



Removal Kinetics and Performance Evaluation of 3D Rotating Cylindrical Anode Reactor for Textile Wastewater Treatment

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ABSTRACT

The removal kinetics of a batch electrocoagulation 3D rotating cylindrical anode reactor for reactive dye effluent was investigated. The cell used a new type of electrode arrangement having a rotating 3D Al cylinder as anode and long rod of aluminium as cathode. The performance of the reactor was studied via various operating parameters, such as current density, anode rotation speed, duration of electrolysis, nature of supporting electrolyte and rate of reaction. The dye removal process in this innovative system follows a second order kinetics with maximum COD removal of 96.40% in a pH range of 6-8 and having a current density of 6 mA/cm². The anode rotation provides the turbulence which helps in removal process.

INTRODUCTION

The rapid rate of industrialization and the discharge of untreated wastewater into the receiving streams strongly affect the water life and groundwater resources. In this contamination process, the textile wastewater is divided with a strong amount of water soiling, which emerges mainly from different textile units after the respective dyeing process. The removal of various dyes from textile wastewater is of great importance and concern since they not only impart colouring effects, but also the high BOD and COD of the wastewater strongly impairs the receiving stream or body of water. The dissociation of many dyes lead to carcinogenic compounds, which in turn have a serious health risk for organisms across the food chain, especially in developing countries (Deb & Majumdar 2013). The annual production capacity for dyes and pigments is around 700,000 and 10,000 tonnes worldwide (Gong et al. 2007). About 15% of these dyes are released into sewage. Since the freshwater resources are limited and must be harvested efficiently, these effluents have to be treated before being released into the environment or recycled or reused.

Conventional processes are available for the treatment of textile wastewater, including biological processes, biodegradation, coagulation and flocculation, adsorption and advanced oxidation (Annadurai et al. 2008, Lin & Peng 1996, Nakagawa et al. 2004). These biological processes are less effective, however, in the treatment of dye wastewater (Elisangela et al. 2009).

The disadvantages of these processes led to the search for an alternative technology for industrial wastewater treatment known as electrocoagulation (EC). It has an advantage of the *in situ* release of reactive agents with less space required for its functioning. The potential of the EC as a treatment technology for different wastewaters has been reported by various researchers. It has been used for the treatment of dyes, heavy metal, oil emulsions, complex organic substances, suspended solids, bacteria, viruses and cysts (Aleboyeh et al. 2008, Bensadok et al. 2008, Yildiz 2008, Zidane et al. 2008).

With the increasing popularity of the EC technology, there exist some disadvantages of the technology, viz., a. dissolution of sacrificial electrodes, b. fouling of the electrode, and c. oxide layer formation leading to loss of efficiency.

This leads to a further improvement of the technology to eliminate these problems. In this study, we have developed a unique reactor to solve these problems, leading to the development of a new advanced EC system with an electrochemical reactor having an innovative design for the treatment of textile wastewater. A rotating three-dimensional perforated cylindrical aluminium anode and cathode was developed to induce high turbulence even at low rotational speed in the textile wastewater/solution (Walsh 1993). This is the first time that this type of system is developed and will be used for the treatment of textile wastewater. In this light, it is expected that the use of a rotating 3D perforated

cylindrical anode would improve the process of textile wastewater treatment by electrocoagulation by increasing the mass transfer of Al^{3+} from the surface of the anode to the solution to be treated (El-Ashtoukhy & Yasmine 2014). This in turn reduces the soiling of the electrode, the formation of the oxide layer as the concentration polarization decreases, and reduces the passivation tendency of the anode which severely impairs the performance of the EC process. This also reduces the dissolution of the anode into the solution. The effects of the anode rotation speed, the current density, the NaCl concentration, the initial pH value, the type of the supporting electrolyte and the reaction rate have been worked out.

MATERIALS AND METHODS

Electrochemical reactor: In this investigation, a 3D perforated cylindrical aluminium anode and cathode was used for the treatment of synthetic textile wastewater with electrocoagulation. The reactor was made of plexiglas having conical structure at the bottom to effectively collect and enhance the settling of the sludge produced at the time of EC. The anode was made of a hollow aluminium cylinder having pores at regular distance in order to enhance the turbulence in the reactor. The effective area of the electrode was 284.52 cm^2 . The cathode was an aluminium rod with 7 mm inner diameter, 1.2 cm outer diameter and 14 cm height. The aluminium rod and perforated aluminium cylinder were isolated by perforated epoxy resin. The inter-electrode distance was fixed at 2 cm. The experimental system used is represented in Fig. 1.

Textile wastewater: The synthetic textile wastewater was prepared in the laboratory using Direct Red 23 dye with tap water. The pH was adjusted using NaOH and H_2SO_4/HCl when required. The conductivity of the wastewater was adjusted using NaCl.

Methods: The required currents were applied by a DC power supply (Kusam Mecco, Model: KM-PS- 305-DII). The analytical determination of the colour and COD removal was made by the standard procedure (5220 D. Closed reflux, Colorimetric method) using a UV spectrophotometer (Shimadzu, Model: UV-1800) (American Public Health Association, American Water Works Association, and Water Environment Federation 1999). The pH and conductivity were measured by a pH meter (Hanna, Model: HI 98128) and conductivity meter (Lutron. Model: CD-4302), respectively.

The COD and colour removal efficiencies (RE%) were calculated using the following equations:

$$\text{COD Removal Efficiency (\%)} = \frac{C_o - C}{C_o} * 100 \quad \dots(1)$$

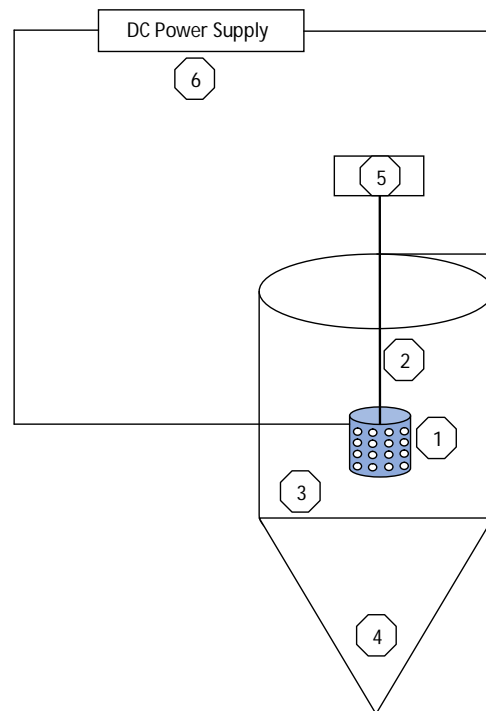


Fig. 1: Experimental setup. 1. 3D aluminium perforated cylindrical anode. 2. Aluminium rod cathode. 3. Textile wastewater. 4. Sludge. 5. Mechanical stirrer. 6. DC power supply unit.

Where, C_o and C are the concentration of COD before and after treatment, respectively, in mg/L.

$$\text{Colour Removal Efficiency (\%)} = \frac{A_o - A}{A_o} * 100 \quad \dots(2)$$

Where, A_o and A are the absorbance of dye before and after treatment, respectively.

RESULTS AND DISCUSSION

Effect of anode rotation speed: The effect of anode rotation on colour and COD removal efficiencies was studied (Figs. 2 and 3). The experiments were carried out at six different anode rotation speeds: 0, 20, 40, 60, 80 and 100 rpm. As the anode rotation speed increases from 0 to 60 rpm, the removal efficiencies increase from 65.53% and 98.65% to 96.40% and 99.86% for COD and colour respectively. This may result in the increment of the diffusion rate of Al^{3+} from the surface of the anode and in turn increase the intensity of the turbulence to induce good mixing conditions within the reactor (Walsh 1993). This leads to a reduction in the diffusion layer thickness. The turbulence generated by the anode rotation increases the collision frequency of the generated flakes to coalesce into larger flakes which are easily buoyant by cathodic hydrogen bubbles (El-Ashtoukhy & Yasmine 2014).

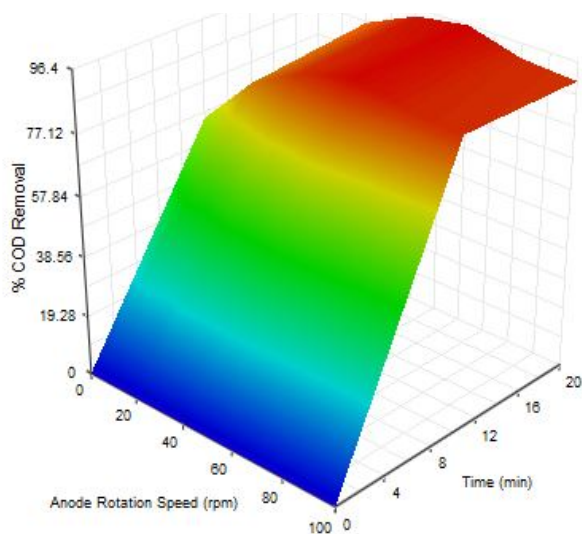


Fig. 2: Effect of anode rotation speed on percentage COD removal. (CD = 6 mA/cm², pH = 8, initial COD = 861 ppm).

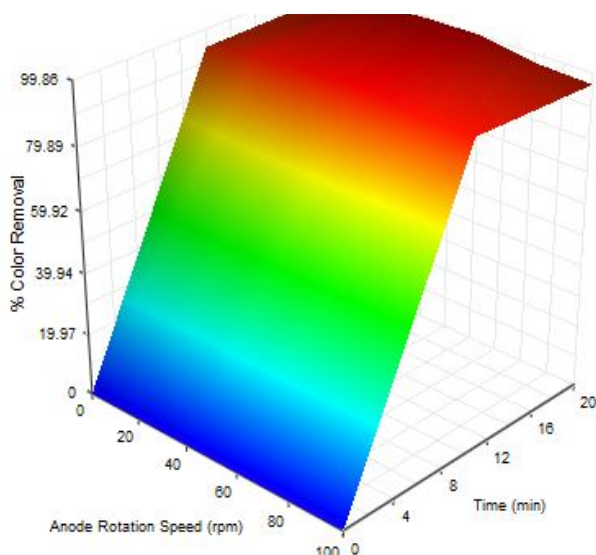


Fig. 3: Effect of anode rotation speed on percentage color removal. (CD = 6 mA/cm², pH = 8, initial COD = 861 ppm).

When the rotational speed was further increased to 80 and 100 rpm, the COD and colour removal efficiencies were reduced due to the high turbulence, which in turn leads to a collapse of the returned flakes. This results in an increase in the axial velocity such that it interferes with the flocs by the induction of the cyclonic action in the reactor at high speed.

Effect of current density: The current density is determined by dividing the measured current to the total effective anode area (El-Ashtoukhy & Yasmine 2014). It controls the reaction rate of the EC (Vasudevan & Lakshmi 2012). As the current

density increases, the efficiency of the system increases as depicted in Fig. 4; and as the current density further increases, the efficiency decreases. This phenomenon can be explained by the following effects:

- (i) The increase in the amount of Al³⁺ content according to Faraday law.
- (ii) The discharge rate of H₂ increases when the current density is increased, which in turn increases the floated electrocoagulated dye molecules to the surface of the solution.
- (iii) The rotation of anode along with generation of H₂ bubbles enhances the mass transfer of Al³⁺ ions. So, the anode concentration polarization decreases, resulting in the elimination of anode passivation (El-Shazly & Daous 2013).

Effect of type of supporting electrolyte: The effect of the supporting electrolyte was studied by using four different electrolytes: NaCl, NaOH, NH₄Cl and KCl. The properties of electrolyte devices and their interaction with electroactive species dominate the electrode reactions (Huang et al. 2009). NaOH provides best removal efficiency as compared to other electrolytes. NaOH electrolyte favours the removal efficiency due to the fact that aluminium is an amphoteric metal that deliquesce electrochemically in NaOH and increases the dissolution rate of Al to Al³⁺. The anode passivity is prevented by the addition of NaOH as it dissolves Al₂O₃ to sodium aluminate. The size of the H₂ bubbles developed from NaOH solution is small and has an effective surface area to float the pollutants to the surface easily as compared to those generated in the acidic range (Janssen & Hoogland 1973). NH₄Cl has the lowest efficiency due to the fact that in acidic range the formation of Al(OH)₃ is hindered, which is the main contributor in the dye removal process.

Adsorption kinetics: Kinetic study plays an important role in the determination of hydraulic retention time in the reactor used for treatment to achieve the removal efficiency (Dash & Chaudhari 2005). The kinetics of the removal of dye are explicitly explained in the literature using first-order and second-order kinetic models. The adsorption of dye is analysed using Lagergran rate equation (Gasser et al. 2007). The first order Lagergran model is (Singh et al. 2006):

$$dq/dt = k_1 (q_e - q_t) \quad \dots(3)$$

Where, q_t is the amount of dye adsorbed at time t (min) and k (1/min) is the rate constant of first order adsorption. The time dependence function of the equation 1 as an integrated form with boundary conditions t = 0 to >0 (q = 0 to >0) is:

$$\log(q_e - q_t) = \log(q_e) - k_1 t / 2.303 \quad \dots(4)$$

Where, q_e is the dye adsorbed at equilibrium.

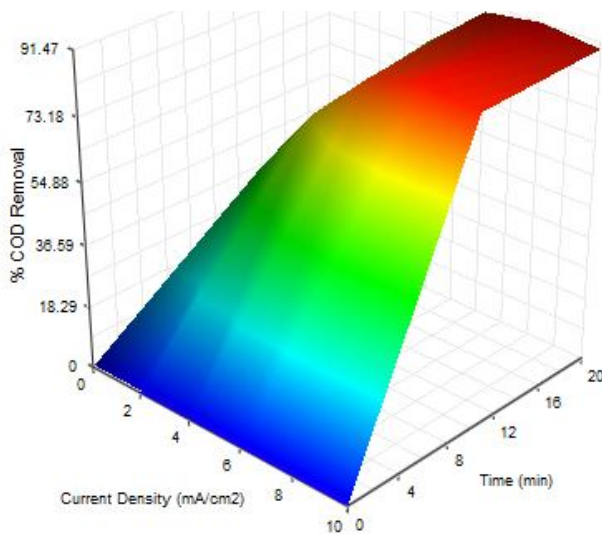


Fig. 4: Effect of current density on percentage COD removal. (Anode rotation speed = 60 rpm, pH = 8, Initial COD = 861 ppm).

The slope of the plots of $\log(q_e - q_t)$ versus time (t) were used to calculate q_e and rate constant (k_1). In our case it was found that experimental q_e value does not agree with the calculated q_e values.

The second order Lagergren kinetic model is expressed as (Ho & McKay 1999):

$$dq/dt = k_2 (q_e - q_t)^2 \quad \dots(4)$$

Where, k_2 is the rate constant of second order adsorption. The integrated form with the boundary conditions $t = 0$ to >0 ($q = 0$ to >0) is:

$$1/(q_e - q_t) = 1/q_e + k_2 t \quad \dots(5)$$

The plot t/q_t versus time (t) shows the straight line. Table 1 depicts the computed results obtained from the first order and second order Lagergren kinetic model. It is observed that calculated q values are in correlation with the experimental q_e values for second order kinetics model in contrast to the first order model. These results indicate that the adsorption system of dye onto aluminium hydroxide belongs to the second order kinetic model.

Adsorption isotherm: To address the adsorption capacity of the adsorbent, various isotherms has been applied and studied. In this study, Freundlich, Langmuir and Dubinin-Radushkevich isotherms were applied for the same.

Freundlich isotherm: The mathematical expression of the model can be written as (Langmuir 1918):

$$q_e = k^n \quad \dots (6)$$

It is an empirical model that relates the adsorption intensity of the sorbent towards adsorbent. This isotherm is not bounded to monolayer formation and is used to describe

reversible adsorption (Vasudevan and Lakshmi 2012).

The logarithmic form is:

$$\log q_e = \log k_f + n \log C_e \quad \dots(7)$$

Where, k_f is the Freundlich constant related to adsorption capacity, n is the energy of adsorption and C is the equilibrium concentration of direct red dye.

Langmuir isotherm: The Langmuir adsorption isotherm model is (Annadurai et al. 2008, Demiral et al. 2008, Tanyildizi 2011):

$$C_e/q_e = 1/q_0 b + C_e/q_0 \quad \dots(8)$$

Where, C_e is the concentration of the dye solution (mg/L) at equilibrium, q_0 is the adsorption capacity (Langmuir constant) and b is the energy of adsorption.

As per experimental data, the Langmuir plot is a better fit in comparison to Freundlich plots. The value of q_m , adsorption capacity was found to be 550.56 mg/g. The Langmuir isotherm can also be expressed as the dimensionless constant R_L .

$$R_L = 1 / (1 + bC_0) \quad \dots(9)$$

Where, R_L is the equilibrium constant that indicates the type of adsorption, C_0 is the initial concentration of the dye solution and b is the Langmuir constant.

The R_L value in between 0 and 1 describes favourable adsorption as depicted in Table 2.

Dubinin-Radushkevich (D-R) isotherm: This isotherm is used to evaluate the equilibrium data and in turn estimates the energy (E) for the adsorption. This model is given by (Tan et al. 2007):

$$q_e = q_s \exp(-B\epsilon^2) \quad \dots(10)$$

Where, ϵ is the Polanyi potential, B is related to the free energy of the sorption and q_s is the Dubinin-Radushkevich (D-R) isotherm constant.

The E is found to be 6.18 KJ/mol, which is lesser than the energy range for adsorption reaction which is in a range of 8 to 16 KJ/mol. So, it is chemical adsorption which is taking place (Golder et al. 2006).

Out of all the models analysed Langmuir isotherm model was found to be a good fit to adsorption data as it has a higher regression coefficient ($R^2 = 0.999$) as compared to other models.

CONCLUSION

The present results demonstrate the beneficial role played by the 3D perforated rotating cylinder anode in improving the EC process for removal of colour and COD from textile wastewater. This improvement is by virtue of the decrease

Table 1: Comparison between the experimental and calculated q_e values for different concentrations of dye in first and second order adsorption kinetics.

Concentration (mg/L)	q_e (exp)	First Order Adsorption			Second Order Adsorption		
		q_e (Cal)	$k_1 \times 10^3$ (min/mg)	R^2	q_e (Cal)	$k_1 \times 10^3$ (min/mg)	R^2
10	7.56	31.58	-0.0032	0.7765	7.52	2.225	0.9997
20	16.14	49.11	-0.0038	0.7986	16.02	4.212	0.9996
30	24.56	53.23	-0.0042	0.7859	24.48	5.351	0.9995
40	35.65	57.48	-0.0046	0.7999	35.60	5.772	0.9989
50	48.58	59.55	-0.0055	0.8078	48.52	5.896	0.9998

Table 2: Comparison of different adsorption isotherm models.

Langmuir	q_m (mg/g)	b (L/mg)	R_L	R^2
	550.56	0.0029	0.8385	0.9998
Freundlich	K_f (mg/g)	n (L/mg)		R^2
	1.356	1.049		0.9785
D-R	$Q_s (\times 10^3 \text{ mol/g})$	$B (\times 10^3 \text{ mol}^2 / \text{kJ}^2)$	E (kJ/mol)	R^2
	0.475	0.2874	6.18	0.8248

in anode passivation tendency as a result of the improved rate of mass transfer between the anode and the wastewater. In addition, the good mixing conditions in the system arises from the turbulence generated at the 3D perforated rotating cylinder anode, speeds up the process of EC.

The system shows a removal efficiency of 96.40% after 20 minutes under optimum conditions. The optimum performance was obtained at a rotation speed of 60 rpm, current density (6 mA/cm²), pH (8.0), NaCl concentration (3.5%) and followed the second order with Langmuir model fitting the system.

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