

TREATMENT OF OILY WASTEWATER FROM METAL PROCESSING BY THERMOCHEMICAL DECOMPOSITION PROCESS

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Abstract

This paper investigates the treatment of oily wastewater (emulsions) originating from metal processing via thermochemical decomposition. The treatment aimed to purify the wastewater to meet the regulatory standards, that is, specifically targeting a hydrocarbon index concentration of less than 10 mg/l. Experimental investigations included testing the influence of flocculant addition, sulfuric acid dosage, temperature and process duration on applied treatment efficiency. The results indicate that the addition of flocculants is not necessary. The optimal parameters for the thermochemical decomposition of oily wastewater are defined as: acid dosage of 2.4 g H₂SO₄/l of emulsion, process temperature of 90 °C and a duration time of 24 hours. Under these optimal conditions, the hydrocarbon index was reduced to 1.89 mg/l. However, due to the resulting low pH value (1.6), an additional neutralization step to a pH range of 6-13 is required before discharging the purified water into the recipient.

Keywords: oily wastewater, emulsions, thermochemical decomposition, treatment

1. INTRODUCTION

Wastewater with an increased oil and grease content is generated in various industrial sectors. The primary industrial sources of oily wastewater include oil refineries, metal processing operations, and food production processes [1-3]. Emulsions are suspensions of droplets with diameters greater than 0.1 µm, consisting of two completely immiscible liquids, where one of two is dispersed within the other [3,4]. Depending on which liquid forms the continuous phase, emulsions are classified into two types: (1) oil in water (O/W) for oil droplets dispersed in water, (2) water in oil (W/O) for water droplets dispersed in oil [3-5].

Spent emulsions (oily wastewater) from metal processing operations contain stable surface-active substances (emulsifiers), mineral oils, fats, organic compounds (mostly hard-to-degrade hydrocarbons), anti-corrosive agents, and metal ions, which prevent the gravitational separation of the oil and water phases. Due to their composition, wastewater emulsions are classified as hazardous pollutants that require responsible management. From an environmental protection perspective, all technological processes

generating oily wastewaters must be accompanied by the treatment of those waters in accordance with ecological regulations [1,3,6]. Chemical treatment is a common method for emulsion destabilization using surface-active compounds. The emulsifier molecules at the phase boundary are replaced by the demulsifier, which destroys the stable film around the water droplets [7]. The thermochemical decomposition process is an effective method for destabilizing oil-in-water system, wherein the combined effect of elevated temperature and specific chemical reagents successfully breaks interphase bonds [3,4,6,8]. Applying the treatment of oily wastewater through the process of thermochemical decomposition, an effective separation of the oily and water phases is achieved, which enables the safe discharge of purified water into receiving water bodies in compliance with environmental regulations [1,2].

This paper investigates and defines the optimal parameters of the thermochemical decomposition process using an actual industrial oily wastewater sample originating from the metal processing plant. The ultimate objective is to obtain purified water with characteristics suitable for the discharge into the environment.

2. EXPERIMENTAL PART

2.1. Characterization of oily wastewater

Characterization of the oily wastewater sample includes determination of pH value, hydrocarbon index and metal concentrations (chromium, zinc and copper). The pH measurements of the original oily wastewater, as well as after the experimental investigations, are performed on a Hanna Instruments digital pH/ORP-meter, model HI 9125 (Italy). The determination of the hydrocarbon index value was carried out according to the international standard ISO 9377-2, while the concentrations of chromium, zinc and copper were determined by the Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) method.

2.2. Thermochemical treatment of oily wastewater

The effectiveness of the thermochemical decomposition process of oily wastewater is influenced by many factors, such as: addition of decomposition agent, addition of flocculant, process time, temperature, and the settling time after the process is completed [4].

In order to determine the optimal parameters for the thermochemical treatment of oily wastewater (emulsions), experimental laboratory investigations were conducted in this paper, including the investigation of the influence of key process parameters. The influence of the addition of $\text{Al}_2(\text{SO}_4)_3$ as a flocculant (with and without addition), the sulfuric acid (as a decomposition agent) dosage (1.2 g $\text{H}_2\text{SO}_4/\text{l}$ of emulsion, 2.4 g $\text{H}_2\text{SO}_4/\text{l}$ of emulsion, 3.4 g $\text{H}_2\text{SO}_4/\text{l}$ of emulsion and 4.6 g $\text{H}_2\text{SO}_4/\text{l}$ of emulsion), temperature (ambient ($\sim 25^\circ\text{C}$), 65°C , 90°C), process time (6 h, 24 h, 48 h). The settling time, i.e. cooling and phase separation, was 24 hours in all experiments.

Thermochemical treatment investigations were carried out on emulsion samples with a volume of 200 ml. After reaching the desired temperature, the flocculant and/or sulfuric acid was added to the emulsion in a certain ratio, mixed, and left to react for the

investigated period at the target temperature to separate the oil and water phases. After the thermochemical decomposition process was completed, the suspensions were left to settle, i.e. to cool down to room temperature for a period of 24 hours. As a measure of the efficiency of the applied process, the separated water phases were sampled, the pH value was measured and the hydrocarbon index concentrations was determined. The obtained results were compared with the values from the Regulation on limit values for the emission of polluting substances into water and deadlines for their achievement ("Official Gazette of RS", no. 67/2011, 48/2012, and 1/2016), Table 7.1: Emission limit values at the point of discharge into surface water [9].

3. RESULTS AND I DISCUSSION

3.1. Characterization of oily wastewater

The results of the characterization of the oily wastewater sample are presented in Table 1.

Table 1. Characterization of the original oily wastewater sample

Content (mg/l)				Measured pH value
Hydrocarbon index	Cr	Cu	Zn	
146.90	<1.00	20.50	9.50	6.59

3.2. Thermochemical treatment of oily wastewater

Table 2 shows the investigated parameters of the thermochemical decomposition process of oily wastewater, as well as the obtained results.

Table 2. Parameters of the thermochemical decomposition process and obtained results

Experiment No.	Process parameters						Measured values after the treatment	
	Flocculant addition (g/l emulsion)	Settling time after flocculant addition (h)	H ₂ SO ₄ addition (g/l of emulsion)	Temp. (°C)	Proces time (h)	Settling time (h)	Hydrocarbon index (mg/l)*	Measured pH value
1	0.1	4	2.4	90	24	24	7.30	1.58
2	0.1	/	2.4	90	24	24	5.85	1.58
3	/	/	2.4	90	24	24	1.89	1.65
4	/	/	1.2	90	24	24	6.86	2.01
5	/	/	3.4	90	24	24	7.82	1.46
6	/	/	4.6	90	24	24	5.50	1.47
7	/	/	2.4	25	24	-	-	-
8	/	/	2.4	65	24	24	76.60	1.93
9	/	/	2.4	90	6	24	12.00	1.68
10	/	/	2.4	90	24	24	1.89	1.65
11	/	/	2.4	90	48	24	8.90	1.65

*According to the Regulation on limit values for the emission of polluting substances into water and deadlines for their achievement ("Official Gazette of RS", no. 67/2011, 48/2012 and 1/2016), Table 7.1: Emission limit values at the point of discharge into surface water [9], the limit value for the hydrocarbon index is <10 mg/l.

The results obtained from investigating the influence of flocculant addition (experiments 1-3) on the thermochemical decomposition process are satisfactory in all experiments, specifically, the hydrocarbon index values are <10 mg/l. For this reason, it can be concluded that the addition of flocculant is not necessary to achieve hydrocarbon index values below the limit value.

Although the measured hydrocarbon index value were below the limit in all experiments investigating the influence of H₂SO₄ addition (experiments 3-6), an H₂SO₄ addition of 2.4 g/l of emulsion was selected as the optimal parameter for the thermochemical decomposition process, as it yielded the lowest hydrocarbon index value. Sulaymon et al. [10] concluded in their research that the process of thermochemical decomposition is favored by the addition of sulfuric acid until a pH value of about 1.5 is reached, which in this study was achieved with an H₂SO₄ addition of 2.4 g/l of emulsion.

Investigations of the influence of temperature (experiments 3,7,8) on the thermochemical decomposition process of the emulsion showed that the process duration exceeds 30 days at ambient temperature. Applying a process temperature of 65 °C did not achieve satisfactory results, as the hydrocarbon index in the aqueous phase obtained after the thermochemical decomposition process is 76.60 mg/l. Also, at this process temperature, a clear separation of the phases into oil and water phase was not achieved. A process temperature of 90 °C is considered optimal, given that a clear separation of the oil and water phases was achieved, and the hydrocarbon index in the water phase is 1.89 mg/l.

During the thermochemical decomposition of the emulsion, the hydrocarbon index remained below the limit values at both 24 and 48 hours. The time of 24 hours was selected as the optimal parameter. A process time of 6 h (experiment 9) did not show satisfactory results.

Based on the experimental investigations of the thermochemical decomposition of oily wastewater and the obtained results, it can be concluded that the optimal process parameters are as follows: no flocculant addition, an acid dosage of 2.4 g H₂SO₄/l of emulsion, a process temperature of 90°C, and a process time of 24h.

In addition to the advantages of using sulfuric acid for the thermochemical decomposition of oily wastewater to achieve hydrocarbon index values below the limit values, this treatment has a disadvantage reflected in the low pH value (about 1.6) of the water phase obtained after the applied treatment. Due to this low pH value, the water phase cannot be discharged directly into the recipient, instead, an additional neutralization process must be carried out to achieve a suitable pH value within the prescribed range of 6-13. Beyond correcting the pH value itself, the subsequent neutralization process plays a key role in removing the heavy metals present in the initial emulsion sample. Since the thermochemical treatment was carried out in an acidic environment, the present copper, zinc and chromium ions remained dissolved in the water phase. Increasing the pH value during the neutralization process in the range of pH 6-13 creates conditions for their precipitation in the form of hydroxides. Consequently, the subsequent neutralization process resolves both the acidity issue and

ensures metal removal prior to discharging the treated water into the receiving environment.

The separated oil phase can be further disposed of or delivered to authorized operators who will handle it in accordance with legal regulations.

4. CONCLUSION

Based on laboratory investigations of the thermochemical treatment of a original industrial sample of oily wastewater from metal processing, it can be concluded that the applied thermochemical decomposition process successfully destabilizes the oil-in-water emulsion and breaks the interphase bonds. The best experimental results were achieved without flocculant addition, using an H_2SO_4 dosage of 2.4 g/l of emulsion, at a temperature of 90 °C, and with a process time of 24 h. By applying optimal process parameters, the hydrocarbon index was drastically reduced from an initial 146.90 mg/l to 1.89 mg/l, which is below the regulatory limit of 10 mg/l. The successful phase separation enables the recovery of the oil layer, which can be managed by handing it over to authorized waste operators. Due to the low pH value (about 1.6), treated water must undergo an additional neutralization process to reach a pH value of 6-13. This step is crucial, as it will also enable the additional precipitation and removal of the present heavy metals prior discharge into the receiving water body.

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