

Separation of Fumaric and Maleic Acid Crystals from the Industrial Wastewater of Maleic Anhydride Production

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In this research, a physicochemical analysis of the industrial wastewater from a factory that produces maleic anhydride was performed. Based on the conducted analysis (pH, electrical conductivity, density of the liquid phase, boiling point of the waste suspension, chemical as well as biological oxygen demand, and dry matter), it can be concluded that the waste stream obtained at the outlet pipe from the plant resulting from the production of maleic anhydride requires appropriate treatments. Some of the parameters measured, e.g. pH (0.97 ± 0.06), boiling point ($106.8 \pm 1.3^\circ\text{C}$) and acidity, indicate the presence of organic acids such as fumaric and maleic acids, which are formed during the production of maleic anhydride. The possibility of extracting crystals by adding urea and thiourea followed by forced cooling in a heat exchanger was investigated. The most effective method was the addition of thiourea when the most significant amount of crystals was obtained, namely 17.29 wt%. The addition of thiourea in combination with forced cooling greatly facilitates the process of separating the solid and liquid phases of the waste suspension, which could later be adequately treated by physical, chemical or biological methods.

Keywords: MAN production, separation, thiourea, cooling, wastewater

1. Introduction

Since the chemical industry and the waste streams generated during chemical production have a harmful effect on the environment, it is necessary to minimize their harmful impact before releasing them into the environment and comply with legal regulations, both locally and globally. Moreover, it is important to conduct environmental impact assessments and environmental management with regard to the practical implementation of environmental regulations [1], e.g. determining the Informative Environment Qualifying Index.

The production process of maleic anhydride (MAN) is based on two different technological processes in the gas phase, namely the oxidation of benzene and the oxidation of n-butane [2]. In 2015, the global capacity of MAN production amounted to 2800 million metric tons [3]. Scientific and technological developments in the manufacture and use of maleic anhydride as well as maleic and fumaric acids have been reviewed over the past 20 years [4]. During MAN production, a certain amount of wastewater is generated, which must be

processed and treated in order to minimize environmental pollution. The increasing need to mitigate environmental impacts has led industries to develop more sustainable processes, which may be an arduous task since economic, safety, social and environmental factors must be considered [5]-[6]. The impact assessment of the chemical industry on the environment is becoming more and more important with regard to projecting and designing processes. A special problem is represented by facilities involved in exploitation, which are in the process of complying with EU regulations on environmental protection. Given that Bosnia and Herzegovina, a country in transition, is increasingly adopting the laws of the European Union, it is necessary to take measures that will reduce the harmful effects of the chemical industry both locally and globally. Furthermore, the Federation of Bosnia and Herzegovina has introduced legislation [7] which is in accordance with EU legislation.

Due to the fact that MAN production facilities have a detrimental impact on the environment, various methods have recently been applied for the treatment of wastewater streams. The wastewater flow from the MAN

production plant consists of a mixture of organic components, containing mainly fumaric and maleic acids, which can be treated by following different physical, chemical and biological methods [8]-[14]. Considering the physical characteristics of fumaric and maleic acids [15], especially their solubility in water (fumaric acid is poorly soluble in water), a waste stream consisting of a crystal suspension as well as a mother liquor of fumaric and maleic acids is obtained at the outlet of the plant. Before any treatment, such a suspension must be separated into the crystal flow and the mother liquor flow, which, if necessary, could be treated later or possibly reused to obtain products that do not require highly pure fumaric or maleic acid.

This research was carried out in order to examine the possibility of separating the wastewater suspension from the industrial MAN production plant and the crystal stream, which consists of a mixture of fumaric and maleic acids along with other organic impurities, from the mother liquor stream. Considering the physical, chemical and biological properties of the waste stream as well as its components, the goals of this research are to choose the most efficient method to separate the crystalline product from the waste stream in addition to making recommendations concerning its processing and further use in the industrial production of unsaturated polyester resins. Another aim is to make recommendations for possible biological treatments by analyzing the liquid component of the waste stream.

2. Experimental

2.1 Treatment of the waste stream

The waste stream of the suspension at the outlet of the MAN production facility owned by the company Global Ispat Koksna Industrija Lukavac (GIKIL) (Bosnia and Herzegovina) was used in this research. The above-mentioned waste stream is generated discontinuously by the process of washing the distillation column and cooler with water at a temperature of 100°C. In the aforementioned industrial plant, the distillation system is washed every 4 days when approximately 70 m³ of water is consumed in an hour, resulting in water with a low pH due to the presence of maleic and fumaric acids. The aftercooler is washed twice a month, consuming 10 m³ of water. Given that wastewater contains fumaric acid, which is the basic raw material for the production of unsaturated polyester resins, it is necessary to investigate the possibility of using this waste stream in terms of extracting (crystallizing) fumaric acid. The total amount of waste suspension generated under industrial conditions on a monthly basis is approximately 300 m³, which has a significant impact on the environment if it is not processed adequately.

Experimental research and analyses were carried out in the Chemical Engineering laboratory of the Faculty of Technology at the University of Tuzla. Samples were taken twice a month directly at the outlet of the tank used to collect the waste stream. Most samples



(a)



(b)

Figure 1. The samples: (a) immediately after being taken from the plant; (b) after being delivered to the laboratory.

were taken after the first wash when the concentration of organic matter is the highest. The samples immediately after being taken from the plant and after being delivered to the laboratory are shown in Fig. 1. They were collected and delivered to the laboratory in plastic containers with a volume of 5L. Certain aliquots were extracted to perform physicochemical and other analyses.

Based on the research objectives, the following tasks were conducted:

- Laboratory modelling of the washing of the distillation column and the discharge of the waste stream was performed;
- Physical and chemical analyses of the waste stream were performed under laboratory conditions;
- The quantity of the resulting crystalline product was determined in relation to the volume of the waste stream under laboratory conditions;
- Examination of the possibility of extracting crystals from the waste stream was carried out in several ways:
 - a) by cooling the flow under laboratory conditions,
 - b) by adding urea and thiourea,
 - c) by cooling the waste stream with water in a system of tubular heat exchangers.

Among the physicochemical analyses, the pH, electrical conductivity, boiling point as well as the chemical and biological oxygen demand were measured. All measurements refer to a homogenized sample, moreover, after separating the liquid and solid phases, the dry matter and acidic properties of the liquid phase were determined.

The density of the liquid phase was determined using a pycnometer and the bulk density of the dried crystalline product was measured according to the ISO 1183-1:2004 standard.

2.2 Materials and Methods

For the purpose of experimental modelling, washing of the distillation column and the discharge of the waste stream, a special system was designed, consisting of a glass container with a volume of 25 liters with openings at the top and bottom. The vessel includes a distillation column and a glass vessel of the same volume was used as a receiving vessel. The amount of sample used was 5 liters and was preheated to 100°C.

To obtain a real picture of the industrial plant, the process of crystal formation was tested by cooling down the waste stream to ambient temperature (laboratory conditions). 250 ml samples that were observed were taken from a 5-liter sample after mixing and heating to a temperature of 100°C. The resulting crystals were filtered and air-dried under laboratory conditions.

Following the addition of urea and thiourea, the 400 ml samples preheated to 100°C, the temperature of the rinsing water, were taken from a 5-liter sample. The test was performed by adding urea and thiourea in different percentages concerning the volume of the sample. After the addition of urea and thiourea, the samples were allowed to settle before the crystals were separated by filtration on filter paper and air-dried.

For the purposes of testing whether the waste suspension stream crystallizes, a cooling system consisting of three laboratory-scale tubular heat exchangers was designed. The cooling conditions and crystal formation were investigated for different flow rates of cooling water. The cooling system is shown in *Fig.2*.

The total area for heat exchange of the laboratory-scale cooling system was about 0.43 m². Once the waste suspension had passed through the tubular cooling system, the resulting crystals were collected on a metal grid and placed on a glass container before being dried and weighed on an analytical scale.

All measurements were performed three times and statistical data processing was conducted in Microsoft Excel, namely the mean and standard deviation were calculated.

Electrometric measurements of the pH and electrical conductivity were carried out by direct measurements using a METTLER TOLEDO FE 20-30/EL 20-30 pH meter/conductometer. The pH was measured using the standard method BAS EN ISO 10523, while the electrical conductivity was determined using the standard method BAS EN 27888.

The Chemical Oxygen Demand (COD) is the oxygen equivalent of the amount of potassium dichromate consumed during the complete oxidation of the organic matter in the measured volume of the sample. The COD and Biological Oxygen Demand (BOD) are determined by the BAS ISO 6060 and BAS EN 1899-1 methods, respectively.

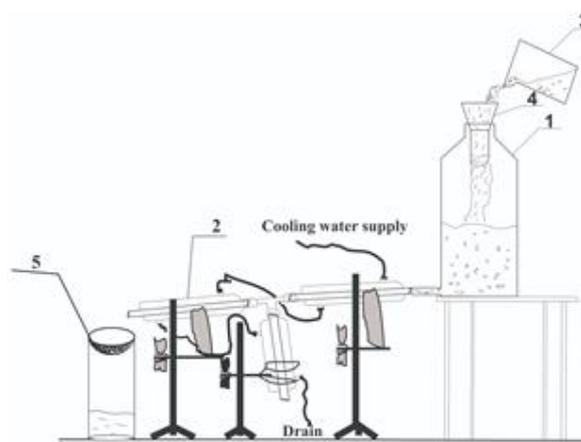


Figure 2. Schematic diagram of the waste-stream cooling system: 1) glass container for rinsing, 2) system consisting of three tubular heat exchangers, 3) cup containing the sample, 4) glass funnel, 5) metal grid for collecting crystals

After separating the liquid and solid phases, the liquid sample was filtered, evaporated at 100°C and dried overnight in an oven before the mass of the dry matter was measured on an analytical scale. The content of the dry matter was determined according to Method 2540-Solid B [16]. Furthermore, the solid phase in the solid sample was analysed gravimetrically by drying it at 105°C for 24 h.

3. Results and evaluation

3.1 Characterization of the waste stream

Considering that the waste stream represents a heterogeneous mixture (suspension) under laboratory conditions, for the purpose of the analysis, the samples were homogenized and heated to a temperature of 100°C because the waste stream was obtained by washing the distillation column in the MAN plant with water at a temperature of 100°C. On the walls of the distillation column, organic substances, predominantly fumaric and maleic acids, are deposited that may occur during the production of MAN. Due to its physical and chemical properties, fumaric acid is insoluble in water, while the solubility of maleic acid in water is 478.8 g/L at 20.0°C, i.e. 3926 g/L at 97.5°C [17]. Therefore, by washing the distillation column, a suspension is formed in which crystals of fumaric acid as well as a solution of maleic and fumaric acids are present. Considering the aforementioned fact and the boiling points of the pure acids, fumaric acid at 287°C and maleic acid at 135°C [15], the boiling point of the suspension was measured to be 106.8±1.3°C under laboratory conditions. This data indicate the presence of other substances that have significantly lower boiling points compared to the components that are primarily present.

As expected, the measured pH is very low, namely 0.97±0.06, due to the presence of organic acids, while the measured electrical conductivity is 33.62±4.03 mS. In view of the pH prescribed in [6], the measured value does

Table 1 Mass of the crystalline product obtained following the addition of urea and thiourea

Mass added (g)	Volume of filtrate collected (ml)		Mass of crystals (g)	
	Thiourea	Urea	Thiourea	Urea
1	100	200	69.0	44.9
3	60	210	71.4	46.7
5	150	200	71.8	46.9

not comply with the legal framework, which indicates that this waste stream of industrial wastewater should be treated in an appropriate way. The relatively low electrical conductivity, for which no legally prescribed limits are found, indicates a low concentration of free ions in the waste stream. A pycnometer measured the density of the liquid phase after separation to be $1038.84 \pm 4.31 \text{ kg/m}^3$, while the bulk density of the solid phase was $394.0 \pm 1.4 \text{ kg/m}^3$.

To further examine the characteristics of the waste stream, the COD and BOD of the homogenized sample were determined to be 233600 and 87280 mg O₂/L, respectively. The permitted limits for the discharge of a waste stream into the environment for COD and BOD are 25-250 and 135-700 mg O₂/L, respectively, which indicates the need for pretreatment of the waste stream before being discharged into the environment.

By separating the solid and liquid phases by filtering and decanting under laboratory conditions, a homogenized 2.5 L sample contains $5.09 \pm 0.05 \text{ wt}\%$ of dry crystalline products. As a result, the total amount of solid matter discharged every month (300 m³) is about 15.27 kg. Therefore, a huge amount of solid waste can be treated or possibly used for other purposes. The amount of dry matter in the liquid phase is $16.3 \pm 0.2 \text{ wt}\%$, which also exceeds the permitted limits.

By titration of the liquid phase with NaOH and phenolphthalein as an indicator, it was determined that 1 g of the liquid solution is titrated with 3.95 mmol of NaOH. In simple terms, if the acidity is due to the presence of maleic acid, this would correspond to a maleic acid concentration of 0.247 mg/ml.

3.2 Separation efficiency

Considering the results of the physicochemical analysis of the industrial waste stream resulting from MAN production, it was observed that this waste stream must be adequately treated before being discharged into the environment. Due to the composition and characteristics of the waste stream, it is necessary to separate it into the solid and liquid phases. In this research, several experiments based on different methods were conducted to obtain an efficient method for separation.

As described earlier in the Experimental section, before testing the aforementioned methods, laboratory modelling of the process by which the distillation column is washed was carried out. The reason for performing the



Figure 3. Crystals obtained by forced cooling

experimental simulation is to experimentally and visually determine how the crystals are formed during the discharge of the waste-stream suspension into the collector. During the simulation, it was observed that immediately after the waste stream comes out of the outlet pipe, a larger amount of crystals were formed, meaning that other organic substances, predominantly maleic acid, also crystallized.

Simply by highlighting the flow, a sudden drop in the temperature of the flow from 100°C to ambient temperature is observed, during which more intense crystallization occurs. Following this observation, a system of three heat exchangers (Fig.2) was designed under laboratory conditions to cool down the waste stream more quickly and test such an efficient way of separating the solid and liquid phases. At the outlet from the cooling system, a container collected the waste flow, on top of which a metal grid to separate the crystals was placed. After the cooling and separation processes, the crystalline product obtained was dried and measured. The mass of crystals obtained by forced cooling (sample volume of 5 L) was $638.37 \pm 2.34 \text{ g}$, that is, 12.3 wt% of the dry crystalline product.

Compared with the amount of crystals obtained by natural cooling to ambient temperature, it can be seen that this method (forced cooling and separation by filtration) is significantly more efficient. This technique of collecting crystals on a metal grid is very simple to perform due to the very structure and size of the resulting crystals. The appearance of the crystals obtained is shown in Fig.3.

After experiments were performed using forced cooling, the influence of the addition of urea and thiourea on the formation and separation of crystals of organic substances in the industrial waste stream was examined. These components were added to better isolate the crystalline product from the mixture of fumaric and maleic acids, that is, thiourea acts as a catalyst in the isomerization of maleic acid to fumaric acid [18].

The masses of the resulting crystalline product following the addition of urea and thiourea are presented in Table 1. Analyses were performed using a sample that

Table 2 Mass of the obtained crystalline product following the addition of smaller quantities of thiourea

Mass added (g)	Volume of filtrate collected (ml)	Mass of crystals (g)
0.25	180	45.2
0.50	160	52.7
0.75	170	60.3

was heated to 100°C and homogenized in a volume of 400 ml.

The masses of urea and thiourea added were 1, 3 and 5 g. Samples where different amounts of urea and thiourea were added (U1 and T1 1g, U2 and T2 3g, U3 and T3 5g) are shown in *Fig.4*.

As can be seen in *Table 1*, the largest amount of crystalline product was obtained following the addition of 5 g of thiourea. As a percentage of the 400 mL sample, this value is 17.29 wt% of dry crystalline product, which is significantly more compared to forced and natural cooling of the waste stream.

The addition of urea also enhances separation of the solid phase from the suspension of the waste stream, however, considering the results obtained, the effect of adding thiourea on the separation process is significantly greater.

As can be seen in the table, given that the amounts of the crystalline product obtained following the addition of all three amounts of thiourea are very similar, an additional experimental optimization of the mass of thiourea to be added to the waste stream was performed. Amounts of less than 1 g were added to see if a larger difference in the amount of crystalline product formed was observed. Amounts of thiourea added of less than 1 g are presented in *Table 2*. As can be seen, even small amounts of thiourea significantly enhance the separation of crystals from the waste stream.

If 1 g of thiourea is added to a suspension sample of 400 ml as an optimal cost price and to achieve separation of the crystals when treating the waste stream generated from an industrial plant, it would be necessary to add 750 kg to 300 m³ of waste suspensions per month, which is a huge amount. However, if 0.25 g of thiourea is added to a suspension sample of 400 mL, which equates to approximately 0.06%, about 1250 kg of thiourea would need to be added annually at a cost of approximately \$98,550 [19]. In this case, this price is reasonable if the separated fumaric acid crystals were to be used for the production of resins.

In light of the research conducted, in the future, some other methods for extracting the mixture of fumaric and maleic acid crystals should be examined, which would be economically profitable and technologically feasible in an already existing plant. Furthermore, the composition of the crystalline product following the addition of thiourea should be tested using appropriate methods and analyses.



Figure 4. Separation of crystals by cooling at room temperature following the addition of urea and thiourea: U1, U2, U3 – samples to which urea was added; T1, T2, T3 – samples to which thiourea was added

4. Conclusions

In this research, a physicochemical analysis of the wastewater flow from an industrial plant resulting from the production of maleic anhydride was conducted. Based on the obtained results, it is evident that a very low pH as well as electrical conductivity indicate the presence of organic acids left over from distilling MAN. Given that the resulting flow is a suspension flow at the temperature of water used to wash the distillation column as well as the physical and chemical properties of fumaric and maleic acids, it can be stated that both are the two dominant components in the waste flow. This was also confirmed by determining the acidity by titration with NaOH. The research determined the density of the liquid phase as well as the bulk density of the separated crystalline product. By carrying out different experimental methods, the crystals were separated from the waste suspension by a combination of cooling and the addition of thiourea, a technique which can be applied in an industrial plant, facilitating the isomerization reaction of maleic to fumaric acid. Furthermore, the installation of a metal grid at the inlet to the receiving court is a simple structural solution whereby the resulting crystalline product, with appropriate analyses, could be used in processes that do not require highly pure fumaric acid, e.g. resin production. The liquid component, that is, the mother solution obtained by separating the waste suspension, due to the high COD and BOD, following the adjustment of other parameters like pH, could be successfully treated by the process of anaerobic digestion or co-digestion. Therefore, the liquid stream could serve as a good co-digestate for adjusting the characteristics of waste sludge that is normally applied in anaerobic digestive processes.

Following a literature review, since it was observed that very few studies have been conducted in this regard or require significant financial resources, this research opens up new possibilities and perspectives for the implementation of simple as well as inexpensive industrial and implementable solutions.

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