Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2021.26600

210 (2021) 134–142
January

Efficient phase separation in metalworking emulsions due to pH-induced destabilization and addition of aluminosilicates specialized demulsifiers

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Received 27 February 2020; Accepted 15 September 2020

ABSTRACT

In this study, effect of pH adjustment and addition of specialized aluminosilicates on the effectiveness of destabilization of metalworking fluids emulsion, in relation to turbidity, as well as chemical oxygen demand (COD) of obtained water phase was investigated. The two different aluminosilicates from C.H. Erbslöh (Germany) were used for the adsorption of oil on silicate structure. The silicates showed different effectiveness, depending on the product, pH of emulsion, and quantity of powder adsorbent used for the same emulsion system. The results of experiments indicated that cutting oil emulsions based on Emulgol ES-12 were stable in pH range from 3.5 to 12.5, in an ambient temperature of 25°C. Below and above-mentioned pH levels, the dispersion started to break. Moreover, the emulsion degradation process was studied with advanced light scattering techniques – with Turbiscan Lab® Expert apparatus, and with photometer PCE-TUM-20. The addition of the specialized silicate based chemicals resulted in excellent separation of phases of an emulsion. The obtained nephelometric turbidity unit dropped by 99.7% from ca. 750 to 2.3 NTU, while COD decreased by 88.5% from ca. 4,760 to ca. 550 mg/L. In this article, the mechanism of oil droplets interactions with aluminosilicates particles was also described. The experiments allowed the estimation of optimal conditions for phase separation with the usage of aluminosilicates as oil adsorbents

Keywords: Aluminosilicates; Demulsification; Adsorption; Metalworking fluids; Turbiscan Lab

1. Introduction

The term "metalworking fluids" (MWFs) refers to various types of liquids that are widely used in machining work, for example during processes such as boring, drilling, or grinding. These fluids are used for three main reasons. First, usage of MWF leads to cooling a metal piece at high speed cutting. Second, the appearance of MWF at low cutting speed benefits in lubrication of machinery. Last, it also reduces the corrosion rate of a metal surface. MWFs can be in the form of straight oils; however, the emulsified oils are most widely used [1–3].

These cutting fluids lose their properties and effectiveness with time. It is caused by shearing forces, thermal degradation and biological or other types of contamination [4]. The necessary replacement of these fluids leads to the occurrence of stable, emulsified, polluted wastewater, that is, known to be harmful to the environment [5–8]. Cutting fluids, in form of emulsion, usually contains from 1% to 10% of oil, with several additives and surfactants. The extra additives are present in the oil concentrate to meet the specifications for commercial applications [9].

Before the disposal of MWFs into the ecosystem, the treatment of the waste emulsions is necessary. In Europe, there already exists a strict environmental regulation for this type of effluent. As an example, Directive 2008/98/EC of the European Parliament from 19 November 2008 called

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"Waste Framework Directive" is implemented. According to the mentioned document, waste oils are considered as hazardous fluids and needs to be managed properly with the best available technique [10]. Considering that, the research on efficient and low-cost processes for the treatment of MWFs is essential.

Usually, three methods of oil separation from waste MWFs emulsion are described: physical, chemical and biological [4–6,8,11]. In many cases, effectiveness of the demulsification process is enhanced by electricity forces [7]. However, the most modern, and presently reported in literature, techniques include usage of freeze-thaw method [12], addition of blast furnace dust (BFD) [13], mixing with seawater followed by usage of microwaves [14] or treatment with nanoparticles [15]. All of the mentioned, novel methods have downsides and limitations. As an example, in the study described by Feng et al. [12], freeze-thaw method was used to break the emulsion system. It is an efficient method, however, the energy consumption is relatively high – about 42.90 kWh per m^3 of treated wastewater. Andrade et al. [13] described the possibility of BFD usage as an adsorbent of oil in wastewater emulsion produced by steel industry. This is a remarkable method of waste BFD usage, however, most of the mentioned dust is recycled by forming it into briquette. Microwave radiation is another technique of separation of oil from metalworking fluids emulsion. As an example, the method of seawater and microwaves usage was described by Chin-Hsing and Chon-Lin [14]. The considerable disadvantage of this method is the low efficiency – it reached only 40%. Moreover, the energy cost of microwave radiation is considerable. The team of Peng et al. [15] designed and tested the process of two-step demulsification, that include magnetic nanoparticles usage, which are recyclable, and further purification of effluent. Although the novel idea of this work has many advantages, it is worth to notice that the cost of nanoparticles and the necessity of their careful recovery make the application of process more difficult.

The low energy method, that does not have the drawbacks of mentioned techniques, might be the adsorption of oil in flock structure after addition of aluminosilicates or pH destabilization of MWFs emulsion.

Aluminosilicates are natural chemical compounds with variable Si/Al ratios that have become increasingly important due to their versatile physical and chemical properties. They have extensive applications as adsorbents, molecular sieves, membranes, ion exchangers, and catalysts in pollution control as well as in soil remediation [16,17]. The high cation-exchange ability and molecular sieve properties of aluminosilicates, especially zeolites, make their use possible for the removal of toxic metal ions such as lead, nickel, zinc, cadmium, copper, chromium and cobalt from wastewater [18]. The usage of aluminosilicate blends as oil adsorbents from MWFs emulsions is a new approach to this issue.

What is more interesting is the fact that the effect of pH on emulsions destabilization was studied very deeply in relation to crude oil emulsions [19,20], but not very intensively in terms of cutting oil emulsions. Therefore, in this paper, the influence of pH on MWFs emulsion is also investigated.

The aim of this work was to analyse the efficiency of MWF emulsion destabilization by two methods: pH adjustment and adsorption with aluminosilicates as adsorbent.

2. Materials and methods

In experiments, efficiency of oil removal from oil-in-water cutting fluid emulsion based on concentrate of Emulgol ES-12 oil was tested. During the analysis, three different dosages of two new class specialized aluminosilicates, delivered by C.H. Erbslöh-GmbH&Co.KG: Neosorb EMU-V and Neosorb EMU-B6, were used. During the studies, the influence of the pH level on stability of emulsion was also examined. Moreover, the advanced optic scanner Turbiscan Lab® was used to observe the instant changes in emulsion behaviour. The interactions of oil droplets with aluminosilicate particles were analyzed and described. The samples after demulsification were subjected to chemical oxygen demand (COD) tests. The conducted measurements give insights on efficiency and feasibility of modern adsorbents to break stable cutting oil emulsion. Fig. 1 presents the simplified methodology of the process.

2.1. Emulsion preparation

In a 250 mL beaker, the emulsion with 2% volume concentration of oil, based on emulsifying oil Emulgol ES-12, delivered by Orlen Group (Poland), was prepared by mixing the mentioned concentrate and tap water with a high speed homogenizer for 120 s. This concentration of oil in

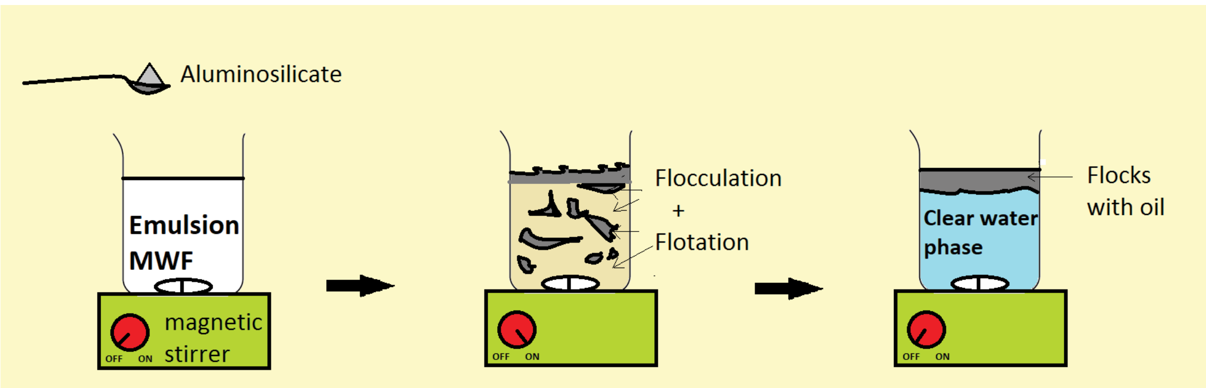

Fig. 1. Experiment of destabilization of emulsion with aluminosilicates.

emulsion has been chosen because it is used in industry for grinding [21]. Emulsion was oil-in-water system, as it was checked with microscope. For each experiment, three 200 mL samples of emulsion were prepared.

The tap water used for emulsion preparation had the temperature of 25°C, the hardness from 2.03 to 2.14 mmol/L, pH level in the range from 7.0 to 7.4 and total mineral content of 320 mg/L, confirmed by tap water supplying company (ZWIK-LODZ).

2.2. Emulsion structure analysis

Emulsion structure was examined with equipment used for microscopic image analysis. The system consisted of optic microscope Levenhuk 740T, with digital camera M1000+ connected to computer. It was found that diameter of the oil droplets was in range from 1 to 5 μm.

2.3. Emulsion stability and demulsification tests

In experiments, to monitor the stability of prepared emulsions, beyond visual observations, also the Turbiscan Lab® Expert apparatus was used. It is an optical measurement device, delivered by Formulaction (France), that allows monitoring the dispersion changes in time. The device uses a multiple light scattering analysis technique. The stability of emulsions can be recorded in time and compared. This advanced scanner detects all degradation processes such as creaming, sedimentation, coalescence and flocculation [22,23]. The Turbiscan Lab® detects the changes in structure of fluid before they can be visible to human eye [24–26].

To conduct phase separation process, two experimental procedures were developed. First, the demulsification due to adjustment of only dispersed fluid pH was investigated. Second, the phase separation induced by regulation of emulsion pH, combined with addition of specialized aluminosilicate chemicals was tested.

In first set of experiments, the prepared emulsion was treated to adjust the system pH. A necessary amount of 1 M NaOH solution (symbol AL) or H_2SO_4 (AC) was added with a syringe in order to obtain exact pH level of the samples. The pH was checked with VOLTCRAFT KBM-100 tester, delivered by Conrad Electronic (Poland), that was calibrated after every experiment. Later, 10 mL of previously prepared emulsion with known pH was placed in a Turbiscan Lab® measuring cell and the light scattering measurement started. Destabilization of sample was analysed according to obtained transmittance (*T*%) and backscattering (BS%) curves in TurbiSoft® program, with emulsion sample scanned every 880 nm of height, every minute for the first hour, every 5 min for next 2 h and every hour for next 21 h. The total time of experiment was 24 h. The process was conducted in an ambient temperature of 25°C. After the required time, the obtained water phase was also tested with turbidity scanner PCE-TUM 20, scaled in nephelometric turbidity unit (NTU). This device was delivered by PCE Holding GmbH (Germany). It uses light scattering technique and gives instant results in NTU. As stated by the manufacturer, there is an infrared LED light source with a wavelength of 850 nm inside the meter. A photodiode positioned in a 90° angle to the measuring ray absorbs the light reflected by the particles in the solution. In the device, diffused light is used for the lower measuring range – below 50 NTU. For the higher measuring range, it means between 50 and 1,000 NTU, an additional photodiode is positioned at the opposite side; therefore, measurement is performed via the transmitted light method.

In the second part of planned experiments, the three emulsions were first treated to obtain a desired pH level, with the procedure mentioned before. After that the aluminosilicates: Neosorb EMU-V (AD-1) or Neosorb EMU-B6 (AD-2) were added to samples, and mixed together for 20 min with a magnetic stirrer. The amounts of added chemicals were between 0.5 and 5 kg/m^3 of emulsion. The concentration of aluminosilicates added to MWFs emulsion, as well as properties of AC and AL are presented in Table 1.

Second set of experiments were planned to be recorded by Turbiscan Lab® device. However, due to issues related to mixing of emulsion and silicates in small 10 mL Turbiscan Lab® measurement cells, only the visual experiments were performed during the experiment. After the experiment, the obtained water phase was tested with NTU scanner mentioned earlier.

3. Results and discussion

3.1. Observations of pH-induced demulsification

In first experiments with usage of Turbiscan Lab® scanner, the changes of backscattering (BS%) and transmittance (*T* %) signal were analyzed according to the procedure from scientific article by Lemarchand et al. [22], and from other reports [23–26].

During studies, first general stability of prepared emulsion was tested. Sample without demulsifier addition, and without pH alternation, was placed in Turbiscan device. This sample had pH at the level of 7.91. In Fig. 2, the result of this test is presented. The description of emulsion breaking processes is described with blue font. As it can be seen in Fig. 2, basically no changes in transmittance (*T* %) or backscattering (BS%) signal can be observed. It was confirmed that emulsion stability in regular conditions is longer than 24 h, which is typical for micro-emulsion of metalworking fluid.

Fig. 3 shows scan of sample after usage of AC and acidification to pH 0.5. As mentioned before, in this first part of experiments no aluminninosilicate was added to emulsion. During the analysis of the signals – transmittance (*T*%) and backscattering (BS%), the coalescence process becomes

Table 1
Type and amount of used demulsifier

Demulsifier type	Symbol	Concentration	State of matter
H_2SO_4	AC	38%	Liquid
NaOH	AL	1 M	Liquid
Aluminosilicate NEOSORB EMU-V	AD-1	5 kg/m^3 2.5 kg/m^3 0.5 kg/m^3	Powder
Aluminosilicate NEOSORB EMU-B6	AD-2	5 kg/m^3 2.5 kg/m^3 0.5 kg/m^3	Powder

visible. It can be mainly seen as lowering the backscattering (BS%) signal in time. The further clarification of the sample is visible as the growth of transmittance (T%) signal is also present. However, it can be seen that degradation process also occurred in highly alkalized sample – Fig. 4. Emulsion with pH above 12.5 was also subjected to destabilization, as it is presented. It can be seen, that similarly to the sample with added acid, the phases separated during the test. However, the sample treated with AL, at the end of the process, was more turbid. This can be seen as a quite low transmittance (T%) of the water phase after demulsification process. It was related to the presence of small oil droplets that were left in water phase. It means that the acidic conditions are more suitable to break stable emulsion of metalworking fluid.

The turbidimetric analysis, such as presented in Figs. 3 and 4, is more precise than visual observation and it might lead to better understanding of the process nature. It is estimated that phase separation processes can be identified and quantified up to 50 times faster with Turbiscan Lab®, than with the naked eye [27].

Fig. 5 presents the emulsion behavior after adjustment of pH to 3.5. It can be seen that very small changes in BS (%) signal are present in time. Such changes are not visible to human eye, but Turbiscan Lab® can identify them. It is worth to mention that transmittance (T%) signal basically did not change, except very bottom of the measurement cell. It means that water phase did not separate from oil phase in that case. Similar situation can be found in Fig. 6, where sample was alkalized to pH 11.5. The modest changes in BS (%) can be observed in the figure. The phase separation did not appear (Fig. 6), as it can be concluded from very low transmittance (T%) signal at the end of experiment.

It is worth to mention that in case of strong alkalization, or acidification, extreme level of fluid pH can lead to corrosion of the equipment and is hazardous to humans health. In case of spillage, such fluid could easily irritate or damage human skin and eyes [28].

The photographs from acidification process of the emulsion – to pH of 0.5 are shown in Figs. 7a and b. In Fig. 7a, the dispersion before addition of AC can be seen, while in Fig. 7b sample after phase separation is presented. However, it can

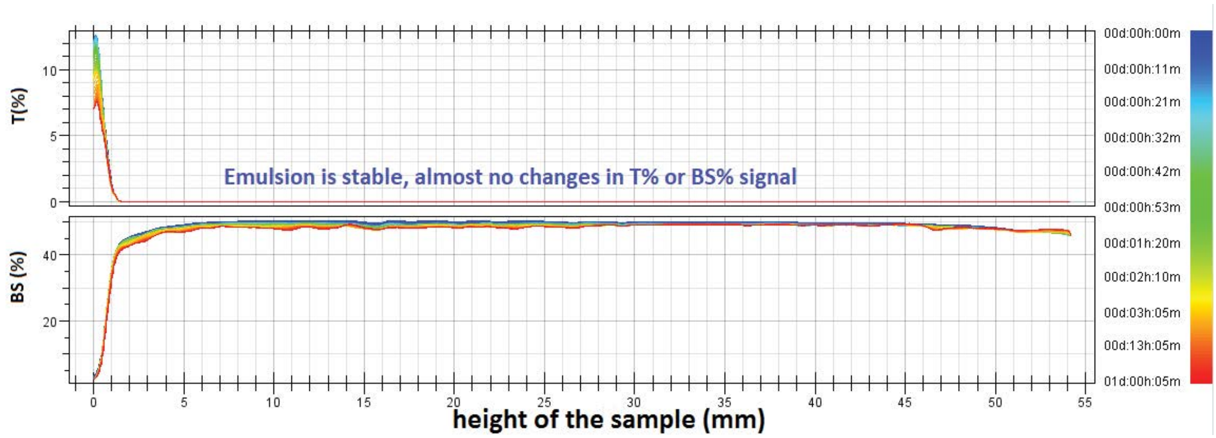

Fig. 2. Scan of emulsion without any additives for destabilization.

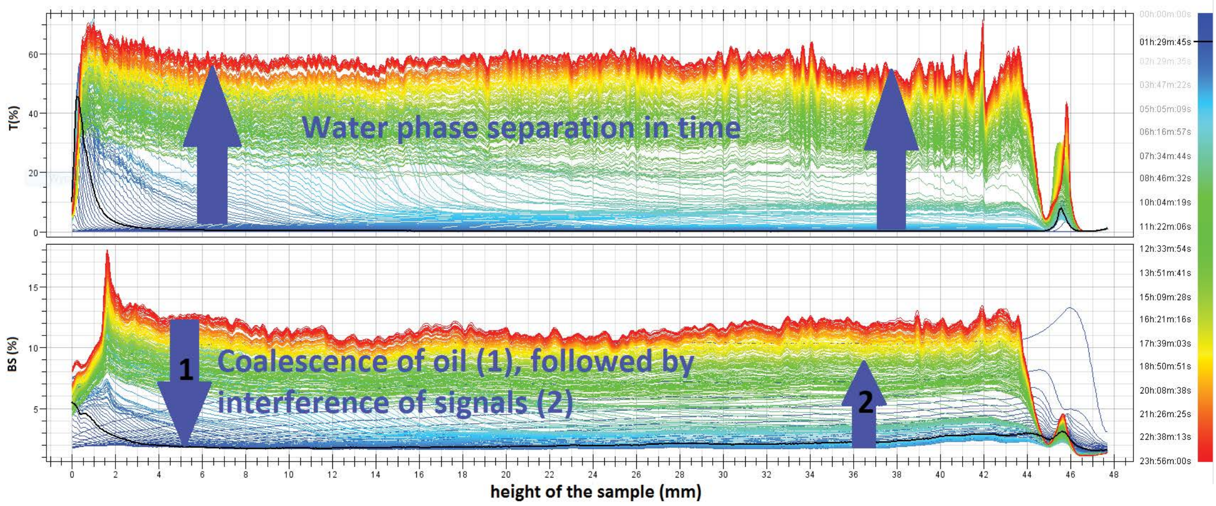

Fig. 3. Scan of emulsion after adjusting pH to 0.5 by AC.

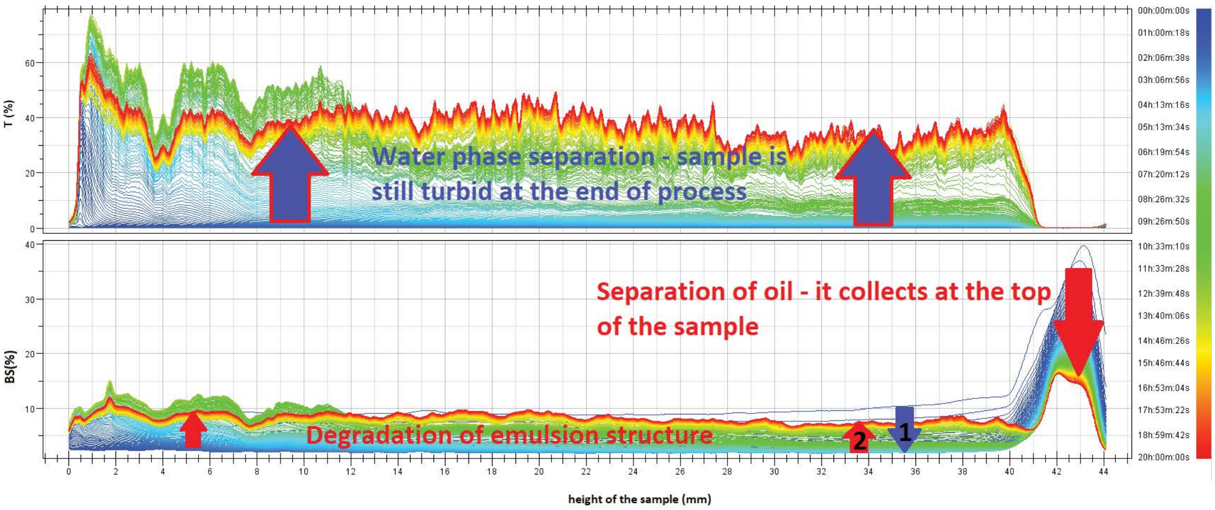

Fig. 4. Scan of emulsion after adjusting pH to 13.5 by AL.

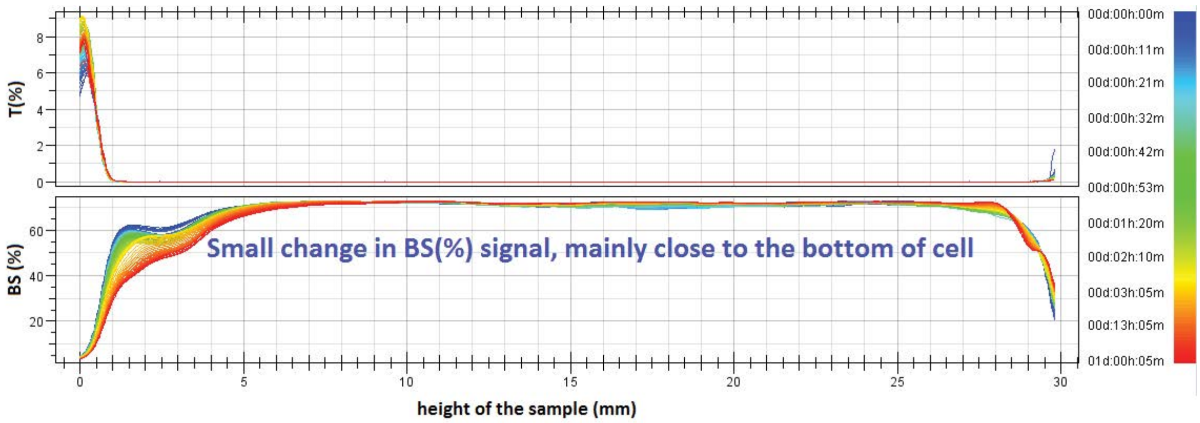

Fig. 5. Scan of emulsion after adjusting pH to 3.5 by AC.

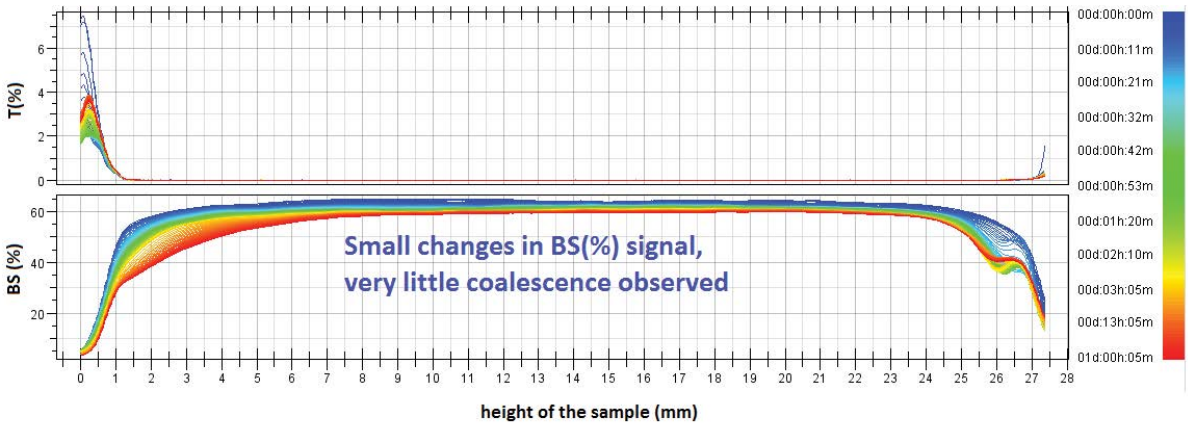

Fig. 6. Scan of emulsion after adjusting pH to 11.5 by AL.

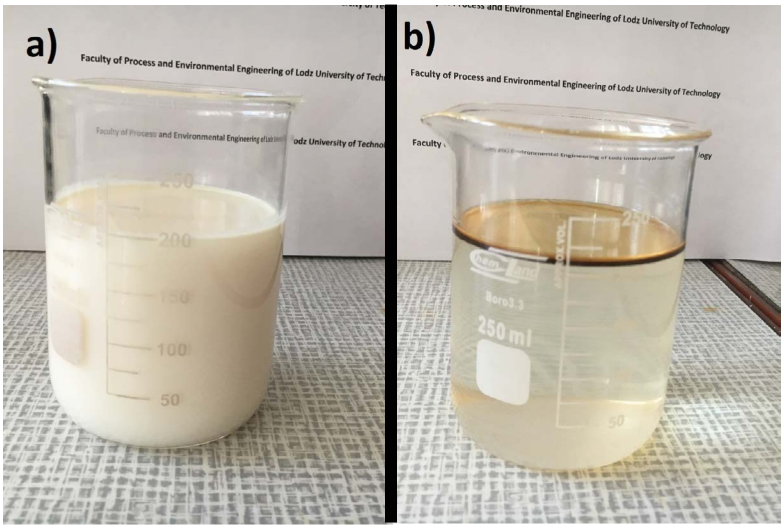

Fig. 7. Photo of emulsion: (a) before AC treatment and (b) after AC treatment to 0.5 pH.

be noticed that water phase after the process is still slightly turbid.

As it was mentioned, results of the experiments with different pH levels confirmed that the emulsion based on Emulgol ES-12 oil concentrate is stable in pH range from 3.5 to 12.5. More alkaline, as well as more acid conditions, lead to phase separation.

3.2. Demulsification with pH adjustment and aluminosilicate addition

In Figs. 8a–c, the results of demulsification of samples with AD-1 are presented. In experiments, the pH of emulsion sample was adjusted with AC to pH 6.5. The photographs clearly show that addition of AD-1 destabilizes the emulsion. At the top of the sample, the flocculated oil can be seen. At the sample bottom, small part of added powder is visible. In Fig. 8a, the amount of 5 kg/m^3 of AD-1 was used, while in Fig. 8b the amount was 2.5 kg/m^3 and whereas in Fig. 8c, the amount was 0.5 kg/m^3. Although the fact that addition of AD-1 leads to phase separation, still the obtained water phase appears to be cloudy. It had turbidity of 360 NTU, for the most suitable – 5 kg/m^3 addition of AD-1. In industrial application such turbid effluent will need purification, as example with filtration. The experiments with AD-1 were continued in different pH range. The results of the experiments showed that at the pH of 7.5 the results were better. In described case, the obtained water phase had 160 NTU. However, this level means that the sample was not clear yet, and still oil was present in form of small droplets in water phase.

Since in the results of experiments, with usage of AD-1, the turbidities of the samples after were still too high, the other product – AD-2 was used. This product is a blend of aluminosilicates, with additives that lower the sample pH. Therefore the experiment was conducted in pH-controlled conditions, with pH adjusted to 7.5. After the addition of AD-2 to emulsion system, pH was checked, and controlled with AL solution. The addition of AD-2 was 0.5 kg/m^3.

This time, the results were acceptable, since the obtained turbidity in 7.5 pH sample was as low as 2.3 NTU. It is worth to mention, that clear tap water used for research has NTU about 1 NTU. It means that the obtained water phase was "clear" for human eye. It also meets the industrial standards, for example Environmental Protection Agency directive for wastewater turbidity (NTU).

The oil concentration after treatment did not exceed the limit for wastewater effluent. The maximum value of oil concentration for industrial wastewater effluent in Lodz, Poland (ZWIK-LODZ), cannot exceed 100 mg/L. According to calibration curve in Fig. 9 that was based on NTU and emulsified oil concentration, the sample after treatment with AD-2 contained 21 mg/L of oil. It means that it was below the maximum limit.

The visual observations from experiments can be seen in Figs. 10a and b. The photographs show the sample before addition of AD-2 – Fig. 10a, and after complete phase separation – Fig. 10b. Clarity of obtained water phase, for human eye, is the same as tap water.

Alternatively, the efficiency of presented phase separation process can be described as 99.7% reduction in turbidity of the sample, compared with the raw sample. The data of obtained water phase turbidity can be seen in Fig. 11. In the figure, the comparison between treatment of emulsion with two aluminosilicates, as well as between only acidification and alkalization can be seen. The best result – turbidity equal to only 2.3 NTU – was obtained during usage of AD-2, in amount of 0.5 kg/m^3, in pH 7.5. In case of addition of AD-1, the lowest NTU was obtained with the highest dosage of aluminosilicate – 5 kg/m^3. However, sample treated with more efficient AD-2 only required addition of 0.5 kg/m^3 of this silicate for the best performance.

As it was stated, the aluminosilicates ability to adsorb oil droplets strongly depends on pH of the sample. The silicate powder is also effective as demulsifier in pH lower than 5.5. However, the efficiency of process is lower in acidic conditions, which can also be concluded from Fig. 11.

The COD test is considered as an important indicator of water quality. It measures the oxygen required to

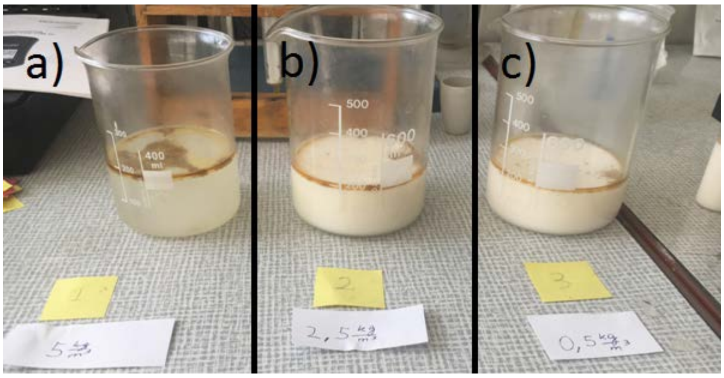

Fig. 8. Photo of emulsion after addition of AD-1: (a) 5 kg/m^3, (b) 2.5 kg/m^3, and (c) 0.5 kg/m^3.

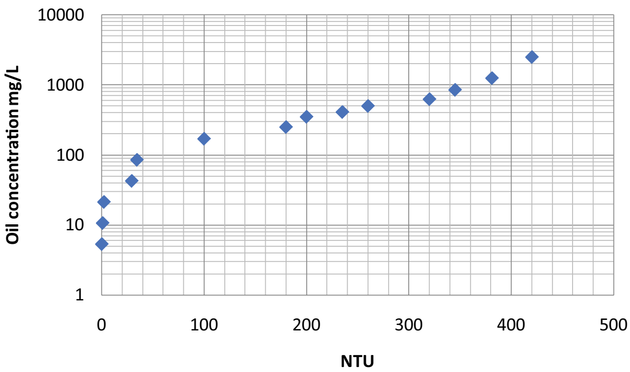

Fig. 9. Standard curve – oil concentration in emulsion vs. NTU.

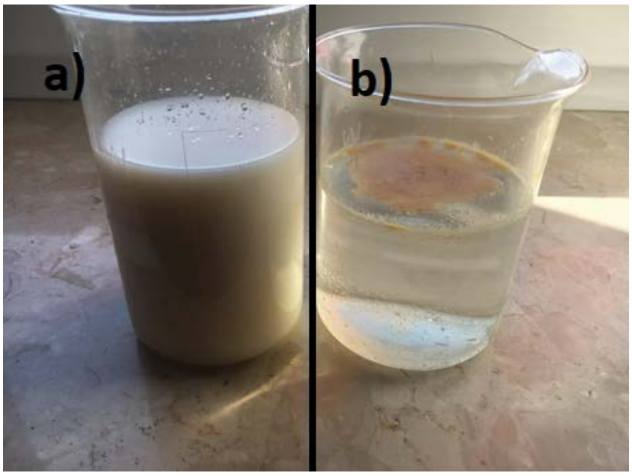

Fig. 10. (a) Emulsion before demulsification and (b) fluid after demulsification with AD-2.

oxidize soluble and particulate organic matter in water. This test shows the electron donating capacity of nearly all the organic compounds in the sample: biodegradable or nonbiodegradable as well as soluble or particulate. This analysis is crucial to be done for water after demulsification [29]. COD in this research was determined by conventional potassium dichromate oxidation process. The test was conducted for our team by Ekokompleks Company (Poland). For the COD measurement, only the three most transparent samples and the reference emulsion were given. The three most transparent samples were: water after acidification to pH 0.5, water after alkalization to pH 12.5, and water after demulsification with AD-2, when pH of emulsion was adjusted to 7.5.

The results of COD in the water after phase separation are presented in Fig. 12. It can be seen that the best results, meaning the lowest COD for sample, were obtained for test with addition of aluminosilicate AD-2. The other methods: alkalization with AL and acidification with AC were also efficient in reduction of COD. Still, for the real waste emulsion, contaminated with artificial particles and microorganisms, probably the superiority of aluminosilicate will be more significant. It is related to ability of silicate particles to attract not only oil droplets, but also other contaminations from dispersion system.

The aluminosilicate Neosorb AD-2 high efficiency in reduction of turbidity, can be explained with the following mechanism: emulsion of metalworking fluids are usually

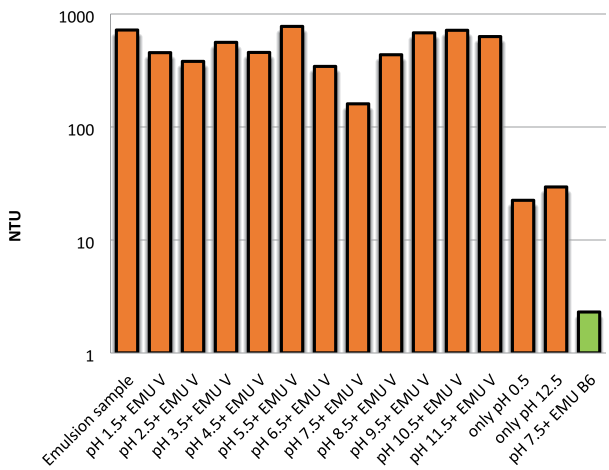

Fig. 11. Turbidity of obtained samples measured with NTU.

negatively charged, while the aluminosilicate blend from C.H. Erbslöh company (Germany) is positively charged powder [30]. When the silicate is added to emulsion, the attraction forces between the solid, and oil droplets appear.

If the amount of aluminosilicate is sufficient, and the process is intensified by mixing, the attraction forces between powder and oil become higher than interfacial tension in emulsion. As a result, degradation of emulsion structure begins. The droplets are being adsorbed on surface of solid, and also begin the coalescence. Since the overall density of obtained oily flock is lower than the density of water, the flotation phenomenon occurs. As it was mentioned, all processes are being intensified by mechanical mixing, which help to better distribute the powder in liquid. Fig. 13 illustrates the described process.

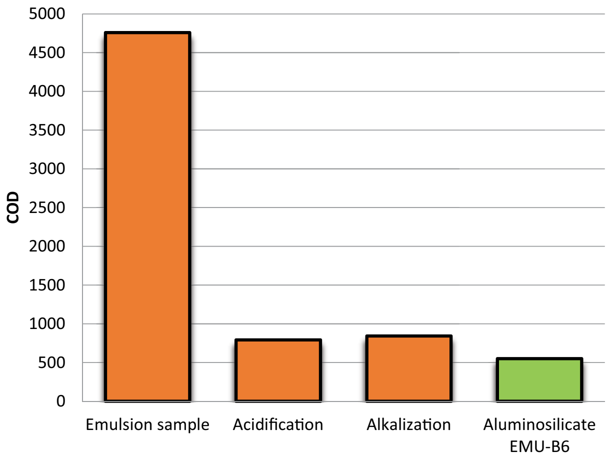

Fig. 12. Chemical oxygen demand of samples of: raw emulsion, after acidification, after alkalization, and after addition of aluminosilicate.

In Fig. 14a picture of aluminosilicate powder AD-2 is presented. It is a microscopic photograph, which shows the particles of powder used during the research. In Fig. 14b the flocks obtained after usage of AD-2 can be seen. As it was stated before, they contain adsorbed oil. It can be noticed on the edges of flocks shapes, as lighter color. These photographs are important for studies, since they confirm the described mechanism of adsorption.

The results of emulsion breaking are generally in common with the observations of other researchers, who studied the adsorption/precipitation behavior of oily wastewater with various silicates blends. Especially in the study of Sun et al. [31], the researchers introduced a novel composite coagulant, commonly known as "polysilicate–metal composite coagulant", to overcome the limitations of traditional coagulants. However, as they stated, very few studies have used similar technique to prepare coagulants and investigate the phase separation/clarification of water. It is also worth to mention that in their experiments researchers used high-oil-containing wastewater, not the low-oil-containing metalworking fluid emulsion, as in this study.

4. Summary and conclusions

In this research, we analyze novel class of demulsifiers: aluminosilicate blends, and we compare results of experiments with acidification and alkalization methods alone. The discussion of emulsion treatment and its efficiency was described. Our work highlights the optimal conditions, in terms of the pH and dosage of aluminosilicates to effectively degrade very stable metalworking emulsion. The experiments showed that both pH and aluminosilicate type had

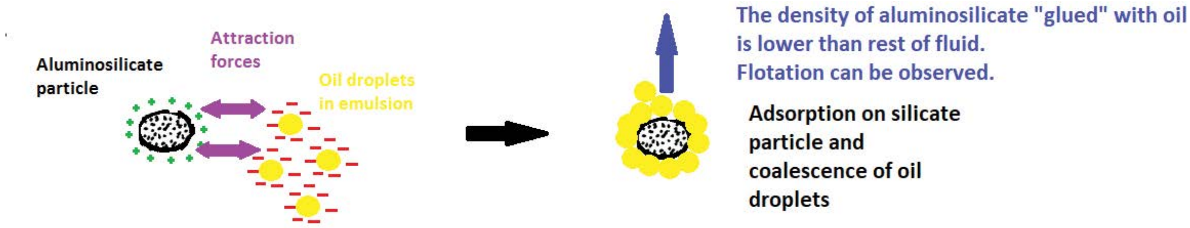

Fig. 13. Schematic representation of electrostatic attraction forces between aluminosilicate and oil droplets in microemulsion.

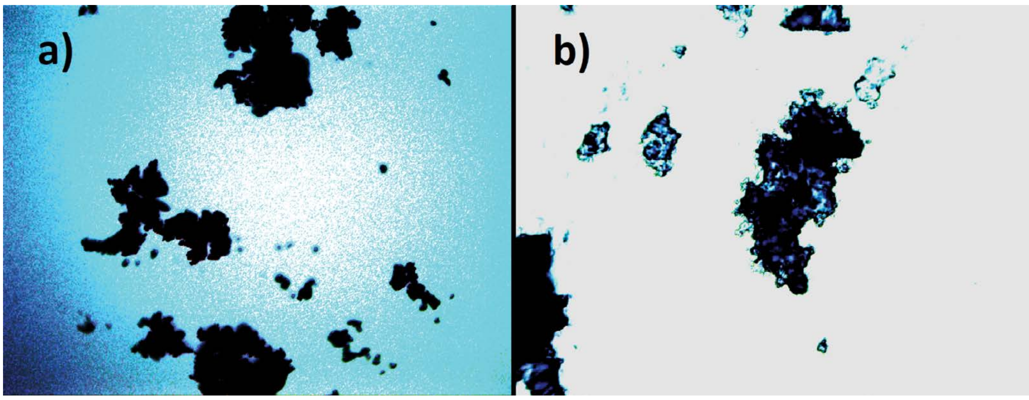

Fig. 14. (a) Aluminosilicate powder AD-2 and (b) flocks with adsorbed oil on aluminosilicate AD-2.

significant effect on destabilization of the metalworking fluid emulsions as quantified by light scattering techniques, as well as by visual observations. Moreover, it was shown that in normal conditions metalworking emulsion based on commercial oil concentrate is very stable. For destabilization of MWFs emulsion with only pH alternation, extreme conditions are required for the phase separation process. It means that below pH of 3.5 or above pH of 12.5 emulsions started to break. Therefore, it is more efficient to add to a dispersion the aluminosilicates blends, in order to separate phases. The electrostatic interactions of oil droplets with aluminosilicate are responsible for degradation of emulsion structure. These forces lead to adsorption of oil droplets on silicate, followed by coalescence, flocks formation and flotation which results in complete phase separation. It was shown, that tested aluminosilicates – AD-1 and AD-2 perform the best in pH between 7 and 7.5. The AD-2 is more efficient than AD-1, simple acidification or alkalization in reduction of COD and turbidity of the sample. The final obtained NTU, after addition of the efficient AD-2 to emulsion, dropped by 99.7% – it means from ca. 750 to 2.3 NTU.

Acknowledgements

The research was financed by the internal grant number NCN/2019/35/D/ST8/01033 of the Faculty of Process and Environmental Engineering of Lodz University of Technology. The authors would like to thank Mr. Arkadiusz Walkiewicz from C.H. Erbslöh for assistance with methodology development.

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