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Iron-Containing Modeled Waste as Raw Material for Coagulant Receiving

S V Svergusova¹, Zh A Sapronova¹, A V Svyatchenko¹, A G Rymarov², E V Fomina¹

¹Belgorod State Technological University named after V.G. Shoukhov, 308012, Belgorod, Kostukova Street, 46, Russia ²National Research University Moscow State University of Civil Engineering, 129337, Moscow, Yaroslavskaya road, 26, Russia

E-mail: sv.anastasiaa@mail.ru

Abstract. The possibility of usage chemically treated dust of electric arc steel smelting furnaces (EASSF) of the electrometallurgical production for sewage of soymilk production cleaning, which are stable colloid-dispersed systems with high COD and BOD values, is investigated. It is shown that by the dust acidizing, it is possible to obtain a coagulating mixture, which achieves 87% model wastewater purification efficiency.

1. Introduction

The depletion of freshwater resources and the World Ocean pollution are global environmental problems of our time. The World Ocean is a key factor in the climate formation processes, the cycle of substances and productivity of the biosphere. However, the massive negative anthropogenic impact on water resources led to their great damage [1]. According to some sources, at present 1/5 of the World Ocean water area is contaminated with various organic, inorganic and biological substances [2].

Global pollution of water resources is caused by a huge number of various pollutants entering surface and underground waters with sewage. Environmentally hazardous contaminants are oil products, heavy metals, fats, oils and other organic and inorganic substances [3, 4]. For example, in the Belgorod region, it can be noted that hundreds and thousands of tons of pollutants enter its waterways (Figure 1 and Figure 2) [5, 6].

Sewage waters of small enterprises are big danger for water objects, because they have not undergone treatment properly or are not treated at all. As a rule such enterprises are located on the banks of low-water streams, so the discharge of these waters causes huge damage to aquatic organisms due to the weak intensity of self-cleaning processes [7]. These industries include soymilk production and other soybean processing products factories.

Because of the large nutritional value of food products derived from soy, the processed soy volume is continuously increasing both in the world and in the Russian Federation (Figure 3) [8]. Along with this, the volume of wastewater generated in the process also increases.

The wastewaters of soybean processing enterprises are characterized by a high level of contamination, because they contain originally included in the soybean substances and their metabolic products (proteins, carbohydrates, sugars, organic acids, etc.). Wastewaters from such enterprises have significant turbidity, high COD and BOD values, contain a large amount of suspended matter and must undergo integrated treatment. To purify such waters, adsorption, flotation, and coagulation can be used [9].

Universally recognized effective sorbents are activated carbons [7]. However, they are an expensive material, after their use, it is necessary to carry out regeneration processes, which lead to a significant increase in water treatment cost and the formation of secondary contaminated wastewater. This is the limitation of their usage possibility. In the works [10-14] other materials were used as adsorbents for water purification.

Coagulation-flocculation followed by sedimentation, filtration and disinfection is used worldwide in the water treatment industry. Coagulants can be classified into inorganic coagulants, synthetic organic polymers, and naturally occurring coagulants [15, 16].



Figure 1. Sewage water discharge into water bodies of the Belgorod region.



Figure 2. The pollutants entering water bodies of the Belgorod region.

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Figure 3. Soybean sales dynamics in the Russian Federation.

The commonly used metal coagulants fall into two general categories: aluminum-based and ironbased ones. The effectiveness of aluminum and iron coagulants arises principally from their ability to form multi-charged polynuclear complexes with enhanced adsorption characteristics. The nature of the complexes formed may be controlled by the pH of the system.

The whole treatment process of coagulation – flocculation can be divided into two distinct procedures, which should be applied consecutively. The first one is the process whereby destabilization of a given colloidal suspension or solution is taking place. The second sub-process, refers to the induction of destabilized particles in order to come together, to make contact and thereby, to form large agglomerates, which can be usually separated easier through gravity settling [17].

Despite the extensive list of used coagulants, the search for inexpensive and effective coagulating agents is an actual task.

We used an iron oxide waste - dust of electric arc steel furnaces of the Oskol Electrometallurgical Combine of the Belgorod Region, containing iron compounds in the equivalent of Fe_2O_3 up to 50% and with the particles size up to 50 µm to produce the coagulant. It is known that compounds of 2 and 3 valent iron are widely used in sewage treatment as coagulants [18].

2. Materials and methods

To determine the chemical composition of the dust, a device such as ARL9900 Intellipower Workstation was used, which allows X-ray fluorescence analysis of elements from B (boron) to U (uranium) with the use of an X-ray tube with Rh-anode and X-ray phase analysis in the range of double angles $2q 8,80^{\circ}$, using a tube with Co-anode.

The investigation involved a coagulating suspension produced on the basis of EAF dust treated by concentrated H2SO4, and model soy milk production wastewater.

The pH factor of water solutions was measured by pH-meter (I-500 ionometric converter, Akvilon, Russia); ξ-potential was measured by Zetatrac analyzer (Microtrac, USA).

The clarification of emulsions was determined by the turbidity (NTU) using HI 98703 Portable Turbidimeter (Hanna Instruments, USA)

3. Experimental

According to the X-ray phase analysis data (Figure 4), iron is included in the dust composition in the form of the following compounds: $FeO \cdot Fe_2O_3$ (magnetite), FeO (wustite). To obtain a coagulating

agent based on dust, it was necessary to partially dissolve the minerals that make up the EASSF dust and obtain a preparation containing Fe^{2+} and Fe^{3+} ions. For this purpose, the dust was treated with concentrated sulfuric acid. The optimal conditions for acid treatment of dust were selected, ensuring a high level of Fe^{2+} and Fe^{3+} ions in the resulting coagulating suspension (CS) [19].



Figure 4. Radiography of EASSF dust.

When the CS was added to distilled water and model emulsions which simulated sewage from soymilk production, it was found that the pH of the first decreases from 7,21 to 6,05 (Figure 5), and in the model emulsions from 7,13 to 6,27 (Figure 6).



Figure 5. Influence of the CS amount on the pH of distilled water.

To purify model emulsions, the CS agent was added in an amount from 0,5 to 2,5 cm³ per 250 cm³ of the emulsion. After mixing and filtration, the residual turbidity was determined in the filtrate. The study results, shown in Figure 7, indicate that with an increase of the CS additive, the model solutions purification efficiency increases.

Obviously, the volume of 1 cm^3 should be considered as the optimal addition amount of the CS, since in this case there is a decrease of turbidity from 949 to 122 NTU units, which is 87%. A further increase in the amount of CS addition does not make sense, because the efficiency increase is 5% only.

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Figure 6. Influence of the CS amount on the model systems pH change.



Figure 7. The effect of the CS addition on the change of model solutions NTU.

The effect of the proposed coagulating mixture can be explained as follows. Under the influence of concentrated sulfuric acid on the EASSF dust and heating it up to 80 °C, there are reactions which are proceeding according to the following schemes:

 $FeO + H_2SO_4 \rightarrow FeSO_4 + H_2O$

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 $Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O$

In the test emulsions coagulation processes occur during the hydrolysis of salts $FeSO_4$ and $Fe_2(SO_4)_3$:

 $2\text{FeSO}_4 + 2\text{HOH} \rightleftharpoons (\text{FeOH})_2\text{SO}_4 + \text{H}_2\text{SO}_4$

 $Fe(OH)_2SO_4 + 2HOH \rightleftharpoons 2Fe(OH)_2 + H_2SO_4$

 $Fe_2(SO_4)_3 + 2HOH \rightleftharpoons 2FeOHSO_4 + H_2SO_4$

 $2\text{FeOHSO}_4 + 2\text{OH} \rightleftarrows [\text{Fe(OH)}_2]_2\text{SO}_4 + \text{H}_2\text{SO}_4$

 $[Fe(OH)_2]_2SO4 + 2HOH \rightleftarrows 2Fe(OH)_3 + H_2SO_4$

The coagulation is caused by the ions $FeOH^+$, $FeOH^{2+}$, $[Fe(OH)_2]^+$, formed in this process, which leads to the coalescence of particles in the system and their sedimentation.

To test an effectiveness of the proposed CS preparation under conditions which are close to production, a model emulsion containing in addition to soymilk ions of PO_4^{3-} , SO_4^{2-} , fats and oils, was prepared.

The sulfates in the model waters before and after purification were determined by the titrimetric method in accordance with the methods [20,21]. The fats and the oils were determined by IR spectrometry method after extraction with carbon tetrachloride in accordance with the method [22]. The COD indicator in contaminated and purified waters was determined by the Expert-003-COD device according to the attached instruction [23,24]. The concentration of orthophosphate ions in the water was determined by the photometric method with ammonium molybdate at a wavelength of 880-890 NM [25, 26].

The model system physicochemical parameters after the purification process using the CS are given in Table 1.

	рН	COD, mg O ₂ /l	Turbidity NTU	PO_4^{3-} ions compounds, mg/dm ³	SO_4^{2-} ions compounds, mg/dm ³	Fats and oils compounds,
Initial wastewater	7,13	14320	949	25,4	80,2	mg/l 192,3
Wastewater after	6,27	2551	122	1,19	4,25	35,7
purification Purification efficiency, %		82,2	87	95,3	94,7	81,4

Table 1. The model system physicochemical parameters after the purification process using the CS.

4. Conclusion

Thus, it is established in the paper that the EASSF dust-based CS is an effective coagulating material for soymilk production and soybean processing products wastewaters treatment. The coagulation process is caused by the ions FeOH^+ , FeOH^{2+} , $[\text{Fe(OH)}_2]^+$, appeared under the influence of concentrated sulfuric acid on the EASSF dust and heating it up to 80°C.

The test of an effectiveness of the proposed CS under conditions which are close to production shows the high purification efficiency: 82,2% for COD, 95,3% of r PO_4^{3-} ions compounds, 81,4% for food fats and oils compounds.

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