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Removal of Crude Oil from Oily Artificial Wastewater by Using Pulse Electrochemical Treatment

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Abstract

In this study electrocoagulation (EC) process with sacrificial aluminum anode was used to separate crude oil from synthetic oily wastewater emulsion. A preliminary experimental study was performed to evaluate the most accurate operating parameters, which are then used for the determination of crude oil removal efficiency. The experimental results indicated that electrocoagulation was very efficient andable to achieve 99% turbidity removal in less than 15 min,pH:7, current density: 125(A/m2). Also the effect of initial concentration of crude oil (2-33 g/L) in wastewater, initial volume of wastewater (600-1800 mL), effect of flow rate (5.5-16.25 mL/s) in semi batch reactor, dose of electrolyte and type of electrolyte were optimized.

During the oil removal process, polarization were occurred around anode, for omitting this problem two types of current were studied as follows: “direct current (DC)” and “pulse current (PC)” however the energy consumption were 0.012 and 0.0042 kWh/m3 respectively.

***Key words**: Turbidity removal, Electrocoagulation, Oily wastewater, Pulse current.*

Introduction

Over the current decades during drilling, discovery and oil production an increase in the demand for crude oil have been observed. Also the mechanical and metallurgical industries generate great quantities of oily wastewater which in the majority of cases are rejected into the environment because of non-adaptation of the processes of treatment [1]. American Petroleum Institute stated that the standard instrument in refinery waste treatment is the API Separator, although effluents from this unit may still contain some of oil. Recently, there is a need to identify new technologies that achieve technically and economically efficient separation of oil from oil-in-water emulsion [2].

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For this purpose, electrocoagulation process is playing a more prominent role in the treatment of oily wastewaters [3-4]. Electrolyticreaction at electrode surface, formation of coagulants by electrolytic oxidation in aqueous phase and adsorption of colloidal particles on coagulant, and removal by sedimentation or flotation. Therefore the appropriate selection of the electrode materials is very important. The most common used materials for electrocoagulation are aluminum. They are cheap and readily available. However, aluminum was found to be a more appropriate electrode material according to the iron electrode performance [1, 5, 6]. The electrochemical reactions with aluminum as anode may be summarized as follows [1]:

At the anode: $M(s) \rightarrow M^{3+}(aq) + 3e^{-}$ (1)

At the cathode: $3H_2O(l) + 3e^{-} \rightarrow 3/2H_2 + 3OH^{-}$ (2)

In the solution: $M^{3+}(aq) + 3H_2O \rightarrow M(OH_3)(s) + 3H^{+}(aq)$ (3)

M^{3+} (aq) and OH−ions generated by the electrode reactions (1) and (2) however the net reaction is (3) react, respectively, to form various monomer species, depending on pH range, which transform finally into $M(OH)_3$ according to complex precipitation kinetics. Freshly formed amorphous $M(OH)_3$ (sweep flocs) with large surface areas which are beneficial for a rapid adsorption of soluble organic compounds and trapping of colloidal particles. Consequently, these flocs can be removed by sedimentation or by flotation using H2 bubbles produced at the cathode [7]. In this study, electrocoagulation using aluminum sacrificial anode was used for the treatment of crude oily emulsion. In order to evaluate the decreasing of turbidity and increasing crude oil removal from the emulsion, Various important electrochemical factors were investigated: current density, initial pH, type of current (direct and pulse), initial concentration of crude oil in the wastewater, initial volume of wastewater, water recovery, effect of flow rate (recycling system) and electrocoagulation time in the batch and semi batch reactors. However, in this research “water recovery” was presented to show the more economic recycling of treated water.

Experimental

Materials

All the chemicals were of analytical grade and purchased from Merck or Sigma Aldrich Company. Crude oil for this study was obtained from a South of Iran (Khoozestan area) and stored under argon.

Batch study

Deionized water was used for preparation of various solutions (synthetic crude oil wastewater). Desired amount of crude oil mixed with cutting oil (ratio 90:10 wt/wt respectively) and deionized water were used under ultrasound agitation for one an hour, for obtaining very stable or soluble synthetic crude oil wastewater. Representative crude oil concentration of aqueous solution was selected as 4 g/L. pH of the solution was adjusted with 0.1N HCl or 0.1N NaOH. The experiments were conducted in 600 and 1800 (mL) initial volume of waste water(reactor volume was 0.7 L and 2 L respectively). The reaction was initiated by adding different electrolyte at the reactor after the pH was adjusted. All tests were performed at room temperature and stirring speed was 120 rpm. PC circuit was exerted for 2 tasks first of all to decrease the polarization around the electrodes or to exfoliation the sludge from anode and cathode and the second one for saving the energy consumption. Initial oily solution conductivity was increased by proper amounts of various electrolytes: NaCl, $NaNO_3$, Na_2SO_4, KNO_3, $Fe(NO_3)_3$, $Zn(NO_3)_2$,$Al_2(SO_4)_3$, K_2SO_4, KCl and Poly aluminum chloride (PAC).

Experiments were performed in a batch system (Figure 1) and also the results compared in semi batch system by using a peristaltic (variable flow rate) pump for wastewater recycling. Effective area of each electrode [Al (cathode) and Al (anode)] used was $36cm^2$ (6cm×6 cm). The gap between the electrodes was 3 cm. One DC power supply package having an input of 220V and variable output of 0–30 V, with variable current0–4 (A)was used. An electro pulse current generator was applied to study the PC type of circuit (purchased from Nano Pushesh Felez, Iran).

Methods of analysis

Samples were periodically taken out from the reactor and then turbidity measurements of the reaction solutions were immediately performed. Residual crude oil measurement was performed by using a Turbidity meter (Model: HACH-Lange). Each experiment lasted 15 min. The turbidity or crude oil removal efficiency percent was determined as follows:

$$\text{Crude oil (Turbidity) removal efficiency (\%)}=\frac{T_0-T}{T_0}*100 \quad (4)$$

Where T0 is the initial turbidity (before EC) and T is the final turbidity (after EC) in NTU.

Consumption of power or electrical energy was calculated as follows:

$$\text{(EE) (kWh/m}^3\text{ wastewater)} =\frac{V}{v} \quad (5)$$

Where V is the applied voltage (volt), I is the applied current(ampere), t (or tEC) is the time of reaction (hr) and v is the initial volume of wastewater (m^3).

The current density (CD) was measured [3,6] according to Eq. (6):

$$C \;=\frac{I}{2S} \qquad (6)$$

Where I is the current (A) and S is the surface area of the electrode (m^2).

The water recovery [7] was measured

according to Eq. (7):

Water recovery = volume of product water (after EC)/initial volume of wastewater (before EC), (7)

Where the clear supernatant is product water or treated water, however, highly dense (or dewatered) sludge remained at the reactor bottom after EC.

SARA (saturate-aromatic-resin-asphaltene) fractionation was used for characterization of crude oil [8]. The different fractions of crude oil for this study are represented in Table 1.

Table 1.SARA fractions of crude oil sample analyzed with TLC-FID Itroscan and traditional open column chromatography-gravimetry.

Saturate %Wt		Aromatic %Wt		Resin %Wt		Asphaltene %Wt	
TLC*	Open column**	TLC	Open column	TLC	Open column	TLC	Open column
70.9	78.90	17.0	4.50	11.2	15.6	0.3	1.00

*:Analyzed by TLC-FID(Thin Layer Chromatography-Flame Ionization Detection) Itroscan,
**: Analyzed by traditional open column chromatography-gravimeter.

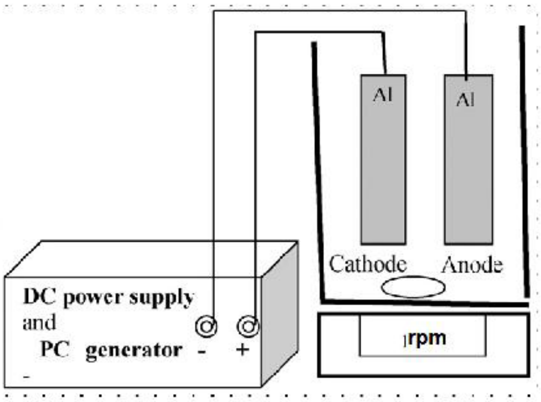

Figure 1. Schematic diagram of the electrocoagulation reactor.

Results and discussions

The electrochemical process was conducted by several operational parameters, such as current density (CD), time of reaction, initial pH, type of current, initial crude oil concentration, conductivity, energy consumption and flow rate in semibatch system. In order to promote the process performances, the influences of these parameters were studied as follows.

Effect of current density

In all electrochemical processes, current density (CD) is the most important parameter for reaction controlling in the reactors. According to Faraday's law [9] CD determines the coagulant production rate and regulates the rate and size of the bubbles and growth of flocs. A series of electrochemical experiments were performed by solution containing constant initial crude oil concentration (4 g/L as an representative concentration) with current densities varied from 60 to 140A/m^2. It is obvious that the removal efficiency increases at higher CD up to 125A/m^2 after 15 min EC reaction, based on maximum removal efficiency 99%. Other optimized parameters are tabulated in Table 2,the results show some improvement over previous attempts, Sangal showed for 99% removal of 1-10% cutting oil waste water the current density increased to 138.8A/m2[4].

Effect of time of reaction

Based on Faraday's law [9], reaction time also influences the turbidity removal efficiency in EC process and it determines the production rate of metal ions from electrodes. To investigate the effect of reaction time a series of experiments were carried out by solution containing constant initial crude oil concentration (4 g/L) by considering fixed optimized current density represented above (125A/m^2). The results show that turbidity removal efficiency was about 99% in the first 15 min and was almost constant after that. In the literature, time of 3 hours was reported to achieve 99% in removal of cutting oily waste water [4].

Effect of initial pH

In this study the dependence of turbidity removal efficiencies on initial pH values were investigated over pH range of 3–9. It can be seen from Figure 2 and Table 2 that the initial pH plays an important role on the performance of EC process. The results show that if pH is less than 5, efficiency decreases. Since the initial pH value of the solutions was near 7,no change in the pHof the solutions was needed and all later experiments were done at this initial pH. Because of hydroxyl ions production in EC process, the final pH increased during electrolysis. The evolution of optimizing operating parameters and also other results are tabulated in Table 2.The best conditions that are based on maximum removal turbidity, maximum water recovery and appropriate energy consumption were highlighted in Table2. Sangal obtained similar result pHinitial=6.5.

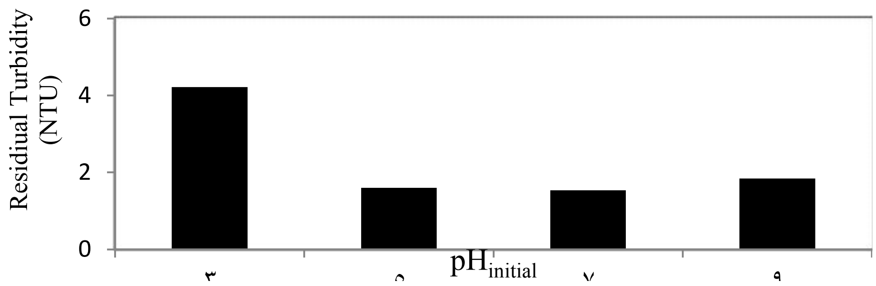

Figure 2. Effect of initial pH versus residual turbidity. Condition :Initial volume of waste water =600 mL،Mixing rate=120 rpm ،Dose of Electrolyte (NaCl)=0.9 g/L،Electrode distance=3cm، Current density=125A/m^2،Contact time=15min.

Table2. The result of several experiments during optimization of operating parameters, the best conditions were highlighted.[Condition: Initial volume of waste water (mL)=600، Mixing rate=120 rpm ،Time(min)=15،Type of Electrolyte=NaCl, Current density (A/m^2)=125,Electrode(Anode/Cathode)= Al /Al، Initial oil concentration (g/L)= 4،Initial turbidity (NTU) =215، Electrode distance (cm)=3].

Crude Oil Removal Efficiency % (Eq.(4))	Water recovery (m^3/m^3 of wastewater) (Eq.(7))	Residual Turbidity (NTU)	Energy Consumption (kwh/m^3 of waste water) (Eq.(5))	pH_{final}	$pH_{initial}$	Dose of Electrolyte (gr/L)
99.25	0.81	1.6	$12*10^{-3}$	8	5	o.9
99.25	0.75	1.6	$15*10^{-3}$	8	5	0.7
-	-	-	-	-	-	0.5
98.03	0.84	4.22	$13*10^{-3}$	6	3	0.9
99.28	**0.84**	**1.54**	$\mathbf{12*10^{-3}}$	**8**	**7**	**0.9**
99.13	0.84	1.85	$11*10^{-3}$	8	9	0.9
99.22	0.84	1.66	$8*10^{-3}$	7	5	0.9
98.18	0.87	3.9	$7*10^{-3}$	4	3	0.9
98.88	0.84	2.4	$7*10^{-3}$	8	7	0.9
96.89	0.84	6.67	$8*10^{-3}$	9	9	0.9
98.37	0.75	3.5	$14*10^{-3}$	8	7	0.8

Type of circuit and its effect on EC: pulse current (PC)

During EC process sludge is produced, while polarization and fouling phenomena are happened around the anode. In other words, passivity and mass transport control [10] can interfere with the EC process. For some systems, an increase in current does not lead to a corresponding dissolution of the electrode. Passivity is caused by a formation of metal oxides on the electrodes, leading to an increase in the resistance to the electrolytic process [11].In this work, pulse current (PC) was performed and proposed to control the passivity [12-13].Figure3illustrates applied PC, where either cathode or anode is typically operating for 3 min, and then it is quieted until EC is completed. The proposed time was obtained during successive experiments (Table 3). In Table 3 various PC time pattern was established, applied voltage was 24–28V based on 4 g/L representative initial crude oil concentration in each batch. Nearly equal turbidity removal efficiency was obtained in direct current and pulse current. The PC mode was found to be more efficient than the DC mode with a lower anode over-voltage, slower an odepolarization and passivity, also the operating time is (30%, 46%, 26%, 60%, 80%) less in PC mode based on different on|off pattern (3|3, 1|1, 2|2, 4|2, 2|4 and 1|5) respectively. All the operating times in PC mode are compared with optimized DC mode in Table 3,however, because of PC mode, sludge was hitched around the electrodes and fouling phenomena were limited. Energy saving was significant in PC mode with 3|3 pattern, 42*10-4kwh/m3 of waste water however, whereas in DC mode energy consumption was12*10-3 kwh/m3 of waste water (see Table 3 for detailed operational parameters). Turbidity of clarified water in PC andDCmodewere1.98 NTU and 1.54 NTU respectively after EC process. To the best of our knowledge there is no report on our search of literature, indicated that there is no report on application of PC for removing crude oily wastewater. Keshmirizadeh reported fairly similar results for removing cutting oily wastewater [14].

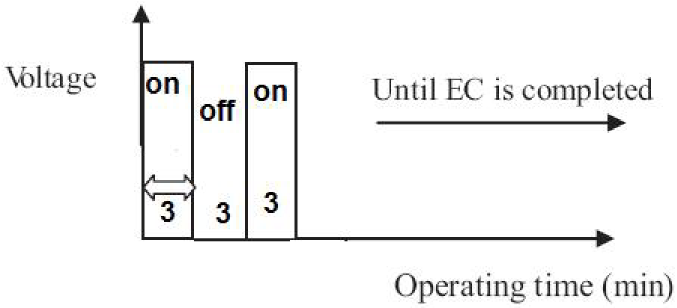

Figure 3. Typical diagram for rectangular pulse current (PC). Cathode oranode is operating for 3min then it shouted down until EC is completed.

Table 3.Optimized operational parameters for various PC time pattern-comparative results of PC and Dc mode, the best selective condition was highlighted. [Condition:Initial volume of waste water=600(mL)‹ Initial crude oil conc.=4g/L, Mixing rate=120(rpm)‹Current density=125 (A/m^2)‹I(A)=0.9‹Electrode distance =3(cm) ‹InitialTurbidity(NTU)=215‹$pH_{Initial}$=7].

		PC				DC		
PC time pattern (min) *on|off*	EC time (min)	Oil Removal Efficiency % *Eq.4*	Water recovery (m3/m3 of waste water) *Eq.7*	Energy Consumption (kwh/m^3 of waste water) Eq.5	EC time (min)	Oil Removal Efficiency % *Eq.4*	Water recovery (m3/m3 of waste water) *Eq.7*	Energy Consumption (kwh/m^3 of waste water) Eq.5
3|3	9	**99.07**	**0.82**	**$42*10^{-4}$**	15	99.28	0.84	$12*10^{-3}$
1|1	8	99.33	0.21	$39*10^{-4}$				
2|2	8	95.25	0.13	$42*10^{-4}$				
4|2	11	97.81	0.06	$23*10^{-4}$				
2|4	6	97.83	0.13	$54*10^{-4}$				
1|5	3	99.23	0.1	$75*10^{-4}$				

**Effect of initial crude oil concentration on turbidity removal efficiency*

In this study, crude oil solutions with different initial concentrations in the range of 2–33 g/L were treated by EC process; however, other studies worked on initial cutting oil concentrations in the range of 0.1-10% [6, 7, 15]. Consequently, optimized operational parameters such as crude oil removal efficiency percent, water recovery, cathode and anode weight loss values are represented based on various initial crude oil concentrations in Table 4 .According to the results, at high initial oil concentrations, 33g/L, water recovery was 0.87 while turbidity removal efficiency percent was near 99%.

Table 4. Optimized operational parameters for various crude oil initial concentrations.[Condition: Initial volume of waste water=600 (mL)، Mixing rate=120(rpm)،Time(min)=15،Current density(A/m^2)=125،$pH_{Initial}$=7،Electrode distance =3(cm)، I(A)=0.9, Energy consumption=12*10^{-3} (kwh/m^3 of waste water)].

Initial crude oil solution concentration (g/L)	Crude oil Removal Efficiency %(Eq4)	Water recovery (m3/m3 of wastewater) (Eq.7)	Cathode Weight Loss(gr)	Anode Weight Loss(gr)
2	97.7	0.84	0.016	0.09
4	99.31	0.84	0.032	0.148
8	98.42	0.84	0.16	0.1
16	98.42	0.87	0.017	0.092
33	98.9	0.87	0.017	0.088

**The effect of type of electrolyte and electrolyte concentration*

In this research, 2 duties were studied: (1) access to maximum Crude oil removal efficiency (2) a study on water recovery (or treated water) reuse. If the conductivity of water recovery is near 2mS/cm or less, recycling is more economically feasible. In this study, electrolyte consumption for enhancement of EC was optimized at 1.3mS/cm for low to high concentrations of crude oil by NaCl, and other operational parameters are reported based on conductivity levels (Table 2). However, other authors [16-17] reported a conductivity level of up to 17 mS/cm. Also in this research, in addition to NaCl, nine different electrolytes were used as supporting electrolytes separately. The performance of each electrolyte was compared in each batch, based on high turbidity removal efficiency and low operating time and energy consumption. The optimized and suggested electrolyte concentration in each batch is represented in Table 2. As Figure 4 demonstrates NaCl is the best electrolyte and because of ease of availability was selected. The ohmic resistance of EC cell increases when polarization takes place. The highest oil removal was observed when NaCl or KNO_3 or $NaNO_3$ were used respectively. The effect of PAC on oil removal efficiency was evaluated. The results showed that for removal of initial crude oil concentrations of 4 g/L, the use of PAC or KCl or $FeNO_3$ or $Zn(NO_3)_2$ are not recommended.

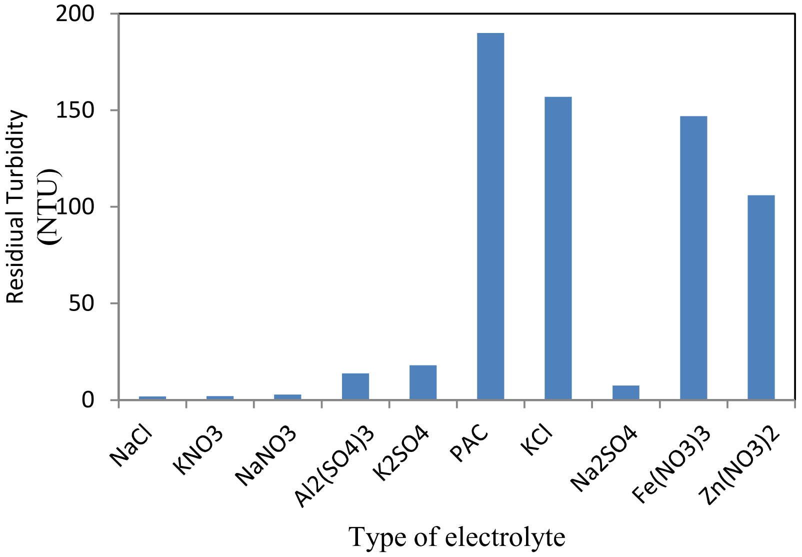

Figure 4. Comparison of electrolytes, residual turbidity development versuselectrolyte type. [Condition: Initial oil concentration 4g/L, Initial volume of waste water =600 mL، Mixing rate=120 rpm,pH=7**,** Electrode distance=3cm ،Current density=125A/m^2، Contact time=15 min].

Effect of flow rate and initial volume of wastewater on the residual turbidity

In order to understand the optimum flow rate of the crude oily waste water that yields maximum turbidity removal efficiency the experiments were carried out at 5, 11.25 and 15 mL/sec with 4g/L crude oil solution and a constant current density of 125 A/m2 was applied in each semibatch system, all experiment were performed in two cases separately for initial volume of wastewater 600 and 800 mL. The residual turbidity as a function of flow rate is shown in Fig.5 comparatively. Fortunately, it can be seen that the residual turbidity in 600 mL initial volume of waste water was increased from 0.8 NTU at 5mL/sec to 1.5 NTU at 15mL/sec, however the allowable residual turbidity for drinking water was 5 NTU. The increase in residual turbidity with increasing flow rate is rather expected, since slower the flow rate higher is the residence time, whereas it means the untreated solution remains in the electrocoagulation cell for more time, otherwise at higher flow rate the residence time is lowered in a flow reactor, which in effect, lowers the rate of coagulation. The residence time was calculated as follows:

$$Residencetime = \frac{volumeofwastewater}{flowrate} \quad Eq\ .(8)$$

Whereas volume of wastewater is in mL, and flow rate is in mL/sec. The residual turbidity for 1800mL initial volume of wastewater increases with increasing flow rate up to 9.9

NTU. These observations are in agreement with the previous researchers for textile waste water treatment [18].

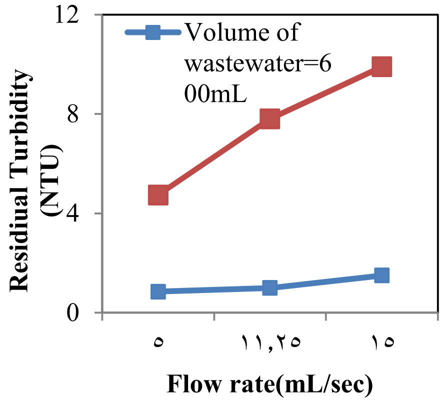

Figure 5. Comparative curve. Effect of wastewater flow rate versus residual turbidity.[Condition: Initial oil concentration 4g/L, Mixing rate=120 rpm, Electrode distance=3cm ،Current density=125A/m2، Recycling or contact time=15 min].

Conclusions

The electrochemical treatment of crude oily waste water in a batch and semi batch (in a flow through EC cell) described can effectively remove 99% crude oil from waste water in a 15 minute and under the optimum conditions. The PC mode was found to be more efficient than the DC mode with a lower anode over-voltage, slower anode polarization and passivity. The operating timeis30% less when PC mode is used, based on initial concentration of 4g/L. Because of the reduction in operating time, less power (or energy) is consumed, which makes the PC mode more cost effective. Accessing to a clear supernatant (Turbidity: 2 NTU) or high quality effluent and water recovery=0.84 which are feasible for reuse as treated water.

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