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ELECTROCHEMICAL NEUTRALISATION OF "SOUR" WASTEWATER

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The article considers the electrochemical method for neutralising "sour" industrial wastewater. The authors analysed the dependencies of the conductivity of industrial wastewater on the neutralisation time on platinum and steel electrodes.

Introduction

Modern oil refining processes often generate toxic waste, the storage and/or disposal of which can be very harmful for the environment. In the Yaroslavl region, there are sour-fertiliser ponds of the oil refinery "PJSC named after D.I. Mendeleyev" [1]. This company specialises in the production of so-called white petroleum oils - transformer, medical, vaseline, insulating, perfumery and a range of other petroleum products. A sulphuric acid method using sulphuric acid and oleum was used for their cleaning [2]. The disadvantage of this method is the generation of a large-tonnage waste, sour tar, which is accumulated in storage ponds belonging to the plant (Fig. 1, 2). As time passed, the contents of the ponds stratified, producing "sour" water in the middle layer. It contains significant quantities of petroleum products and sulphuric acid.

The ponds are located in close to the Pechegda River. It is flowing into the Volga River [3]. When snow melts and/or precipitation is present, the level of "sour" water in the ponds rises, thus creating the risk of its overflowing into the Pechegda, further polluting the Volga [1, 2].

Fig. 1. A storage pond for "sour" sludge and "sour" water

Fig. 2. The "sour" water drains into the Pechegda River and then into the Volga River

Experimental part

In order to eliminate this problem, we developed an original electrochemical method of "sour" water neutralising [4]. The method includes the acid number and electrical conductivity of the raw material and ensures the necessary purification of water suitable for further use.

We preliminarily cleaned water of oil products by adsorption using different adsorbents. The composition and properties of the "sour" water were determined according to the standard methods (Table 1).

Table 1. Pollutants in "sour" water

№ Sample	pH	Oil products, mg/dm^3	Surface-active substances, mg/dm^3	Sulphates, mg/dm^3
1	2.9	14.4	60.3	944.8
2	2.7	14.1	57.7	980.1
3	3.0	11.3	59.7	937.6

"Sour" water from the storage ponds of oil refinery "PJSC named after D.I. Mendeleyev" is an electrically conductive medium, as it has an acid number of about 60 mg KOH/g. The authors made an attempt to neutralise water electrochemically without the neutralising reagent [5]. We used 60 V AC at 50 Hz on 0.165 m^2 platinum or steel electrodes, spaced 5 cm apart. The current was up to 40 A. The neutralisation time was 45 min on platinum electrodes and 40 min on steel electrodes [6].

The process was accompanied by an intense release of hydrogen, which in this case plays the role of a flotation gas.

Hydrogen release is a multistage process consisting of the transport of water molecules or hydroxonium ions to the cathode surface; the conversion of the hydroxonium ion into a hydrogen atom adsorbed on the metal surface.

Hydrogen diffusion causes the mixing of "sour" water. The neutralisation of the acidic components is achieved by the formation of OH-groups [7].

During electrolysis of "sour" wastewater, at the anode:

$$4OH^- - 4e \rightarrow 2H_2O + O_2\uparrow$$
$$2SO_4^{2-} - 2e \rightarrow S_2O_8^{2-}$$

The probability of the sulphate groups being discharged at the anode is low, so the hydroxyl groups are discharged first, according to the extraction potential, and the anode stream is acidified. At the cathode, electrons are attached to positively charged solution ions:

$$2H^+ + 2e \rightarrow H_2\uparrow$$

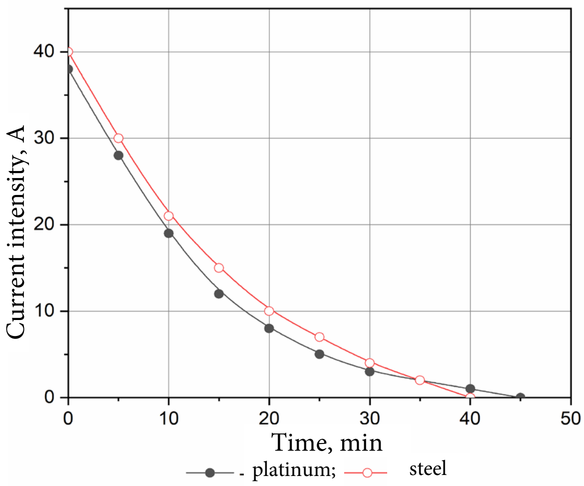

Fig. 3. Current intensity changes as a function of neutralisation time

The reduction of the electrode current to zero (40 min for steel electrodes and 45 min for platinum electrodes) indicates the end of the neutralisation process. The conductivity decreased to zero simultaneously (Fig. 3-5).

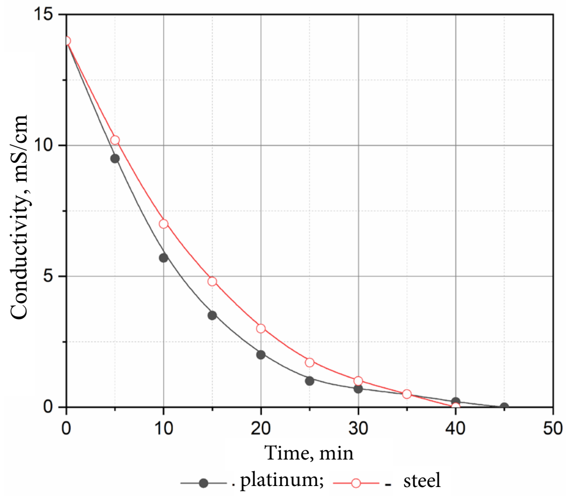

Fig. 4. "Sour" water conductivity change

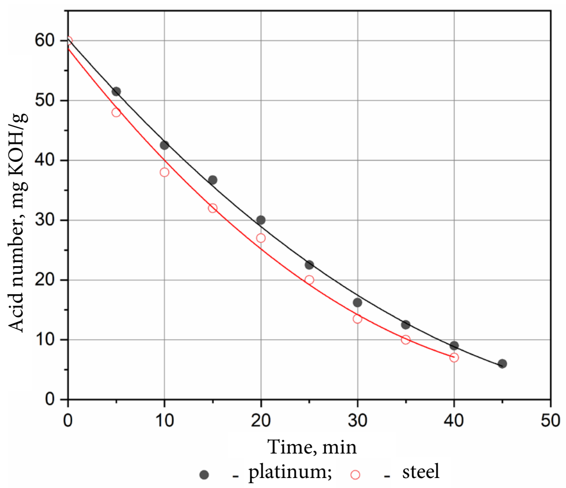

Fig. 5. Acid number change as a function of neutralisation time

Tables 2, 3 show the results of the electrochemical neutralisation and its efficiency parametres.

Table 2. Electrochemical neutralisation efficiency

Pollutant	Content, mg/dm^3			Efficiency neutralisation, %	
	before neutralisation	after 45 minutes (platinum electrodes)	after 40 minutes (steel electrodes)	platinum electrodes	steel electrodes
Oil products	5	1.2	1.6	76	68
Sulphate ions	330	0	30	100	90.9
Surface-active material	26	15.5	17	40.4	34.6
Sulfuric acid (H_2SO_4)	38	3	4	99.2	98.9

Table 3. Parameters of "sour" water after electrochemical neutralisation

Parameters	Parametres value		
	before neutralisation*	after 45 minutes (platinum electrodes)	after 40 minutes (steel electrodes)
Current, A	38/40	0	0
Electrical density, A/m^2	230/242	0	0
Electrical conductivity, mS/cm	14	0	0
Acid index, mg KOH/g	60	6	6
Electrode resistance, Om	0,79/1,5	200	200
Temperature,°C	+18	+98	+95
pH	2	7	7

* Numerator is for platinum electrodes; denominator is for steel electrodes.

Conclusion

The results suggest the electrochemical neutralisation of "sour" water is effective (particularly on platinum electrodes). The difference compared to the process on steel electrodes is up to 8% in compare with methods based on the neutralising agents use [8]. The industrial application of platinum electrodes is eliminated. However, the neutralisation on steel electrodes is faster.

The developed technology for neutralising “sour” water, a large-tonnage waste product of the oil refining industry, provides environmental protection, sustainability and preservation of public health.

References

1. About the Yaroslavl Oil Refinery named after D.I. Mendeleev. URL: http://npz-mendeleev.ru/?a=about (in Russian).
2. **Filippova O.P.** Complex utilization of acid tar - a large-tonnage waste of the process of oil production: doctoral thesis: 03.00.16. Ivanovo, 2008. 32 p. (in Russian).
3. **Singh S., Sharma L.K., Saraswat A., Siddiqui I.R., Singh R.K.P.** Electrochemical behaviour of aldenite-n-arylhydrazones at platinumelectrode and their characterisation. Elektrokhimiya. 2014. T. 50. N 9. P. 924-931. DOI: 10.7868/S0424857014090096 (in Russian).
4. **Galikova E.V., Filippova O.P.** Acidic sludge formation in acidic ponds, neutralization of acidic sludge by electrochemical method. Pyataya Vserossijskaya studencheskaya nauchno-tekhnicheskaya konferenciya "Intensifikaciya teplo-massoobmennyh processov, promyshlennaya bezopasnost' i ekologiya", Kazan, May 23-25, 2018: sb. materialov konf., sekciya 4. Kazan: KNITU, 2018. P. 364-366 (in Russian).
5. **Kuz'mina E.V., Karaseva E.V., Chudova N.V., Ivanov A.L., Kolosnitsyn V.S.** Petroleum coke as the active material for negative electrodes in lithium-Sulfur batteries. Elektrokhimiya. 2021. T. 57. N 3. P. 131-141. DOI: 10.31857/S0424857021030063 (in Russian).
6. **Tyunina E.Y., Chekunova M.D.** Electrical conductivity and decomposition potentials of LIASF6 solutions in a mixed solvent propylene carbonate-N,N-dimethylformamide. Elektrokhimiya. 2021. T. 57. N 3. P. 152-161. DOI: 10.31857/S0424857021030129 (in Russian).
7. **Sakhibgareev S.R., Tsadkin M.A., Badikova A.D., Osipenko E.V.** Some regularities of destructive-catalytic processing of petroleum raw materials on modified catalysts based on alkali earth metal chlorides. Bashkirskij khim. zhurn. 2020. T. 27. N 3. P. 47-51. DOI: 10.17122/bcj-2020-3-47-51 (in Russian).
8. **Pochitalkina I.A., Artamonov A.V., Bessolova Y.A., Torochkov E.L.** Technology of waste water neutralisation with sludge recycling. Trudy Kol'skogo nauchnogo centra RAN. 2020. T. 11. N 3-4. P. 18-23. DOI: 10/37614/2307-5252/2020/4/4/003 (in Russian).

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