Electrochemical Oxidation Post-Treatment of High Concentration Waste Oil/Water Emulsion Treated with Ultrafiltration

Yang Liua, Lian jun Wang [a, *], Lihua Liu [b, **], Weiqing Han [a], Xiuyun Sun [a], Jiansheng Li [a], Jinyou Shen [a]

[a] Key Laboratory of Jiangsu Province for Chemical Pollution Control and Resources Reuse, School of Environmental and Biological Engineering, Nanjing University of Science & Technology, Nanjing, 210094, Jiang Su Province, China
bFasten Group of China, Jiangyin, Jiang Su Province, China, 214433
* Corresponding authors. Tel./fax: +86 25 84315351.
** Corresponding authors. Tel./fax: +86 510 86057003.
E-mail addresses: wanglj@mail.njust.edu.cn (L. Wang),
liulh@chinafasten.com (L. Liu).

***Abstract* - Integration of ultrafiltration (UF) with electrochemical oxidation process is investigated as treatment of stabilized high concentration waste oil/water emulsions, collected from metal drawing industry. Results show that at optimum conditions for different ultrafiltration membranes treated, the effluent still contains high CODCr and ammonia nitrogen (NH3-N) that is above the emission standard. Electrochemical oxidation process using Ti/SnO2+Sb2O3/β-PbO2 electrodes is tested as effluent post-treatment in reducing these high pollutant concentrations. Electrodes showed the perfect property. CODCr, NH3-N were affected during electrochemical oxidation process. Through a single-factor electrolysis experiment with optimal running conditions (current density of I=400A/m2, pH=6, CNaCl=10g/L, electrode spacing 5mm), after 15minutes the final CODCr and NH3-N concentrations were 18 and 2.4 mg/L and down to the discharge standards. A combined process consisting of UF and electrochemical oxidation can be a technical suitable solution for stabilized high concentration waste oil/water emulsions and yield a very high-quality aqueous effluent that could be reused for emulsion reformulation or others.**

Keywords* - *waste oil/water emulsion; ultrafiltration ; electrochemical oxidation; single-factor experiment; COD removal;

I. INTRODUCTION

The high concentration waste oil/water(o/w) emulsion was discharged during metal forming and machining processes and mainly used to lubricate, cool, clean, improve surface finish against corrosion and surface oxidation etc. The emulsion consisted of a complex mixture of emulsifier, preservative, antifoaming and extreme pressure agents. Long time used, undergo thermal degradation products, metal chips, bacterial growth and other impurities towards the active ingredients decreased, the emulsion had lost the functional properties [1].

The waste o/w emulsion was coded of Hazardous Waste 09(HW09) and toxic or harmful for the environment. They required more than a single separation step to treat[2,3]. Several conventional methods of metal drawing emulsions treatment [4] could be classified as electrochemical technique [5,6], heating, vacuum evaporation [7], hybrid-modified resin, activated carbon system [8], biochemical degradation [9], gas flotation [10], demulsification [11], as well as membrane separation [12]. Since the emulsion's droplets were finely dispersed and their concentration and constituent are different each time [13], the treatment process was additionally complicated. Hence there is lack of a perfect efficient methods yet in removal hazards from waste emulsions. Ultrafiltration (UF) membrane separation seem to be a promising method for the separation from emulsion [14-16]. The pilot operation had obtained satisfied results which different materials of UF membranes had been applied to emulsion [17,18]. Hence, to combine another operation to increase the efficiency of treatment of waste o/w emulsion meanwhile to had prior producing water quality of the emulsion is advisable[19].

During the electrolysis processes, the pollutants are destroyed through either the direct or indirect oxidation [20]. The main oxidizing agent in electrochemical oxidation process is Water electrolysis, hypochlorite ion or hypochlorous acid produced from chloride ions, Chloride ion oxidation and hydrolysis of the produced chlorine yields hypochlorous acid or the hypochloride ion depending on the solution pH. The chlorine, oxygen, hydrogen and hypochlorite oxidize are thus reduced to chloride ion. Hydroxyl radicals or other reactive species also participate in the electrochemical oxidation of organics. Resulting reaction as follows (reaction(1)-(5)):

$$2Cl^- - 2e = Cl_2\uparrow \quad (1)$$
$$4OH^- - 4e = 2H_2O + O_2\uparrow \quad (2)$$
$$Cl_2 + H_2O = HClO + HCl \quad (3)$$
$$HClO + OH^- = H_2O + ClO^- \quad (4)$$
$$12ClO^- + 6H_2O - 12e = 4HClO_3 + 8HCl + 6(O) \quad (5)$$

The aim of the present work discusses the treatment of waste emulsions by UF and post-treatment of electrochemical oxidation to identify the main parameters of influencing the performance of this integrated process, through single-factor experiment integrated electrochemical oxidation process was investigated after UF as treatment of oil/water waste emulsion.

II. MATERIALS AND METHODS

A. Materials

A waste drawing o/w emulsion was prepared from a steel wire drawing plant of Jiangyin Fasten Group Co. Ltd. It contains oil, surfactants, water, extreme pressure additive preservative and other components. The main characteristic of the waste o/w emulsion is shown in Table 1.

TABLE 1. WASTE EMULSION'S MAIN COMPOSITION DETERMINATION OF PARAMETERS

Parameters	Average	Range
Chemical Oxygen Demand (CODCr)[mg/L]	20000~50000	25000
NH3-N[mg/L]	20~60	50
Turbidity[NTU]	2000~3000	2500
pH	7.5~9.5	8.5

The COD concentration and the turbidity were measured by standard methods. The conductivity was measured using a conductivity meter EC-1385. The pH was measuring using a portable pH meter KL-009(I)ATC.

B. UF Process

This UF system with automatic control operation, when the waste o/w emulsions were adjusted and filtered by centrifugal separation machine, then the percolate fluid into the tubular UF membrane recycling pool, with a range temperature and circulated pump into tubular UF device, after membrane filtration of water flow to the clear water reserves; UF membrane concentrate back into the pool, and then into the UF equipment. In the section process main macromolecular of emulsion and biological fungus, colloid and suspended particle are removed. The experimental UF membranes were provided by Jinshui Membrane Co. Ltd. The physical properties of the membranes were shown in Table 2.

Each membrane module had different available membrane area but identical flux in common conditions. The molecular cut-off of membranes were 100000 diameter and its mean apparent pore size is 20-50 nm. The operating parameters of UF system were as follow: flow velocity ≥ 3 m/s, feed pressure 0.1-0.8MPa, output pressure 0.07~0.16MPa, circulation of material in the range temperature of 25~90℃.During the pilot experimental, UF system run continuously 20 hours a day and washed as needed with EDTA-4Na, sodium alkyl benzene sulfonate, NaOH and HCl in frequently. The permeate solution was continuously intercept oil and the mass of permeate each time was measured. As for the dialysate, they were collected and used for the experiment of electrochemical oxidation experiment. The actual photograph of UF equipment as follows Fig.(2).

C. Electrochemical oxidation apparatus

The electrochemical oxidation experiments were conducted in a electrolytic bath and carried out at a constant current using a digital DC power supply. Before the continuous test, the optimization of operating conditions of electrochemical oxidation was performed through the unit process study. Experimental schematic of electrochemical oxidation as Fig.(1) follows. The apparatus consisted of a reactor (Ø1 0 cm×25 cm), three electrodes and DC rectifier [21]. Two piece of anodes were made of plate of titanium (6 cm×22 cm, 132 cm2) coated with SnO2, Sb2O3 andβ-PbO2, while plate of stainless steel (6 cm×22 cm) was used as cathodes; distance between electrodes was 5to 20 mm. NaCl was added as an electrolyte. HCl solution is added to adjust pH of the solution to the desired value.

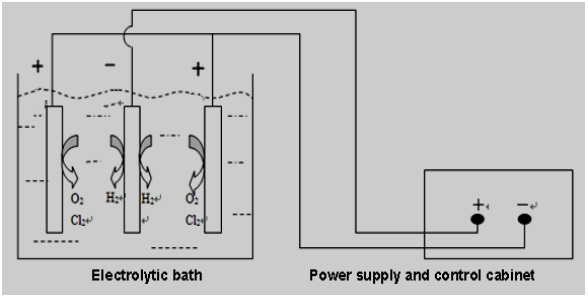

Fig.(1). Electrochemical Oxidation Experimental Schematic

TABLE 2. PROPERTIES OF UF MEMBRANES

Membrane	aMaterial	AMA[m2]	Water flux[L/m2·h]	Max temperature[℃]
GUJPF-8-85-3-BL-30	PVDF	42	1000	50
JWUF-12	ZrO2	12	1000	85
F20-A-121M	Stainless steel	8.4	1000	90

Fig.(2). Photograph Of One Of UF Equipments In The Workshop

D. Pilot Experiments

The pilot experiments combined UF and electrochemical oxidation were carried out in the workplace located in Fasten Group Co. Ltd.. Schematic diagram of the proposed of UF and electrochemical oxidation for the treatment of o/w waste emulsion is shown in Fig.(3). The emulsion outflow from drawing machine for 1m3 /hour was first pumped into the centrifugal machine, 15minutes later the effluent was second pumped into a horizontal type storage tank, few minutes stewing and then pumped into a steam heating tank. When heated of 10℃ to 60℃, the UF begin separating, later 95% of UF permeate was used of electrochemical oxidation for treatment. The Pilot of UF and electrochemical oxidation, water quality analysis were performed throughout a control panel. Periodically, some experimental data of steady permeate such as permeate flux, COD concentration and turbidity was determined regularly[22]. Once the recovery rate of water was obtained up to 90%, and reach the water discharge standard, the concentrate was then returned to the water reuse store tank, and the treatment process was finished.

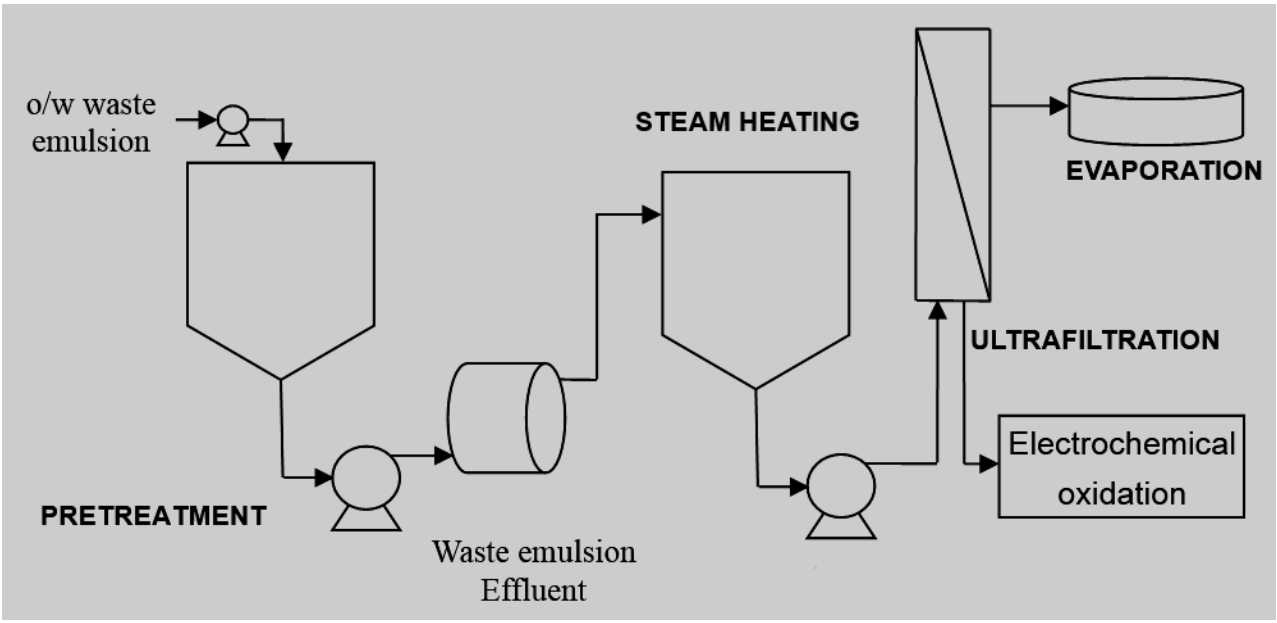

Fig.(3). Schematic Diagram Of The Proposed Of UF And Electrochemical Oxidation For The Treatment Of Waste O/w Emulsions.

III. RESULTS AND DISCUSSION

A. Ultrafiltration Treatment

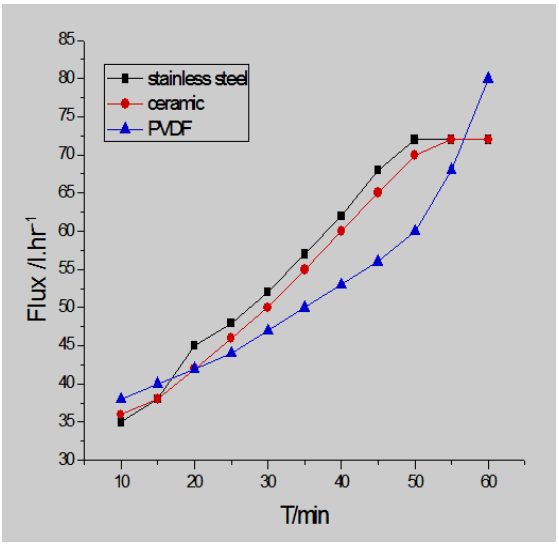

Fig.(4). The Flux vs.Time Of Three Series UF Membranes Run Before Pretreatment.

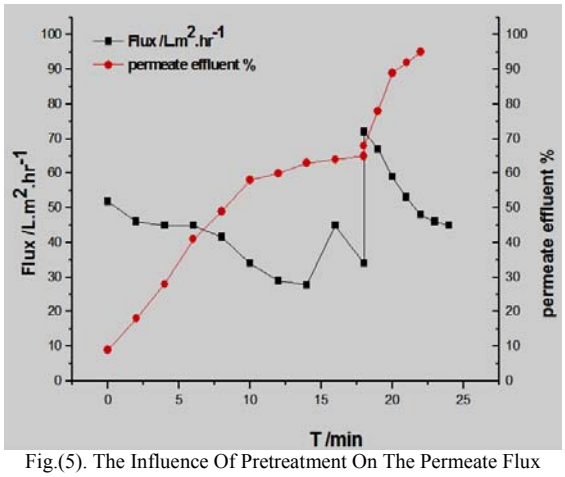

Fig.(5). The Influence Of Pretreatment On The Permeate Flux

In this study, membrane of PVDF affected the temperature resistance of the membrane pore size and then influenced the membrane flux. Given a different UF membrane with the same production rate of membrane area, indicated that the flux changes by the processing of treatment of waste emulsion below different temperature. Each kind of membrane own the same newly flux, after a test running, cleaning, measured of normal flux. shown as Fig.(4) and Fig.(5),the influence of UF pretreatment on the permeate flux. It can be observed that with the increasing of operation time, led to decline of membrane flux, after cleaning of membrane, permeate restored to the original, in the case of high permeate, membrane water production rate is normal and steadily rising, but after fouled, permeate is reduced, water production rate decline or slow. This indicated that although the major fouling was removed by the regeneration route. After numerous experiments, main composition determination of parameters by UF showed in Table 3., it was finally found out that the pretreatment has a strong influence on the characteristics of the filtration of waste emulsion by stainless steel UF membrane.

The possible reasons for these phenomenon are suggested to be: (1) with a high temperature, the oil droplets in the emulsion may be a high mobility which will help to improve the flux; (2) pretreatment also changes the wettability of the droplets surface from hydrophobic to hydrophilic, which will enhance both the flux and the oil rejection efficiency. It is observed by microscope that the size of the oil droplets in the emulsion before pretreatment is usually below 1 mm, and the droplets are almost transparent. These observations are complied with the above analyses.

TABLE 3. INFLUENCE OF WASTE EMULSION'S MAIN COMPOSITION DETERMINATION OF PARAMETERS BY UF

Parameters	Average concentration	
	Raw waste emulsion	UF permeated
aCODCr[mg/L]	40000	2000~4000
NH3-N[mg/L]	50	40~48
Turbidity[NTU]	2500	1~20
pH	8.5	7.5~9.5

B. Optimization Of Electrochemical Oxidation

B1. Effect of current density

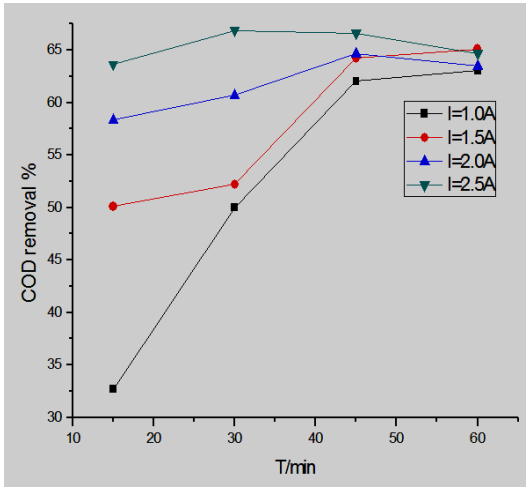

Fig.(6). Effect Of Current Density On COD Removal Efficiency

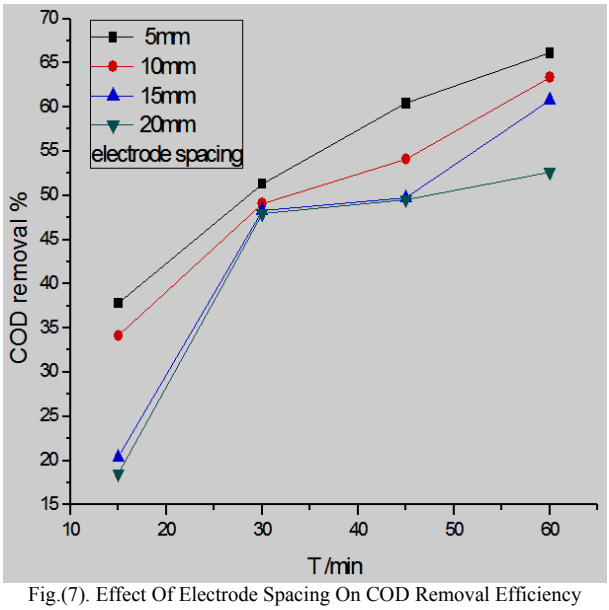

Fig.(7). Effect Of Electrode Spacing On COD Removal Efficiency

In this study, showed in Fig.(6). it can be seen the higher the current density and scaling-up the removal of COD. According to Faraday's law of electrolysis rate, during electrolytic process, the electrode on the precipitation or dissolved material quality is proportional to the energy crossed, the electrolysis energy more greater the products followed. And the larger current density, did the greater electrolysis energy, the electrolysis of [O], OH-, H2O2 and other strong oxidizing particle, it promote more of the oxidation of organic matter in waste emulsion. Electrolysis current density is low, be required for a long time, in order to achieve better treatment effect, and 15 min or processing under high current density has better treatment effect. Considering the current density, the greater the energy consumption is higher, considering from energy-saving and treatment effect, to choose the optimum current density of I=400A/m2.

B2. Effect of Electrode Spacing

In this study a effect of electrode spacing is discussed to deal with waste emulsion, result showed in Fig. (7). It can be seen that with the decrease of the plate electrode spacing, constantly the removal rate of COD of waste emulsion and electrolytic time was improved, COD removal efficiency is more obvious. Academically electrode spacing should near possible, to reduce the resistance between the electrode. When fixed voltage between the electrodes, increased electrode spacing lead to increase the resistance while consume more electricity. Furthermore with the increase of plate spacing, tank pressure is also a linear rising that may lead to negative electrode surface reaction, and even dissolve oxide electrodes, affecting the service life of the electrode. Therefore, distance of electrode is advisable to 5 mm with no affect to the operation conditions.

C. Effect Of Solution pH

In this study , result was tried and shown in Fig. (8). Lower initial samples pH value (pH 3 and 5) lead to oxidation efficiency highest of all. The removal efficiency of COD decreased from 85% to 50% when the pH was increased from 3 to 8 and after oxidation time of 45 minutes. It appears that the increase of the pH decreased the potential oxygen generation obtained from [•OH] radicals oxidation and consequently increased the flow rate of oxygen at the electrode surface. As a result, the diffusion flow towards the electrode decreased. Furthermore, it is well known that the decrease of the solution pH favors oxidation reactions; This can be indicated by the decrease of COD measured between pH 3 to8.

TABLE 4. EFFECT OF OPTIMUM TREATMENTS OF HIGH CONCENTRATION WASTE EMULSION

	COD （mg/L）	NH3-N （mg/L）
Raw O/W waste emulsion	25000	50
UF permeated	1973	48
electrochemical oxidation	18	2.4
Removal %	99.1%	95.9%

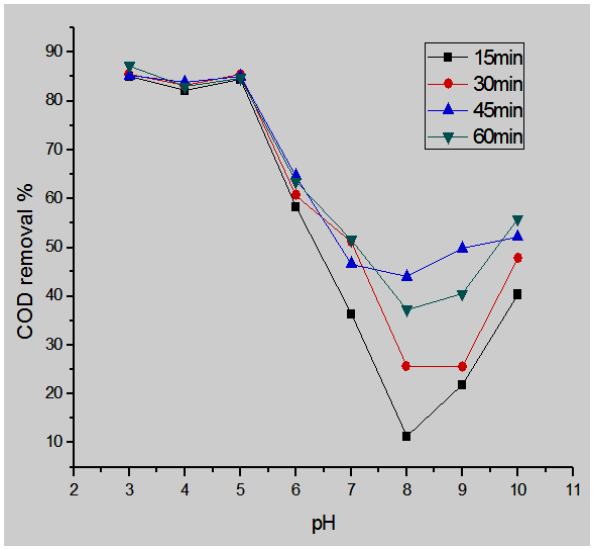

Fig.(8). Effect Of pH On COD Removal Efficiency

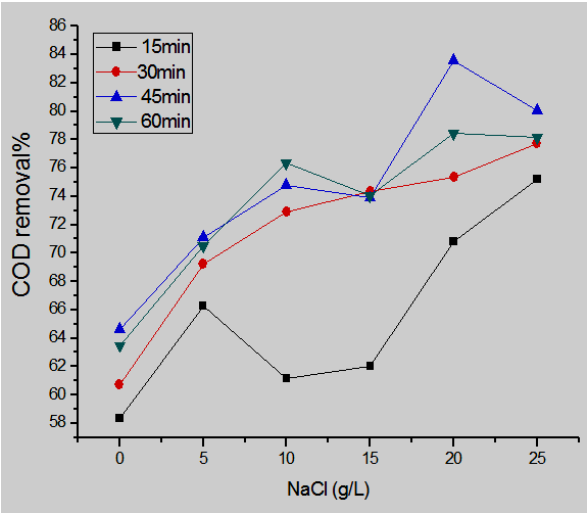

Fig.(9). Effect of fortified concentration of NaCl

D. Effect of Concentration of NaCl

Early research has shown that adding cast salt electrolytic test can reduce power consumption, promote the effect of electrolytic occurred at the same time. In this study, NaCl was added as an electrolyte. When adjust current density I=400 A/m2, plate spacing is 5mm, electrolytic experiment was carried out, at applied NaCl as electrolyte concentration of 0, 5, 10,15,20,25 g/l and the corresponding COD removal efficiencies were appeared after electrochemical oxidation from 15 to 60min. With concentration of NaCl and increase of electron transfer. But the concentrations of Cl-, in the raw wastewater were higher than that in conventional chemical wastewater. Overmuch salt resulted in adsorption of a mass of Cl− on an anode surface. It prevent creation of hydroxide radical. The effects of electrolyte concentration turn to invalid. As the electrolyte concentration was increased, the electrochemical oxidation efficiency was not increased, but reduced.

E. Test Results of Waste Emulsion Process

According to the single factor experiment, the optimum electrolytic conditions namely the pH=5, current density I=400A/m2, the plate spacing is 5 mm, with NaCl as electrolyte concentration of 10 g/L, under the optimum condition of the electrolytic, 15 minutes was cost best for the solution of high concentration waste emulsion, the results are under Table 4.

Table 4. shows under the condition of optimum electrolytic, COD removal rate Show the extremely high advantages of removal rate of 99.1%, 15 min after the waste emulsion COD value dropped below to 18mg/L. The electrolytic process of waste emulsion ammonia nitrogen also has good removal effect, electrolytic 15 min of ammonia nitrogen removal rate was totally to 95.9%. In addition, under optimum treatments condition, pH as a reaction parameters was adjusted. After penetrating, the turbidity was reach a perfect value till the end of electrochemical oxidation. As we know, electrochemical oxidation method is mainly used for processing hard organic biodegradable materials, in this section, NaCl as electrolyte increased electrical conductivity, that not tested.

IV. CONCLUSION

Treatment of waste drawing o/w emulsions may be implementation by various techniques, depending on the emulsion Composition. However, process performance can be improved by a combination of techniques as UF with post-treatment electrochemical oxidation. From the results reported in this work, a hybrid process including UF and Electrochemical oxidation are proposed for waste emulsion treatment (Fig. 3.). Due to high concentration, the waste emulsion after electrolytic treatment water COD still has about 1973 mg/L, still cannot direct emissions, subject to further processing is up to standard. Through a treatment of electrochemical oxidation of high concentration waste o/w emulsion , the optimal pilot conditions as follows: the current density of 400A/m2, pH = 5, 10 g/L NaCl dosing quantity, electrode spacing is 5 mm, electrolytic time only 15 min. Adopt the electrolytic device processing waste emulsion, can under the condition of no other inflatable and dosing, make the COD removal rate up to 99.1% in the water, ammonia nitrogen removal rate as high as 95.9%.It was concluded that the high concentration organic pollutant were removed and destroyed much effectively in combine UF with post-treatment of electrochemical oxidation. And the concentration of COD and NH3-N was much effectively decreased by the treatment. And this combined process was successfully employed and was highly practicable.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

ACKNOWLEDGEMENTS

This research was supported by Fasten Group Co. Ltd. The authors acknowledge their financial support. Authors thank the financial support.

REFERENCES

[1] M. Greeley, N. Rajagopalan, “Impact of environmental contaminants on machining properties of metalworking fluids”, Tribol. Int. 37 (2004) 327–332

[2] J.M. Benito, G. Ríos, E. Ortea, E. Fernández, A. Cambiella, C. Pazos, J. Coca, "Design and construction of a modular pilot plant for the treatment oil-containing wastewaters", Desalination, 147 (2002) 5–10.
[3] J.M. Benito, A. Cambiella, A. Lobo, G. Gutiérrez, J. Coca, C. Pazos, "Formulation, characterization and treatment of metalworking oil-in-water emulsions", Clean Technol. Environ. Policy 12 (2010) 31–41.
[4] F.R. Ahmadun, A. Pendashteh, L.C. Abdullah, D.R.A. Biak, S.S. Madaeni, Z.Z. Abidin, "Review of technologies for oil and gas produced water treatment", J.Hazard. Mater. 170 (2009) 530–551.
[5] H.Z. Ma, B. Wang, "Electrochemical pilot-scale plant for oil field produced wastewater by M/C/Fe electrodes for injection", J. Hazard. Mater. B 132 (2006) 237–243.
[6] C.L. Yang, "Electrochemical coagulation for oil water demulsification", Sep. Purif. Technol. 54 (2007) 88–395.
[7] G. Gutiérrez, A. 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.
[8] Y.B. Zhou, X.Y. Tang, X.M. Hu, S. Fritschi, J. Lu, "Emulsified oil wastewater treatment using a hybrid-modified resin and activated carbon system", Sep. Purif. Technol. 63 (2008) 400–406.
[9] X.F. Huang, J. Liu, L.J. Lu, Y. Wen, J.C. Xu, D.H. Yang, Q. Zhou, "Evaluation of screening methods for demulsifying bacteria and characterization of lipopeptide bio-demulsifier produced by Alcaligenes sp", Bioresour. Technol. 100 (2009) 1358–1365.
[10] R. Moosai, R.A. Dawe, "Gas attachment of oil droplets for gas flotation for oil wastewater cleanup", Sep. Purif. Technol. 33 (2003) 303–314.
[11] A.A. Hafiz, H.M. El-Din, A.M. Badawi, "Chemical destabilization of oil-in-water emulsion by novel polymerized diethanolamines", J. Colloid Interface Sci. 284 (2005) 167–175.
[12] U. Daiminger, W. Nitsch, P. Plucinski, S. Hoffmann, "Novel techniques for oil/water separation", J. Membr. Sci. 99 (1995), pp197–203.
[13] M. Gryta, K. Karakulski and A.W. Morawski, "Purification of oily wastewater by hybrid UF/MD", Water Res., 35(15) (2001) 3665-3669.
[14] P. Lipp, C.H. Lee, A.G. Fane and C.J.D. Fell, "A fundamental study of the ultrafiltration of oil-water emulsions", J. Membr. Sci., 36 (1988) 161-177.
[15] G. Gutiérrez, A.Lobo, J.M. Benito, José Coca, Carmen Pazos, "Treatment of a waste oil-in-water emulsion from a copper-rolling process by ultrafiltration and vacuum evaporation", J.Hazard.Mater. 185 (2011) 1569–1574
[16] Y. Lee and M.M. Clark, "Modeling of flux decline during crossflow ultrafiltration of colloidal suspensions", J. Membr. Sci., 149 (1998) 18 l-202.
[17] J. Marchese, N.A. Ochoa, C. Pagliero and A. Almandoz, "Pilot-scale ultrafiltration of an emulsified oil wastewater", Environ. Sci. Technol., 34 (2000) 2990-2996.
[18] X. Hu, E. Bekassy-Molnar, Gy. Vatai, L. Meiszel and J. Olah, "The study ofoil/water separation in emulsion by ultrafiltration membranes", Chem. Technik (Leipzig), 50 (1998) 119-123.
[19] A. Lobo, A. Cambiella, J.M. Benito, C. Pazos, J. Coca, "Ultrafiltration of oil-in-water emulsions with ceramic membranes: influence of pH and crossflow velocity", J. Membr. Sci. 278 (2006) 328–334.
[20] Chen, G., 2004. "Electrochemical technologies in wastewater treatment". Sep. Purif.Technol. 38, 11–41.
[21] W. Han, L. Wang , X. Sun, J. Li, "Treatment of bactericide wastewater by combined process chemical coagulation, electrochemical oxidation and membrane bioreactor", J. Hazard.Mater 151 (2008) 306–315
[22] I.A. Alaton, S. Dogruel, E. Baykal, G. Gerone, "Combined chemical and biological oxidation of penicillin formulation effluent", J. Environ. Manage.73 (2004) 155–163.