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Modeling of Tubular Electrochemical Reactor with a Spiral Design of Anode for Treatment of Petroleum Refinery Wastewater

[1] Ghazi Faisal Naser *, [2]Thamer J. Mohammed, [3]Ali H. Abbar

[1] Chemical Engineering Department, Faculty of Engineering, Al-Muthanna University, Iraq
[2]Chemical Engineering Department, University of Technology, Iraq
[3]Department of Biochemical Engineering, Al-Khwarizmi College of Engineering, University of Baghdad, Baghdad, Iraq

Article information

*Corresponding Author:
Ghazi Faisal Naser
ghazi_faisal@mu.edu.iq

Abstract

Petroleum effluent is often made up of a complex combination of metals and organic molecules. In the present work, modeling of a tubular electrochemical reactor (TER) with a novel design operated at batch recycle for petroleum refinery effluent treatment by anodic oxidation was investigated. The reactor is composed from a cylindrical stainless steel cathode and a spiral porous graphite anode at its center. The impact of flow rate on the chemical oxygen demand (COD) reduction and mass transfer coefficient (k) was studied. Results showed that increasing flow rate led to higher removal efficiency of COD and higher mass transfer coefficient where COD removal of 70% and k with value of 6.283×10^{-4} cm/s were obtained at flow rate of 4l/min. A power low correlation was obtained between mass transfer coefficient(k) and Reynolds number (Re) with coefficient of determination (R2) equal to 0.994869.This relation can be described as $k=1.906 \times 10^{-6}(Re)^{0.545}$ with range of Re $10000 \leq Re \leq 40000$ prevailing turbulent conditions.

1. Introduction

Wastewaters generated by petroleum refineries have high COD and salinity therefore they are considered as major risk pollutants to the environment. Numerous toxic organic compounds were found in these effluents, hence treatment such effluents before discharging to revisers is mandatory [1]. Refineries often produce hazardous

wastewater with COD levels between 300 and 600 mg/L, phenol levels between 20 and 200 mg/L, benzene levels between 1 and100 mg/L in addition to heavy metals of intervals between 0.1 and100 mg/L for chrome and (0.2–10) mg/L for lead, and other contaminants. [2]. Different Physicochemical and biological approaches were used to treat refineries effluents. [3]. Recently, electrochemical treatment methods of wastewaters from petroleum refineries consider as attractive and environmentally friendly processes that can be performed in industrial areas under ambient temperature and pressure. Besides these methods offer many typical benefits such as versatility, environmental compatibility and energy efficiency [4]. In comparison to traditional techniques, electrochemical oxidation, one of the electrochemical treatment technologies have gotten a lot of attention in recent years as a good way to treat wastewater [5].

Generally, direct and indirect electrochemical ways are utilized for removing organic contaminants from wastewater depending on the type of anode used and existing of NaCl salt [6]. Besides, various configurations of electrochemical reactors were utilized at anodic oxidation process such as the traditional parallel plate reactor, stack cell and flow cell with mesh anode (rotating disc reactor) tubular electrochemical reactor (TER), and three dimensional electrodes [7].

The tubular electrochemical reactor has been utilized by numerous researchers to treat many forms of organic wastewater using electrochemical oxidation techniques, such as Cr(VI) from wastewater [8,9], petroleum refinery waste-water [10,11], textile wastewater [12], phenol removal from wastewater [13,14], also pharmaceutical effluents[15], in addition paint wastewater [16]. Excepting work of Martínez-Delgadillo and their coauthors [8], most of these tubular electrochemical reactors consist of concentric cylindrical cathode and anode. Martínez-Delgadillo et al., [8] in their work on removing [Cr (VI)] from wastewaters used a tubular TER consisted of a cathode represented by central polished carbon steel rod and spiral wire like material used as anode. They concluded that for low intake velocities, reactor dispersion is strongly dependence influenced by inlet position and using spiral wire anode gives better reduction in the dispersion leading to lower residence time within the reactor. In further research the same authors used the same reactor and found that the best performance comes from an electrochemical reactor with a tangential intake in comparison with central and lateral inlets [9].In present study, treatment of petroleum refinery wastewater was investigated by using a new design of TER composed from a central spiral rode anode surrounded by hallow cylindrical cathode.

Studying the modeling of electrochemical oxidation of petroleum refinery wastewater is essential for scale up the process depending on geometric and hydrodynamic similarities. Besides, modeling of any electrochemical reactor used for anodic process depends solely on the mechanism of oxidation since it considers as a complex phenomenon due to the occurring of dissociate chemisorption step combined with electron transfer reaction. Essentially two kinds of oxidation processes could be occurred at the anode depending whether the anode having a high electro-catalytic activity or it is a non-active anode, in the first type oxidation takes place at the electrode surface called (direct electrolysis); while in the second type, the oxidation happens via surface intermediary on the anodic surface that generated constantly called as (indirect electrolysis). In the indirect oxidation, the rate of oxidation is governed by parameters like pH, temperature and diffusion rate of the created oxidants while in case of direct electrolysis, current density, electrode action, and contaminants diffusion rate determine the rate of oxidation. Moreover, specifically in the indirect-anodic-oxidation, NaCl is added to the wastewater to generate hypochlorite ions as well as to get better conductivity [17].The main objective of this work is to model a novel tubular electrochemical reactor with a spiral design of anode in removal of COD from waste water and finding a mathematical correlation that relates between mass transfer coefficient and Reynolds number via varying the flow rate and measuring the corresponding COD values at different intervals of time.

2. Theoretical Part

The modeling of indirect anodic oxidation starts from the creation of chlorine gas by anodic- oxidation of Cl ions (Eq.(1)):[18]

$$2Cl^- \xrightarrow{k_1} Cl_2 + 2e^- \tag{1}$$

Hypochlorous acid is then generated via reaction of chlorine gas with H2O (Eq.(2)):

$$Cl_2 + H_2O \xrightarrow{k_2} H^+ + Cl^- + HOCl \tag{2}$$

Hypochlorite ion is then formed by dissociation of HOCl(Eq.(3))

$$HOCl \frac{k_3}{k_3'} H^+ + OCl^- \tag{3}$$

Hypochlorite ions serve as a strong oxidizing agent that degrade the pollutants existing in wastewater.

The mechanism of indirect electrochemical oxidation with chloride as sustaining electrolyte has been proposed for wastewater processing [19-21]. The hypo-chlorite reacts with organic pollutant according to the following equation:

$$Organic\ polutant + OCl^- \xrightarrow{k_4} Cl^- + CO_2 + H_2O + Product \tag{4}$$
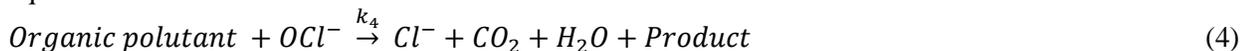
Because the OCl (pKa 7.44) ion is readily formed in basic solution, the rate response is faster in

Eq. (3) while it is less rapidly in acidic solution as a result of instability of OH^- hence indirect oxidation is favored in basic or neutral pH conditions. A loop of chloride–chlorine–hypochlorite–chloride develops, resulting in OCl. The pseudo steady state method can be useful to any of the intermediate products (OCl and HOCl). The rates of reactions r_i exclusively for the series are (Eqs. (1)–(4)) if all other reactions are irreversible processes.

$$-r_{Cl_2} = k_2[Cl_2] \tag{5}$$
$$r_{HOCl} = k_2[Cl_2] - k_3[HOCl] + k_3'[H^+][OCl^-] = 0 \tag{6}$$
$$r_{OCl^-} = k_3[HOCl] - k_3'[H^+][OCl^-] - k_4[Polu.][OCl^-] = 0 \tag{7}$$
$$-r_{polu.} = k_4[Polu.][OCl^-] \tag{8}$$

Then using equations 6 and 7 give the following:

$$-r_{Cl_2} = -r_{polu.} = k_4[Polu.][OCl^-] \tag{9}$$

Consequently, according to the bulk solution, $-r_{Cl_2} = r_{Cl^-}$ can be calculated from material balance in eq.4

$$-r_{Cl_2} = r_{Cl^-} = k_2[Cl_2] = -r_{polu.} = k_4[Polu.][OCl^-] \tag{10}$$

The rate expression for basic electrode reaction as stated by the Eq. (1) can be written as

$$-r_{Cl^-}' = -r_{Cl_2}' = k_1[Cl^-] \tag{11}$$

The preceding equations were used to develop a connection between the active species in bulk and at the electrode surfaces. Faraday's law is the essential relationship applied to all electrochemical reactions in which the weight of material reacted at the surface is related to the charge ($I_A t$) transmitted to be ($M_A I_A t/nF$) (assuming 100% current efficiency) and takeover the current density (i_A), which is I_A/A_e as a measurable parameter. As a result, the electrochemical reaction mechanism (for reactant A disappearance) can be represented as

$$-\left(\frac{V_R}{A_e}\right)\frac{d[A]}{dt} = \frac{i_A}{zF} \tag{12}$$

Where V_R the reactor volume, A_e the electrode area, z the multiple of electrons transported per mole of reaction, (F) is the Faraday (96,500 C or A s/mol), while (I_A) is the current passed in time t, and (M_A) acts the molecular weight.

From a material balance of species Cl^-, it could be concluded that:

$$\frac{i_A}{zF} = k'[Cl_2] \tag{13}$$
$$\frac{i_A}{zF} = k''[Polu.][OCl^-] \tag{14}$$

When operating ate constant current over electrolysis and under a certain group of experimental status, the rate of creation of $[OCl^-]$ will kept constant. Then

$$\frac{i_A}{zF} = k_{obs}[Polu.] = k[COD] \tag{15}$$

For batch recirculation reactor, the electrochemical reaction rate (for elimination of COD) can be presented as

$$-\left(\frac{V_R}{A_e}\right)\frac{d[COD]}{dt} = \frac{i_A}{zF} = k[COD] \tag{16}$$

OR

$$ln\frac{[COD]}{[COD]_o} = -kat \tag{17}$$

where : a acts the specific area of working electrode (A_e / V_R), COD estimation was taken as a measurement of the progress of organic pollutant destruction[22].

Scare literatures on modeling of electrochemical oxidation using TER for treatment of wastewaters. Ramesh Babu et al., 2009[23] investigated the electro-oxidation for processing of pharmaceutical wastewater in a cylindrical shape of reactor in continuous mode with single pass. The flow rate and current density were discovered to affect the mass transfer coefficient. However, no mathematical correlations describing these behaviors were found.

Skban Ibrahim et al.,2013[7] studied the performance of (TER) with a cylindrical configuration of mesh electrode

worked at batch circulation mode for wastewater processing using computational fluid dynamics (CFD) in addition ,residence time distribution (RTD) as tools. As a performance evaluation of TER, they studied the mass transfer coefficient and found an improvement in mass transfer coefficient at higher levels of flow rates with no mathematical presentation of such behavior. Skban Ibrahim et al., 2014[11] adopted an electro-oxidation as a processing technology for petroleum refinery wastewater (PRW) using TER at batch circulation. They found that increasing of flow rate resulted in decreasing specific energy expending and enhancing mass transfer coefficient. Besides, their findings shown that electrochemical technology may be used to recycle and recover petroleum refinery wastewater.

Vijayakumar, et al., 2017 [24] investigated the modeling of TER for synthetic dye wastewater treatment. The reactor was run in a batch with circulation then modeled and analyzed using finite difference way. They concluded that modeling of TER especially in dye removal might be beneficial in the design and scale up of electrochemical process. However no mass transfer correlation was found in their work.

All previous works have not reported a mass transfer correlation that relates between Reynolds number (Re) and mass transfer coefficient (k). Therefore, the purpose of this work is to modeling of a novel tubular electrochemical reactor with a spiral design of anode in removal of COD from waste water and finding a mathematical correlation that relates between k and Re. In this context, the impact of flow rate on the reduction of COD and mass transfer coefficient was investigated.

3. Experimental Procedure

3.1 Materials and Apparatus

A quantity of 40 liters of wastewater have been collected from Al-Muthanna petroleum refinery plant emptying point. Table 1 displays the properties of AlMuthanna petroleum refinery wastewater. The conductivity of raw water is 4.25 m S/cm which is at the acceptable interval for generating low cell potential [25] hence no further addition of supporting electrolyte like Na2SO4 is required.

Table 1. Wastewater properties of Al-Muthanna petroleum refinery.

Parameter	COD $(\frac{mg}{l})$	pH	T.D.S $(\frac{mg}{l})$	Cl⁻ $(\frac{mg}{l})$	SO₄⁻² $(\frac{mg}{l})$	Turbidity NTU	Conductivity $(\frac{mS}{cm})$
value	340	7.2	3180	1160	425	98	4.25

The electrochemical system is presented clearly in Figure (1). It consists of a tubular electrochemical cell, 5liters Perspex tank for the wastewater, a recirculation pumps (GRANDFAR: X15GR-10), a flow meter with a flow interval from 0.5 to 7 L/min, for controlling the electrolyte flow rate. The batch recycle mode of operation is offered by this configuration, which permits wastewater to be recirculated through the electrochemical reactor.

A new tubular electrochemical reactor was composed of cell body and cover both of them made from Teflon. It was closed from the bottom and provided with inlet portion located on the lateral side of the body near the bottom. At the upper, the body cell was joined with a flange provided with four holes for fixing the body with the cover. An outlet portion was located on the lateral side below the flange of the cell body. The cover was provided with a hole for joining anode and four holes for fixing cover with cell body via four bolts and nuts. A system based on concentric electrodes arrangement was constructed in the present work. The cathode was a tubular 316 stainless steel. It was fixed inside the cell body via bolt and nut located at the center of its length. A spiral porous graphite rode was used as a new design of anode. It was purchased from Tokai Carbon Co., Ltd. with a porosity of 20-26% and BET surface area of 22.751 m²/g [26]. This design makes the electrolyte to flow along the lateral surface of the anode in a spiral movement, so the anode and cathode distances were kept constant. The graphic illustration of a tubular electrochemical reactor is shown in Figure (2).
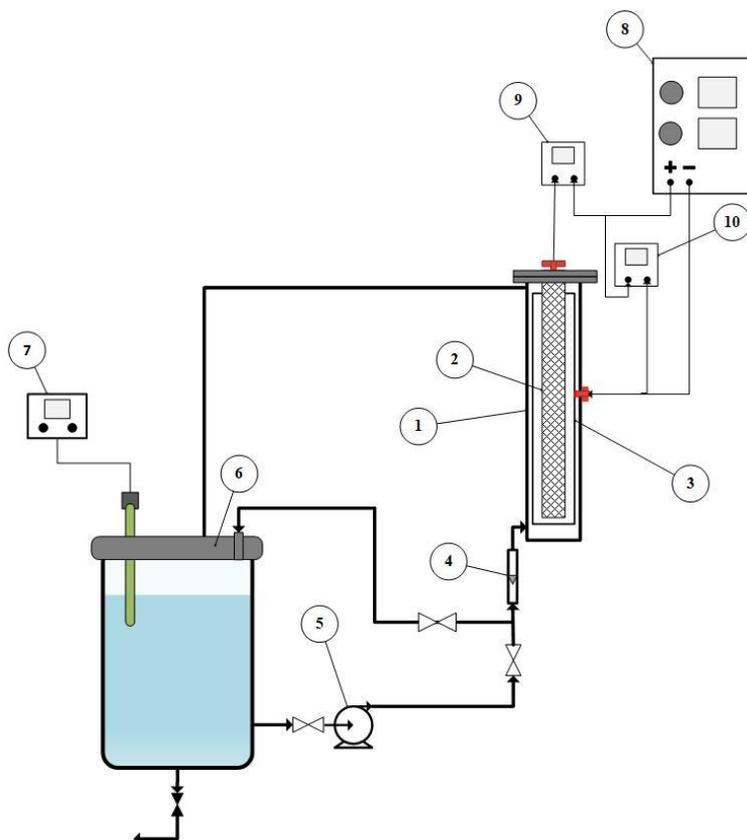
Figure 1 The electrochemical system's diagram.1) cell body,2) anode,3) cathode ,4)flow meter, 5) pump,6)reservoir,7) pH-meter,8)power supply,9) Ammeter,10) voltmeter
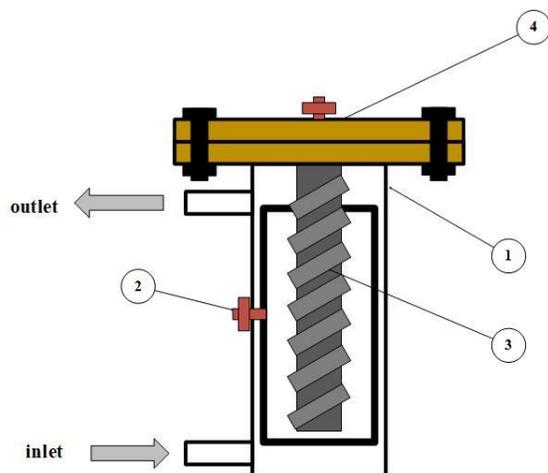
Figure 2 The electrochemical cell's diagram,(1) cell body, (2) cathode, (3) anode, (4) cell cover

During each run, a digital power supply with range (0–30 Volt), (0–5 Amp.) (UNI - T, UTP1305) was utilized to supply stable current (4.49A) which gives anodic current density of 26mA/cm^2. To obtain the required combining conditions, a 3 L solution was mixed with a magnetic stirrer at rotation value (500 rpm) for each experiment, then 1.9g/l NaCl was added followed by pH adjustment to 10 using either 1M HCl or 1M NaOH using a digital pH meter (HM Digital Inc.PH-200) with continuing the mixing at the same rotation speed then finally putting the solution in the reservoir and circulating it through the cell at the required value of flow rate. All of the tests were conducted at a fixed temperature of 25 ±2 ºC. The selecting of the above conditions is based on our prior research [27].
Based on eq.18, the removal efficiency of COD was evaluated [26]**:**

$$R\,E\,\% = \frac{COD_i - COD_f}{COD_i} \times 100 \tag{18}$$

COD_i indicates the initial COD(mg /l) , COD_f indicates the final COD (mg /l) and R E % denotes for the elimination efficiency of COD.

The energy consumption for a kilogram of COD that needs to be digested acts the amount of energy consumed in the process. Eq. 19 can be used to evaluate SEC in (kWh/kgCOD). [26]**:**

$$SEC = \frac{E.I.t \times 1000}{(COD_i - COD_f)\,V} \tag{19}$$

Where SEC refers to the specific energy consumption (kWh/kgCOD), E: acts the cell voltage (volt), t: acts the time (hr.), I: acts the current (Amp.), V: acts the effluent volume (L), and COD_f and COD_i acts the final and initial chemical- oxygen- demand (mg/l) respectively.

4. Results and Discussion

The aim of the present work as mentioned previously is to state a correlation between mass transfer coefficient (k) and Reynolds number as a design equation for scale up of such electrochemical reactor for large scale processes. Figure (3) shows the degradation of COD with time at different flow rates (1,2,3 and 4l/min).
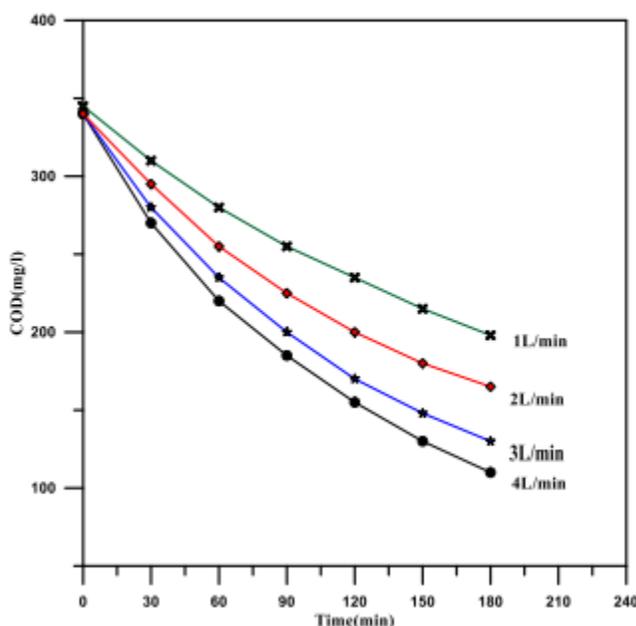

Figure 3:COD concentration decay with time at various flow rates Conditions: C.D. = 26mA/cm2,pH=10,[NaCl]=2g/l

From Figure 3, it can be shown that the COD readings reduced with increasing the time of the operation and electrolyte flow rate. The destruction of organic content occurred more quickly at high flow rates because of high rate of oxidants production leading to increase the mass transfer coefficient. Similar observations were found in previous studies [11, 26]. Hypochlorite ions are the principal reagent for decomposing organic contaminants in indirect oxidation in the presence of chloride. Hence increasing electrolyte circulation results in transport of the Cl^-ion from the bulk to the surface of electrode more rapidly which ease generation of chlorine gas and its dissolution to form ($OCl-$) for reaction with the organic pollutants. Similar behavior was noted by Vijayakumar et al [24]

Figure 4 displays the relation between the removal efficiency and flow rate where higher removal efficiency was obtained at 4l/min (70%) while Table 2 presents the values of SEC which is increased with decreasing the flow rate. This behavior is expected since lower flow rate results in high voltage applied and low reduction in COD. Similar behavior was found by Skban Ibrahim et al. [11]
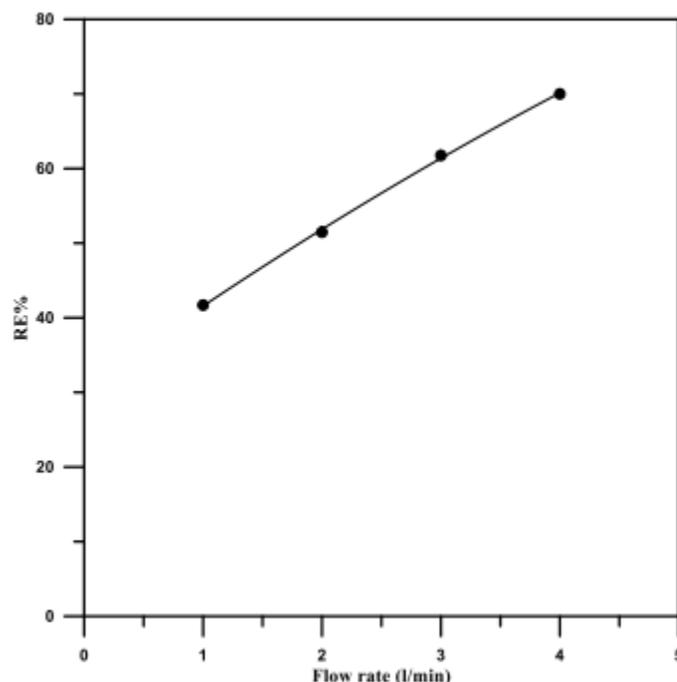
Figure 4 COD removal efficiency (RE%) verses flow rate
Conditions: current density 26mA/cm^2,pH=10,NaCl=2g/l

Table 2 SEC at various flow rates
Conditions: C.D. 26mA/cm^2,pH=10,[NaCl]=2g/l

Flow rate (l/min)	E (Volt)	SEC (kWh/kgCOD)
4	10.87	212.2
3	11.86	253.6
2	11.595	297.49
1	11.475	362.836

The mass transfer coefficient (k) was evaluated from the plot of ln (COD/COD$_o$) and time of electrolysis process as shown in Figure 5. In predicting of k, the value of (a) was taken as 0.171 cm^{-1} for the present system. The relation between ln COD/COD$_o$ and time is linear with coefficient of determination (R^2) higher than 0.997 for all flow rates as shown in Table 3. From Table 3, it can be seen that mass transfer coefficient increased with rising the flow rate. Similar behavior was found by Ramesh Babu et al. [23] that they used in their work continuous mode of flow and by Skban Ibrahim et al [11] which batch recycle mode was applied in their work. When comparison was made the work of Skban Ibrahim et al.[7] ,the values of mass transfer coefficient in the current work were higher than those gained by Skban Ibrahim work at flow rates 1,2 l/min. The reason for this may due to the high turbulence promotion of the present design.
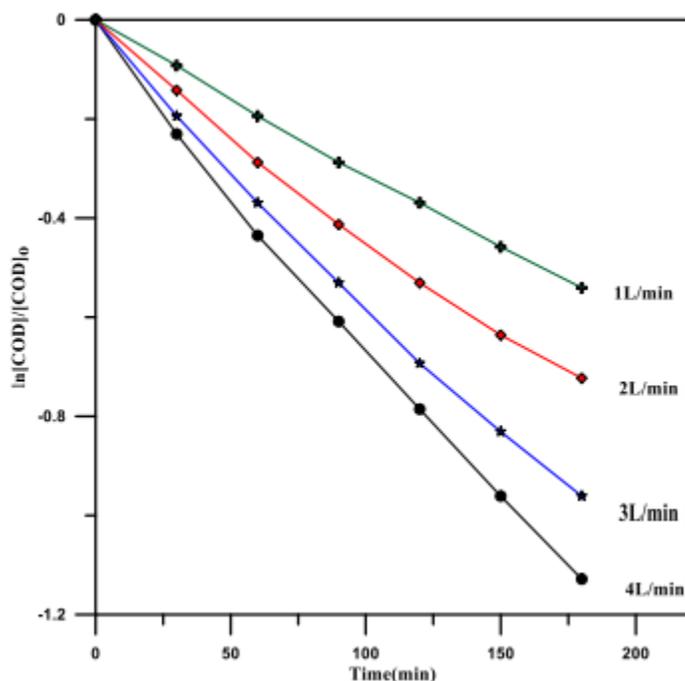
Figure 5 Plots of $\ln[COD]/[COD]_o$ against time for different flow rates
Conditions: C.D.= 26mA/cm^2,pH=10,[NaCl]=2g/l

Table 3 mass transfer coefficient at multiple flow rates
Conditions: current density 26mA/cm^2,pH=10,NaCl=2g/l

Flow rate (l/min)	k.a(min^{-1})	k(cm/min)	k(cm/s)	R^2
4	0.006463	0.0377	6.283x10^{-4}	0.998332
3	0.005574	0.0325	5.416x10^{-4}	0.997966
2	0.004248	0.0248	4.133x10^{-4}	0.997039
1	0.0030596	0.01785	2.975x10^{-4}	0.999518

Figure 6 shows the relation between (k) and (Re). the value of Re was estimated by taking the density of electrolyte 1.2 g/cm^3 and its viscosity equal to 0.0009 Pa.s measured by using viscometer. The results showed that the correlation between them is power type with exponent of 0.545 and R^2=0.994869 and it could be correlated mathematically by the following equation:

$$k=1.906\text{x}10^{-6}(Re)^{0.545} \qquad 10000\leq Re\leq 40000 \qquad\qquad (20)$$

In comparison of results in the present work in anodic oxidation using TER with our previous work for cathodic reduction of zinc using packed bed cathode in batch recycle mode of operation [29], the power of Reynolds number is higher than that obtained in packed bed (0.4227). The reason may be the high turbulence promotion of the new design which permit turbulent conditions that couldn't be achieved in packed bed electrode. Recently Anke Arts et al, 2020[30] used parallel plate electrochemical cell operated at batch recycle mode for oxidation of formic acid on BDD anode. They found that mass transfer coefficient correlates with Reynolds number to the power 0.44. In a parallel plate cell, mass transfer is less efficient than in a TER. so lower exponent of Re was observed in their

work. Besides the new design of TER in this work has enhancement mass transfer in comparison with traditional TER.
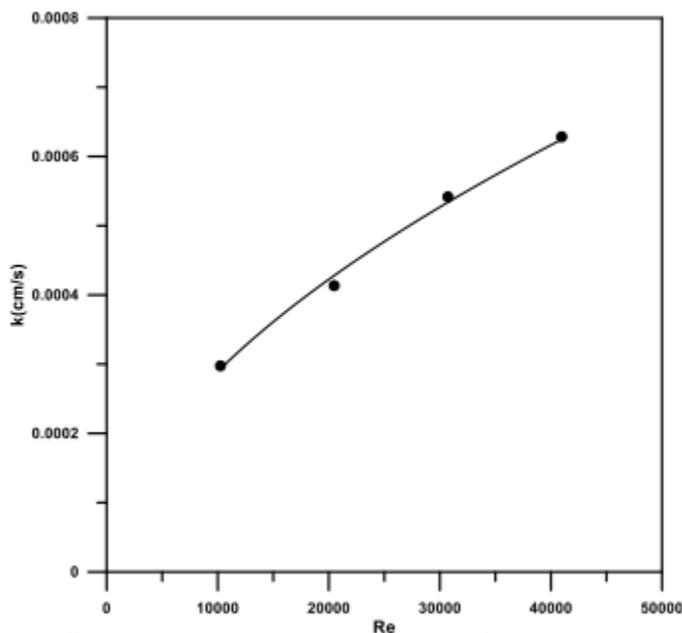

Figure 6 Mass-transfer coefficient against Reynolds number
Conditions: current density $26mA/cm^2$,pH=10,NaCl=2g/l

5. Conclusions

The electrochemical processing of petroleum refinery wastewater collected from Al-Muthanna refinery in a batch recycle mode utilizing a tubular reactor made of a stainless steel cylinder cathode with a spiral porous graphite anode at the center was examined. Effect of flow rate on the reduction of COD and mass transfer coefficient was investigated. The results showed that raising the flow rate reduces COD, with a highest removal effectiveness of 70% achieved at a flow rate of 4l/min. Effect of flow rate was found to be vital where higher removal of COD occurred at high flow rate due to the turbulence promotion action of the new design of the anode. Increasing flow rate leads to increase mass transfer coefficient. A mathematical correlation between mass transfer coefficient and Reynolds number was achieved which is a power relation with exponent of 0.545 revealing high mass transfer using the present design of TER.

Conflict of Interest: There are no conflicts to declare.

Nomenclatures

symbol	definition	unit
COD	Chemical Oxygen Demand	mg/l
C.D.	Current density	mA/cm^2
E	voltage	volt
k	Mass transfer coefficient	cm/s
Re	Reynolds number	
SEC	Specific energy consumption	kWh/kgCOD
T.D.S	Total dissolved solid	mg/l
t	Time	hr
I	Current	Amp.
V	Volume	L

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