RESEARCH ON THE DISPOSAL OF ACIDIC WASTEWATER FROM THE SEPARATION OF FATTY ACIDS FROM COTTON SOAPSTOCK IN THE OIL INDUSTRY

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Abstract. *When raw cottonseed is processed, the resulting crude oil is subjected to refining to precipitate free fatty acids. If from 1 ton of seeds 18% crude oil is obtained, and from the same oil 9% of the total soapstock is extracted. The process of converting soap stock into fatty acids is accompanied by copious amounts of acidic runoff. This article presents the results of a study of wastewater treatment for the production of crude fatty acids using the sulfuric acid method.*

The mineralized mass of phosphorites of the Central Kyzylkum was used as a neutralizing agent. After neutralization and separation of phosphorite sediment, the water was further purified with coagulants such as $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, $FeCl_3$ *and PAA. It was found that after the use of aluminum sulfate, the indicators observed a decrease in hardness from 9.91 to 8.83 mEq/l, turbidity from 4.3 to 3.4; COD from 280 to 86, and pH from 8.80 to 8.40, and on the other hand, an increase in the degree of purification from 86.12 to 89.03%. The optimal dose of coagulants can be considered 4 g/l.*

Key words: *soapstock, acid wastewater, coagulant, chemical oxygen demand, biochemical oxygen demand.*

INTRODUCTION

In Uzbekistan, there are 19 main enterprises, which are intended to process soapstock and refine it as a raw material. And the rest are more than 100 new enterprises opened on a cluster basis. The total number of oil and fat enterprises today is more than 240, which produced approximately 280 thousand tons of vegetable oils and more than 650 thousand tons of meal in 2020. According to statistical data from

the «Uzyogmoysanoat» UE, oil producing enterprises produced a total annual capacity of more than 4.3 million tons of oil seeds[1].

Such valuable intermediates as crude fatty acids (CFAs), glycerin for the production of detergents (laundry soap, etc.), emulsifiers, and surfactants are obtained from soap stock [2-7].

Cotton soap stock, unlike other types, contains neutral fat ranging from 25 to 65%, fatty acids (bound in the form of soap) from 13 to 33%, water from 40 to 60%, phospholipids from 0.45 to 0.85%, unsaponifiables substances from 2.9 to 6.8%, tocopherol from 4.0 to 8.9%, free gossypol from 0.21 to 0.29% [2,8,9]. Also, the content of phosphorus 1.198%, nitrogen 0.723% and carbohydrates, sucrose 0.24%, raffinose 0.56% and stachyose 0.087% was found in cotton soapstock [10].

The main method of obtaining fatty acids from soap stock is sulfuric acid decomposition. However, to do this, you usually need to saponify cotton soapstock in two ways - adhesive and sound. They differ in the initial stage of processing, where in the adhesive method the soapstock is first saponified with a 40–42% NaOH solution, and in the case of the core method, the process includes, after saponification, a salting-out procedure (NaCl) followed by settling and separation of the soap liquor. After deep saponification of soapstock using the adhesive method, the resulting mass is called “soap glue,” while the pre-saponified soapstock using the core method is called “soap core.” This method is still widely used in the oil and fat industry of the CIS countries [11].

To do this, the soap stock is saponified with a 40-42% alkali solution for 4-5 hours while thoroughly mixing the contents of the boiler with steam until a soap glue is obtained with an excess free alkali content of 0.2-0.3%. The saponified soap stock thus obtained is subjected to deoxidation using concentrated fatty acid to 95–98% [11] at a temperature of 80 ºC for an hour. The reactor-boiler is a cylindrical vessel with a conical bottom, lined on the outside with stainless steel and on the inside with acid-resistant ceramic materials. In this case, sulfuric acid is fed into the reactor in a thin stream, in order to avoid excessive foaming, which leads to the release of mass from the reactor. Sulfuric acid decomposition of soap stock occurs in stages with the formation of “acid soap” and the subsequent production of FFA according to the following equation [12]:

$$nRCOONa + H_2SO_4 = mRCOOH + Na_2SO_4$$

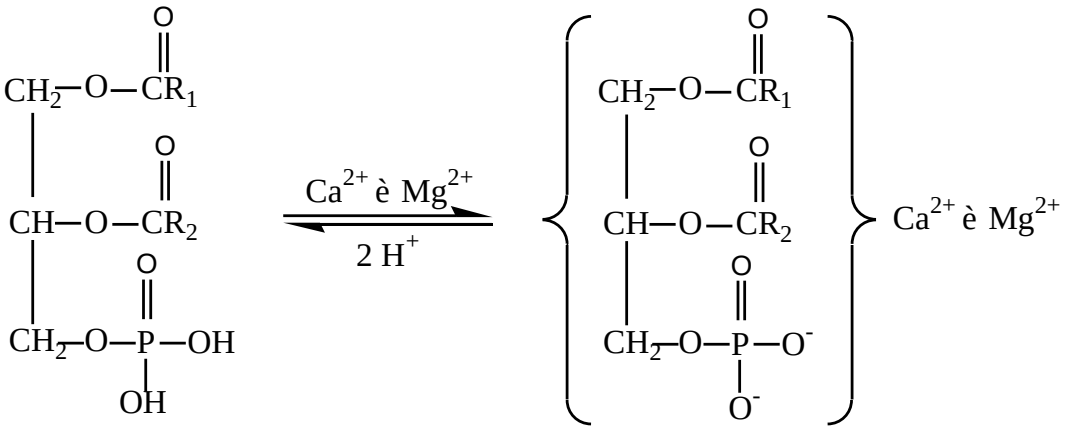
$$mRCOOH + nRCOONa = mRCOOH \cdot nRCOONa$$

$$mRCOOH \cdot nRCOONa + 1/2\ H_2SO_4 = (n+m)\ RCOOH + 1/2\ Na_2SO_4$$

In general, the process of deoxidation of saponified soapstock can be described as follows:

$$2RCOONa + H_2SO_4 \longrightarrow 2RCOOH + Na_2SO_4$$

In addition, a change occurs in phosphatides during their acidic decomposition, which contain calcium and magnesium. Acid decomposition produces unhydrated phosphatide [13].



The completion of the decomposition process is usually determined by taking a sample from the reactor, during which the formation of two layers can be observed - a fatty mass on the top layer and non-turbid acidic water in the bottom. After completion of the process, the mass is allowed to settle for 1 hour and the lower acidic layer is drained into a grease trap, and then transferred to a wastewater treatment plant [11].

As follows from the above methods of processing soap stock with the production of crude fatty acids from it, it is closely related to the associated formation of acidic wastewater with a significant content of organic impurities and salts. Various methods have been proposed for the treatment of oil and fat industry wastewater, which are coagulation/flocculation, adsorption, membrane, advanced oxidation, biological treatment and electrochemical treatment [14].

METHODS

The sample was taken from the acidic wastewater (AWW) of the soap production plant for processing soapstock of JSC "Urganch yog'-moy", formed from the 2nd stage of washing the FFA and mixed with the main concentrated wastewater under the settling tank. Their composition and technological properties have been fully studied. Table 1 shows the wastewater performance.

Table 1

Indicators of waste water from the first settling process of the deoxidation plant for saponified soap stock

solution pH	Transparency	Taste	Color	Smell	COD, O_2/l	BOD $_5$, O_2/l	Rigidity mEq/l		Dry residue mg/l		Suspended solids mg/l
							Carbonate	Non-carbonate	experimental	Calculated	
2,0	Red	brine	brown	specific	947,2	380,2	56,50	108,50	140,51	134,24	6185

Since AWW is acidic, first of all it is necessary to neutralize it with a more suitable substance, which could be accessible and promising for its further processing into target products with good technical and economic indicators.For this purpose, we selected phosphorites of the Central Kyzylkum (CK), which have a high carbonate content. Table 2 shows the chemical composition of CK phosphorites.

Table 2

Chemical composition of CK phosphorites

Types of Phosphate raw materials	Component content, weight. %									$\frac{P_2O_{5aviable.}}{P_2O_{5total.}}$ %
	P_2O_5	CaO	Al_2O_3	Fe_2O_3	MgO	F	CO_2	SO_3	H.O.	
Mineralized mass (MM)	15,09	43,17	1,22	1,34	1,21	1,7	14,01	2,17	1,02	9,11

Chemical oxygen demand (COD) content was determined by the dichromate method using 0.25 N. solution of $K_2Cr_2O_7$, in which, after adding a solution of silver sulfate and Mohr's salt, the solution is titrated until the color changes from blue-green to reddish-blue. The COD value is calculated using the formula:

$$x = \frac{(V_1 - V_2)HK \cdot 8 \cdot 1000}{V}$$

where: V_1 is the amount of Mohr's salt solution spent on titrating the control sample, ml;

V_2 - the amount of Mohr's salt solution spent on titration of the test sample, ml;

H - normality of Mohr's salt solution;

K - wastewater dilution coefficient;

V - is the volume of the sample taken for analysis, ml.

Biochemical oxygen consumption (BOD) was determined after 1, 3, 5, 10, 15, 20, 25 and 30 days. After which, for each of these periods, three bottles were placed: one with diluting water and one for each dilution. BOD of wastewater was calculated using the formula:

$$x_1 = \frac{[(V_1 - V_2)K \cdot 0{,}08 \cdot 10 - x] \cdot 1000}{V}$$

where: V_1 - volume 0.01 N. sodium thiosulfate solution used to titrate the diluting water sample before incubation, ml;

V_2 - the same after incubation.

K - correction to titer 0.01 n. sodium thiosulfate solution;

V is the volume of wastewater taken for analysis before dilution, ml.

Chlorine content in the AWW using the bichromate method, where silver nitrate is used as a titrant [15] using the formula:

$$x = \frac{(V_1 - V_2) \cdot 1000}{V}$$

Also in the study, the following reagents (coagulants/flocculants) were used for wastewater disposal and purification:

Aluminum sulfate, with the chemical formula $Al_2(SO_4)_3$ nH2O, iron (III) chloride $FeCl_3$, iron (III) sulfate $Fe_2(SO_4)_2$, calcium oxide and polyacrylamide (PAA). All reagents were classified as “chemically pure” with a purity of at least 99%.

It should be noted that depending on the type of coagulant, the working pH of wastewater varies. For example, for aluminum sulfate, wastewater must have a pH in the range of 5.0-7.5. And for iron salts, the pH of the purified cloudy and coloring water should be in the pH range of 3.5-6.5 or 8-11. In order to create a working pH environment for coagulants, lime was used as a medium regulator and additive. The use of lime also helps to reduce the consumption of coagulants by 2.0-2.5 times.

Turbidity and degree of water purification were determined using a portable device AMTAST AMT21 (USA). Accuracy ± 3%

Hardness was determined using a portable device Hanna Instruments HI 96741 (Italy). Accuracy - ± 0.11 mg/l.

Since AWW is acidic, first of all it is necessary to neutralize it with a more suitable substance, which could be accessible and promising for its further processing into target products with good technical and economic indicators.

RESULTS AND DISCUSSION

The indicators and chemical composition of neutralized wastewater are presented in table. 3.

Table 3

Indicators of neutralized wastewater MM

solution pH	Transparency	Taste	Color	Smell	COD, O_2/l	BOD_5, O_2/l	Oily substances, mg/l	Hardness, mEq/l	Dry residue, mg/l	Suspen-ded solids mg/l
5,62	opacity	brine	brown	specific	334	101	450	10,2	2431	385

Further studies were studied using a pH regulator (CaO) and $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, $FeCl_3$ with and without the use of PAA. The results are summarized in Tables 4 and 5.

From the research results it follows that with an increase in the amount of coagulants, there is a significant change in the quality of hardness indicators and coagulation properties such as turbidity, COD, degree of purification and pH of purified water. For example, an increase in the amount of aluminum sulfate from 1.0 to 5.0 g/l, on the one hand, leads to a decrease in hardness from 9.91 to 8.83 mEq/l, turbidity from 4.3 to 3.4; COD from 280 to 86, and pH from 8.80 to 8.40, and on the other hand, an increase in the degree of purification from 86.12 to 89.03%. This similarity is observed when using iron (III) sulfate. However, when using iron (III) chloride, the degree of purification exceeds relatively 1.5–2%.

Table 4

The influence of various types of coagulants, without the use of PAA, on the efficiency of neutralized waste water

Coagulant	pH after CaO addition	Amount of coagulant, g/l	Rigidity, mEq/l	Turbidity	COD, mg/l	Degree of purification, %	pH purified water
$Al_2(SO_4)_3$	9,0	1,0	9,91	4,3	280	86,12	8,80
	9,0	2,0	9,53	4,1	210	86,77	8,70
	9,0	3,0	9,17	3,7	146	88,06	8,70
	9,0	4,0	8,94	3,5	95	88,70	8,60
	9,0	5,0	8,83	3,4	86	89,03	8,40
$Fe_2(SO_4)_3$	9,0	1,0	9,18	4,2	276	86,40	8,91
	9,0	2,0	9,93	3,9	208	87,41	8,70
	9,0	3,0	9,64	3,7	143	88,06	8,64
	9,0	4,0	9,12	3,4	93	89,03	8,45
	9,0	5,0	8,98	3,3	84	89,35	8,29
$FeCl_3$	9,0	1,0	9,92	3,8	269	87,74	8,87
	9,0	2,0	9,54	3,5	206	88,70	8,01
	9,0	3,0	9,17	3,1	139	90,01	8,61
	9,0	4,0	9,02	2,7	90	91,29	8,33
	9,0	5,0	8,81	2,5	83	91,93	8,19

Comparing the data, the optimal dose of coagulants can be considered 4 g/l. The degree of purification of purified water in this case is 88.70; 89.03 and 91.29%, respectively, when using $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$ and $FeCl_3$.

Based on the optimal dose of coagulant (4.0 g/l) with the use of PAA from 0.1 to 0.5 g/l as a compactor and accelerator of the particle sedimentation rate, one can see a significant change in all of these indicators (Table 5). In this case, in addition to pH, we see a change in hardness, turbidity, COD, degree of purification and pH of purified water from 9.20 to 8.21; from 9.11 to 8.14; from 8.92 to 8.09; from 3.4 to 2.3; from 3.3 to 1.9; from 2.85 to 1.89 and from 89.03 to 92.58; from 89.32 to 93.74; from 90.8 to 93.90%, respectively, when using $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$ and $FeCl_3$.

Table 5

The influence of various types of coagulants using PAA on the efficiency of neutralized waste water

Coagulant	pH after CaO addition	Amount of coagulant, g/l	Amount of PAA g/l	Rigidity, mEq/l	Turbi-dity	COD, mg/l	Degree of purifica-tion, %	pH purified water
$Al_2(SO_4)_3$	9,0	4,0	0,1	9,20	3,4	93	89,03	8,80
	9,0	4,0	0,2	8,80	3,1	86	90,01	8,70
	9,0	4,0	0,3	8,52	2,7	81	91,29	8,70
	9,0	4,0	0,4	8,37	2,4	76	92,25	8,40
	9,0	4,0	0,5	8,21	2,3	75	92,58	8,30
$Fe_2(SO_4)_3$	9,0	4,0	0,1	9,11	3,3	91	89,32	8,90
	9,0	4,0	0,2	8,82	3,0	85	90,06	8,92
	9,0	4,0	0,3	8,66	2,8	80	90,93	8,64
	9,0	4,0	0,4	8,31	2,0	75	93,45	8,45
	9,0	4,0	0,5	8,14	1,9	74	93,74	8,27
$FeCl_3$	9,0	4,0	0,1	8,92	2,8	88	90,80	8,92
	9,0	4,0	0,2	8,71	2,4	83	92,16	8,73
	9,0	4,0	0,3	8,44	2,2	79	92,77	8,61
	9,0	4,0	0,4	8,15	2,0	73	93,51	8,33
	9,0	4,0	0,5	8,09	1,8	72	93,90	8,19

Thus, the optimal experimental condition can be considered in which the amount of PAA is 0.4 g/l. At the same time, we obtain the following indicators of purified water:

When using $Al_2(SO_4)_3$, the hardness, turbidity, COD, purity and pH are 8.37; 2.4; 76, 92.25 and 8.40.

When using $Fe_2(SO_4)_3$, the hardness, turbidity, COD, purity and pH are 8.31; 2.03; 75, 93.45 and 8.45.

When using $FeCl_3$, the hardness, turbidity, COD, purity and pH are 8.15; 2.01; 73, 93.51 and 8.33.

CONCULUSION

Research has been carried out on the purification of the liquid phase using CaO, $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, $FeCl_3$ and PAA. The effect of a dose of coagulants from 1 to 5 g/l was studied without and with the use of PAA at a temperature of 60 °C. It was revealed that after the use of aluminum sulfate, the indicators observed a decrease in hardness from 9.91 to 8.83 mEq/l, turbidity from 4.3 to 3.4; COD from 280 to 86, and pH from 8.80 to 8.40, and on the other hand, an increase in the degree of purification from 86.12 to 89.03%. This similarity is observed when using iron (III) sulfate.

However, when using iron (III) chloride, the degree of purification exceeds relatively 1.5–2%. The optimal dose of coagulants can be considered 4 g/l. Based on this dose, the effect of the amount of PAA was studied and an improvement in hardness, turbidity, COD, degree of purification and pH of purified water was found from 9.20 to 8.21; from 9.11 to 8.14; from 8.92 to 8.09; from 3.4 to 2.3; from 3.3 to 1.9; from 2.85 to 1.89 and from 89.03 to 92.58; from 89.32 to 93.74; from 90.8 to 93.90%, respectively, when using $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$ and $FeCl_3$.

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