

# Studies on three-phase three-dimensional hybrid electrochemical reactor for treating textile effluent

Padmanaban Sivakumar<sup>a</sup>, S. Deepalakshmi<sup>b</sup>, Anirbid Sircar<sup>c</sup>, N. Yasvanthrajan<sup>d</sup>, Min Suk Shim<sup>a,\*</sup>, Pandian Sivakumar<sup>c,\*</sup>

<sup>a</sup>Division of Bioengineering, Incheon National University, Incheon 22012, Republic of Korea, email: siva02siva@gmail.com (P. Sivakumar), msshim@inu.ac.kr (M.S. Shim) <sup>b</sup>Department of Chemical Engineering, Coimbatore Institute of Technology, Coimbatore, 641014, India, email: deepalakshmis.24@gmail.com (S. Deepalakshmi) <sup>c</sup>School of Petroleum Technology, Pandit Deendayal Petroleum University, Gandhinagar, 382002, India, email: anirbid.sircar@spt.pdpu.ac.in (A. Sircar), sivakumar.p@spt.pdpu.ac.in (P. Sivakumar) <sup>d</sup>Department of Chemical Engineering, National Institute of Technology, Tiruchirappalli-620015, India, email: yasvanthnatarajan@gmail.com (N. Yasvanthrajan)

Received 15 February 2018; Accepted 22 May 2018

## ABSTRACT

In this study, a bipolar airlift type three-phase three-dimensional electrode reactor was used to investigate the colour removal of Acid Black 210 dye and overall chemical oxygen demand (COD) in the simulated textile effluent. Polyvinyl alcohol (PVA) beads containing activated carbon (AC) are used for the fabrication of three-dimensional electrodes in the reactor. The experimental results show that the removal efficiency depends on the initial dye concentrations, bead loading, supporting electrolyte concentration, applied cell voltage, initial pH, air flow rates and AC (wt%) in beads. The results reveal that the three-phase three-dimensional electrodes effectively remove the colour of 100 ppm Acid Black 210 dye and overall COD by 100 and 92.1%, respectively, at optimum operating conditions (bead loading: 30.0 g L<sup>-1</sup>; NaCl: 2000 ppm; cell voltage: 20.0 V; pH: 7.0; air flow rate: 4.0 L min<sup>-1</sup>; 1.25 wt% of AC) within 10 min. The colour and COD removal efficiencies of the three-dimensional reactor were higher compared to those of a two-dimensional reactor at similar reaction conditions (i.e., 72.92% of colour removal efficiency and 64.16% of COD removal efficiency for a two-dimensional reactor). The results also indicate that the optimum conditions for colour removal may not be necessarily the same as those of overall COD. The rates of COD and colour removal were very well-fitted with pseudo-first order kinetics.

*Keywords*: Electrochemical treatment; Three-phase three-dimensional electrode; Hybrid beads; Textile effluent

#### 1. Introduction

Textile industries use an enormous amount of water and chemicals for the wet processing of textiles. They also use various types of dyes to give attractive colours. The wastewater from textile industries generally contains about 10% of dyes used for textile colouration. These dyestuffs include

\*Corresponding author.

various types of acidic, basic, azo, reactive, and anthraquinone based compounds. Frequent changes of dyestuff employed in the dying process cause considerable variation in wastewater characteristics, particularly in colour, pH and COD value.

Traditional methods used for the treatment of textile wastewater include biological, physical, chemical and their various combinations [1–3]. Electrochemical oxidation of industrial effluents can take place through two different

1944-3994 / 1944-3986 © 2018 Desalination Publications. All rights reserved.

mechanisms. In direct anodic oxidation, the pollutants are destroyed at the anode surface whereas in in-direct oxidation a mediator (HOCl, H2S2O8 and others) is electrochemically generated to oxidize the pollutants. It should be noted that in electro-oxidation of aqueous effluents both oxidation mechanisms may coexist [4,5].

However, some dyes have higher water solubility and lower molecular weight and such dyes cannot be treated by traditional electrochemical methods due to their refractory natures [6]. This treatment method can be improved by using a three-dimensional electrode. In the present study, hybrid polyvinyl alcohol-activated carbon (PVA-AC) beads were prepared and used as a three-dimensional electrode inside a three-phase electrochemical airlift reactor to treat the textile effluent. These beads also have an elastic rubber-like property that prevents breakage during electrolysis. The three-dimensional electrode is rather attractive for industrial applications since it can provide a more extensive interfacial electrode surface area compared to a two-dimensional electrode [7-10]. The current study makes use of an airlift type three-phase three-dimensional electrochemical reactor that could degrade textile dyes simultaneously by direct anodic oxidation and by indirect cathodic electro generated H<sub>2</sub>O<sub>2</sub> to treat the textile effluent.

#### 2. Materials and methods

# 2.1. Materials

Analytical grade PVA (Mol. Wt. 13000–23000), boric acid, finely powdered AC, sodium alginate, acetic acid, HCl, ethylene dinitrilo tetraacetic acid, sodium carbonate, sucrose, NaOH and NaCl were purchased from Ranboxy Fine Chemicals Ltd., New Delhi, India. Acid Black 210 (CAS No. 300285), an acid application group dye belonging to azo (metalocomplex) chemical groups, was chosen for the present study. Acid Black 210 (98% purity), along with other textile chemicals used to prepare simulated effluent was purchased from a local textile chemical supplier in Coimbatore, India.

#### 2.2. Preparation of simulated textile wastewater

Textile industry wastewater was systematically prepared by taking the real-time process information to simulate exact real-time composition. Here, model mercerized and non-mercerized cotton dyeing processes were considered where sizing, desizing, singeing, scouring, bleaching, mercerization, dyeing and washing steps were performed methodically [11]. The data for the different compositions of textile wastewater were collected from literatures [12–21]. The Acid Black 210 dye used in dyeing cotton fabrics was taken for preparing simulated wastewater. The exact chemicals equivalent to the composition of textile waste water is shown in Table 1. These constituents were mixed with tap water and warmed to 50°C for 1 h to get better homogeneity. The simulated water was then cooled and stored in a polypropylene container at freezing temperature. It was further used for conducting different runs of the experiments. The characterization of the wastewater was determined as per the guidelines of APHA (2005) handbook [22]. The physical and chemical properties of the simulated textile effluent are presented in Table 2.

COD was determined by closed reflux method using QuickCODultra (LAR Process Analysers AG, Germany). The pH of the solution was measured using LI 120 pH meter (Elico Ltd., India). Colour was determined by the absorbance values at 460 nm in a Scanning Mini Spec SL 177 (Type: 212, Elico Ltd., Hyderabad, India). Before determining the residual intensity of the colour, each sample was adjusted to pH 6.8 using phosphate buffer after which the intensity of the colour was calculated from calibrated curves. The values of the initial and final colour were measured as described above and were used to calculate the colour removal percentage using Eq. (1).

Colour removal (%) = 
$$\frac{(C_o - C_f) \times 100}{C_o}$$
 (1)

where  $C_o$  and  $C_f$  are the initial and final colour intensities respectively.

During the electrochemical process, colour (pigmentation) of the dye in the effluent was removed by interchang-

Table 1 Composition of simulated textile effluent

Contents	Concentration (mg L <sup>-1</sup> )
Acetic acid	150
Acid Black 210 dye	100
Biozyme	350
Catalase	40
Cottoclarin 22	500
Foryl FP (detergent)	300
Securon 540	200
Dextrin	1500
Ethylene dinitrilotetraacetic acid	300
Silicone oil	25
Sodium carbonate	750
Sodium chloride	1000
Sodium hydroxide	800
Sodium silicate	5
Sucrose	550

Table 2

Physical and chemical properties of simulated textile effluent

Parameters	Concentration
COD, mg $O_2 L^{-1}$	2972
Dissolved oxygen, mg $O_2 L^{-1}$	1.35
pH	10.45
Total solids, mg L <sup>-1</sup>	6450
Suspended solids, mg L <sup>-1</sup>	185
Fixed solids, mg L <sup>-1</sup>	6265
Volatile solids, mg L <sup>-1</sup>	3880
Turbidity, FTU	26
Conductivity, µS cm <sup>-1</sup>	14016

ing the molecular structure or by completely or partially degrading the dye. Therefore, colour intensities are different from actual dye concentrations. Preparation of definite dye concentrations requires an accurate quantity of dye that is measured gravimetrically and added for varying the initial dye concentration studies.

# 2.3. Preparation of hybrid beads

Different concentrations (2-16% w/v) of PVA solutions were prepared by dissolving PVA in warm distilled water. Once the PVA powder was completely dissolved, sodium alginate (0.05% w/v) was added to the solution for the preparation of beads in required shape. Finely powdered activated carbon was then mixed with the PVA-alginate solution and stirred sufficiently to obtain the PVA-alginate-AC suspension solution. This mixture was maintained at 80°C and stirred for 2 h to get a uniform suspension. Then the mixture was cooled down to 50°C and injected into gently stirred saturated boric acid solution to form spherical beads through a 50 mL glass syringe. The injection speed was controlled by a laboratory syringe pump at the rate of 30 drops/min and the air gap from syringe tip to water was 10 cm. The hybrid particles were incubated in boric acid over 24 h under gentle stirring to crosslink PVA-AC beads. The hybrid beads taken from the solution were washed with distilled water. Beads having a spherical size between 0.5 and 0.6 cm were taken for studies.

# 2.4. Experimental setup and procedures

The schematic diagram of the experimental set up is shown in Fig. 1. It consists of a tubular bipolar airlift type three-phase three-dimensional electrode reactor made up of polycarbonate material. The anode and cathode are  $RuO_2$ +TiO<sub>2</sub> (1:1 w/w) coated titanium mesh plates of 5× 15 cm having an active surface area of 48 cm<sup>2</sup> as shown in Fig. 2 and placed 10 cm apart inside the reactor. PVA-AC hybrid beads are suspended as a bed electrode to form a three-dimensional electrode [23]. The compressed air was uniformly sparged through a fine pore air diffuser from the bottom of the reactor. The diameters of the air bubble size are between 1 and 5 mm. The air flow was varied from 1-5 L min-1 which was regulated by a rotameter. When an electric potential is applied across the PVA-AC hybrid particles, every particle gets polarized and behaves as an anode in one side and as a cathode on the other side. The electric power was regulated by a DC power supply. All experiments were conducted at room temperature.

To ascertain the purpose of reproducibility of reported results, five independent experiments were conducted for the same sample and their standard deviation taken for further investigations. This is indicated by error bars representing the standard deviation of a data set is incorporated in the figures.

# 3. Results and discussion

### 3.1. Effects of PVA concentrations on bead formation

For the preparation of PVA-AC hybrid beads by PVA-boric acid method, the concentration of PVA is the most important factor. It is impossible to form a PVA-AC hybrid bead mixture using high concentrations of PVA due to its high viscosity. Six PVA-AC mixtures at different PVA concentrations (4, 6, 8, 10, 12 and 14% w/v) with a constant of 1 wt% activated carbon were prepared.





Fig. 1. Schematic diagram of the airlift type three-phase three-dimensional electrode reactor .

Fig. 2. Electrode used in hybrid electro-chemical reactor.

Table 3 Bead formation and strength at different concentrations of PVA

PVA ConcentrationBeadBead(w/v),%Formationstrength4Not good and not stableNo bead formation6Irregular beadsIrregular beads8Good and not stableSoft1Good and stableStrong12Good and stableStrongest14Not good and stableStrongest			
(w/v),%Formationstrength4Not good and not stableNo bead formation6Irregular beadsIrregular bead8Good and not stableSoft1Good and stableStrong12Good and stableStrongest14Not good and stableStrongest	PVA Concentration	Bead	Bead
4Not good and not stableNo bead formation6Irregular beadsIrregular bead8Good and not stableSoft1Good and stableStrong12Good and stableStrongest14Not good and stableStrongest	(w/v), %	Formation	strength
6Irregular beadsIrregular bead8Good and not stableSoft1Good and stableStrong12Good and stableStrongest14Not good and stableStrongest	4	Not good and not stable	No bead formation
8Good and not stableSoft1Good and stableStrong12Good and stableStrongest14Not good and stableStrongest	6	Irregular beads	Irregular bead
1Good and stableStrong12Good and stableStrongest14Not good and stableStrongest	8	Good and not stable	Soft
12Good and stableStrongest14Not good and stableStrongest	1	Good and stable	Strong
14 Not good and stable Strongest	12	Good and stable	Strongest
	14	Not good and stable	Strongest

The formation of the beads and their strength were examined and are shown in Table 3. These results show that the strength of PVA-AC beads below 10.0% (w/v) of PVA concentration is weak and bead formation becomes impossible and irregular when PVA concentration is above 14% (w/v). Good and stable beads were at 12% (w/v) of PVA and this was used for further studies.

# 3.2. Effect of initial dye concentration on COD removal and decolourization

The influence of initial dye concentration on COD removal and decolourization of Acid Black 210 were investigated from 10 to 150 ppm. Fig. 3 shows the effects of initial dye concentrations on the decolourization and corresponding COD removal. It is observed that at lower concentrations higher decolourization occurred which is due to the faster electrochemical reaction rather than diffusion. During anodic dissolution, a constant value of removal agents such as oxidative, perceptive and adsorbent was also available [24]. Therefore, the increase in the initial concentration of dye lowers the rate of COD removal as well as decolourization. It is observed that COD reduction is relatively proportional to initial concentration up to 100 ppm and begins to behave independently over 100 ppm. This is due to the generation of the powerful oxidizing agent Cl- ions on electrode surface that remains constant at constant current density. Therefore, 100 ppm dye concentration was taken up for further studies based on the above observations.

### 3.3. Effect of bead loading on COD removal and decolourization

Fig. 4 shows that efficiencies in COD removal and decolourization increased when the bead loading increased from 10 to 40.0 g L<sup>-1</sup>. But the result showed that for 30.0 g L<sup>-1</sup> of bead loading, a maximum of 71.05% decolourization and 62.16% COD removal were observed within 10 min of electrolysis. There was no further increase in the COD removal when bead loading was increased above 30.0 g L<sup>-1</sup>. Thus, 30.0 g L<sup>-1</sup> of bead loading was considered to be the optimum for further experiments.

#### 3.4. Effect of run numbers on COD removal and decolourization

The results obtained for 50 trial runs are presented in Fig. 5. The electrolysis time for each run was 10 min. The



Fig. 3. Effect of initial dye concentration (operating conditions: Bead loading 25 g L<sup>-1</sup>; NaCl 1000 ppm; Cell voltage 20 V; pH 11; Airflow rate  $3 L \text{ min}^{-1}$ ; AC 1 wt%; 10 min).



Fig. 4. Effect of bead loading (operating conditions: Dye 100 ppm; NaCl 1000 ppm; Cell voltage 20 V; pH 11; Airflow rate 3 L min<sup>-1</sup>; AC 1 wt%; 10 min).



Fig. 5. Effect of different runs (operating conditions: Dye 100 ppm; bead loading 30 g L<sup>-1</sup>; NaCl 1000 ppm; Cell voltage 20 V; pH 11; Airflow rate 3 L min<sup>-1</sup>; AC 1 wt%; 10 min).

observation shows that COD removal and decolourization efficiency decreased with an increase in the number of runs. The results also indicate that electro-oxidation of simulated wastewater using PVA-AC hybrid beads decreased rapidly when used repetitively. In the first run, 71.05% decolourization and 62.16% COD removal were observed up to the 5<sup>th</sup>run of electrolysis. The concentrations of pollutants decreased dramatically due to the combined effect of adsorption and electrosorption [25]. With the increase in the number of runs, COD removal and decolourization decreased gradually due to saturation in the uptake capacity of the adsorbent (i.e., PVA-AC beads), indicating that adsorption was not the main contributor to the removal of pollutants in the later stages. Moreover, the titanium electrodes used in this study are dimensionally stable, corrosion resistant and biocompatible [26]. Therefore, the decrease in efficiency with continual trials is closely associated with hybrid beads. This is indicated by the change in colour of the beads during the repeated runs. It is noteworthy that the PVA-AC hybrid beads could maintain decolourization and COD removal efficiencies above 55 and 59.56% respectively even at the 50<sup>th</sup> run.

# 3.5. Effect of supporting electrolyte concentration on COD removal and decolourization

A possibility of increasing the degradation performance by hybrid beads was investigated by using NaCl as supporting electrolytes. The possibility of accomplishing the electrochemical processes in this medium results in the formation of different powerful oxidizing species such as chlorine radicals, hypochlorous acid and hypochlorite ions. The chlorine evolution reaction and the subsequent formation of oxidizing species in solution are represented as follows:

$$2Cl^{-} \leftrightarrow Cl_{2(el)} + 2_{e^{-}} \tag{2}$$

$$Cl_{2(el)} \leftrightarrow Cl_{2(sol)}$$
 (3)

$$Cl_{2(sq)} + H_2O \to HClO + Cl^- + H^+$$
(4)

$$HClO \leftrightarrow H^+ + ClO^-$$
 (5)

Fig. 6 shows the results obtained using NaCl as a supporting electrolyte. At a constant potential of 20.0 V, different concentrations of NaCl were added to the electrolysis medium, and the efficiency of dye removal was determined over 10 min. It was confirmed that COD removal and decolourization efficiencies increased with an increase in electrolyte concentrations. It was also observed that there was no further increase in the COD removal with an increase in the concentrations of supporting electrolytes beyond 2000 ppm. This may be due to the increase in the concentration of supporting electrolytes above a particular level that leads to the formation of several intermediates, followed by their subsequent mineralization. Therefore, 2000 ppm NaCl was taken as the optimum supporting electrolyte concentration, which resulted in 70.23% COD removal and 79.23% decolourization. There was no significant change in colour removal when NaCl concentration increased beyond 2000 ppm indicating that the maximum colour removal is related to oxidation of chromophore groups.



Fig. 6. Effect of supporting electrolyte concentration (operating conditions: Dye 100 ppm; bead loading 30 g L<sup>-1</sup>; Cell voltage 20 V; pH 11; Airflow rate 3 L min<sup>-1</sup>; AC 1 wt%; 10 min).

# 3.6. *Effect of applied cell voltage on COD removal and decolourization*

COD removal and decolourization efficiencies were significantly affected by cell voltages. Electrolysis was carried out with various cell voltages from 5.0 to 25.0 V. The results are presented in Fig. 7. It was observed that increase in applied cell voltages increased COD removal and decolourization efficiencies. For 20.0 V, 79.32% decolourization and 70.32% COD removal were observed within 10 min but COD removal and decolourization efficiencies were only 44.22 and 48.28% respectively for 5.0 V. This may be attributed to the increase in the driving force of the electrode reaction in addition to the increase in current and cell voltage.

AT 25 V maximum, colour removal remains approximately the same (79.5%) and COD removal increased to 75.55%. Since the main aim of the study is to reduce both the colour and COD removal with minimum energy, 20 V is chosen as the optimum.

# 3.7. Effect of initial pH on COD removal and decolourization

Experiments were carried out to study the effect of initial pH for COD removal and decolourization efficiencies. The actual pH of simulated effluent was corrected to pH 11 and chosen as the maximum which was then varied at different intervals up to pH 3.0 for finding its effect. Fig. 8 shows that the increase in the pH of the solution from 3.0 to 7.0 increases COD removal and decolourization. On the other hand, a further increase in pH of the solution decreases COD removal and decolourization. Thus, pH 7.0 was chosen as the optimum at which point the colour removal was 95.2% and COD removal was 89.32%. These results can be explained based on the following reasons: passivation of electrode surface and formation of OH radical scavengers. The OH radical scavenger is an active species for the degradation of dye molecules in a carbon electrode.

#### 3.8. Effect of airflow rates on COD removal and decolourization

The sparged air serves two purposes. One is to stir the solution in order to speed up the mass transfer and the other



Fig. 7. Effect of applied cell voltage (operating conditions: Dye 100 ppm; bead loading 30 g L<sup>-1</sup>; NaCl 2000 ppm; pH 11; Airflow rate 3 L min<sup>-1</sup>; AC 1 wt%; 10 min).



Fig. 8. Effect of initial pH (operating conditions: Dye 100 ppm; bead loading 30 g L<sup>-1</sup>; NaCl 1000 ppm; Cell voltage 20 V; Airflow rate 3 L min<sup>-1</sup>; AC 1 wt%; 10 min).

is to supply the essential oxygen for electrochemical reactions. This is because oxygen can be converted into stronger oxidizing agents (ie.  $H_2O_2$ ) on activated carbon electrode by two electron reduction of oxygen as suggested by previous studies [27,28]. The three-phase three-dimensional electrodes could simultaneously make use of direct anodic oxidation and electrogenerated  $H_2O_2$  to degrade dye molecules [29]. As a result, it is expected that the sparged compressed air can play an important role in the degradation of effluent. According to Eq. (6), oxygen is adsorbed on the electrode via a "2-electron" pathway where hydrogen peroxide is formed as an intermediate. This process achieves high rates of degradation.

$$O_2 + 2e^- + 2H^+ \leftrightarrow H_2O_2 \tag{6}$$

The COD removal and decolourization efficiencies obtained for different air flows are shown in Fig. 9. The results indicate that increasing the sparging rate of air from 1.0 to 4.0 L min<sup>-1</sup> increases COD removal and decolourization efficiencies. For 4.0 L min<sup>-1</sup> air flow rate, 90.83% COD removal and 90.83% decolourization were obtained within 10 min while it was only 50.27 and 55.42% respectively for 1.0 L min<sup>-1</sup> air flow rate. Thus, 4.0 L min<sup>-1</sup> air flow rate was



Fig. 9. Effect of airflow rates (operating conditions: Dye 100 ppm; bead loading 30 g L<sup>-1</sup>; NaCl 2000 ppm; Cell voltage 20 V; pH 7; AC 1 wt%; 10 min).

taken as the optimum. At  $5 L min^{-1}$  COD and colour removal decreased to 86.23 and 90.7% respectively. This was due to the agglomeration of small bubbles to form larger bubbles which in turn decreased the conductivity of the electrochemical reactor.

#### 3.9. Effect of AC (wt%) on COD removal and decolourization

The AC material having low mass densities, high surface areas, great mesopore volume and high electrical conductivity makes it a better choice as a particle electrode in a three-phase three-dimensional hybrid electrochemical reactor. At higher concentrations of supporting electrolyte, electrochemical oxidation reaction between water and chloride at anode discharges Cl- to the AC in beads, leading to the formation of  $\ensuremath{\text{ClO}}\xspace^-$  ions in the reactor causing indirect oxidation of pollutants. Thus, concentration of AC in PVA-AC beads plays a predominant role. Therefore, a high concentration of AC powder is desirable for the preparation of PVA-AC hybrid beads. However, they have a few limitations when used in excess as a result of which the beads were prepared between 0.25 and 1.25 wt% of AC powder. Increasing the concentration of AC beyond this range results in improper bead formation as it suffers from the loss of fluidity and so AC concentrations above 1.25 wt% are not preferred. It was apparent that increasing the concentration of AC increases COD removal and decolourization efficiencies. 92.1% COD removal and complete decolourization were found at 1.25 wt% of AC as shown in Fig. 10. Thus, electrochemical treatment with PVA-AC beads system offers an efficient way to remove colour and COD by both adsorption and electrochemical redox reactions. AC serves as microelectrodes when because of contact resistance, it polarizes under the influence of electric field in between the anode and cathode.

# 4. Comparison of two-dimensional and three-dimensional electrochemical reactor

When compared to the two-dimensional electrochemical process, particle electrodes were introduced to increase the higher specific surface area and decrease mass transfer



Fig. 10. Effect of initial concentrations of AC (operating conditions: Dye 100 ppm; bead loading 30 g L<sup>-1</sup>; NaCl 2000 ppm; Cell voltage 20 V; pH 7; Airflow rate 4 L min<sup>-1</sup>; 10 min).

making the three-dimensional electrochemical reactor more effective with more potential for wastewater treatment. To validate this, experiments were performed for the simulated effluent in the same reactor with similar parameters and with and without PVA-AC beads. The experimental results show 92.1% of COD removal and complete decolourization are obtained for three-dimensional electrochemical reactors within 10 min. In contrast, COD removal and decolourization efficiencies are only 64.16 and 72.92% respectively for two-dimensional electrochemical reactors. This is due to the addition of PVA-AC beads that enhance conductivity providing more reactive sites leading to the formation of polarized microelectrodes where every bead behaves like an individual micro-electrolytic cell. Therefore, the three-dimensional electrochemical reactors exhibit higher COD and colour removal efficiency when compared to two-dimensional electrochemical reactors.

### 5. Kinetic investigations

In solutions containing chloride, direct electron-transfer oxidation is negligible and the pollutants are removed only by indirect electrolyses mediated by electrogenerated active chlorine [30,31]. Therefore, the rate of colour and COD removal are proportional to the concentration of pollutants and oxidizing agents (i.e., hypochlorite or hydrogen peroxide). Since NaCl is used as a supporting electrolyte, the kinetics of colour and COD removal as suggested by Parasa et al. [32] are used and expressed in Eq. (7). These terms describe the decrease of the concentration colour and COD ([C] and [COD]) due to the indirect electro-oxidation by chemical reactions involving active chlorine (Cl<sub>2</sub>).

For colour removal the rate equation can be written as

$$-\frac{d[C]}{dt} = k[C][Cl_2]$$
<sup>(7)</sup>

For COD removal the rate equation can be written as

$$-\frac{d[COD]}{dt} = k[COD][Cl_2]$$
(8)



Fig. 11. Kinetic analysis for colour removal.



Fig. 12. Kinetic analysis for COD removal.

If the pollutant removal takes place by the formation of hydrogen peroxide (when carbon is used as a cathode), the kinetics of colour and COD removal may be expressed as follows:

For colour removal the rate equation can be written as

$$-\frac{d[C]}{dt} = k[C][H_2O_2]$$
<sup>(9)</sup>

For COD removal the rate equation can be written as

$$\frac{d[COD]}{dt} = k[COD][H_2O_2]$$
(10)

It is assumed that the reaction occurs mostly via an indirect electro-oxidation and that the reduced intermediates after the reaction with a pollutant are continuously reoxidized at the anode. It is assumed that under stationary conditions there is no accumulation of reaction intermediates in the solution and the rates of their production (which is proportional to the applied current I) and consumption are equal. During electrolysis, the produced hypochlorite or hydrogen peroxide oxidizes the pollutants continuously. Accordingly, the concentration of hypochlorite or hydrogen peroxide can be assumed to be constant and  $Cl_2$  or  $H_2O_2$  and k may be merged into a pseudo-first order kinetic constant ( $k_{obs}$ ) as shown in Eqs. (11) and (12).  $k_{obs}$  can be obtained for colour and COD

248

removal by plotting  $\ln[C_o]/[C_l]$  and  $\ln[C_oD_o]/[COD_l]$  vs time respectively.

$$-\frac{d[C]}{dt} = k_{obs}[C] \tag{11}$$

$$-\frac{d[COD]}{dt} = k_{obs}[COD]$$
(12)

Under the present study conditions, colour and COD removal follow pseudo-first order kinetics. Values in the Figs. 11 and 12 represent kobs, and the regression co-efficient obtained for pseudo-first order kinetics were 0.9978 and 0.988 for colour and COD removal respectively. Thus, the colour and COD removal fitted very well with pseudo-first order kinetics.

### 6. Conclusion

An airlift type, bipolar three-phase three-dimensional electrochemical reactor was used to remove colour and COD from simulated wastewater containing Acid Black 210 dye. Hybrid PVA-AC beads were prepared and used as particle-type electrodes inside the reactor. It was observed that the removal efficiency depended on initial dye concentration, bead loading, supporting electrolyte concentration, applied cell voltage, initial pH, air flow rate and AC (wt%) in hybrid beads. It was concluded that 100% decolourization and 92.1% COD removal within 10 min were observed in three-dimensional electrochemical reactor at optimal conditions. It is also confirmed that this process follows pseudo-first order kinetics for which the regression co-efficient values obtained were 0.9978 and 0.988 for decolourization and COD removal respectively.

#### Acknowledgements

This work was supported by the Post-Doctor Research Program (2018) through Incheon National University (INU), Incheon, Republic of Korea.

#### References

- B.N. Malinovic, M.G. Pavlovic, T. Djuricic, Electro coagulation of textile wastewater containing a mixture of borganic dyes by iron electrode, J. Electrochem. Sci. Eng., 7 (2017) 103– 110.
- [2] B.K. Nandi, S. Patel, Effects of operational parameters on the removal of brilliant green dye from aqueous solutions by electrocoagulation, Arab. J. Chem., 10 (2017) S2961–S2968.
- [3] B.K. Korbahti, P. Demirbüken, Electrochemical oxidation of resorcinol in aqueous medium using boron-doped diamond anode: reaction kinetics and process optimization with response surface methodology, Front. Chem., 5 (2017) 1–14.
- [4] M.P. Pavithra, Electrochemical oxidation of dye by using graphite and titanium based electrodes, Int. J. Adv. Sci. Res. Eng., 3 (2017) 247–255.
- [5] C.A. Basha, J. Sendhil, K.V. Selvakumar, P.K.A. Muniswaran, C.W. Lee, Electrochemical degradation of textile dyeing industry effluent in batch and flow reactor systems, Desalination, 285 (2012) 188–197.

- [6] D.C. Moura, M.A. Quiroz, D.R. Silva, R. Salazar, C.A.M. Huitle, Electrochemical degradation of Acid Blue 113 dye using TiO<sub>2</sub>-nanotubes decorated with PbO<sub>2</sub> as anode, Environ. Nanotechnol. Monit. Manage., 5 (2016) 13–20.
- [7] Y. Ling, H. Xu, X. Chen, Continuous multi-cell electrochemical reactor for pollutant oxidation, Chem. Eng. Sci., 122 (2015) 630–636.
- [8] Y. Ling, J. Hu, Z. Qian, L. Zhu, X. Chen, Continuous treatment of biologically treated textile effluent using a multi-cell electrochemical reactor, Chem. Eng. J., 286 (2016) 571–577.
- [9] I. Elaissaoui, H. Akrout, S. Grassini, D. Fulginiti, L. Bousselmi, Role of SiO<sub>x</sub> inter layer in the electrochemical degradation of Amaranth dye using SS/PbO<sub>2</sub> anodes, Mate. Des., 110 (2016) 633–643.
- [10] A.A. Najafpoor, M. Davoudi, E.R. Salmani, Decolorization of synthetic textile wastewater using electrochemical cell divided by cellulosic separator, J. Environ. Health Sci. Eng., 15 (2017) 1–11.
- [11] B.K. Korbahti, A. Tanyolac, Electrochemical treatment of simulated textile wastewater with industrial components and Levafix Blue CA reactive dye: Optimization through response surface methodology, J. Hazard. Mater., 151 (2008) 422–431.
- [12] N. Daneshvar, A. Oladegaragoze, N. Djafarzadeh, Decolorization of basic dye solutions by electrocoagulation: An investigation of the effect of operational parameters, J. Hazard. Mater. B., 129 (2006) 116–122.
- [13] Z.M. Shen, D. Wu, J. Yang, T. Yuan, W.H. Wang, J.P. Jia, Methods to improve electrochemical treatment effect of dye wastewater, J. Hazard. Mater., 131 (2006) 90–97.
- [14] H.S. Awad, N.A. Galwa, Electrochemical degradation of Acid Blue and Basic Brown dyes on Pb/PbO<sub>2</sub> electrode in the presence of different conductive electrolyte and effect of various operating factors, Chemosphere, 61 (2005) 1327–1335.
- [15] P.A. Carneiro, M.E. Osugi, C.S. Fugivara, N. Boralle, M. Furlan, M.V.B. Zanoni, Evaluation of different electrochemical methods on the oxidation and degradation of Reactive Blue 4 in aqueous solution, Chemosphere, 59 (2005) 431–439.
- [16] A. Alinsafi, M. Khemis, M.N. Pons, J.P. Leclerc, A. Yaacoubi, A. Benhammou, A. Nejmeddine. Electro-coagulation of reactive textile dyes and textile wastewater, Chem. Eng. Process., 44 (2005) 461–470.
- [17] A. Fernandes, A. Morao, M. Magrinho, A. Lopes, I. Goncalves, Electrochemical degradation of C. I. Acid Orange 7, Dye. Pigm., 61 (2004) 287–296.
- [18] L. Szpyrkowicz, C. Juzzolino, S.N. Kaul, A comparative study on oxidation of disperse dyes by electrochemical process, ozone, hypochlorite and Fenton reagent, Water Res., 35 (2001) 2129–2136.
- [19] S. Ledakowicz, M. Gonera, Optimization of oxidants dose for combined chemical and biological treatment of textile wastewater, Water Res., 33 (1999) 2511–2516.
- [20] M. Ceron-Rivera, M.M. Davila-Jimenez, M.P. Elizalde-Gonzalez, Degradation of the textile dyes Basic yellow 28 and Reactive black 5 using diamond and metal alloys electrodes, Chemosphere, 55 (2004) 1–10.
- [21] K. Mojsov, Application of enzymes in the textile industry: a review, II International Congress, Engineering, Ecology and Materials in the Processing Industry, Jahorina, (2011) 231–239.
- [22] American Public Health Association (APHA). Standard Methods for the Examination of Water and Wastewater, 21st ed.; American Public Health Association: Washington, DC, (2005).
- [23] P. Sivakumar, P.N. Palanisamy, Packed bed column studies for the removal of Basic blue 29 and Acid red 92 using non-conventional adsorbent, Ind. J. Chem. Technol., 16 (2009) 301–307.
- [24] S. Song, J. Fan, Z. He, L. Zhan, Z. Liu, J. Chen, X. Xu, Electrochemical degradation of azo dye C.I. Reactive Red 195 by anodic oxidation on Ti/SnO<sub>2</sub>-Sb/PbO<sub>2</sub> electrodes, Electrochim. Acta, 55 (2010) 3606–3613.
- [25] R.N. Nageswara, M. Rohit, G. Nitin, P.N. Parameswaran, J.K. Astik, Kinetics ofelectrooxidation of landfill leachate in a three-dimensional carbon bed electrochemical reactor, Chemosphere, 76 (2009) 1206–1212.

- [26] F. Demirel, G. Saygili, S. Sahmali, Corrosion susceptibility of titanium covered by dental cements, J. Oral Rehabil., 30 (2003) 1162–1167.
- [27] E. Yeager, Electrocatalysis for  $O_2$  reduction, Electrochem.
- [27] E. Teager, Electrocatalysis for O<sub>2</sub> reduction, Electrochem. Acta., 29 (1984) 1527–1537.
  [28] P.C. Foller, R.T. Bombard, Process for the production of mix-tures caustic soda and hydrogen peroxide via the reduction of oxygen, J. Appl. Electrochem., 25 (1995) 613–627.
  [29] Y. Xiong, C. He, X. Zhu, H.T. Karlsson, X. Zhu, Performance of three phases three dimensional electrode reactor for the reduction.
- three-phase three-dimensional electrode reactor for the reduction of COD in simulated wastewater containing phenol, Chemosphere, 53 (2003) 131-136.
- [30] M. Panizza, G. Cerisola, Electrochemical oxidation of 2-naphthol with in situ electrogenerated active chlorine, Electrochim. Acta, 48 (2003) 1515-1519.
- [31] M. Panizza, C. Bocca, G. Cerisola, Electrochemical treatment of wastewater containing polyaromatic organic pollutants, Water Res., 34 (2000) 2601–2605.
- J.B. Parasa, M. Rezaei, A.R. Soleymani, Electrochemical oxi-[32] dation of an azo dye in aqueous media investigation of operational parameters and kinetics, J. Hazard. Mater., 168 (2009) 997-1003.

250