

The use of encapsulated sodium ferrate in wastewater treatment in the production of animal feed

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Abstract: The article presents the results of studies devoted to the use of ferrate in wastewater treatment in the production of animal feed. A method of wastewater treatment from various substances is proposed using the example of phenol. The possibility of obtaining of encapsulated sodium ferrate based on hexane, ethylcellulose and paraffin was revealed; its stability in air and in an alkaline solution was established. It has been proven that the reuse of industrial wastewater is a determining direction in preserving the health of animals and birds and the ecological cleanliness of the environment in general.

Keywords: WASTE WATER PURIFICATION METHOD, CAPSULATED SODIUM FERRATE BASED ON HEXANE, ALKALINE SOLUTIONS, ELECTROCHEMICAL GENERATION OF FERRATE IONS

1. Introduction

With the rapid growth of the world's population and the rapid development of industry, the problem of drinking water (i.e., free from pollutants and sludge) has arisen. The main sources of water supply are the central source or water intake from rivers and wells, where the main wastewater discharge is carried out by local industrial enterprises.

Industrial wastewater is contaminated with products of processing raw materials, as well as various impurities of substances used in technological processes. The production of finished feed produces wastewater with a high organic content. They pose a significant risk if they enter water bodies without pretreatment, since they may contain: particles of organic materials (e.g. grain, proteins, food); medical supplements; detergents; solvents and oils used in the operation of equipment; oils, fats and molasses from mixed foods. The discharge of wastewater into water bodies leads to their pollution, which, even if the requirements for maximum permissible concentrations are met, causes irreversible changes in the water body [1]. Water from water bodies is used not only for the life of the local population, but also for the needs of feed production, including for conditioning grain with steam during the granulation process; adding water to the mixture to increase the moisture content of the feed to the level required for granulation; preparation of a starter culture for processing a feed mixture, etc.

Since the water used for the preparation of feed must be suitable in terms of its qualities, the problem of water purification is urgent.

Wastewater generated during washing, surface water runoff and steam condensation in feed production, as well as in technological operations of other industrial enterprises, is a complex mixture of insoluble mineral and organic contaminants, true and colloidal solutions. Such mixtures may even include fibers, particles of lubricants, dyes, synthetic surfactants, finishing agents, reagents, and other insoluble impurities. Wastewater has a pH value in the range of 6 ... 12 and may differ in pronounced coloration. Unevenly flowing effluents from production are not discharged directly into city-wide treatment facilities, but are preliminarily purified [2].

For the complete treatment of wastewater from enterprises, biological methods are used. However, biological wastewater treatment in most cases is hampered by their high hydration alkalinity and lack of biogenic elements. Therefore, biological treatment, as a rule, should be preceded by preliminary mechanical or chemical treatment of effluents.

Currently, electro-chemical wastewater treatment is gaining popularity, but it, like reagent treatment, does not completely remove surfactants [3]. A high degree of wastewater treatment from surfactants and other contaminants is achieved using the ion exchange and hyperfiltration method, i.e. filtration of waste water under pressure through semi-permeable membranes. In this case, the treated wastewater is returned to production, which leads to water savings.

2. Results and discussion

The analysis of scientific, technical and patent literature showed that the number of publications devoted to the use of ferrates for water purification is increasing every year. Many foreign companies are interested in ferrate technology. Foreign practice shows that the purification of industrial effluents requires the involvement of expensive technologies and equipment, which leads to additional significant investments. However, enterprises in Kazakhstan do not have sufficient funds to equip production with new environmentally friendly equipment [4].

In the scientific literature, the issues of effective wastewater treatment are devoted to the anodic dissolution of iron silicides in an alkaline electrolyte [5].

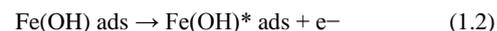
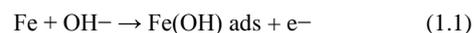
Analysis of the features of anodic dissolution of iron in alkaline electrolytes in the work of Shein A.B., Rakityanskaya I.L., Lomaeva S.F. [6] shows that the anodic process at the potentials of the initial section of the polarization curve cannot be identified only with the dissolution of the metal in the active state. The maximum current i depends on the potential sweep rate, and there is no maximum at all on the stationary curve.

The possibility of $\text{Fe}(\text{OH})_2$ formation also follows from an analysis of the E-pH diagram for the Fe-H₂O system. In the initial part of the polarization curve, one can expect the simultaneous oxidation of iron by reactions:



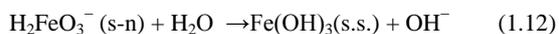
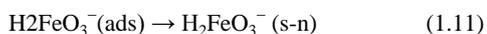
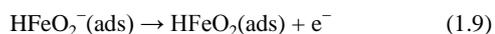
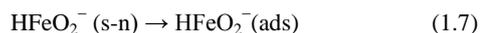
$\text{Fe}(\text{OH})_2$ hydroxide forms a passivating film and partially dissolves in the electrolyte with the formation of γ - FeOOH and $\text{Fe}(\text{OH})_4^-$. Subsequently, in the section where the current is independent of the potential on the surface of the iron electrode, according to the studies by Shein A.B. [7], there are 3 oxide phases: a passivating film γ - FeOOH , loose Fe_3O_4 and a film γ - Fe_2O_3 , covering magnetite.

According to the results of the work of Freire L. [8], the anodic process of iron dissolution proceeds according to the following scheme:



Iron goes into solution according to equation (1.3) in alkaline solutions, the concentration of which is $\leq 5\text{N}$. In more concentrated and hot solutions, the FeO_2^{2-} ion is formed. The course of the process according to equation (1.4) leads to the passivation of the metal. The speed of the first anodic process is limited by the stage.

The second anodic process occurs at more positive potentials in the following stages:



These processes are carried out with low overvoltage. The rate of the process is limited by the diffusion of iron ions in concentrated solutions (> 2N), and in more dilute solutions, perhaps, one should take into account the slow diffusion through solid oxides.

During the course of the second anodic process, spontaneous processes of dehydration and crystallization of $\text{Fe}(\text{OH})_3$ still take place, as a result of which the potential of the electrode shifts to the negative side and the process also begins, without significant overvoltage.



In a number of works by Freire L. it is shown that such an anodic process is also possible [8]:

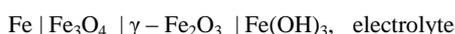


which runs at 20°C and alkali concentrations up to 4N. During this process, a black precipitate forms on the electrode, which is γ - Fe_2O_3 :



An active iron electrode in alkaline solutions can be passivated relative to the above processes due to the formation of FeOOH , δ - FeOOH and γ - Fe_2O_3 . Passivation of an iron electrode in alkaline solutions occurs if trivalent oxides or oxide hydrates are formed on the surface.

Recently, the following structure of the passivating layer on iron in neutral and alkaline Massot L. solutions has been proposed. [nine]:



However, the formula $\text{Fe}(\text{OH})_3$ is often considered unfounded. In alkaline media, hydrated FeOOH is offered instead of $\text{Fe}(\text{OH})_3$.

It should be noted that the composition of individual layers may be non-stoichiometric and there is no sharp transition between them. The first peak of active dissolution on the CVA curve of the Fe electrode practically degenerates already in the 2nd cycle, which indicates a deep passivation of the electrode. With a decrease in the anodic polarization on the CVA curve in the 1st cycle, peaks are observed (at more negative values of the potential than the peaks in the section of the forward stroke curve). The latter indicates the possibility of reduction of the formed oxide films.

A clearly pronounced anodic peak is also observed on the CV curve of FeSi , which disappears already in the second cycle. The peak potential is close to that for Fe; however, the current density of this peak is 3.3 A/m², that is, it is much lower than that for Fe ($i_a = 14$ A/m²). As the anodic polarization of FeSi decreases, a weak cathodic peak appears in the CV curve.

An even greater decrease in the anodic peak currents occurs for higher silicides with a decrease in the content of Fe atoms (FeSi_2 and $\text{FeSi}_2\text{-Si}$) in them.

So, in the case of FeSi_2 , the value of i_a , max is ~ 0.3 A/m², and for $\text{FeSi}_2\text{-Si}$, i_a , max = 0.45 A/m². A certain increase in i_a , max for $\text{FeSi}_2\text{-Si}$ compared to FeSi_2 can be associated with an increase in the

heterogeneity of the eutectic alloy surface and an intensification of the anodic process along the phase boundaries.

To clarify the role of silicon in the process of anodic dissolution of iron silicides, anodic CV curves were taken on pure silicon in 0.1-5.0 N NaOH. It is known that, in contrast to acidic electrolytes, where silicon is stably passivated due to the formation of a stable passive film consisting of SiO_2 , in alkaline media it is quite well soluble by the reaction:



Silicon has a high affinity for oxygen. Its surface in air is always covered with an oxide film, the thickness of which reaches 30Å under normal conditions. The study of the mechanism of coupled electrochemical reactions in potassium hydroxide solutions in the work of Nikolić-Bujanović, L., Čekerevac, M., Vojinović-Miloradov, M., Jokić, A. Simičić, M. [10] showed that for p- and n-types of silicon, the rate of self-dissolution is practically the same, that is, the process does not depend on the type of conductivity of silicon. At the anodic sites, the silicon dissolution reaction occurs with the formation of SiO_2 , and at the cathode sites, the process of hydrogen evolution occurs.

The results presented in this work make it possible to make an assumption about the mechanism of anodic dissolution of iron silicides in an alkaline electrolyte.

Thus, the above experimental data show that the mechanisms of anodic dissolution of iron silicides in acidic and alkaline electrolytes are different. In acidic electrolytes, as it was established earlier, selective dissolution of iron from the sublattice in silicide occurs, while silicon remains on the electrode surface and, being oxidized, forms a silicon dioxide (SiO_2) film. Since SiO_2 is characterized by high stability in acidic fluoride-free environments, iron silicides are also slightly soluble in acidic electrolytes.

In alkaline electrolytes, despite the increased activity of silicon (its increased solubility), the rate of the anodic process is determined by the formation of protective films of iron oxides and hydroxides, which passivate the surface and make iron silicides sufficiently stable in alkalis. One should not forget about the high strength of the Fe - Si bond, which also determines the resistance of silicides.

The results of electrochemical studies carried out on iron and iron silicides reveal the general regularities of their anodic behavior in alkaline media. These include: the presence of an anodic dissolution peak, which is most pronounced in the first cycle, an increase in the peak current and a shift in the peak potential to a more positive side with an increase in the potential sweep rate, a decrease in anode currents with a decrease in the pH of an alkaline electrolyte. These regularities do not appear for the Si-electrode, the dissolution rate of which increases in more concentrated alkaline solutions.

In Kazakhstan, there is enough secondary iron-containing raw materials, including scrap metal, from which anodes for the production of ferrates can be made at low cost. In addition to the mention in the scientific literature on the use of electrodes made of pressed steel chips [11] and galvanized wire in order to increase the true surface of the anode, to date, detailed studies on the use of VS in the technology of obtaining ferrates by electrochemical method have not been carried out. Obviously, such studies are relevant, since a variety of waste, in addition to iron, can contain other metals, for example, zinc, tin, etc., widely used for anticorrosion protection, which, in parallel with Fe, can participate in chemical and electrochemical transformations and have a certain effect on basic electrode processes.

A promising method of water purification is the use of ferrates (VI) of alkali metals, which have a multifunctional effect. Ferrates (VI) are one of the most powerful known oxidants (in an acidic medium the potential of FeO_4^{2-} an ion is higher than the potential of ozone) and is capable of decomposing many toxic chemicals to low-toxic products (oxidizing effect), as well as causing the death of microorganisms (disinfecting effect). The product of the decomposition of the ferrates themselves in solution is iron hydroxide, that is, a low-toxic product. In addition, iron hydroxide is

released in the form of colloidal aggregates with a very developed surface, which effectively adsorb heavy metal ions, suspension particles and organic residues, providing additional water purification by coagulation of pollutants (coagulating action).

One of the most promising, but at the same time poorly studied, is the electrochemical method for producing alkali metal ferrates.

3. Conclusion

The conducted literature review showed that the problem of water purification by electrochemically generated ferrate ions is complex, and a number of problems must be solved for a successful choice of purification conditions [12]. First, the material of the soluble anode must be selected. The composition of the anode, namely, the content of silicon and carbon in it, pays great attention to the current efficiency of ferrate ions. It is necessary to select the conditions under which the reaction of oxygen evolution during the anodic polarization of the electrode would proceed at a minimum rate in order to avoid a significant decrease in the current efficiency of ferrate ions.

Large problems in the electrochemical generation of ferrate ions are caused by the anode passivation in an alkaline medium. In 10-20 minutes after the start of electrolysis, the yield of ferrate ions drops sharply due to the formation of a passivating film on the anode surface. In this case, the dissolution of the steel anode deteriorates sharply, and almost all the current goes to the side reaction of oxygen evolution. The development of measures that reduce the degree of anode passivation during electrolysis in an alkaline electrolyte is not an easy task. It can be solved by careful selection of the electrode material, as well as its preliminary polarization (pre-polarization).

Ferrates (VI) are one of the most powerful known oxidizing agents of alkali metals (in an acidic medium, the potential of FeO_4^{2-} ion is higher than the potential of ozone), and is the largest among the currently used compounds and is capable of decomposing many toxic chemicals to low-toxic products (oxidizing effect), and also cause the death of microorganisms (disinfecting effect). The product of the decomposition of the ferrates themselves in solution is iron hydroxide, that is, it is possible to obtain a low-toxic product. In addition, iron hydroxide is released in the form of colloidal aggregates with a very developed surface, which effectively adsorb heavy metal ions, suspension particles and organic residues, provide additional water purification by coagulation of pollutants (coagulating action). Sources of drinking water supply disinfected with sodium ferrate by the example of phenol are non-toxic.

Ferrates (VI) of alkali metals can replace widely used oxidizing agents (pyrolusite, bleach), the use of which leads to secondary contamination of solutions with manganese and chlorine compounds. The use of ferrates will eliminate secondary contamination of the treated solutions.

In connection with the above, the development of a wastewater treatment technology, as a result of obtaining encapsulated sodium ferrate based on hexane, ethylcellulose and paraffin, will be of great importance not only for feed production, but also for all industrial enterprises. Treatment of reused industrial wastewater will reduce its discharge into water bodies, improve its sanitary condition, and also contribute to the natural circulation of water in nature.

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