

Scaling up the chemical treatment of spent oil-in-water emulsions from a non-ferrous metal-processing plant

Vesna B. Lazarević¹, Ivan M. Krstić², Miodrag L. Lazić³, Dragiša S. Savić³, Dejan U. Skala^{4*}, Vlada B. Veljković³

¹Centre for Preventive and Medical Protection, Niš, Serbia

²University of Niš, Faculty of Occupational Protection, Niš, Serbia

³University of Niš, Faculty of Technology, Leskovac, Serbia

⁴University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Serbia

Abstract

The treatment of spent oil-in-water emulsion (SOWE) from a non-ferrous metal-processing plant by using aluminum sulfate and hydrated lime was studied in order to determine the purification efficiency, optimize the operating conditions and scale up the treatment process. The purification efficiency was estimated by comparing the compositions of the SOWE and the processed wastewater. The treatment efficiency does not depend on the type of mineral oil and filter aid. The optimum doses of aluminum sulfate and hydrated lime must be experimentally determined for each batch of SOWEs, but the results obtained at laboratory level are applicable at pilot level. The processed wastewater and the filter cake from the process can be safely disposed into public sewage systems and at municipal waste landfills, respectively. The purification efficiency was higher than 98% with respect to total suspended solids, chemical oxygen demand and oil and grease, and was comparable to the known treatment processes based on coagulation/flocculation followed by sedimentation.

Keywords: aluminum sulfate, chemical wastewater treatment, coagulation, flocculation, mineral oil-in-water emulsion, sedimentation..

Available online at the Journal website: <http://www.ache.org.rs/HI/>

Mineral oil-in-water emulsions (OWEs) are used in the metal-processing industry as cooling and lubricating agents [1]. They also have secondary functions, such as to ensure the corrosion protection of both processed metal parts and operating tools, and to provide assistance in taking away metal scraps and chips from the metal-processing area. OWEs help to improve the function of the tool and to prolong its service life.

OWEs can have the above-mentioned positive effects on metal processing, but can also negatively affect the environment. During utilization, an OWE undergoes changes under the influence of mechanical, thermal, chemical and biological factors, is no longer safe to be used because of reduced operating functions and emerging health hazards and it must be replaced [2,3]. Because of a small concentration of mineral oil in spent OWEs (SOWEs), also known as used or waste OWEs, mainly as a result of microbial contamination, their regeneration is not recommended. Therefore, from time to time or on every day bases, SOWEs are

disposed from manufacturing plants into the basins as wastewater, where they are exposed to uncontrolled natural processes of destruction. Generally, SOWEs contain residual mineral oil, tramp oils, greases, biocides, emulsifiers, metal ions, other components of original OWEs and the products of their degradation. When irresponsibly and non-professionally handled, SOWEs appear as environmentally hazardous wastewaters. To reduce their negative impact on the environment, SOWEs must not be discharged into sewage systems, rivers or lakes without previous extensive treatment. Environmental and economical importance of the pretreatment is extremely important due to the impact of SOWEs on traditional wastewater treatment processes caused by their volume and high contamination levels [4]. The SOWE amount is estimated to be more than ten times the worldwide usage, which exceeds $2 \times 10^6 \text{ m}^3$ per year [5]. Greeley and Rajagopalan [3] reported that eleven dollars would be spent on management and disposal of SOWEs for each dollar spent on purchasing OWE concentrate.

Different methods (physical, chemical and biological) are used for SOWEs treatment before disposal [5]. The most often used methods are vacuum evaporation [2,6,7], membrane separation [2,8], chemical destabilization/separation [2,8–10] and biological treatment [11,12]. To achieve higher separation efficiency,

SCIENTIFIC PAPER

UDC 628.316.12:546.62:66

Hem. Ind. 67 (1) 59–68 (2013)

doi: 10.2298/HEMIND120317055L

Correspondence: V. Veljković, University of Niš, Faculty of Technology, Bulevar oslobođenja 124, Leskovac, Serbia.

E-mail: veljkovicvb@yahoo.com

*Present address: University of Belgrade, IChTM, Center for Catalysis and Chemical Engineering, Njegoševa 12, Belgrade, Serbia.

Paper received: 17 March, 2012

Paper accepted: 21 May, 2012

coagulation pretreatment is coupled to deep bed filtration [10], membrane separation [4,13] and vacuum evaporation [7]. Treatment plants involving combinations of physical and biological processes are also employed [5]. So far, the SOWE treatment studies have been performed primarily at laboratory level, while modular pilot plant for the treatment of oil-containing wastewaters has been only reported [14].

Among the most common methods, chemical treatment is frequently used because of its relatively low operating costs, small capital investment and simplicity [15]. This method can be used for volumes of SOWE from 190 L per day to more than 3.8 million L per day [16], but it is extremely economic for large SOWE volume producers, *e.g.*, higher than 1135 m³ per day [17]. The treatment has three main phases [18,19]: coagulation, flocculation and phase separation. Coagulation is caused by adding a coagulant agent to intensively agitated SOWE. The coagulating agent neutralizes negatively charged colloids by cationic hydrolysis products and/or forms an amorphous hydroxide precipitate, which drags down oil droplets, colloids, soluble organic compounds and other impurities [20]. During the flocculation phase, the obtained floccules grow while the suspension obtained is moderately agitated. Once the floccules have reached a size large enough, they are removed from the water by gravitational settling or centrifugation.

Chemical treatment usually takes place in batch reactors [19]. Strong inorganic acids (sulfuric acid), inorganic salts (aluminum sulfate or chloride, ferric chloride, calcium chloride or sulfate) and organic chemicals (ionic polymers) are usually used as coagulating agents to destabilize or break SOWEs. Industrial chemical treatment processes frequently employ salts for coagulation [18,19]. Aluminum salts (sulfate or chloride) are traditionally used as coagulating agents in emulsified wastewater treatment. At the same salt dose, lower values of the residual COD were achieved when a model SOWE (based on a commercial mineral oil Fesol 05 and Fesol 09, produced by FAM Kruševac, Serbia) was treated by aluminum sulfate, and after that with ferric chloride [21]. Aluminum sulfate has already been shown to be effective in separation of oil and greases from SOWEs via destabilization of oil droplets and destruction of emulsions [22].

The present paper deals with chemical treatment of the SOWE from a non-ferrous metal-processing plant at laboratory and pilot levels. Aluminum sulfate was used as a coagulant to destroy the emulsion while hydrated lime was used as a base and a precipitating agent. Both model and real SOWEs were used; the former were prepared in the laboratory by emulsifying mineral oils in distilled water, and the latter were taken from the basin of the non-ferrous metal-processing plant where

they have been collected. The attention was paid to the effects of the coagulant dose, the hydrated lime dose, the speed and time duration of agitation as well as type and dose of filter aid on the efficiency of the SOWE treatment. The treatment efficiency was estimated by comparing the composition of SOWEs with that of the processed wastewater. The main goals were to determine the efficiency of purification of both model and real SOWEs by coagulation/flocculation, to optimize the process operating conditions, to develop an effective chemical treatment of the SOWE from the non-ferrous metal-processing plant and to get the chemical engineering data needed for the design of an industrial process.

MATERIALS AND METHODS

Materials

Two commercial mineral oils, Fesol 05 and Fesol 09 (FAM, Kruševac, Serbia) were used in this study. The basic properties of the mineral oils used are given in Table 1 [23]. Aqueous emulsions of the mineral oils, used as models of the SOWE, were prepared by mixing the oil with distilled water; the oil concentration was 10.0 g/L, if not differently specified. A real SOWE was taken from the basin located within a metal-processing plant (FOM, Prokuplje, Serbia). Floating tramp oil was separated from the SOWE.

Table 1. Basic properties of mineral oils used [23]

Property	Fesol 05	Fesol 09
Viscosity at 40 °C, mm ² /s	29	24
Density at 20 °C, kg/m ³	915	950
pH Value (5% in water)	9.5	8.8

Aluminum sulfate, Al₂(SO₄)₃·18H₂O, p.a. or technical grade, was purchased from Merck or Marking (Užice, Serbia), respectively; an aqueous solution, 0.75 mol/L (500 g/L), was prepared. Hydrated lime, technical grade, was purchased from Veljko Dugošević Co. (Kučevo, Serbia). Celite filter-cel, Celite Standard super-cel and Celite 512 (Celite Corp., Lompoc, USA) were used as filter aid. Sawdust (common beech; particle size: 0.6–2.0 mm), used as a filter aid and an adsorbent, was taken from a local sawmill.

Equipment

A jar test apparatus (Velp C6F, Italy) with six two-flat-blade stirrers, having a maximum speed of 200 rpm, was used in the laboratory studies of the chemical treatment of both model and real SOWEs. Glass beakers (1 L) were employed as reactors. All experiments were carried out at room temperature (about 20 °C). Three reactors (5, 50 and 1000 L) equipped with stirrers

were used in the scaling-up studies of the chemical treatment of the real SOWEs.

Laboratory studies

Model SOWE

The model SOWE (0.5 L) was poured into a number of glass beakers. The coagulant solution was added while the emulsion was intensively agitated at 120 rpm to favor the coagulation. In some experiments, the filter aid was added immediately after the coagulant solution. The suspension formed was agitated for 3 min. Then, the agitation speed was slowed down at 30 rpm and the agitation was continued for 30 min to favor the flocculation. Finally, the solid phase obtained was separated by filtration under vacuum using a Seitz K200 filter sheet. The filtrate was collected for determining the chemical oxygen demand (COD).

Real SOWE

The real SOWE (0.5 L) was poured into a number of glass beakers (1 L), and the coagulant solution and hydrated lime were added while the SOWE was intensively agitated. The effect of aluminum sulfate was studied at doses in the range between 0.2 and 2.0 g/L at the hydrated lime dose of 1.0 g/L. The effect of hydrated lime was investigated at doses of 1.0, 2.0 and 3.0 g/L and at the coagulant dose of 1.0 g/L. During the coagulation phase, the SOWE was agitated at 120 rpm

for 5 min. The resulted suspension was then stirred at 30 rpm for 30 min during the flocculation phase. The solid phase obtained was separated by filtration under vacuum using the Seitz K200 filter sheet. The filtrate was collected for determining pH, COD, biochemical oxygen demand (BOD), total organic carbon (TOC), oil and grease and sulfates.

Scaling-up of SOWE treatment process

The real SOWE was poured into a coagulation/flocculation tank, and while the SOWE was intensively agitated, the coagulant solution, hydrated lime and filter aid were added at doses of 1.0, 3.0 and 1.0 g/L, respectively. The suspension was intensively agitated for 5 min at the same agitation speed in order to enhance the coagulation. The agitation speed was then slowed down to favor the growth of the floccules formed; sawdust (3.0 g/L) was added and the agitation was continued for 30 min. The suspension was filtrated under vacuum using the Seitz K200 filter sheet to separate the solid phase (filter cake) from the purified wastewater (filtrate). The latter was used for determining pH, total suspended substances (TSS), COD, BOD, TOC, oil and grease, sulfate, aluminum, copper, zinc and lead. Only the filter cake from the laboratory experiment was used for determining moisture, ash, organic load, copper, zinc and lead. The operating conditions are given in Table 2.

Table 2. Quality parameters of SOWE and processed wastewater

Parameter	Method	Processed wastewater produced				SOWE	Maximum allowed value	
		Operating/Total volume of reactor, L/L						
		0.5/1	3/5	30/50	800/1000			
Working conditions		Agitator type						
		Two flat blade paddles ^a	Marine	Ultra turex	Marine			
		Agitation speed/Time duration, min ⁻¹ /min						
		Coagulation phase						
		200/5	Intensivly ^b /5	Intensivly ^b /5	180/5		Leskovac, Serbia [29]	Hungary [36]
		Flocculation phase						
		30/30	Slightly ^b /30	Slightly ^b /30	45/30			
pH	SRPS H.Z1.111:1987	7.6	7.5	7.6	7.6	6.9	6.5–9.0	5.0–10.0
Total suspended matter, mg/L	SRPS H.Z1.160:1987	<1	<10	<10	<10	11,900	400	100–500
COD, mg O ₂ /L	SRPS ISO6060:1994	234	174	276	276	14,500	550	50–100
BOD, mg O ₂ /L	SRPS ISO5815:1994	174	137	113	162	3,400	300	–
TOC, mg/L	SRPS ISO8245:1994	118	100	37	176	2,400	–	–
Oil and grease, mg/L	SRPS H.Z1.150:1972	–	8.9	–	9.8	571	40	2–10
SO ₄ , mg/L	SRPS H.Z1.131:1974	–	353	341	306	42	350	–
Al, mg/L	SRPS H.Z1.115:1984	–	0.1	0.0	0.0	0.1	4	–
Zn, mg/L	EPA 3051 A	–	0.07	0.8	0.9	12.9	2	1.0/5.0
Cu, mg/L	EPA 3051 A	–	0.02	0.06	0.06	5.5	1	0.5/2.0
Pb, mg/L	EPA 3051 A	–	0.01	–	0.0	0.07	0.5	0.05/0.2

^aJar test apparatus; ^bthe agitation speed was not possible to be measured

Analytical methods

The quality parameters of the SOWE, the processed wastewater and the filter cake such as TSS, COD, BOD, TOC, oil and grease, sulfate, metal ions (zinc, copper, aluminum and lead), pH, moisture, ash and organic were measured by the standard methods (Tables 2 and 3). The oil concentration, c_{oil} (g/L), in model SOWEs based on mineral oils Fesol 05 and Fesol 09, was calculated from the measured values of COD (mg O₂/L), using the following equation [21]:

$$COD = 2393c_{oil}$$

which is valid for $c_{oil} \leq 5$ g/L. To develop the above correlation, the COD of the OWE of different concentrations (0.1, 0.25, 0.5, 1.0 and 5.0 g/L) was determined by the standard method. The proportionality coefficient was calculated by the least squares method.

RESULTS AND DISCUSSION

Treatment of model SOWEs

Type and dose of coagulant and mineral oil, as well as time duration and speed of agitation and the pH of the solution, are expected to be among the key process factors affecting chemical treatment of model SOWEs. Since it was observed that model SOWEs were destroyed immediately after adding the coagulant to the vigorously agitated emulsion [21], hydrated lime was not included in these experiments. Also, the type and the dose of filter aid were expected to be an influential factor for clarification and sludge filtration stages of chemical treatment of SOWEs, although it may be an adsorption agent. The presence of a Celite filter aid had a negative effect on the clarification of the suspension of flocculated particles obtained by the chemical treatment of SOWEs, but they had a positive effect on its filtration [24]. The usage of sawdust in the treatment of an OWE model by calcium sulfate as coagulant, oil and COD reduction efficiencies greater than 99 and 95% were achieved [10]. The use of bentonite and sawdust is highly effective for the coagulation of oil in water,

giving removal efficiency of 92% or above [25]. The above factors were optimized on the base of the residual COD of the processed wastewaters.

Influence of coagulant dose

The effect of the coagulant dose in the range between 1.0 and 5.0 g/L on the COD reduction efficiency from two model SOWEs (*i.e.*, water emulsions of Fesol 05 or Fesol 09, 10 g/L) can be seen in Figure 1. Independently of the mineral oil type, the residual COD in the processed wastewater decreased rapidly when the coagulant was added at its doses up to approximately 2.0 g/L. At higher coagulant doses, however, the residual COD was reduced negligibly. Thus, once the model SOWEs were destabilized and the lowest residual COD values were achieved, further addition of the coagulant did not influence emulsion destabilization. The coagulation action of aluminum sulfate could be explained by two distinct mechanisms [20]. According to the first mechanism, the coagulant reduced the electrostatic repulsion among oil drops, which could then coalesce, grow in size and settle if large enough. The second mechanism, known as sweep flocculation, emphasized the role of coagulant hydrolysis in alkaline pH, which generated an amorphous aluminum hydroxide precipitate. The coagulant floccules collided and incorporated with the majority of the oil drops, colloids and soluble organic compounds. Once the floccules had reached a size large enough, the floccules containing the oily phase quickly settled after the stirrer was switched off.

Influence of type of mineral oil

The two kinds of OWE based on two different commercial mineral oils – Fesol 05 and Fesol 09 – are used in different parts of the manufacturing plant, and the SOWEs containing different mineral oils are collected in a common basin. In order to test whether the type of mineral oil would affect their efficiency, the model SOWEs containing the two mineral oils (10 g/L) have been purified under the same conditions (aluminum sulfate, 5 g/L; Celite standard super-cel, 10 g/L) in tri-

Table 3. Results of chemical analysis of filter cake; means from duplicate measurements, volume of SOWE: 3 L; volume of coagulation tank: 5 L; aluminium sulfate: 1.0 g/L; Celite standard super-cel: 2.0 g/L; hydrate lime: 2.0 g/L; sawdust: 3.0 g/L

Parametar	Method	Content		Maximum allowed concentration in ground ^a , mg/kg	Limiting value for sludge ^b , mg/kg
		%	mg/kg		
Moisture	EN 14346:2006	48.9±0.4	–	–	–
Ash	EN 15169:2006	33.9±0.4	–	–	–
Organic load ^c	EN 15169:2006	15.3±0.3	–	–	–
Zn	DM 0109	0.135±0.005 ^d	910	50-140	2.500-4.000
Cu	DM 0109	0.047±0.001 ^d	320	150-300	1.000-1.750
Pb	DM 0109	0.002±0.000 ^d	13	50-300	750-1.200
pH	ISO 10523:2008	11.9±0.1	–	–	–

^aDirective EU 86/278/EEZ Appendix 1A; ^bDirective EU 86/278/EEZ Appendix 1B; ^cBased on dry filter cake; ^dBased on ash

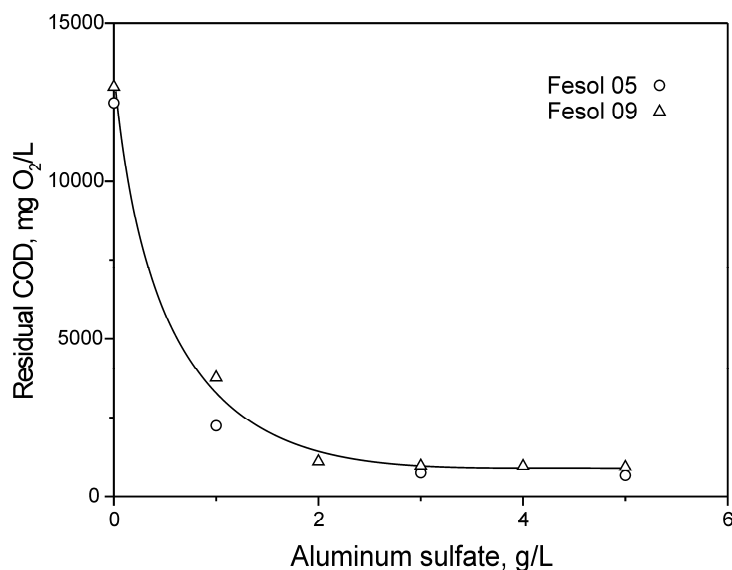


Figure 1. The effect of the aluminum sulfate dosage on the residual COD (model OWE, 10 g/L; agitation conditions: 3 min at 120 rpm, and then 30 min at 30 rpm).

plicate. The model SOWEs containing Fesol 05 and Fesol 09 had the initial COD of $24,650 \pm 2,120$ mg O₂/L and $26,145 \pm 1654$ mg O₂/L, respectively, while values of the residual COD after purification were 523 ± 41 mg O₂/L and 726 ± 45 mg O₂/L, respectively. The values of purification efficiency of 97.9 ± 0.4 and $97.2 \pm 0.3\%$ were achieved for the model SOWEs containing Fesol 05 and Fesol 09, respectively. The effect of the mineral oil type on the COD reduction efficiency was statistically tested by comparing the two means. For both mineral oils, the calculated value of $t_0 = 2.16$ were lower than the t -value at a 99% confidence level and four degrees of freedom ($t = 3.75$), showing that there was no significant difference between the two means, *i.e.*, the COD reduction efficiencies for the two mineral oils differed to each other by chance and not because of

their different compositions. Thus, it was expected that the COD reduction efficiency would not depend on the fractions of the two mineral oils present in the SOWE.

Influence filter aid type

In the present study, three types of diatomaceous earth of different particle size were used as filter aids, namely Celite filter-cel, Celite standard super-cel and Celite 512 (10 g/L). The model SOWE was prepared using Fesol 05 (10 g/L), and the coagulant dose was 5 g/L. Approximately the same values of the residual COD (1653 ± 113 mg O₂/L) were achieved in the purification processes in the presence of different filter aids. Therefore, in further studies, only Celite standard super-cel was used, which has been recently reported [24] to be the most efficient filter aid for treating the SOWE from the non-ferrous metal-processing plant. Figure 2 shows

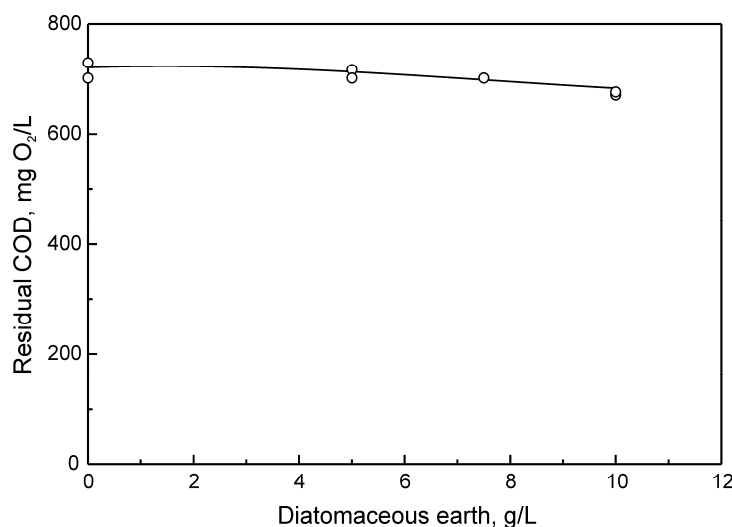


Figure 2. The effect of the filter aid (Celite standard super-cel) dose on the residual COD (Fesol 05, 10 g/L; aluminum sulfate dose, 5 g/L; agitation conditions: 3 min at 120 rpm, and then 30 min at 30 rpm).

the influence of the filter aid (Celite standard super-cel) dose added initially to the model SOWE (Fesol 05, 10 g/L) in the range between 0 and 10 g/L on the residual COD. The coagulant dose was 5 g/L. The residual COD value decreased very slightly with increasing the filter aid amount.

Influence of time duration and speed of agitation

Figures 3 and 4 show the effect of the time duration and speed of agitation during the coagulation phase, respectively on the residual COD after the chemical treatment of a model SOWE (Fesol 05, 10 g/L). The residual COD did not reduce significantly when the time duration of the agitation was increased from 1 to 8 min (Figure 3). With increasing the agitation speed in the range between 60 and 150 rpm, the residual COD remained constant (525 ± 19 mg O₂/L) or very slightly increased from 500 to 550 mg O₂/L (Figure 4).

Efficiency of SOWE treatment at the laboratory level

This study of the effects of the coagulant dose and the pH of the reaction mixture on the treatment efficiency has been carried out with real SOWEs in the jar test apparatus. In conjunction with aluminum sulfate as a coagulant, hydrated lime is often used in wastewater treatment to maintain the proper pH for most satisfactory coagulation conditions. Also, hydrated lime can precipitate some metal ions such as copper, zinc and lead and anions such as sulfate in the form of hydroxides and insoluble calcium compounds (calcium sulfate), respectively. Finally, hydrated lime can facilitate clarification and filtration on pressure filters. Both the clarification and filtration rate increased with increasing pH, *i.e.*, the hydrated lime dose, while the sludge volume was reduced [24]. Also, the filtration properties of the filter cake, such as porosity and incompress-

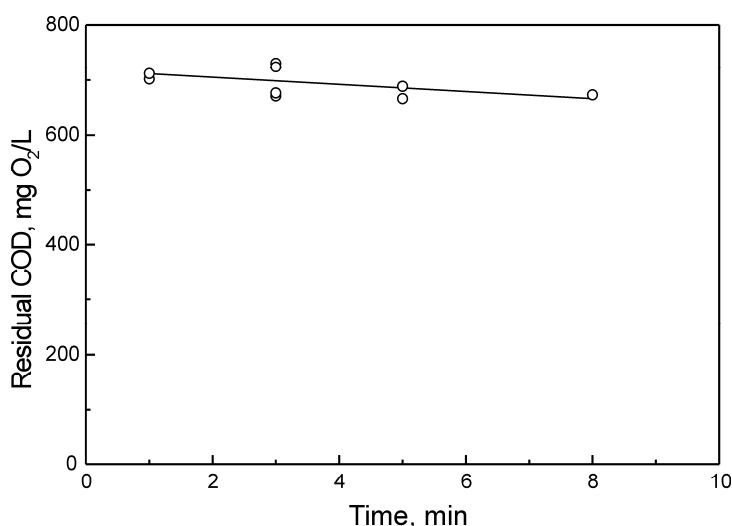


Figure 3. The effect of the time duration of agitation in the coagulation stage on the residual COD (Fesol 05, 10 g/L; aluminum sulfate dose: 5 g/L; Celite standard super-cel: 10 g/L; agitation speed).

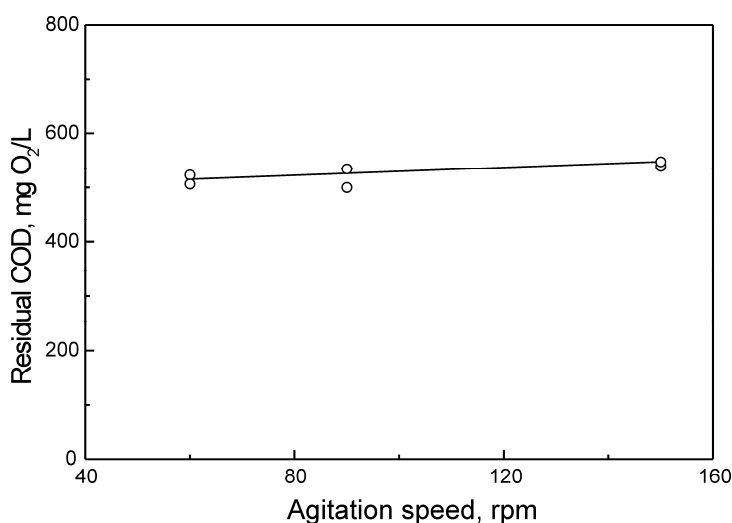


Figure 4. The effect of the agitation speed in the coagulation stage on the residual COD (Fesol 05, 10 g/L; aluminum sulfate dose: 5 g/L; Celite standard super-cel: 10 g/L; agitation speed during the flocculation phase: 30 rpm in 30 min).

sibility, were significantly improved by adding sawdust to the suspension of flocculated particles before filtration, enhancing the filtration rate [21].

Influence of coagulant dose

The effect of the coagulant dose on the treatment efficiency was studied in the range between 0.2 and 2.0 g/L. As can be seen in Table 4, with increasing the coagulant dose, the COD, BOD, TOC and oil and grease reached a minimum and then increased, probably due to a re-stabilization of particles. The lowest values of COD, BOD, TOC, oil and grease and sulfates were achieved when the SOWE was treated at the coagulant dose of 1.0 g/L. The efficiency of COD reduction from the SOWEs was 97.4%, which was close to the efficiency of the model SOWE treatment (under optimal conditions about 98 to 99%). The efficiency of BOD removal was lower (about 90%). At the coagulant dose of 2.0 g/L, the residual sulfate concentration was higher than the coagulant dose of 1.0 g/L. Therefore, the coagulant dose of 1.0 g/L was applied in further experiments. This optimum dose for real SOWEs treatment is even lower than the one determined for the model SOWEs, probably due to the presence of calcium ions from hydrated lime. Calcium ions contributed to the compression of the electrostatic double layer and to the reduction of electrostatic repulsion among oil droplets, causing their coalescence and growth, in OWEs prepared from commercial products from Spain [9,10,13].

Influence of pH

The effect of pH on the removal efficiency of coagulation/flocculation by aluminum sulfate was studied in the range of pH between 6.3 and 9.5. Different pH values of the reaction mixture were adjusted by adding different doses of hydrated lime. The suggested pH conditions for this coagulation process are in the region of $\text{Al}(\text{OH})_3$ precipitation and optimum sweep flocculation, and the latter mechanism is dominant at $\text{pH} > 6$ [26]. As can be seen in Table 5, the reduction efficiency, measured via the residual COD, BOD and TOC, appeared to be slightly increased with increasing the pH value from 6.3 to 9.5. At these pH values, $\text{Al}(\text{OH})_4^-$ are dominantly generated, which favor the formation of the Al_{13} polymer [20], which are the most efficient Al-

species for organic matter removal because of their larger size and higher positive charges [27]. However, levels of the residual COD, BOD and TOC were close at different pH, and it was concluded that the pH could be adjusted in the range between 8.0 and 9.5, by adding a corresponding amount of hydrated lime (between 1.0 and 3.0 g/L), to ensure an acceptable purification efficiency.

Scaling-up of SOWE treatment process

To find out the possible problem related to scaling up, the chemical treatment process developed was carried out at four levels using the tanks for coagulation and flocculation of 1, 5, 50 and 1000 L filled with 0.5, 3, 30 and 800 L of real SOWE. The values of quality parameters for both SOWEs and the wastewater obtained by the treatment along with the operating conditions are given in Table 2. The values of quality parameters for the filter cake from the 5 L laboratory treatment process are given in Table 3. The organic load of the SOWE was decreased by the chemical treatment. The COD, BOD, TOC and oil and grease were significantly reduced at all process levels. At the pilot level, suspended matters were almost completely removed (99.9%), while the reduction efficiencies of COD, BOD, TOC and oil and grease were 98.1, 95.2, 92.7 and 98.3%, respectively. The concentrations of metal ions originated from the metal processing such as zinc and copper were also reduced with the removal efficiency of 93 and 99%, respectively, by precipitation with hydrated lime in the form of the hydroxides. The lead ion concentration was also reduced below the maximum allowed level due to the lead hydroxide precipitation. The high metal removal efficiency was attributed to a favorable pH of about 9.0 in the coagulation/flocculation tank. The highest efficiency of zinc, copper and lead removal from aqueous solutions by hydroxide precipitation was obtained in a range of 8.7 to 9.6, 8.1 to 11.1 and 7.8 to 8.8, respectively [28].

Regardless of the process scale, the processed wastewater was appropriate for disposal to the public sewage system. This provided the appropriate regulations on sanitary and technical requirements for wastewater discharge into public sewerage of the municipality of Leskovac, Serbia [29]. Furthermore, it was very important that the addition of aluminum sulfate did not

Table 4. The effect of the coagulant dose on the removal efficiency of SOWE at pH 8.0

Quality parameter of the wastewater after the treatment	SOWE	Coagulant, g/L			
		0.2	0.5	1.0	2.0
COD, mg O ₂ /L	12,100	725	730	320	405
BOD, mg O ₂ /L	3,100	505	520	315	388
TOC, mg/L	2,200	320	335	260	320
Oil and grease, mg/L	488	2.4	2.0	1.1	1.8
SO ₄ , mg/L	0	290	289	289	392

Table 5. The effect of pH on the treatment efficiency of SOWE

Quality parameter of the wastewater after the treatment	SOWE	Hydrated lime, g/L		
		1.0	2.0	3.0
pH	7.6	6.3	8.8	9.5
COD, mg O ₂ /L	12,100	910	900	860
BOD, mg O ₂ /L	3,100	435	405	370
TOC, mg/L	2,200	435	405	370

create new environmental problems related to aluminum and sulfate ions. As it can be seen in Table 2, the sulfate concentration in the processed wastewater (although increased in comparison to the influent SOWE) was below the maximum allowed level for industrial wastewaters that could be disposed into the public sewage. The addition of hydrated lime contributed to the sulfate level reduction because of calcium sulfate precipitation. The aluminum ions concentration was very low because of their precipitation as aluminum hydroxide. However, the processed wastewater did not meet most standards prescribed by the relevant Hungarian law, a country which is similar in size to Serbia; therefore, it should be subjected to further purification for disposal into rivers, lakes or groundwater.

With respect to the removal efficiency of oil and grease, the present purification technology of SOWEs from the non-ferrous metal-processing plant is comparable to the already known treatment processes involving coagulation followed by sedimentation applied in metal-processing industry using aluminum sulfate and/or hydrated lime such as paint manufacture (aluminum sulfate: 99%; aluminum sulfate+hydrated lime: 98%) and steel pickling (lime: 66%) (Sutton and Mishra, 1994). The treatment efficiency of coagulation/flocculation process changes dramatically from one wastewater to another, for instance the COD reduction of 15, 40, 60, 65 and 75% were achieved by treating wastewaters from compositing plants [30], cheese whey production [31], landfills [32], slaughterhouse [33] and tanneries [34], respectively. In addition, the efficiency of oil removal from a palm oil mill effluent was higher than 95% [35], while the efficiency of TOC reduction from a waste coolant effluent was 87% [4].

The results of the physico-chemical analysis of the filter cake obtained by the laboratory treatment are shown in Table 3. Limiting values for heavy metals (zinc, copper and lead) described by the appropriate European Union directive on the protection of the soil, when sewage sludge is used in agriculture, are also presented. The cake contained about 50% of water, 15% of the organic load and 34% of ash. Zinc, copper and lead concentrations were found to be 0.13, 0.05 and 0.002% (based on ash), respectively. The aluminum concentration in the treated wastewater was very low (<0.1 mg/L), as it can be seen in Table 3, indicating that

produced sludge would contain almost all the aluminum from the aluminum sulfate dose (estimated to be 5–6 mg/kg of dry filter cake).

The dry filter cake from the SOWE treatment plant could be burnt or disposed at a landfill if it satisfies the prescribed law limitations. The zinc and copper loadings of the dry filter cake were below the limit values for sewage sludge which could be used in agriculture, but about 3 times higher than the maximum allowable concentrations in the soil. The content of lead in the dry filter cake was far below the prescribed limits for both the soil and the sewage sludge. Due to the lack of all necessary data (flue gas composition and calorific value of dried filter cake), it was not possible to estimate the possibility of its incineration or use as a fuel. In addition, if the filter cake was used in this way, new environmental problems appeared – such as ash that contained toxic heavy metals and the flue gases of unknown purity. The general solution and recommendation could be proper disposal of the filter cake at municipal waste landfills.

CONCLUSION

The chemical treatment of model and real SOWEs using aluminum sulfate, combined with hydrated lime filter aids have been studied. The results obtained showed that treatment efficiency does not depend on the type of mineral oil (Fesol 05 or Fesol 09) and the type and amount of filter aid based on the Celite diatomaceous earth. The optimum doses of aluminum sulfate and hydrated lime must be experimentally determined for each batch of SOWEs, but their acceptable doses are 1.0 g/L and 1.0 to 3.0 g/L, respectively. The optimum conditions for the coagulation/flocculation process determined in the jar test are applicable at the pilot level. The process was confidently scaled-up from the laboratory to the pilot level, and the chemical engineering data obtained can be credibly used for designing the industrial SOWE treatment process comprising a coagulation/flocculation/sedimentation sequence.

The chemical treatment process for SOWE from non-ferrous metalworking plants should involve: equalization of SOWEs from different batches, secondary oil separation, SOWE destruction (coagulation/floccula-

tion) and heavy-metal ions precipitation, sedimentation of flocculated particles, sludge filtration, neutralization of the processed wastewater and filter cake disposal. The processed wastewater and the wet filter cake, which are 98 and 2% of the inlet SOWEs, can be safely disposed into public sewage systems and at municipal waste landfills, respectively. The purification efficiency is higher than 98% with respect to TSS, COD and oil and grease and is comparable to the known chemical treatment processes based on coagulation/flocculation followed by sedimentation.

Abbreviations

BOD – Biochemical oxygen demand

COD – Chemical oxygen demand

OWE – Oil-in-water emulsion

SOWE – Spent oil-in-water emulsion

TOC – Total organic carbon

TSS – Total suspended substances

REFERENCES

- [1] J.S. McCoy, Introduction: Tracing the Hystorical Development of Metalworking Fluids, in: J.P. Byers (Ed.), *Metalworking Fluids*, Marcel Dekker Inc., New York, 1994, pp. 1–23.
- [2] J.M. Burke, Waste treatment of metalworking fluids, a comparison of three common methods, *Lubr. Eng.* **47** (1991) 238–246.
- [3] M. Greeley, N. Rajagopalan, Impact of environmental contaminant on machining properties of metalworking fluids, *Tribol. Int.* **37** (2004) 327–332.
- [4] N. Hilal, G. Busca, F. Talens-Alesson, B. P. Atkin, Treatment of waste coolants by coagulation and membrane filtration, *Chem. Eng. Proc.* **43** (2004) 811–821.
- [5] C. Cheng, D. Phipps, R.M. Alkhaddar, Treatment of spent metalworking fluids, *Water Res.* **39** (2005) 4051–4063.
- [6] G. Gutiérrez, Á. Cambiella, J.M. Benito, C. Pazos, J. Coca, The effect of additives on the treatment of oil-in-water emulsions by vacuum evaporation, *J. Hazard. Mater.* **144** (2007) 649–654.
- [7] G. Gutiérrez, J.M. Benito, J. Coca, C. Pazos, Vacuum evaporation of waste oil-in-water emulsions from a copper metalworking industry, *Ind. Eng. Chem. Res.* **48** (2009) 2100–2106.
- [8] J.M. Benito, A. Cambiella, A. Lobo, G. Gutierrez, J. Coca, C. Pazos, Formulation, characterization and treatment of metalworking oil-in-water emulsions, *Clean Techn. Environ. Pol.* **12** (2010) 31–41.
- [9] Á. Cambiella, J.M. Benito, C. Pazos, J. Coca, Centrifugal separation efficiency in the treatment of waste emulsified oils, *Chem. Eng. Res. Des.* **84** (2006) 69–76.
- [10] Á. Cambiella, E. Ortea, G. Ríos, J. M. Benito, C. Pazos, J. Coca, Treatment of oil-in-water emulsions: Performance of a sawdust bed filter, *J. Hazard. Mater.* **B131** (2006) 195–199.
- [11] B.R. Kim, N.R. Devi, F.Z. Jerome, L. Frank, P.V. Harvath, Biological removal of organic nitrogen and fatty acids from metal-cutting-fluid wastewater. *Water Res.* **28** (1994) 1453–1461.
- [12] C. Cheng, D. Phipps, R.M. Alkhaddar, Thermophilic aerobic wastewater treatment of waste metalworking fluids, *Water Environ. J.* **20** (2006) 227–232.
- [13] A. Lobo, Á. Cambiella, J.M. Benito, C. Pazosa, J. Coca, Effect of a previous coagulation stage on the ultrafiltration of a metalworking emulsion using ceramic membranes, *Desalination* **200** (2006) 330–332.
- [14] J. Benito, G. Ríos, E. Ortea, E. Fernández, A. Cambiella, C. Pazos, J. Coca, Design and construction of a modular pilot plant for the treatment of oil-containing wastewaters, *Desalination* **147** (2002) 5–10.
- [15] Michigan Departments of Commerce and Natural Resources. Ten Ways to Reduce Machine Coolant Cost, Fact Sheet No. 9402, Office of Waste Reduction Services, Environmental Services Division, Michigan Departments of Commerce and Natural, Resources, Lansing, 1994.
- [16] G. Foltz, Treatment and disposal of used metalworking fluids. *Moldmak. Technol.* No. 6, 2003, <http://www.moldmakingtechnology.com/articles/060303.html> (accessed on August 06, 2011).
- [17] M. Cheryan, N. Rajagopalan, Membrane processing of oily streams. *Wastewater treatment and waste reduction*, *J. Membrane Sci.* **151** (1998) 13–28.
- [18] J.W. Patterson, *Industrial Wastewater Treatment Technology*, second ed., Butterworth Publishers, Boston, 1985, pp. 273–297.
- [19] P.M. Sutton, P.N. Mishra, Waste Treatment, in: J.P. Byers (Ed.), *Metalworking Fluids*, Marcel Dekker, Inc., New York, 1994, pp. 367–391.
- [20] J. Duan, J. Gregory, Coagulation by hydrolyzing metal salts, *Adv. Colloid Interface Sci.* **100–102** (2003) 475–502.
- [21] V. Kovačević, Purification of spent oil-in-water emulsion from non-ferrous metal-processing plants, MSc. Thesis, University of Niš, Faculty of Technology, Leskovac, Serbia, 2003 (in Serbian).
- [22] W.J. Eilbeck, G. Mattock, *Chemical Processes in Wastewater Treatment*, Ellis Horwood Limited, England, 1987.
- [23] V.N. Rajaković, D. Skala, Demulsification based on the thermal treatment (cooling and heating) of W/O emulsions, *Hem. Ind.* **58** (2004) 343–350 (In Serbian).
- [24] V.B. Lazarević, I.M. Krstić, L.M. Takić, M.L. Lazić, V.B. Veljković, Clarification and filtration of the flocculated particles suspension from a chemical treatment of waste oil-in-water emulsions from a non-ferrous metalworking plant, *Hem. Ind.* **65** (2011) 53–60 (in Serbian).
- [25] Y. Fu, D.D.L. Chung, Coagulation of oil in water using sawdust, bentonite and calcium hydroxide to form floating sheets, *Appl. Clay Sci.* **53** (2011) 634–641
- [26] J. Bratby, *Coagulation and flocculation in water and wastewater treatment*, second ed., IWA Publishing, London, 2006.
- [27] A. Matilainen, M. Vepsäläinen, M. Sillanpää, Natural organic matter removal by coagulation during drinking water treatment: A review, *Adv. Colloid Interface Sci.* **159** (2010) 189–197.

- [28] F.M. Pang, S.P. Teng, T.T. Teng, A.K. Mohd Omar, Heavy Metals Removal by Hydroxide Precipitation and Coagulation–Flocculation Methods from Aqueous Solutions, *Water Qual. Res. J. Can.* **44** (2009) 174–182.
- [29] Official Gazzete of the Municipality of Leskovac, No. 10/93 (July 27, 1993), pp. 311–312 (in Serbian).
- [30] M.A. Zazouli, Z. Yousefi, Removal of heavy metals from solid wastes leachates coagulation-flocculation process, *J. Appl. Sci.* **8** (2008) 2142–2147.
- [31] J. Rivas, A.R. Prazeres, F. Carvalho, F. Beltrán, Treatment of cheese whey wastewater: Combined coagulation - flocculation and aerobic biodegradation, *J. Agr. Food Chem.* **58** (2010) 7871–7877.
- [32] S. Ghafari, H. Abdul Aziz., M.J.K. Bashir, The use of poly-aluminum chloride and alum for the treatment of partially stabilized leachate: A comparative study, *Desalination* **257** (2010) 110–116.
- [33] O.S. Amuda, A. Alade, Coagulation/flocculation process in the treatment of abattoir wastewater, *Desalination* **196** (2006) 22–31.
- [34] S. Aber, D. Salari, M.R. Parsa, Employing the Taguchi method to obtain the optimum conditions of coagulation-flocculation process in tannery wastewater treatment, *Chem. Eng. J.* **162** (2010) 127–134.
- [35] A.L. Ahmad, S. Sumathi, B.H. Hameed, Coagulation of residue oil and suspended solid in palm oil mill effluent by chitosan, alum and PAC, *Chem. Eng. J.* **118** (2006) 99–105.
- [36] B. Dalmacija, Control of water quality within the quality management, University of Novi Sad, Faculty of Sciences, Department of Chemistry, Novi Sad, 2000, pp. 191–221 (in Serbian).

IZVOD

POVEĆANJE RAZMERE HEMIJSKOG PREČIŠĆAVANJA OTPADNE VODENE EMULZIJE MINERALNOG ULJA IZ FABRIKE ZA OBRADU OBOJENIH METALA

Vesna B. Lazarević¹, Ivan M. Krstić², Miodrag L. Lazić³, Dragiša S. Savić³, Dejan U. Skala⁴, Vlada B. Veljković³

¹*Centar za preventivnu i medicinsku zaštitu, Niš, Srbija*

²*Univerzitet u Nišu, Fakultet zaštite na radu, Niš, Srbija*

³*Univerzitet u Nišu, Tehnološki fakultet, Leskovac, Srbija*

⁴*Univerzitet u Beogradu, Tehnološko–metalurški fakultet, Beograd, Srbija*

(Naučni rad)

Proučavano je prečišćavanje otpadne vodene emulzije mineralnog ulja (OVEMU) iz fabrike obrade obojenih metala pomoću aluminijum-sulfata i hidratisanog kreča radi određivanja efikasnosti prečišćavanja, optimizovanja radnih uslova i povećanja razmere procesa prečišćavanja. Efikasnost prečišćavanja je ocenjivana na osnovu poređenja sastava OVEMU i dobijene otpadne vode. Utvrđeno je da efikasnost prečišćavanja ne zavisi od vrste mineralnog ulja i pomoćnog filtracionog sredstva. Optimalne količine aluminijum-sulfata i hidratisanog kreča moraju biti eksperimentalno određene za svaku šaržu OVEMU, s tim što su rezultati dobijeni na laboratorijskom nivou primenljivi na poluindustrijskom nivou. Otpadna voda, odnosno filtraciona pogača iz procesa prečišćavanja mogu se bezbedno ispustiti u kanalizaciju, odnosno odložiti na deponiju komunalnog otpada. Efikasnost prečišćavanja je bila veća od 98% u odnosu na ukupno suspendovane čvrste čestice, hemijsku potrošnju kiseonika i ulja i masti, a može se porediti sa efikasnošću poznatih procesa prečišćavanja baziranih na primeni koagulacije, flokulacije i sedimentacije.

Ključne reči: Aluminijum-sulfat • Hemijsko prečišćavanje otpadne vode • Koagulacija • Flokulacija • Vodena emulzija mineralnog ulja • Sedimentacija