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Methods of Reducing the Impact of Waste Water of Metallurgical and Coke Production on the Environment of Surface Waters and the Waters of Azov Sea

Key words*: Wastewater, sulfide, anaerobe, sorbent, oxidation.*

Annotation: *The paper deals with the problem of the influence of metallurgical and coke plants of METINVEST HOLDING (Mariupol, Ukraine) on the ecological situation of water bodies - the Kalchyk and Kalmius rivers and the coastal zone of the Sea of Azov. Various methods (anaerobic microbiological method, using sorbents and oxidation method) of elimination of sulfur compounds from industrial wastewater was shown and their effectiveness was assessed.*

1. Introduction

The current environmental situation in Ukraine can be described as a critical, formed over a long period due to neglect of the objective laws of development and reproduction of natural resources of Ukraine. There was a structural deformation of the economy of Ukraine, in which the priority was granted to the development of raw materials extraction. Just this industry is considered to be the most environmentally dangerous.

Iron and steel industry (including ferrous and nonferrous metallurgy, coking and rolling production, as well as related ancillary facilities and processes) is one of the most polluting industries which emissions from stationary sources of pollution reaches up to 38 % of the total amount of pollutants (1).

Currently, since 2004 Mariupol is the city which is characterize by the highest level of air pollution and water bodies from stationary pollution sources on the background of other regions in Ukraine and Europe. The reason for this is the fact that in Mariupol there are situated two largest steel companies of the Donetsk region - AZOVSTAL IRON & STEEL WORKS and ILYICH IRON & STEEL WORKS (METINVEST HOLDING, System Capital Management). In 1999 enterprises of Mariupol discharged into surface water bodies (the rivers Kalchyk, Kalmius and coastal zone of the Sea of Azov) about 885,0 mln m^3 of

wastewater (including 403,9 mln m³ of untreated waste water) (2,3). The content of chlorides, sulphates, phenol, petroleum products and nitrates exceed the maximum permissible concentrations (MPC) of harmful substances established by in the national legislation acts (Table 1).

Table 1

Concentrations of pollutants in the Kalmius river below the discharge of industrial wastewaters of METINVEST HOLDING

Polluting substances	Concentration, mg / l	MPC, mg / l
Chlorides	440	356
Sulphates	987	930
Phenol	0,009	0,001
Petroleum products	0,33	0,3
Nitrates	77	45

The most common index for determining the quality of water used in Ukraine is the Water Pollution Index (WPI) (4). On the base of WPI value equal to 3-5 the hydrochemical state of the of Kalmius river within Mariupol urban area was classified as very dirty.

2. Methods of protection of waters from pollution

The aim of this work is to study the basic methods for removing sulfur and its compounds from wastewater of metallurgical and coke production, which are used at enterprises of Mariupol.

The present study was dike of industrial wastewater of AZOVSTAL IRON & STEEL WORKS. The content of sulfur compounds in the protective dam is 97 mg/l, above normal content equal to 10 mg/l (5). This fact shows the necessity for development of cleaning processes. Moreover, it is possible to clean not only the industrial wastewater, but also as a preventive measure in the Sea of Azov, closed to the protective dam. This is due to the fact that sulfur may harm not only to human health but also to the environment in general.

2.1 Anaerobic microbiological method

Anaerobic biological treatment processes are characterized by a compact hardware design, a minimum amount of activated sludge and the lack of energy for aeration (6).

The experimental procedure consisted of the introduction of autotrophic organisms (Thiobacillus "X", Thiobacillus concretivorus) in cleaned medium containing samples of water from the dam safety. The efficiency of wastewater treatment in the changing process conditions of cleaning (concentration of sulfides, reactor type, pH) was determined. Scrubbing medium is artificially introduced into a high concentration of microbial communities, effectively assimilating organic substances in the environment as a primary energy source, turning them into products of their own activity. Preparations for degradation occur due to the activation mechanisms of interaction between two or more microorganisms. Degradation of sulfide components of object occurs by increasing the concentration and biological activity of these microorganisms.

Under certain conditions (pH from 6.6 to 9, the temperature range from 23 to 28° C (7)) activity of microorganisms of the activated sludge (namely the selectivity of enzymatic systems and their readjustment based on the substrate) enables transformation "sulfides - sulfates - sulfur" in the shortest possible time period, without the need to adapt to harsh environmental conditions.

The growth and development of the culture of microorganisms is limited not only by their concentration, but also the accumulation of metabolic products. At concentrations above 10 mg of sulphide/l the reduction in the total number of microorganisms on 10 % of control in six days takes place. At receipt of sulfide ions in amounts more than 200 mg/l decrease in the total number of microorganisms occurs by 60 % in three days. Only individuals are in the activated sludge, they are facultative anaerobes, as sulfides in the biological treatment are not only showing a toxic effect on the bacterial cells but also are active consumers of dissolved oxygen.

Increased number of anaerobes is strongly dependent on the reactor type - whether it is closed or is in contact with atmospheric air, which is a natural inhibitor of the process. The growth of anaerobic microorganisms is shown in Fig. 1.

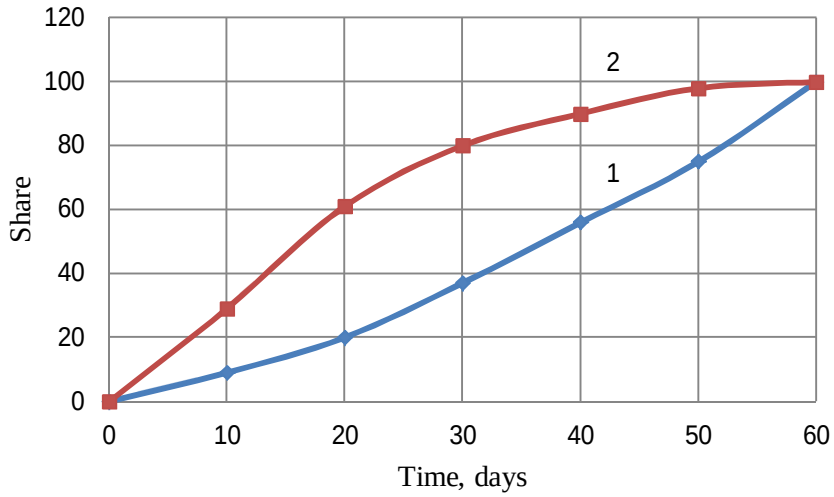

Figure 1. The growth of anaerobic bacteria
(1 - methane tank; 2 - open reactor)

At pH is from 9 to 11, autotrophs develope synthesizing inorganic substances necessary for living organic matter. Next, at pH from 5 to 9, Thiobacillus "X" develop. Then, at pH less than 5 developing Thiobacillus concretivorus (Thiobacillus thiooxidans) form sulfuric acid.

Microbial activity depends on temperature, type of substrate, the availability of oxygen quantities of pH. When the temperature varies from 15 to 20 °C the bacterial activity increases at least by 2 times. Formation of sulfuric acid by the bacteria proceeds optimally at temperature from 30 to 37 ° C, but at temperature of 18 ° C can be formed of 6 % sulfurous acid.

After equilibration, shown in Fig. 1, the following results of anaerobic treatment were obtained:

- the initial sulphide concentration - 97 mg / l;
- the final concentration of sulphides - 10 mg / l;

- the initial concentration of ammonium salts - 357 mg / l;
- the final concentration of ammonium salts - 221 mg / l.

Efficiency of removal of sulfides from waste water is 89.6 % and in the case of ammonium salts is 38 %.

2.2 Method of elimination of sulfur compounds using sorbents

One of the perspective directions of elimination of sulfur compounds from the water is using of different sorbents. Layered double hydroxides (LDHs) can be obtained from chemical production waste containing magnesium and aluminum salts, and used as sorbents (8).

To determine the parameters of the process were conducted kinetic studies of sorption. Investigation of sorption of sulfide ions in the LDH was performed in mixing reactor with periodic sampling, the sulfide ion concentration was determined spectrophotometrically. From the data presented in Fig. 2, it is seen that the rate of sorption of sulfide is high, the system quickly reaches a state of equilibrium.

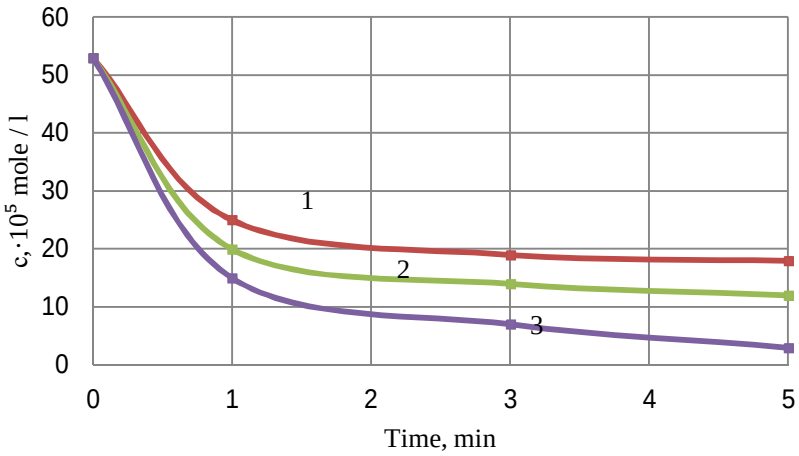

Figure 2. The change in concentration of sulfide ions in time at different sorbent mass: 1 - 0.1 gm; 2 - 0.15 gm; 3 - 0.2 gm

During studies rate constants were calculated for sorption of sulfide ions of the first and second order for sorbents with different contents of Mg/Al mole/mole. These rate constants are presented in Table. 2.

Table 2

The values of the rate constants of the first and second order for sorbents with different content of Mg/Al, mole/mole

Mg/Al, mole/mole	0,52	0,72	0,81	0,86
$k_{1,}$ s^{-1}	0,04	0,04	0,03	0,01
$k_{2,}$ l / mole·s	210,53	245,40	200,00	82,64

Study of sorption processes for LDH of different composition made possible to determine the rate constants of sorption of the second order for the sulfide ions, from which it follows that the optimal molar ratio Mg/Al is 0.72.

2.3 The elimination of sulfur compounds from waste water by oxidation

Studies of the oxidation rate of hydrogen sulfide with air in distilled water showed that the process proceeds very rapidly and almost completes within 20 minutes. Moreover, the process proceeds in a diffusion region with a low value of specific surface interface is less than 0.2 m^2 / m^3.

Also, experiments were conducted using samples of water from the dam protecting of AZOVSTAL IRON & STEEL WORKS. The rate of oxidation of sulfides determined by the concentration of dissolved oxygen. Determination of soluble salts in aqueous solution results in salting-out effect of dissolved oxygen, and, consequently, to decrease the speed of oxidation.

The dependence of the solubility of the gas in the aqueous salt solution the salt concentration expressed by equation of Setchenov (9). On the basis of this equation constants of Setchenov were calculated for the average solution of industrial waste water (Table. 3).

Table 3

Calculation of constant of Setchenov for industrial waste water protection dam

μ	0,005	0,01	0,02	0,04
μ_o	0,916	1,792	2,148	2,568
$\lg(\mu/\mu_o)$	-2,263	-2,253	-2,031	-1,808
$K \cdot 10^3$	-15,5	-15,4	-13, 9	-12,3

The obtained value of the constant is $K = -(14,2+2,3) \cdot 10^3$; knowing the value of the constant of Sechenov, we can calculate the effect of salting out of oxygen at any concentration of salts in the protective dam of industrial wastewater.

Effect of temperature on the process of removing sulfide oxidation method is double. On the one hand, an increase in temperature leads to an increase in the overall speed of the process in accordance with the Arrhenius law. On the other hand, with an increase in temperature decreases the solubility of oxygen in solution industrial wastewater protective levees and the oxidation rate decreases. Because the process takes place in the diffusion region, and thus the activation energy is less than the enthalpy of dissolution, the total effect of increasing the temperature will decrease the overall speed of the process.

As can be seen from the experiments conducted, the oxidation rate of sulfides in saturated industrial wastewater of protective dam insufficient to develop technology based only on oxidative processes. Therefore, studies were conducted alternative removal of sulfides from aqueous solutions.

Summary

1. The environmental situation was analyzed, and the main sources of pollution of surface waters and the waters of the Sea of Azov (Mariupol, Ukraine) were set.

2. The efficiency of removal of sulfur compounds from wastewater was determined. It amounted to 89.6 % for sulfur compounds and 38 % for ammonium salts.

3. It is found that the optimum for the elimination of sulphides and compounds is the use of sorbents containing Mg / Al = 0,72 mole / mole.

4. It was found that for effective wastewater treatment and metallurgical coke production of sulfur compounds is insufficient use of technologies based only on oxidative processes.

References:

1. *Resolution of the Verkhovna Rada of Ukraine on March 5, 1998 №188 / 98-VR "On the main directions of state policy in the field of environmental protection, natural resource management and environmental security": Bulletin of the Verkhovna Rada of Ukraine, 1998, №38-39; 248.*
2. *The official website of AZOVSTAL IRON & STEEL WORKS [Internet] Available from: http://azovstal.metinvestholding.com/ua.*
3. *The official website of ILYICH IRON & STEEL WORKS [Internet] Available from: http://ilyichsteel.metinvestholding.com/ru.*
4. *Gagarin OV. Review of integrated Assessment of surface water quality: Bulletin of Udmurt University, 2005, № 11; 45-58.*
5. *Bandman AL. Harmful chemicals. Inorganic compounds of elements of groups V-VIII: Reference books: AL. Bandman, NV. Volkova, TD. Grehova and others. Leningrad, Chemistry, 1989; 592.*
6. *Kalyuzhny SV. Highly efficient of anaerobic biotechnology industrial wastewater treatment: Catalysis in Industry, 2004, № 6; 42-50.*
7. *Perushkina EV. Biological treatment processes of sulfur-containing wastewater in the process of cultivation sulfur-oxidizing of microorganisms: dis… tehn. science. Kazan, KSTU, 2008; 120.*
8. *Nakayama H. Intercalation of amino acids and peptides into Mg–Al layered double hydroxide by reconstruction method: Nakayama H, Wada N, Tsuhako M: Int. J. of Pharm, 2004, V.269; 469–478.*
9. *General Chemistry: Textbook: AV. Zholnin; ed. VA. Popkov, AV. Zholnina. Moscow, GEOTAR Media, 2012; 400.*