 g l⁻¹ of metal ions, we used direct electrolysis on installations equipped with metal cathodes and graphite anodes. Discharge of metal ions (Cu, Ni, Zn, or Cr) and deposition of a metal occurred on the metal cathode. The current efficiency by metal was determined by gravimetry.

The experiments demonstrated that use of cathodes with smooth surface at a cathode current density of 0.3–1.5 A dm⁻² allows recovery of up to 80–85% of metals at current efficiency of 30–70%. In this case, the specific energy consumption for metal recovery is 4–8 kW h kg⁻¹.

With bulk flow-type complex-shape cathodes, the current density can be decreased to 0.02–0.5 A dm⁻², with the degree of metal recovery of 95–98% and current efficiency of 50–80%.

Metals deposited at the cathode had relatively high purity (up to 99.5%), and, therefore, could be used as soluble anodes in metal plating.

Spent etching solutions formed in printed circuit board manufacture can be recovered by direct electrolysis with cooled titanium cathodes and graphite anodes at 40–45°C, current density of 9.5–11 A dm⁻², and rate of spent solution supply of 5–10 l min⁻¹.

In this case, cathode deposition of copper and anode recovery of etching reagent occur simultaneously. The productivity of copper recovery was 3 kg h⁻¹ at a current efficiency of 85%.

The results of the investigations performed allowed us to design an automated compact (required area of 95 m²) installation for physicochemical purification of wastewater containing heavy metals.¹

¹ The project will be implemented at the galvanic shop of Krasnoe znamya plant (Ryazan).

CONCLUSIONS

(1) Conditions were found for the effective joint use of reverse osmosis, ion exchange, and electrolysis for deep purification of wastewater containing heavy metal ions and for recovery of these metals.

(2) A low-waste technology for purification of wastewater of galvanic industry and printed circuit board manufacture, assuming recycling of purified water and recovered metals, was proposed for practical implementation.

REFERENCES

1. *Rekomendatsii po sokrascheniyu sbrosa metallov pri rabote gal'vanicheskikh predpriyatii* (Recommendations for Diminishing Metal Wastes at Galvanic Plants), Baev, A.S., Ed., St. Petersburg: Ekopolis i Kul'tura, 2000.
2. *Gibkie avtomatizirovannye linii* (Versatile Automated Lines), Zubchenko, V.L., Ed., Moscow: Mashinostroenie, 1989.
3. Sinyakova, M.A., Mikryukova, E.B., Vol'f, I.V., and Manvelova, N.E., *Zh. Prikl. Khim.*, 2000, vol. 73, no. 3, pp. 388–391.
4. Kazakov, E.V. and Pekarskii, L.D., *Promyshlennost' stroitel'nykh materialov: Ochistka stochnykh vod gal'vanicheskikh proizvodstv i regeneratsiya metallov iz nikh*, (Building Material Industry: Purification of Wastewaters of Galvanic Manufactures and Regeneration of Metals from them), Moscow: VNIINTI Ekonomiki Promyshl. Mater., 1988, ser. 10, no. 2.
5. Povarov, A.A., Kolomiitsev, A.G., Kuznetsov, M.S., et al., *Progress. Prirodookhran. Tekhnol., Akad. Nauk SSSR*, 1991, no. 9, ref. 95, pp. 131–135.
6. Naidenko, V.V., Bednova, L.I., Erekhinskii, A.V., et al., *Vodosnabzh. Santekhn.*, 1984, no. 6, pp. 3–6.
7. Manvelova, N.E., *Materialy konferentsii "Khozyaistvennopit'eve i stochnye vody, problemy ochistki i ispol'zovaniya"* (Proc. Conf. "Industrial, Drinking, and Waste Water: Problems of Purification and Use"), Penza, 2000, pp. 90–92.
8. Manvelova, N.E. and Vol'f, I.V., *Materialy mezhdunarodnoi konferentsii "Membrannye i sorbtionnye protsessy"* (Proc. Int. Conf. "Membrane and Sorption Processes"), Krasnodar, 2000, pp. 18–19.
9. RF Patent 2 088 537.
10. Sinyakova, M.A. and Vol'f, I.V., *Ionn. Obmen Ionometr.*, 2000, no. 10, pp. 96–107.