UDC 628.31

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EXTRACTION OF AMMONIA SULFATE FROM MOTHER LIQUOR IN METHYLACRYLATE PRODUCTION

In methylacrylate production liquid wastes containing considerable amounts of sulfuric acid and organic compounds are formed. Neutralization of sulfuric acid and removal of organic compounds from the effluent water are the essential phases of ammonia sulfate preparation. Methods of purifying waste water formed in methylacrylate production are proposed. Waste water purification is performed by oxidation, floatation and extraction. Combining several physical and chemical methods the most perfect purification is attained. By removing organic impurities from waste water high grade ammonia sulfate may be obtained as by-product.

Introduction. The production of polymericmaterials as well as their raw materials is a leading branch of chemical industry in the Republic of Belarus. A commonly known method of preparing acrylicesters is based on the sulfuric hydration of acrylonitrileintoacrylamidesulfate with its subsequent saponification and etherification into methylacrylate. This method is used when producing methylacrylate at the OJSC "Polymir" (Novopolotsk).

The technological process of the production of methylacrylate has two stages:

– hydration of acrylonitrile in water containing at least a stoichiometric amount of sulfuric acid which results in the formation of acrylamide:

$$CH_2{=}CH{-}CN + H_2O + H_2SO_4 \rightarrow$$
$$\rightarrow (CH_2{=}CH{-}CONH_3)HSO_4 \rightarrow CH_2{=}CH{-}CONH_2$$

– etherification of acrylamide by methanol in water in the presence of H_2SO_4 as a catalyst with simultaneous distillation of them ethylacrylate formed. The products of thistransformationare methylacrylate and ammonium hydrosulfate:

$$CH_2{=}CH{-}CONH_2 + H_2SO_4 + CH_3OH \rightarrow$$
$$\rightarrow CH_2{=}CH{-}COOCH_3 + NH_4HSO_4$$

The main and by-products of these processes arethe polluting substances present in waste waters (so-called mother liquors). The mother liquor inproducing methylacrylate at OJSC "Polymir" (Novopolotsk) is characterized by the following composition: sulfuric acid – up to 15 wt %; ammonium hydrosulfate – up to 30 wt %; dimethyl sulfate – up to 1 wt %; methylsulfate – up to 2.5 wt %; methanol and otherorganic matters (in terms of carbon) – up to 4 wt %; polymers – up to 5 wt %.

As a result ofether ification of acrylamide, ammonia is formed, it reacting with sulfuric acid forming ammonium hydrosulfate. A line for producing ammonium sulfate from waste water formed in the synthesis of methyl acrylate by neutralizing this water with ammonia is installed at the enterprise.

The basic amount of ammonium sulfate is formed during the interaction of gaseous ammonia with ammonium hydrosulfate and sulfuric acid. The reactions take place at atmospheric pressure and temperatures up to 100ºC:

$$NH_3 + H_2SO_4 \rightarrow NH_4HSO_4$$
$$NH_3 + NH_4HSO_4 \rightarrow (NH_4)_2SO_4$$

The technological process of preparing ammonium sulfate includes the following stages:

1) collection and neutralization of methylacrylate production waste;

2) vacuum crystallization of the ammonium sulfate solution;

3) centrifuging, drying, packaging, transportation of ammonium sulfate.

The organic impurities and polymers contained in the mother liquor substantially complicate the process of the formation and isolation of crystalline ammonium sulfate, and the ammonium sulfate obtained is contaminated with organic impurities, microcrystalline, has high acidity, which reduces its commercial qualities. After the separation of ammonium sulfate, the waste water is utilized by burning, the process involving economic and power consumptions.

To obtain a high quality product it is necessary to isolate the organic compounds from the mother liquor, which will also allow to use a much smalleramount of water in the technologicalprocess.

The purpose of the research is to develop techniques for purification of waste water formed during the production of methylacrylate in order to obtain high quality ammonium sulfate.

Main part. According to references [1–4] priority technologies for the purification of the waste water formed as a result of the synthesis of methylacrylate were identified: flocculation, extraction

and oxidation. Each of these methods was tested in laboratory conditions, and on the basis of the experimental data conclusions on its effectiveness were made.

Although processes of flocculation and coagulation of organic acids occur more efficiently in acidic media, the results of the preliminary experiment showed the need of partial neutralization of waste water. Neutralization was performed with concentrated ammonia solution of pH = 2–3, the processes of flocculation and extraction being the most efficient in this range.

Since the investigated waste water is contaminated with impurities (acrylic acid and its derivatives), cationic type of flocculant has been used for purification. When infiltrating cationic flocculant into the mother liquor, the formation of polyelectrolyte complexes takes place, producing flakes that precipitate in the gravitational forces field. Thus, the cationic type flocculant acts both as a coagulant and as a flocculant and permits to remove the derivatives of acrylic acid present in the water.

An experimental selection of flocculant was performed. For this purpose the comparison of the flocculating capacity of three types of flocculants was made: Amiflock (copolymer of methacrylamide and diethylamineethyl methacrylate), PSP (pyridinic salt polymer) and Praestol 230. 1 ml of each flocculant solution of different concentration was injected into 100 ml of mother liquor and stirred intensely. Dependence curves of the organic substances content in terms of acrylic acid (AA) in the mother liquor on the flocculant solution content are shown in Fig. 1.

From the curve concerned it can be seen that the most effective flocculant is Praestol 230.

To determine the optimal dose of the flocculant, a number of solutions with different contents of flocculant (from 0.001 to 1 wt %.) were prepared.

The degree of purification was determined as the ratio of differences in the concentration of organic substances present in the initial and purified aqueous solutions tot he concentration of organic substances in the initial solution.

The results are shown in Fig. 2.

As it can be seen from the graph, with the flocculant dose of 1 mg/l the degree of purification equals to 65%. This is an optimal result, because with further increase of the flocculant dose by up to 10 times, only insignificant improvement in the efficiency of purification is observed.

Thus, 1 kg of flocculant is required for 1,000 m^3 of purified waste water (partially neutralized mother liquor).

Molecules of organic acids in acidic aqueous solutions are weakly hydrated by water molecules, but when in contact with organic solvents acid molecules solvate easily, thus being extracted by the organic solvent. By choosing an extracting agent, it is theoretically possible to achieve complete removal of the acrylic acid and its derivatives from the solution.

Experiments on the extraction of acrylic acid and its derivatives from the mother liquor allowed choosing the extractant – tetrabutyl phosphate (TBP). The advantages of the selected extractant include its low volatility, non-flammability, non-toxicity. During the experiment, the optimum volume ratio of mother liquour and extractant 5 : 1 was established.

The effectiveness of the method was evaluated by comparing the content of organic impurities in terms of acrylic acid in the purified solution (raffinate) and the content of acrylic acid in the extract. The degree of purification of the mother liquor by extraction of organic impurities, using TBP amounted to 95% (in terms of AA).

The content of organic compounds in terms of AA in the raffinate was determined by oxidation of the solution with potassium permanganate and subsequent titration of the oxidizer excess by using oxalic acid.

The concentration of AA in the extract was established by the titration method. Titration was performed with alcohol solution of sodium hydroxide.

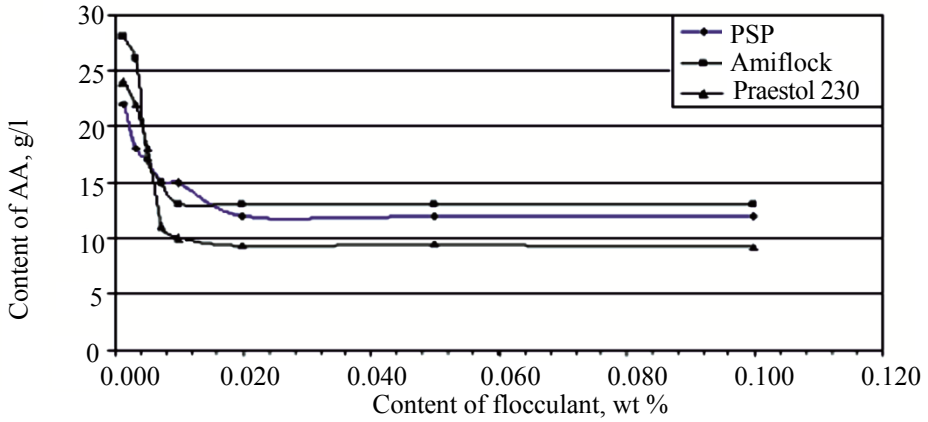

Fig. 1. Change of the content of organic substances in the mother liquor according to the content of the flocculant

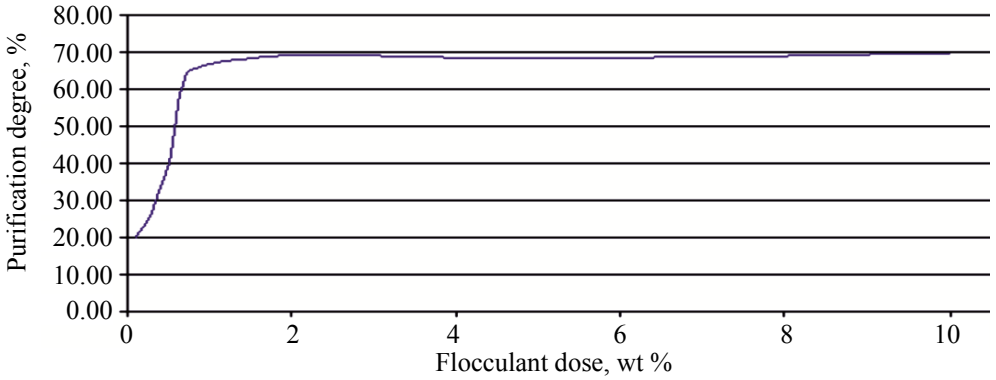

Fig. 2. Dependence of purification degree of mother liquor on flocculant dose

The results are given in Table 1. (Initial concentration of organic substances in terms of AA – 26.3 g/l.)

As it is seen from Table 1, the extract purification degree calculated using the results of AA titrationis some what less than the degree of purification, calculated according to the results ofoxidation. This can be explained by the fact that organic compounds other than AA are also extracted from the waste water, but their concentration can not be determined by acid-base titration.

The used extractant was subjected to regeneration. Sodium carbonate solution (Na_2CO_3) saturated at 20°C was used as the regenerating agent. The amount of sodium carbonate was calculated based on the stoichiometric ratio with a 10% excess. The ratio of volumes of the extract and the saturated sodium carbonate solution amounted to 20 : 1. The weight ratio of sodium carbonate in the solution saturated at 20°C equals to 23%.

After regeneration the extractant used was applied for purifying waste water. During the experiments it was found that the regenerated extractant does not lose its extracting ability during its repeated uses for more than 20 cycles of purification. Moreover, the lossof the extractant after 10 purification cycles amounted to 10%.

In developing the operating conditions for mother liquor purification the oxidation method was used as an additional one after extraction and flocculation, as the complete oxidation of the initial mother liquor is economically unprofitable due to the large consumption of oxidizing reagents. Hydrogen peroxide (H_2O_2) was use das an oxidizer.

The oxidation process was carried out within several hours, after which the residual concentration of organic substances was determined by using the method of reverse titration of the hydrogen peroxide residue with potassium permanganate. The results are presented in Table 2.

According to the Table 2, the average degree of purification from organic substances using hydrogen peroxide amounts to 98%.

After using each of the described methods of purification and subsequent tneutralization of ammonia solutions to pH = 8.0–8.5 they excreted ammonium sulfate. Crystalline ammonium sulfate was obtained on a laboratory apparatus by removing the water under vacuum at 34°C.

Table 1

Results of mother liquor purification by extraction method

Number of purification cycle	Concentration of organic compounds in terms of AA in raffinate, g/l	Purification degree in organic substances, %	AA concentration in extract, g/l	Purification degree in AA, %
1	1.17	95.55	86.4	65.70
2	1.13	95.70	85.9	65.32
3	1.20	95.43	87.0	66.16
4	1.15	95.62	86.3	65.63
5	1.17	95.55	86.5	65.78
6	1.16	95.58	86.3	65.63
7	1.14	95.66	86.1	65.48
8	1.16	95.58	86.4	65.70
9	1.18	95.51	87.0	66.16
10	1.17	95.55	86.5	65.78
Average value	1.16	95.58	86.4	65.73

Table 2

Results of using the oxidation method

Purification stage	Concentration of organic substances, g/l	Volume of water sample for analysis, ml	Volume of H_2O_2, used for oxidation, ml	Concentration of H_2O_2 solution, %	Concentration of organic substances after oxidation, g/l	Degree of purification from organic substances, %
Mother liquor partially neutralized	26.3	100	5.20	10	0.54	97.95
Mother liquor after flocculation	8.3	100	1.64	10	0.17	97.95
Mother liquor after extraction	1.16	100	22	0.1	0.023	98.02
Mother liquor after extraction and flocculation	0.01	500	10	0,01	0.0002	98.00

During crystallization about 37–40 g of ammonium sulfate of various degrees of purity were obtained from 100 ml of the neutralized solution, depending on the mother liquor purification method. And the crystals were rather large

The purity of ammonium sulfate obtained was analyzed by determining the content of SO_4^{2-} and NH_4^+ ions in the extracted product. On an average the weight ratio of nitrogen in terms of the dry substance of ammonium sulfate extracted from the purified mother liquors amounted to (with the normative content of nitrogen in terms of the dry substance of at least 21%):

20% – after purifying the mother liquor by flocculation method;

22% – after purifying the mother liquor by extraction method;

23% – after purifying the liquor by flocculation and extraction methods step-by-step;

24% – when using hydrogen peroxide as after purification stage (after preliminary extraction purification).

The solid wastes formed after the use of the flocculant and regeneration of the extractant can be utilized in a regular mannerin the dumps.

Conclusion. Based on the data obtained it may be concluded that each of the methods we proposed form ethylacrylate production waste water treatment is efficient. However the best option for mother liquor purification is the combination of all the methods analyzed. Application of the methods concerned will make it possible to produce high grade ammonia sulfate and save fuel for waste water incineration.

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Received 02.03.2012