UDK 628.3:621.78
DOI: 10.7562/SE2018.8.01.04
Review article
www.safety.ni.ac.rs

VESNA LAZAREVIĆ[1]
MIODRAG STANISAVLJEVIĆ[1]

[1]Military Hospital Nis
[2]High Technical School of Professional Studies, Požarevac

[1]*vesna.toxicology@gmail.com*
[2]*vode@gmail.com*

THE TREATMENT OF WASTE OIL-IN-WATER EMULSIONS IN THE METALWORKING PROCESS

Abstract: *Used water emulsions obtained in the metalworking process contain oils and grease, organic compounds as well as secondary oils and anti-corrosion fluids, metal ions and other things. Since they can have a negative effect on the environment before released into the recipients, they need to be processed through the primary, secondary and tertiary phase of treatment. The primary treatment procedure of waste oil-in-water emulsions is used for the separation of free and non-emulsifying oils as well as for balancing the course of wastewater and oil concentration. In the secondary phase of treatment of waste oil-in-water emulsions, the emulsifying oil and a large fraction of dissolved oil are carried out. What follows is the tertiary biological treatment based on the basic biological processes present in nature.*

Key words: metalworking, waste oil-in-water emulsions, treatment

INTRODUCTION

The most common types of cooling and lubricating fluids can be classified in four groups:

- pure oils for cutting and deforming (mineral oils, greasy oils and oil mixtures),
- dissolved oils (e.g. water emulsions of mineral oils),
- synthetic and semi-synthetic fluids and
- gas fluids (air under pressure, emulsion or oil fog, carbon- dioxide (CO2), argon (Ar) and nitrogen (N2).

Pure oils are the oldest class of cooling and lubricating fluids and they contain the highest level of mineral or vegetable oil. They provide excellent lubrication and good corrosion control. Pure oils are available in different forms based partially on their viscosity. Pure oils of lower viscosity are used for whetting and polishing, whereas pure oils of higher viscosity are used in the heavy metalworking.

Dissolved or emulsifying oils are most commonly used metalworking fluids. They represent a combination of 30-85 % of refined mineral oils and emulsifiers (the dominant one is sodium sulfonate) which enable the dispersion of oil into water. In order to improve their performances, these fluids contain other additives. Dissolved oils enable good lubrication as well as improved cooling compared to pure oils. On the other hand, dissolved oils sometimes have low corrosion control and can "smoke", while emulsions can be unstable or short term. It should be pointed out that there is a difference between "regular" dissolved oils which do not contain any or contain a few additives to improve their characteristics and "special" dissolved long-term oils with excellent performances in metalworking [1].

Figure 1. *Metalworking fluids*

Physical and chemical properties of metalworking fluids

The quality of metalworking fluids depends on the chemical and physical properties of mineral oil, oil concentration in emulsion, oil stability and water emulsion stability.

The appearance of emulsion is influenced by **the size of dispersed particles** and the way of their distribution. The size of particles is from 0.1-1.0 µm. The higher the size of the particles, the less clear the emulsion is, whereas with particles bigger than 1,0 μm it becomes creamy-colloid.

The density of water emulsions of mineral oils in normal temperatures is close to the density of water.

The viscosity is the most important individual property of metalworking fluids. Its significance decreases if the fluid is diluted by water before use.

Most metalworking fluids are bases and their **pH value** is between 8.0 and 9.5. The common reason for pH decrease is microbiological increase, which leads to the formation of acids. Keeping pH level at 8.8 or higher is an efficient way of controlling bacterial increase.

A metalworking fluid may contain acids or bases, and these compounds can be formed by degrading certain components during usage. **Alkalinity** can increase during the ageing period of the metalworking fluid, because it not very likely for the alkaline components to be separated by secondary oil, carbonates from water or other contaminants.

By measuring conductivity the information about the presence of all ions is obtained. **Conductivity** increases during the application until a saturated solution has been reached. After that, conductivity remains constant since the "excess" of non-organic ions is lost through precipitation, whereas the excess of organic ions is transformed from water to oil phase through adding enormous amounts of non-organic salts. When this ion loss occurs, the performances of the metalworking fluid worsen, so that the emulsion may become unstable.

The foaming of metalworking fluids can lead to high operative costs due to liquid loss, shortening of working time of pumps due to cavitation and decreasing cooling and lubricating properties on the surface of the tools. The factors influencing the intensity of foaming during the cutting and grinding processes are: water hardness, the composition of water emulsion, the reaction of emulsion components over time etc.

It is very important to control the **concentration of mineral oil** in water emulsion. All water emulsions of mineral oil react usually problem-free when the ratio of mixing mineral oil with water is defined. Corrosion, microbiological increase and emulsion instability can occur when oil concentration is smaller, while high oil concentration can result in foaming and skin irritation.

Knowing **the emulsion instability** represents a crucial factor which enables decomposition (treatment) of waste emulsions. Instability of emulsions is reflected in three ways: by forming creams, inversion and demulsifying (separating emulsion). The formation of creams represents decomposition of emulsion into two layers due to coagulation and creation of aggregates (flocculation) in the presence of electrolytes. Inversion is reflected through the transfer of one type of emulsion (oil in water) into the opposite one (water in oil) due to high heating accompanied by constant and intensive stirring. Demulsifying is a process of complete decomposition of emulsion, which can be followed by the creation of cream or inversion due to elevated temperatures, low or high amount of emulsifiers and presence of a larger number of bivalent cations [2].

Wastewaters in the metalworking

Water emulsions used in the metalworking must satisfy not only high criteria of the industry regarding heat exchange (cooling) and lubrication, but also the criteria regarding working and living environment. Out of the overall amount of waste fluids in the metalworking, 28 % disappears in nature without control. The largest part of these waste fluids is water emulsions, which account for 20 % of used industrial metalworking fluids. After use, enormous amounts of these emulsions remain unprocessed and as such enter the waterways [3].

Reduction, or possibly a complete removal, of harmful effects of water emulsions on the environment can be achieved in different ways such as: development and application of new water environmentally safe emulsions, oil recycling and treatment of waste oil-in-water emulsions before disposal. By using semi-synthetic and synthetic fluids "oil fogs" in the workshop and danger of fire have been eliminated. Despite these benefits, there is a concern about the environment even when using synthetic fluids. From the point of view of waste treatment, many synthetic fluids are not compatible with the operations of treatment of wastewaters which are designed to work with the metalworking fluids with mineral oils. Regardless of the performances and efficiency of these operations, complex soluble organic compounds, which comprise synthetic fluids, go through the process of wastewater treatment. This results in the additional treatment on the spot, otherwise the treated wastewater will contain complex organic substances which will negatively affect further treatment processes. New lubricating fluids, harmless for the environment, should meet the following requirements: to provide maximum protection of water, air and soil, to minimally influence the health of people, animals and plants, as well as to ensure a safe technological procedure and easy treatment of the used processing fluids. It is necessary to make efforts so as to reduce the release of the used metalworking fluids from production workshops with a view to decreasing their negative effect on the environment. If recycling is not possible or is not justified from the finacial point of view, wastewaters must be treated in a suitable way so that they could be poured into the sewage system or waterways.

Treatment of wastewaters in the metalworking

The procedures of treatment of water emulsions obtained in the metalworking can be: physical, chemical and biological, whereas according to the level of gradation they can be primary, secondary and tertiary.

The primary treatment of waste oil-in-water emulsion is used for the separation of floating or free and non-emulgated oils as well as balancing the course of wastewater and oil concentration. What is used here for their separation in the field of gravity is the difference in oil and grease density in relation to water. The most commonly used devices in this treatment are gravitational separators. The treatment usually involves retaining oil waste in the separator, which is then removed (skimmed) from the water surface using a sutable device (“skimmer“). The efficiency of a gravitational separator depends on the correct hydraulic design of the projected period of water retention. A short period of retention, less than 20 minutes, results in oil and water separation of less than 50 %, whereas longer periods improve the separation of oil from water. Gravitational separators are equally efficient in the elimination of grease and non-emulgated oils.

In the phase of **secondary treatment** of waste emulsion oil-water, which was subjected to the primary treatment first, what happens first is the decomposition followed by the separation of oil and water phase. The removal of emulgated oil and a big fraction of dissolved oil is achieved in the phase of secondary treatment. Emulsions can be decomposed by means of chemical, electrical and physical methods. Electrical methods are usually used if the emulsion is with low water content. Physical methods are heating, centrifugation and filtration.

A chemical treatment of used water emulsions is based on the decomposition of emulsion into oil and water phase using electrolytes. Acids, salts and organic compounds (polyelectrolytes) are used as decomposing fluids. The essence of this procedure is to neutralise the effect of the emulgator or its decomposition. The procedure consists of three phases:

- coagulation, which involves adding the chemicals to waste water, accompanied by intensive stirring,
- flocculation, which involves the growth of the particles (“floccules“), accompanied by moderate stirring and
- separation of the phases by flotation or sedimentation.

Coagulation consists of the decomposition of water emulsions. In this process, under the influence of certain reagents, the neutralisation of the effects of the emulgators in the emulsion occurs and the stability of the colloid particles is affected. The stability of emulsion is the result of the protective effects of certain absorbed components as well as mutual repulsion of the particles under the influence of electrostatic forces. In natural water, colloid particles are always negatively electrically charged, which is often the case with the colloids of wastewaters [4]. In the coagulation process, by adding oppositely charged ions, the electricity of the colloid particle decreases (Z-potential), which leads to the creation of agglomerate. This process is the result of the bačance disturbance in the balance ocurring by adding chemical reagents which undo the effects of the repulsion forces or influence the hydrophility of the colloid particles by aggregational or adsorptional mechanisms. Intensive stirring of the system and adding substances, so called coagulants, improves the process. Coagulants are chemical compounds which cause destabilisation and sedimentation of colloid particles in the system by neutralising them. Two primary roles of coagulants are the stabilisation of particles and strengthening of floccules. Flocculation happens immediately after the coagulation process and provides the increase in the number of contacts between coagulated particles suspended in water by means of gentle and long stirring so as to prevent the formed aggregates from breaking and decomposing. The floccules created by aggregating particles between which a successful collision occurred will more easily and more successfully grow if the following is provided:

- establishing the contact between water and formed sediment, which increases the concentration of floccules in water and, therefore, the possibility of successful collisions,
- homogenous and gentle stirring of the whole mixture so as to increase the possibility of colloid particles, free of electricity, meeting a floccule and
- using flocculants.

Flocculants are additional flocculating fluids used as the basis on which floccules grow, enhancing in this way the speed of their sedimentation. Flocculants affect the speed of the creation process and the quality of floccules, which are characterised by a bigger volume, bigger hardness and consistency. They are usually organic, but there is a number of them which are not organic such as sodium-silicat. They can be natural (sodium-alginate) and synthetic, which are considered to be the most effective polymers. When conducting a flocculation procedure, pH values and temperature which determine the reaction of the flocculants should be monitored.

A chemical treatment is usually performed in a batch reactor and involves determination of necessary doses of chemicals for each batch in laboratory conditions [5].

Oil-water emulsions can be decomposed by acidifying, adding sulphur acid. By adding a strong acid, carboxylate ions of the emulgator are transferred into non-ionised form, after which agglomeration of oil drops occurs. The advantage of this procedure is that oil is separated in pure form so it can be burnt or mixed with fuel oil and used as energetic fluid. Generally, acids separate emulsions more efficiently than coagulation salts, but are more expensive and the acid wastewater obtained in the process must be neutralised after the separation of oil and water. The necessary pH value for acid deemulgation depends on the type of waste. Adding a non-organic coagulant, such as aluminium (III)-sulfate, instead of or after adding the acid, facilitates the agglomeration of oil drops. Efficient emulgators are also organic compounds of polyamine type. Decomposition of oil-water emulsions using organic deemulgators is common with lower doses, where a smaller amount of sediment is formed.

Alternative chemical deemulgation processes include:

- adding coagulation salts (aluminium or iron salts),
- adding acids,
- adding salts and heating emulsion,
- adding coagulation salts and electro-treatment and
- adding acids and organic compounds.

The most commonly used procedure for the treatment of industrial wastewaters, including wastewaters in the metalworking, is the one involving adding coagulation salts. For example, coagulation with aluminium (III)-sulfate in concentration 35 mg/dm^3, followed by sedimentation, reduces the oil content form 50-100 mg/dm^3 to less than 15 mg/dm^3. Deemulgation or flocculation are improved by adding polymers. The drawback of the procedure with coagulation salts is the formation of hydroxide sedimentation, which appears as solid waste and is difficult to dehydrate. Adding great amounts of non-organic salts can create an additional problem of pollution due to a significant increase of salts in the effluent. Organic deemulgators are extremely efficient deemulgating reagents, but due to their high price are considered to be impractical in big flow and low oil concentration.

Within the chemical treatment of waste oil-in-water emulsion, physical-chemical procedures using the combination of decomposing and adsorbing materials can be applied. Adsorbing materials used are: silicic acid, active bentonites and clay flour. Because of its big surface and oleophilic character, silicic acid absorbs a big amount of oil. The remaining oil amount in this procedure is less than 20 mg/dm^3. Wastewater contains little amount of salts and does not need to be neutralised. The oil separated on filters is destroyed by burning. This way of separation is not economical and is used for small amounts of emulsions. Another type of adsorption is done by using bentonite and adding polyacrylamid (a macromolecule which connects floccules) to facilitate the separation. Electrochemical decomposition includes subjecting emulsion to the process of electrolysis and is usually applied in emulsions which contain mostly oil, with small amounts of water. Electroflotation and electrocoagulation use electricity for destabilisation of oil in wastewater.

Physical treatment involves evaporation and mechanical procedures.

Evaporation is becoming more and more significant because it can be used for the treatment of all kinds of emulsions (no chemicals are necessary; the obtained wastewater can be used or poured). During the evaporation process we should take care that easily vaporable carbo-hydrogen and emulgator parts do not go away. That is why additional devices for treatment are attached to the evaporators. Due to high level of energy consumption, the process is carried out in several evaporators or in the vacuum.

Mechanical treatment is based on the physical properties of the substances which are dissolved in water. Mechanical treatment includes: sedimentation, flotation, filtration, ultrafiltration, centrifugation and using ultrasound.

Sedimentation is the oldest and most widely used procedure of wastewater treatment primarily because of its low costs and low level of energy consumption. It is based on the separation of diluted suspension into pure liquid and thickened suspension with higher concentration of solid phase. In order to define more clearly different properties of water systems, particles that can be found in water can be classified into three groups:

- rigid particles, in relatively low concentration do not flocculate and sediment independently of each other,
- flocculated particles, created through natural agglomeration or due to the presence of coagulants, and present in relatively low concentration and
- more or less flocculated particles, present in high concentration.

Depending on the concentration of the solid phase, sedimentation can be diffusive or hydraulically decelerated sedimentation. In low concentration of the solid phase, a flocculated particle is sedimented as if it was alone, but its sedimentation speed grows with the increase in its dimensions due to agglomeration (diffusive or free sedimentation). In higher concentrations, due to a larger number of floccules, compacted sedimentation occurs and it is characterized by a prominent contact surface between the oil sediment and the liquid above it (hydraulically decelerated sedimentation).

During flotation, air bubbles are introduced in wastewater. The “catching“ of the drops of emulgated oil occurs on the surface of the air bubble in the presence of superficial active compounds. Released floccules and air bubbles come to the surface and are mechanically removed. Filtration is a procedure of mechanical separation of solid from liquid particles. Depending on the treatment and medium characteristics, there are two types of filtration:

- filtration through the cake and
- filtration through the medium.

Filtration through the cake involves retaining solid particles from suspension (usually with solid phase content higher than 1 % vol.) on the filtration medium, on which a filtration cake is formed, while the liquid (filtrate) goes through the filtration medium. The filtration cake that has been created serves as a filtration medium. Filtration through the medium represents the separation of solid particles from suspension (about up to 0.1 % vol.) using the filtration medium, without the formation of a filtration cake..

Adding coal as an adsorbent in the process of waste oil-in-water emulsion treatment and its subsequent removal through the filtration process enable economical and highly efficient separation of oil from wastewaters [6].

Biological treatment. After the mechanical and chemical treatment, biological treatment of waste oil-in-water emulsion, which is considered as the tertiary type of treatment, can be applied. This treatment is based on the basic biological processes in nature. Independent of human influence, the decrease or disappearance of polluting substances occurs in waters as a result of physical, chemical and biological actions. Esentially, the processes in treatment devices represent just a simulation of natural processes [7]. Biological wastewater treatments are:

- processes using active sludge,
- processes of biological filtration and
- processes in lakes and lagoons.

In these processes, polar biodegradable oils and grease are removed up to the level of 2-8 mg/dm^3 in the treated wastewater, whereas non-polar oils and grease are removed through primary clarification or are incorporated in biological floccules.

Biological wastewater treatment is based on certain basic principles:

- active sludge population consists of different microrganisms from the natural environment whose growth and development do not happen in optimal physiological conditions,
- the substrate is wastewater whose chemical composition and other characteristics can be very different,
- the substrate concentration is usually low in relation to the values for the growth of microorganisms and
- the process is directed at decomposition of organic substances, which are difficult to remove in a chemical or mechanical way, such as fatty acids and amines, and not at creating a biomass or using the products of metabolism.

The most important engineering problems in the biological treatment of wastewaters deal with providing a big contact surface and efficient dissolving of oxygen. Besides this, significant problems are connected with particle flocculation and sedimentation of microrganisms.

The application of membrane processes, ultrafiltration, reverse osmosis and electrodialysis does not only enable the regeneration of toxic metals, but also produces the high quality effluent which can be recycled in the technological process of galvanisation. In this way, through the application of the tertiary treatment preceeded by quality pre-treatment, the efficiency of the technological process increases and the demands of pure technologies are met. If a classical wastewater treatment is used, secondary environment pollution occurs in the form of sludge, which can be destabilised through chemical transformations into eco-friendly products [8-12].

CONCLUSION

Based on the physical-chemical properties of cooling and lubricating fluids used in metalworking, the paper provides an overview of treatments of waste oil-in-water emulsions by means of conventional systems. Since these systems cause secondary environmental pollution, we should use block schemes for unconventional systems such as ultrafiltration, reverse osmosis and electro dialysis, if it is financially justified. If these systems are used, we could meet the demands of pure technologies, with 99.9 % efficiency, and the incoming elements could be recirculated.

REFERENCES

[1] E. Brinksmeier, D. Meyer, A.G. Huesmann-Cordes, C. Herrmann, Metalworking fluids-Mechanisms and Performance, CIRP Annals - Manufacturing Technology, 2015, 64, 605–628.

[2] Bittorf P., Shiv G. K., R. E. DeVor, Transiently Stable Emulsions for Metalworking Fluids, Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, 2011, pp. 7-10.

[3] G. Libralato, A. V. Ghirardini, F. Avezzu, To Centralise or to Decentralise: An Overview of the Most Recent Trends in Wastewater Treatment Management, Elsevier, Journal of Environmental Management Vol. 94 (1), 61-68.

[4] M. Kobyaa, C. Ciftcia, M. Bayramoglub, M.T. Sensoya, Study on the Treatment of Waste Metal Cutting Fluids Using Electrocoagulation, Separation and Purification Technology, Vol. 60, Issue 3 p.p. 285-291, 2008.

[5] V. K. Gupta, I. Ali, T. A. Saleh, A. Nayaka and S. Agarwalc, Chemical Treatment Technologies for Waste-water Recycling – an Overview, RSC Advances, 2, 6380-6388, 2012. DOI: 10.1039/C2RA20340E

[6] X. Li, C. Zhang, J. Liu, Adsorption of Oil from Waste Water by Coal: Characteristics and Mechanism, Elsevier, Mining Science and Technology (China), Vol. 20, 5, p.p. 778-781, 2010.

[7] C. P. Leslie Grady, Jr., Glen T. Daigger, Nancy G. Love, Carlos D. M. Filipe, Biological Wastewater Treatment, Third Edition, CRC Press, Technology & Engineering, 2011.

[8] M. Tira, N.Moulai-Mostefab, Optimization of Oil Removal from Oily Wastewater by Electrocoagulation Using Response Surface Method, Journal of Hazardous Materials, Vol. 158, 1, p.p. 107-115, 2008.

[9] F.A. D.Amaral, V. S. Santos, A. M. Bernardes, Metals Recovery from Galvanic Sludge by Sulfate Roasting and Thiosulfate Leaching, Elsevier, Minerals Engineering, Vol.60, p.p. 1-7, 2014.

[10] M. Stanisavljevic, I. Krstic, S. Zec, Eco-technological Process of Glass-ceramic Production from Galvanic Sludge and Aluminium Slag, Science of sintering, International Institute for the Science of Sintering (IISS), ITN SANU, p.p. 125-130, 2010.

[11] I. Krstić, V. Lazarević, G. Janaćković, N. Krstić, N. Anastasijević, D. Djordjević, D. Dulanović, Toxicological Analysis of the Risk of Lead Exposure in Metal Processing, Tropical Journal of Pharmaceutical Research, 16 (12), p.p. 2959-2966, 2017.

[12] A. Murića, I. Petrinića, M. L. Christensenb, Comparison of Ceramic and Polymeric Ultrafiltration Industry, Chemical Engineering Journal, Vol. 255, 2014, p.p. 403-410.

BIOGRAPHY

Vesna Lazarević was born in Niš, Serbia, in 1970.
She was awarded the PhD in technical sciences - environmental protection, at Faculty of Occupational Safety, University of Niš.
Her main areas of research include wastewater, ecotoxicology, etc.
She is currently working in Military Hospital in Nis as a toxicological chemist. She is engaged in testing the quality of drinking water and determining the energy value for daily meals in military. Also, she cooperated in the development of a number of projects in the field of environmental protection at the Ministry of Defence of the Republic of Serbia.

POSTUPCI PREČIŠĆAVANJA OTPADNIH VODENIH EMULZIJA IZ PROCESA OBRADE METALA

Vesna Lazarević, Miodrag Stanisavljević

Rezime: *Iscrpljene vodene emulzije iz procesa obrade metala sadrže, po pravilu, ulja i masti, organska jedinjenja, kao i sekundarna ulja i antikorozivna sredstva, jone metala i drugo. Obzirom da mogu imati negativan efekat na životnu sredinu, one se moraju obraditi pre ispuštanja u recipijente, primarnim, sekundarnim i tercijalnim prečišćavanjem. Primarni postupak prečišćavanja otpadnih vodenih emulzija koristi se za separaciju slobodnih i neemulgovanih ulja, kao i za uravnotežavanje toka otpadne vode i koncentracije ulja. U fazi sekundarnog prečišćavanja otpadnih emulzija ulje-voda, postiže se uklanjanje emulgovanog ulja i velike frakcije rastvorenog ulja. Nakon toga primenjuje se tercijalno biološko prečišćavanje koje se zasniva na osnovnim biološkim procesima koji se javljaju u prirodi.*

Ključne reči: obrada metala, otpadne vodene emulzije, prečišćavanje.