Full Paper

ELECTROCHEMICAL TECHNIQUES FOR DECOLOURING AQUEOUS SOLUTIONS

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ABSTRACT

Usefulness of carbon-resin (CR) as an electrode for colour removal from solutions was investigated in this paper. Carbon-resin electrodes were developed from used and discarded (R20 UM-1) dry cells using a non heat treatment method. Coloured solutions were prepared from standard indicators (methyl blue, methyl orange and solochrome black T). Each of these solutions was subjected to electrochemical treatment in a batch system using aluminium/ CR electrodes. Efficacy of the system based on colour removal was monitored. Kinetics of colour removed from solutions were obtained and evaluated statistically using total error, coefficient of determination (CD) and model of selection criterion (MSC). Effects of separation distance between the electrodes, contact surface area of the electrodes and the presence of an electrolyte on the kinetics were studied and applicability of the system was tested on selected industrial (paint and textile) wastewaters.

The study revealed that the electrochemical treatment process reduced initial colour of the solutions by 38 %, 36% and 40 % for methyl orange (MO), methyl blue (MB) and solochrome black T (SB) respectively. The presence of an electrolyte (10g/L of NaCl) in the process increased the percentage of the colour removed from the solutions to 84.1; 82.2 and 80.1 for MO, MB and SB, respectively. It was observed that an increase in the contact surface area increased the amount of colour removed while an increase in separation distance between the electrodes decreased the amount of colour removed from the solutions. Statistical evaluation revealed that total error, CD and MSC were in the range of 2.805 to 117.217, 0.130 to 0.983 and -1.834 to 5.964 respectively.

It was concluded that the best kinetic model that predicted removal of colour from textile and paint wastewaters electrochemically should be intraparticle diffusion based on higher CD and MSC values and lower total error.

Keywords: *Electrochemical treatment, wastewaters, colour removal, electrolyte, carbon-resin electrodes, efficacy.*

1. INTRODUCTION

Characterisation of wastewaters could be in the form of physical, chemical or biological. Colour and odour as physical properties are among the major parameters that could influence the degree of acceptance of a particular wastewater to be discharged into the environment (Oke, 2007; Lee et al., 2007). It is well known that Fenton reagents and technique, chemical coagulation, adsorption, ozonation, chlorination, chemical oxidation and electrochemical treatment methods can be used to remove colour from solutions (Oke, 2007; Metcalf and Eddy, 1991; Noyes, 1994). Out of all these methods adsorption and electrochemical have been reported to be cost effective and electrochemical is the most economical method. This singular factor has led to various studies on electrochemical treatment (Oke et al., 2007a). Chen (2004) has reviewed the development, design and applications of electrochemical technologies in water and wastewater treatment. In his review, a particular focus was given to electrodeposition (ED), electrocoagulation (EC), electroflotation (EF), electroadsorption (EA), electrooxidation (EO) and over 300 related publications were reviewed. He reported that electrodeposition is effective in recovering heavy metals from wastewater streams. ED is an established technology with possible further development in the improvement of space-time yield. For EC, he reported that it has been used in the water production or wastewater treatment and the method is finding more applications in the use of aluminium, iron or the hybrid Al/Fe electrodes.

In case of EF, Chen (2004) stated that separation of the flocculated sludge from the treated water can be accomplished by using EF and the technology is effective in removing colloidal particles, oil and grease, as well as organic pollutants. EF is proven to perform better than dissolved air flotation, sedimentation and impeller flotation (IF) and the newly developed stable and active electrodes for oxygen evolution would definitely boost the adoption of this technology. Also it was documented that electrooxidation is finding its application in wastewater treatment in combination with other technologies and is effective in degrading the refractory pollutants on the surface of a few electrodes. It is well known that titanium-based boron-doped diamond film electrodes (Ti/BDD) show high activity and give reasonable stability during EO and its industrial application calls for the production of Ti/BDD anode in large sizes at a reasonable cost and high durability (Chen 2004). Chung et al (2007) and Yoo et al (2007) discuss more on application of electrochemical treatment process. Some studies on colour removal electrochemically by various researchers can be summarised as follows:

i. Sheng and Chi (1994 , 1996) used polyelectrolyte to assist electrochemical;
ii. Vlyssides et al (1999) used expensive electrodes (titanium/platinum against stainless steel).
iii. Sanroman et al (2004 a and b) and Zhan et al (2001) used high NaCl concentration.
iv. Other studies on colour removal can be found in literature such as Xiong et al (2001); Kupferle et al (2004), Chen et al (2005); Lei et al (2006) ; Lee et al, (2007).

However, with a lot of documents on applications and usefulness of electrochemical process, kinetics of colour removed electrochemically was not documented in the literature. The kinetics of colour removal electrochemically, therefore calls for documentation. The main objective of this study as a follow up on the development and performance-testing of electrochemical treatment for selected industrial wastewaters is to use inexpensive electrodes (carbon-resin) for colour removal from solutions with a specific attention to their kinetics.

2. MATERIALS AND METHOD

Carbon resin electrodes were developed from used and discarded dry cells using a non heat treatment method (Oke et al., 2007a; Oke et al., 2007c; Oke, 2009). Its stability was studied, described, analysed and factors that have significant influence on the stability of the electrodes were identified statistically (Oke et al., 2007b; 2007c; Oke, 2009; Oke et al., 209a, b and c). Stock coloured solutions were prepared individually from methyl blue (MB), methyl orange (MO) and solochrome black T (SB) indicators (specifically, 5.00 grams of each of the indicators was dissolved in 100ml of distilled water and make to 1000ml mark with distilled water) and working solutions were prepared from the stock solutions. Each of these working solutions was subjected to electrochemical treatment using aluminium (cathode) and carbon-resin (anode) at 20 volts, 23.6 x 10^{-4}m^2 of electrode contact area and 10 mm separation distance between the electrodes. Figure 1 presents the laboratory set-up and the schematic diagram. Kinetics based on colour removed from the solution was developed and evaluated statistically using total error, root mean squared error (RMSE), coefficient of determination (CD), and model of selection criterion (MSC). Effects of selected factors (presence of electrolyte, separation distance between the electrodes and contact surface area of the electrodes) on these kinetics were conducted. Selection of these factors was based on literature (Oke, 2007; Lee et al., 2007) and these factors were optimised. Optimum values of these selected factors were used to test the practicability of the process on selected typical industrial wastewaters (paint and textile).

In the determination of colour, method specified in APHA (1998) was used (specifically, 1.26 gram of potassium chloroplatinate (K_2PtCl_6) and 1.00 gram of Cobaltous chloride ($CoCl_2$-$6H_2O$) both of analytical reagents were dissolved in 100 ml of hydrochloric acid (HCl) and diluted to 1000ml mark with distilled water). A set of standard solutions (0, 1, 10, 20, 30 and 50 colour unit) was prepared from the stock solutions and was used to calibrate the colorimeter (JENWAY 6051, available at Department of Food Science and Technology, Obafemi Awolowo University, Ile-Ife, Nigeria). Computations of the colour of the solutions (X) and colour removed from the solutions (R, %) were conducted using equations (1) and (2) respectively.

$$X(colour \quad unit) = 50\frac{AD}{B} \tag{1}$$

$$R(\%) = 100\frac{\left(C_o - C_t\right)}{C_o} \tag{2}$$

3. RESULTS AND DISCUSSION

Results from the study is presented in three categories:

i. Colour removal using normal and electrolysed (assisted) electrochemical treatment method
ii. kinetics models of removing colours electrochemically
iii. Statistical evaluation of the kinetics models

3.1. Colours removal using electrochemical treatment method

Figure 2 presents relationship between colour removed (in percent) and time (hours) of electrochemical treatment. From the figure it can be seen that removal of colour from SB is higher than removal of colour from MO and removal of colour from MO is higher than removal of colour from MB. This phenomenon can be attributed to composition and nature of the material in the solution (Otutu et al., 2008). Solochrome Black T (SB) is known as Erichrome Black T ($C_{20}H_{12}N_3NaO_7S$). It is an azo-naphthol dye with a naphthol on both sides of the azo link, one of which has both a sulphonate and nitrate substituent. It is an acid-base indicator, which changes from wine-red to blue at a pH of 6.3 and from blue to orange at pH 11.3. It is used in conjunction with ethylenediaminetetraacetic acid (EDTA) for metal ion analysis. The complex is red and the dye reverts to blue when the metal is complexed with EDTA provided the pH is in the right range.

Methyl orange ($C_{14}H_{14}N_3NaO_3S$,) is a pH indicator frequently used in titrations and named as 4-dimethylaminoazobenzene-4'-sulfonic acid sodium salt with another name as p-dimethylamino-azobenzenesulfonic acid. It is often chosen to be used in titrations because of its clear colour change. Methyl orange (MO) changes colour at the pH of a mid-strength acid and is usually used in titrations for acids. Unlike a universal indicator, methyl orange does not have a full spectrum of colour change, but has a sharper end point.

Methyl blue (MB), is known as Cotton blue, Helvetia blue, or Acid blue 93 is a chemical compound with the molecular formula $C_{37}H_{27}N_3Na_2O_9S_3$. It is used as a stain in histology. Methyl blue is also available in mixture with water blue, under name

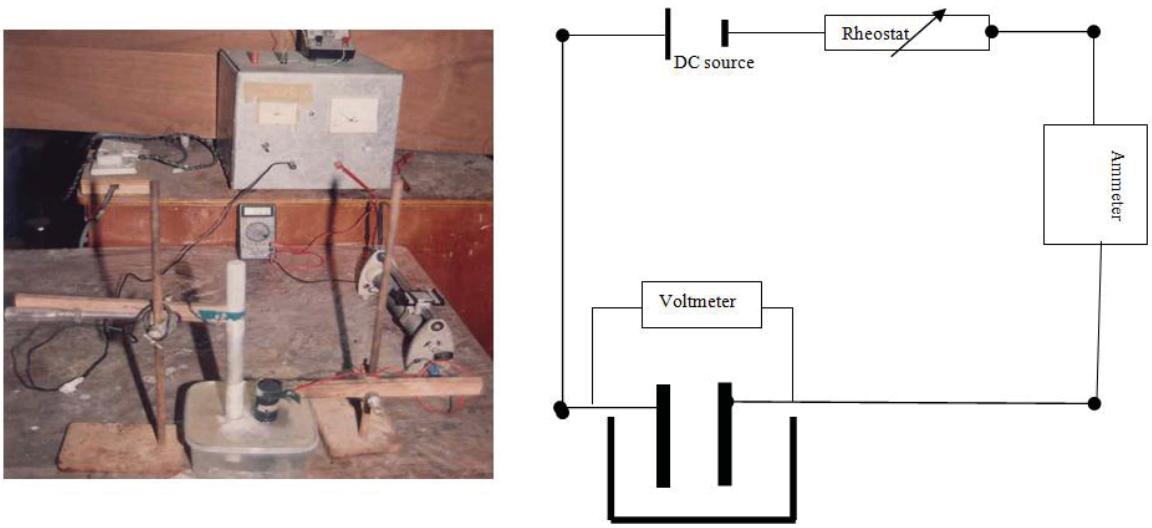


Figure 1 Laboratory Setup of the treatment process (a) Setup of the instruments (b) Schematic diagram

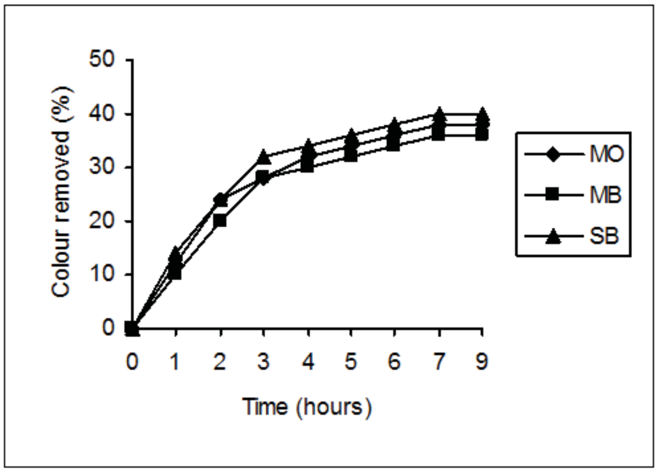


Figure 2 Removal of colour using electrochemical in the absence of an electrolyte

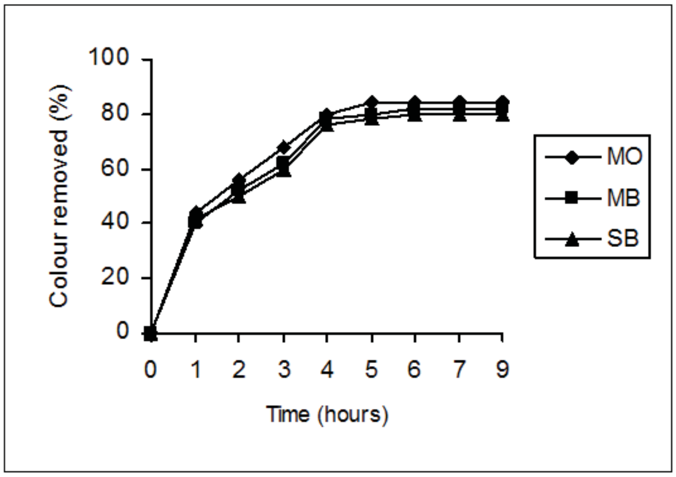


Figure 3 Removal of colour using electrochemical in the presence of an electrolyte

Aniline Blue WS, Aniline blue, China blue, or Soluble blue. Methyl blue stains collagen blue in tissue sections, soluble in water and slightly soluble in ethanol, use in the Mallory's connective tissue stain and Gomori's one-step trichrome stain and in differential staining. It can also be used to mediate electron transfer in microbial fuel cells and is also used to treat thallium poisoning. It binds to the thallium and a strong oxidising agent (Windholz, 1983).

From all these it can be said that removal of colour electrochemically depends on R'-NaOS and ratio of oxygen (O) to sulphur (S), that is the higher the ratio of oxygen to sulphur the higher the removal of colour (SB> MO>MB; O:S 7:1, 3:1 and 3:1). It can be seen also from the figure (fig 2) that equilibrium conditions were reached after 7 hours of continuous electrochemical treatment and the shape of the figure provides information on the mechanism of colour removal. It can be said that removal of these colours from solutions during electrochemical treatment is in three stages as follows:

i. The first stage is an exponential function, which occurs within the first three hours (0-3 hours). This can be attributed to higher concentrations of the colour; lack of colloidal materials and suspended solids that would help in the coagulation of the coloured materials, which indicates that removal of colour, is due to electrochemical process such as electro-coagulation and electro-adsorption.

ii. The second stage which occurred between 3-7 hours is a linear function in nature, which can be attributed to the presence of colloidal materials and high suspended solids that aid colour removal, indicating that removal of these colours are due to electrochemical and electro-adsorption processes, couple with sedimentation, coagulation and flocculation processes.

iii. The third stage is an equilibrium stage. At this stage colour removal has reached its peak and influences of colloidal materials, suspended solids and electrochemical process cannot be felt. The maximum percentages of colour removed from the solutions (MB, MO and SB) were 36, 38 and 40 respectively.

Like figure 2, figure 3 shows relationship between colour removed and the time of electrochemical treatment in the presence of an electrolyte (10g/L of NaCl). From the figure it can be seen that equilibrium conditions were reached after 5 hours of assisted electrochemical process and maximum colour removed from the solutions increased from 40 % to 80.1%, 36% to 82.2 % and 38 % to 84.1 % for SB, MB and MO respectively. Reduction in the time of equilibrium can be attributed to the presence of more solids, which increased the conductivity of the electrolyte and the presence of more colloidal particles during assisted electrochemical treatment process.

Also these higher percentages in the removal of colours (figure 3) can be attributed to differences in electrochemical treatment processes (electrochemical only and assisted electrochemical), which can be explained as thus:

i. electrochemical only: oxidation and reduction reactions took place at the electrodes. These reactions can be expressed as:

$$nH^{+} + n\overset{-}{e} \xrightarrow[reduction]{} \frac{n}{2}H_2 \qquad (3)$$

$$nOH^{-} - n\overset{-}{e} \xrightarrow[oxidation]{} \frac{n}{2}H_2O + \frac{n}{4}O_2 \qquad (4)$$

These expressions indicate that possible intermediate products from electrochemical process are oxygen and hydrogen gases. Lei et al (18) reports that the presence of radicals such as ClO^{-},OH, O_3, H_2O_2, Cl_2 and other oxidants help in removing pollutants from wastewaters during electrochemical treatment. In addition it has been mentioned that the presence many metal ions of variable valences (such as Fe^{2+} , Al^{3+} etc) help in oxidation process directly during electrochemical treatment process. It can then be said that removal of the colours by electrochemical process can be attributed to oxidation or reduction of organic and inorganic compounds present in the form of colour or colour development compounds, which indicates that EO dominated in this reaction (Figure 2).

ii. Assisted electrochemical treatment process: In assisted electrochemical treatment (chloride ions were added) oxidation and reduction reactions took place at the electrodes as:

$$nCl^{-} + 2n\overset{-}{e} \xrightarrow[oxidation]{} (n)Cl_2 \qquad (5)$$

$$nCl_2 + nH_2O \xrightarrow[oxidation]{} nHOCl + nHCl \qquad (6)$$

$$nHOCl \xrightarrow[oxidation]{} nH^{+} + nOCl^{-} \qquad (7)$$

These expressions indicate that possible intermediate products are chlorine gas, residual chlorine and hydrochloric acid, which indicates that reduction of colour intensity, can be attributed to evolvement of chlorine gas, which was used for chlorination as:

direct oxidation of colour exerting compounds;

- formation chloroamines with nitrogen compounds (substitution reaction);
- formation of substances that are no longer decomposable with carbon compounds (substitution reaction); and
- addition of chlorine to unsaturated compounds to form non- decomposable substances

This indicates that in Figure 3, chlorination as well as EO dominated in this type of reaction.

3.2. Kinetics models of removing colours electrochemically

Electrochemical kinetics model describes the solute or pollutant removal rate, which controls the residence time of solution in the reactor and uptake at the solid-solution interface. In order to establish kinetics of colour removal electrochemically, electrochemical kinetics of colour removal was investigated using pseudo first-order, pseudo second-order, Elovich and intraparticle diffusion kinetics. The conformity between experimental data and the model predicted values was expressed by the squared correlation coefficients (R^2). A relatively high squared correlation coefficients (R^2) value indicates that the model successfully describes the kinetics of colour removal electrochemically.

The pseudo first-order equation is generally expressed as follows:

$$\frac{dq}{dt} = k_i\left(q_e - q_t\right) \qquad (8)$$

After integration and applying boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of Equation (8) becomes (Erhan et al., 2004; Alam et al., 2007; Oke et al., 2008):

$$q_t = q_e - q_e \exp^{\frac{k_i}{2.303}t} \qquad (9a)$$

$$\log_e\left(q_e - q_t\right) = \log_e\left(q_e\right) - \frac{k_i}{2.303}t \qquad (9b)$$

The values of $\log_e (q_e - q_t)$ were linearly correlated with t. The plot of $\log_e (q_e - q_t)$ vs. t gave a linear relationship and the values of k_i and q_e were determined from the slope and intercept of the respectively. Tables 1 and 2, and Figure 4(a and b) show the pseudo-first order model and their values respectively.

Like pseudo first order, the pseudo second-order kinetic rate equation is expressed as shown in equation (10):

$$\frac{dq}{dt} = k_2\left(q_e - q_t\right)^2 \qquad (10)$$

Integrating equation (10), and rearrangement gives equation (11) and let h (mg/g· h) is $h = k_2 (q_e)^2$

$$\left(\frac{t}{q_t}\right) = \frac{1}{h} + \frac{1}{q_e}t \qquad (11)$$

The plot of (t/q_t) and t of equation (11) produced a linear relationship from which q_e and k_2 were determined from the slope and intercept of the plot respectively. Figure 5 (a and b) and Tables 1 and 2 show more on the model.

The Elovich model equation is generally expressed as:

$$\frac{dq_t}{dt} = \alpha \exp\left(-\beta q_t\right) \qquad (12)$$

Erhan et al (2004) simplifies Elovich equation as shown in equation (13)

$$q_t = \frac{1}{\beta}\log_e\left(\alpha\beta\right) + \frac{1}{\beta}\log_e\left(t\right) \qquad (13)$$

If colour removal fits the Elovich model, a plot of q_t vs. $\log_e (t)$ should yield a linear relationship with a slope of (1/ β) and an

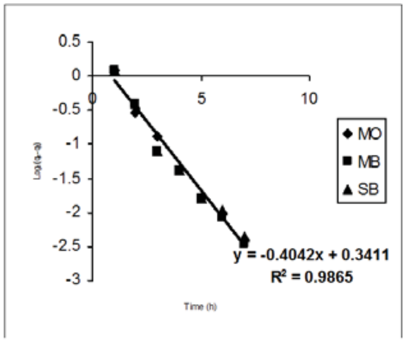


Figure 4a First Pseudo order of electrochemical treatment only

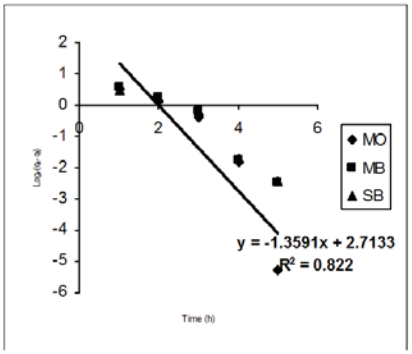


Figure 4b First Pseudo order of assisted electrochemical treatment

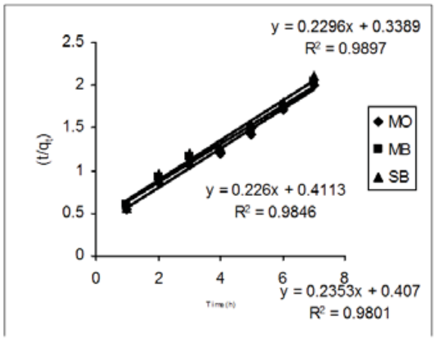


Figure 5a Second Pseudo order of electrochemical treatment only

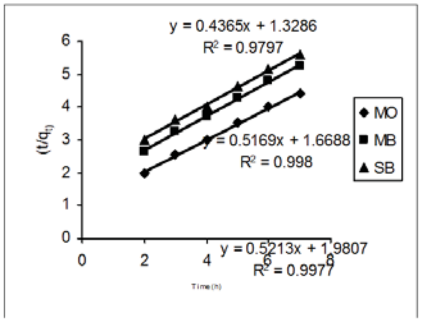


Figure 5b Second Pseudo order of assisted electrochemical treatment

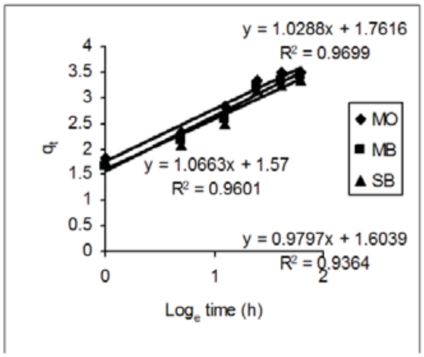


Figure 6a Elovich model of electrochemical treatment only

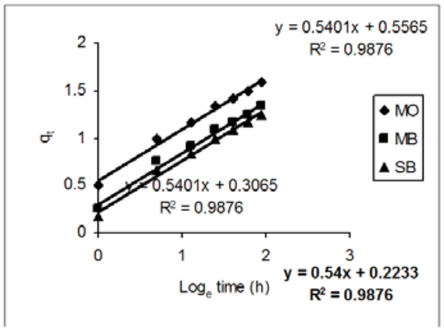


Figure 6b Elovich model of assisted electrochemical treatment

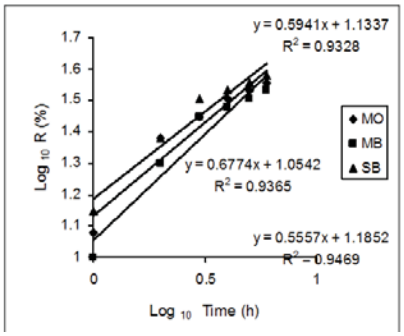


Figure 7a intraparticle diffusion model electrochemical treatment

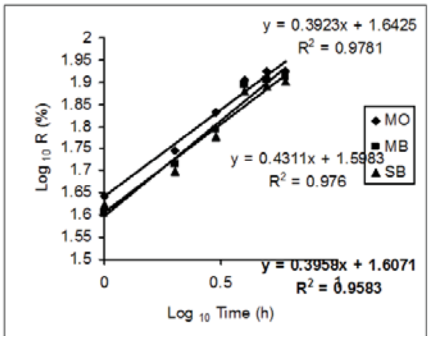
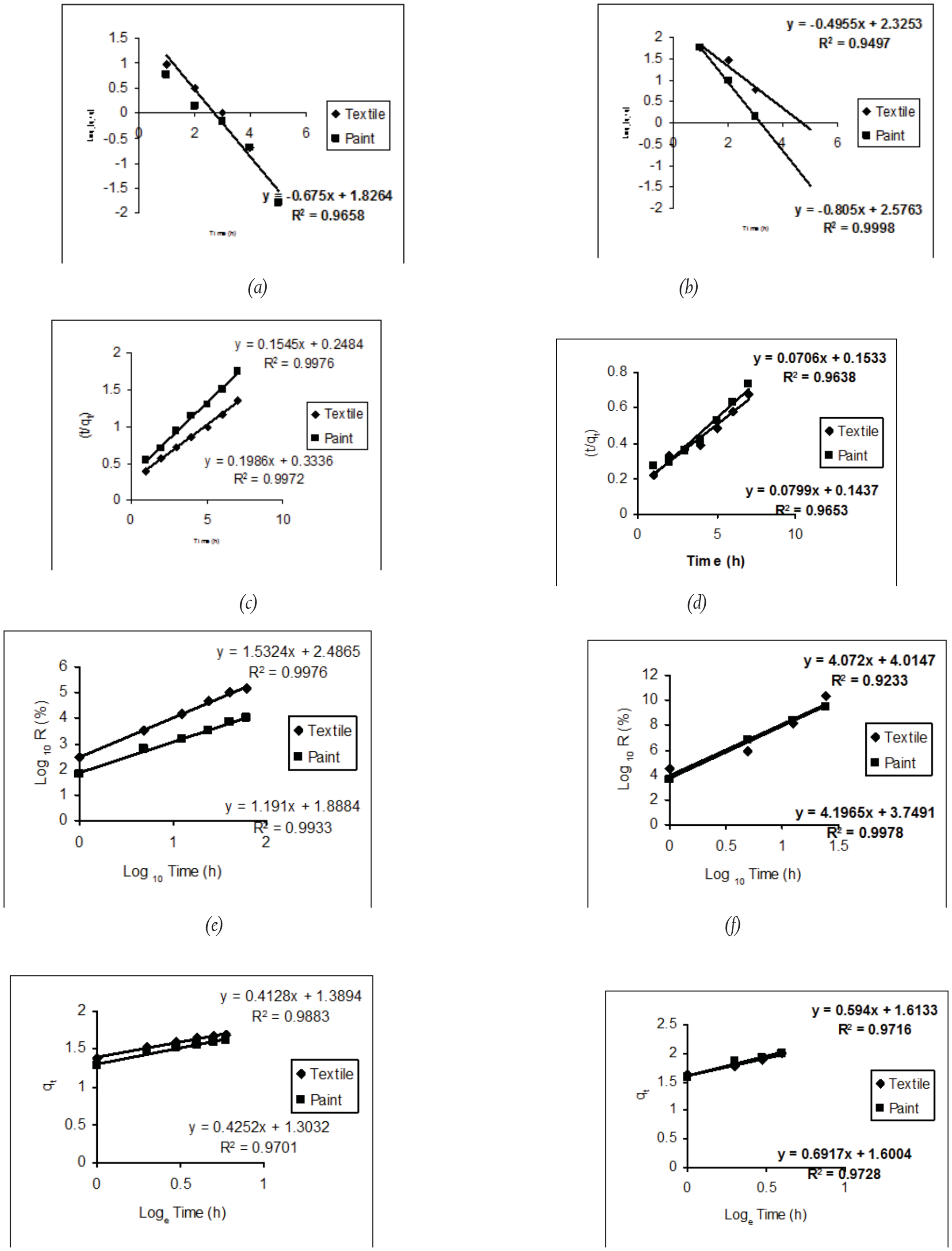


Figure 7b intraparticle diffusion model assisted electrochemical treatment



(a) (b)

(c) (d)

(e) (f)

(g) (h)

Figure 8 Treatment of Industrial wastewaters
(a) *First Pseudo order of electrochemical treatment only*
(b) *First Pseudo order of assisted electrochemical treatment*
(c) *Second Pseudo order of electrochemical treatment only*
(d) *Second Pseudo order of assisted electrochemical treatment*
(e) *intraparticle diffusion model of electrochemical treatment only*
(f) *intraparticle diffusion model of assisted electrochemical treatment*
(g) *Elovich model of electrochemical treatment only*
(h) *Elovich model of assisted electrochemical treatment*

Table 1 the kinetics models and their parameters

Descriptions		Pseudo first-order			Pseudo second-order				Elovich mode	
		k_1 (L/h)	q_{e1} (col./v)	R^2	k_2 (v/col..h)	h^{-1} (col./v.h)$^{-1}$	q_{e2} (col./v.)	R^2	β (v/col.)	α (col./v.h)
Electrochemical treatment of MO solution at 20 volt , 10 mm separation distance and 23.6 x 10^{-4} m^2 contact surface area	In the absence of NaCl	0.931	1.406	0.987	0.500	0.339	4.355	0.990	0.972	5.701
	In presence of NaCl	3.130	15.079	0.822	0.247	1.329	0.753	0.980	1.852	1.513
Electrochemical treatment of MB solution at 20 volt , 10 mm separation distance and 23.6 x 10^{-4} m^2 contact surface area	In the absence of NaCl	0.913	1.421	0.989	0.749	0.411	4.435	0.985	0.938	4.667
	In presence of NaCl	3.007	15.943	0.832	1.436	0.517	0.600	0.998	1.852	0.952
Electrochemical treatment of SB solution at 20 volt , 10 mm separation distance and 23.6 x 10^{-4} m^2 contact surface area	In the absence of NaCl	0.908	1.401	0.978	0.704	0.407	4.250	0.980	1.021	5.035
	In presence of NaCl	2.991	13.613	0.812	2.044	0.521	0.505	0.998	1.852	0.816
Electrochemical treatment of industrial wastewater at 20 volt, 5 mm separation distance and 47.8 x 10^{-4} m^2 contact surface area	Textile	1.555	6.209	0.966	0.399	0.248	6.472	0.998	0.653	5.066
	Paint	1.561	6.340	0.967	0.560	0.334	2.998	0.997	0.246	10.896
	Electrolysed Textile wastewater	1.141	10.227	0.950	0.333	0.153	6.523	0.964	0.840	4.882
	Electrolysed paint wastewater	1.854	13.144	0.999	0.258	0.144	0.258	0.965	0.238	10.266

Table 2 effects of selected factors on the kinetics models

Descriptions		Pseudo first-order			Pseudo second-order				Elovich model		
		k_1 (L/h)	q_{e1} (col./v)	R^2	k_2 (v/col..h)	h^{-1} (col./v.h)$^{-1}$	q_{e2} (col./v.)	R^2	β (v/col.)	α (col./v.h)	
Electrochemical treatment of MO solution at 5 mm separation distance	23.6 x 10^{-4} m^2 contact surface area	1.014	1.651	0.976	0.312	0.419	3.213	0.991	0.772	5.971	0.
	47.8 x 10^{-4} m^2 contact surface area	1.111	1.762	0.967	0.278	0.486	3.456	0.966	0.758	5.988	0.
Electrochemical treatment of MO solution at 23.6 x 10^{-4} m^2 contact surface area	5 mm separation distance	1.014	1.651	0.976	0.312	0.419	3.213	0.991	0.772	5.971	0.
	10 mm separation distance	0.931	1.406	0.987	0.500	0.339	2.951	0.990	0.972	5.701	0.
Electrochemical treatment of MB solution at 5 mm separation distance	23.6 x 10^{-4} m^2 contact surface area	0.989	1.601	0.977	0.474	0.373	2.523	0.981	0.812	4.867	0.
	47.8 x 10^{-4} m^2 contact surface area	0.999	1.644	0.974	0.433	0.401	2.556	0.986	0.781	4.960	0.
Electrochemical treatment of MB solution at 23.6 x 10^{-4} m^2 contact surface area	5 mm separation distance	0.989	1.601	0.977	0.474	0.411	2.523	0.981	0.812	4.867	0.
	10 mm separation distance	0.913	1.421	0.989	0.749	0.401	2.431	0.985	0.938	4.667	0.
Electrochemical treatment of SB solution at 5 mm separation distance	23.6 x 10^{-4} m^2 contact surface area	0.978	1.498	0.986	0.637	0.603	2.645	0.988	0.897	5.635	0.
	47.8 x 10^{-4} m^2 contact surface area	0.997	1.567	0.981	0.601	0.665	2.846	0.982	0.692	5.769	0.
Electrochemical treatment of SB solution at 23.6 x 10^{-4} m^2 contact surface area	5 mm separation distance	0.978	1.498	0.986	0.637	0.603	2.645	0.988	0.897	5.635	0.
	10 mm separation distance	0.908	1.401	0.978	0.704	0.407	2.457	0.980	1.021	5.035	0.

intercept of $(1/\beta)\log_e(\alpha\beta)$. Figure 6 (a and b), Tables 1 and 2 present more on this kinetics.

The intraparticle diffusion model is expressed as equation (14)

$$R = k_{id}(t)^a \tag{14}$$

A linearised form of the equation is $\log R = \log k_{id} + a\log(t)$. Erhan et al (2004) reports that " a" depicts the process mechanism and k_{id} may be taken as a rate factor (per cent colour removed per unit time). Higher values of k_{id} illustrate an enhancement in the rate of colour removal, whereas larger k_{id} values illustrate a better electrochemical mechanism, which is related to an improved bonding between pollutant and the process. Like figure 6 (a and b), Figure 7 (a and b) and Tables 1 and 2 present more on this kinetics. Figure 8 presents kinetics of removing colour from selected industrial wastewaters.

Tables 1 and 2 present kinetics models and their parameters for the three indicators used. From the tables it can be seen that k_1 and q_{e1}(parameters for Pseudo first model) have 0.931(**L/h**) and 1.406(col./v) ; 0.913(**L/h**) and 1.421(col./v) and 0.908(**L/h**) and 1.401(col./v) for MO, MB and SB in the absence of NaCl and 3.130(**L/h**) and 15.079 (col./v); 3.007(**L/h**) and 15.943(col./v) and 2.991(**L/h**) and 13.613(col./v) in the presence of the electrolyte. From the Tables it can be seen that an addition of NaCl increased the values of the model parameters. It can also be seen that for MO about 0.931 of the colour solution can be treated per hour in the absence of NaCl but increased to 3.130(**L/h**) in the presence of the electrolyte. For MB and SB it was increased from 0.913(**L/h**) to 3.007(**L/h**) and 0.908(**L/h**) to 3.007(**L/h**) respectively. These results show that the presence of NaCl would give room for more colour removal electrochemically, which can be attributed to a decrease in the resistance (due to dielectric substance such as water and pollutants). In addition the values of the model parameters increase with increasing contact surface area and decreases with increasing separation distance (Table 2). Changes in the values of the model parameters due to these two factors can be attributed to higher conductivity and higher rate of reaction. In summary, it can be deduced that these selected factors have effects on electrochemical treatment processes. For typical industrial wastewaters these parameters were 1.555(**L/h**) and 6.209(col./v); 1.561(**L/h**)and 6.340(col./v) for textile and paint wastewaters respectively in the absence of NaCl and 1.141(**L/h**) and 10.227 (col./v); 1.854(**L/h**) and 13.144(col./v) for textile and paint wastewaters respectively in the presence of NaCl. These higher in the values of model parameters than synthetic coloured solutions in the absence of NaCl and lower than synthetic coloured solutions in the presence of NaCl can be attributed to heterogenic nature of industrial wastewaters compared to synthetic coloured solutions (Otutu et al., 2008). The values of R^2 ranged from 0.822 to 0.999, which indicates that correlation coefficient of the study parameters is a function of the solution and nature of the wastewater.

Like first Pseudo model, k_2, q_{e2},and h^{-1} for second Pseudo model, β and α for Elovich model, and k_{id} and a for intraparticle model are presented in Tables 1 and 2 for the three indicators and selected industrial wastewaters. From the tables it can be seen that these values of k_2, q_{e2},and h^{-1} for second Pseudo model, β and α for Elovich model and k_{id} and a for intraparticle model increased with NaCl addition (i.e. from the Tables it can be seen that an addition of NaCl increased the values of the model parameters). These changes can be attributed to utilisation of chloride oxidised to chlorine gas and influences of other chemical reactions which took place during the reaction. Although, it might be argued that more potential will be required in the presence of NaCl the benefit there is that chlorine gas as an end product of the process helps in removing colours and excess of the gas can be stored for commercial purposes or can be used disinfectants. Correlation coefficients (R^2) range from 0.965 to 0.991, 0.936 to 0.998; 0.933 to 0.988 for second Pseudo, Elovich and intraparticle model respectively.

3.3. Statistical evaluation of the kinetics models

Statistical evaluation which can be used to describe how well a model predicted the experimental values. Statistical evaluations has been presented as follows total error, coefficient of determination (CD), model of selection criterion (MSC) and root means squared error (RMSE). The total error, which is the sum of the squares of the errors between the obtained values and the predicted values, can be interpreted as a measure of variation in the values predicted unexplained by the values obtained data (Babatola et al., 2008; Oke 2007c). The lower the value of total error the higher the accuracy, validity and goodness of fit of the method. Total error (Err^2) can be computed using equation (15):

$$Err^2 = \sum_{i=1}^{n}\left(Y_{obsi}-Y_{cali}\right)^2 \tag{15}$$

Table 3 shows the values of total error for each of the methods. The total errors are in the range of 2.805 to 117.217, standard deviation, mean and coefficient of variation are 25.091 , 21.454 and 116.953 respectively. The least total error (2.805) is from intraparticle diffusion model of colour removal from textile industry and the highest (117.217) from Elovich model of paint wastewater.

The coefficient of determination (CD) can be interpreted as the proportion of expected data variation that can be explained by the obtained data. Higher values of CD indicate higher accuracy, validity and good fitness of the method. CD can be expressed as follows:

$$CD = \frac{\sum_{i=1}^{n}\left(Y_{obsi}-\overline{Y_{cali}}\right)^2 - \sum_{i=1}^{n}\left(Y_{obsi}-Y_{cali}\right)^2}{\sum_{i=1}^{n}\left(Y_{obsi}-\overline{Y_{cali}}\right)^2} \tag{16}$$

Like total error, CD values range from 0.130 to 0.983 (Table 3), standard deviation, mean and coefficient of variation are 0.212 , 0.661 and 32.040 respectively. The least CD value came from Elovich model of MO and the highest coming from intraparticle diffusion model of textile wastewater.

The model of selection criterion (MSC) can be interpreted as the proportion of expected data variation that can be explained by the obtained data. Like, CD the higher the value of MSC, the higher the accuracy, validity and the good fitness of the method. MSC can be computed using equation (17) as follows:

$$MSC = \ln\frac{\sum_{i=1}^{n}\left(Y_{obsi}-\overline{Y_{obs}}\right)^2}{\sum_{i=1}^{n}\left(Y_{obsi}-Y_{cali}\right)^2} - \frac{2p}{n} \tag{17}$$

Like total errors and CD, MSC values are in the range of -1.834 to 5.964 (Table 3), standard deviation, mean and coefficient of variation are 1.937 ,1.752 and 110.594 respectively. The lowest value of MSC is from Elovich model of MO and the highest value is from intraparticle diffusion model from textile wastewater.

A root mean square error (RMSE) is used as a performance index to compare the prediction capability of a model. It is known to be descriptive when the prediction capability among predictors is compared. RMSE can be expressed as:

$$RMSE = \frac{1}{n}\sqrt{\sum_{i=1}^{n}\left(Y_{obsi}-Y_{cali}\right)^2} \tag{18}$$

Table 3 statistical evaluation of the models

Descriptions	Kinetics models	Total error	Coefficient of determination (CD)	Model of selection criterion (MSC)	Root mean square error (RMSE)
MO	First Pseudo order	13.556	0.742	0.981	1.695
	Second Pseudo order	22.172	0.498	-0.003	2.772
	Elovich model	55.377	0.134	-1.834	6.922
	Intraparticle diffusion	14.436	0.644	0.855	1.805
MB	First Pseudo order	8.368	0.887	1.988	1.046
	Second Pseudo order	13.119	0.713	1.089	1.640
	Elovich model	20.267	0.536	0.220	2.533
	Intraparticle diffusion	16.816	0.547	0.592	1.102
SB	First Pseudo order	20.068	0.577	0.239	2.509
	Second Pseudo order	21.489	0.479	0.103	2.686
	Elovich model	12.117	0.760	1.248	1.515
	Intraparticle diffusion	14.270	0.666	0.921	1.784
Textile	First Pseudo order	9.332	0.837	3.560	1.167
	Second Pseudo order	20.343	0.486	2.002	2.543
	Elovich model	23.251	0.461	1.734	2.906
	intraparticle diffusion	2.805	0.983	5.964	0.351
Paint	First Pseudo order	5.545	0.909	4.239	0.693
	Second Pseudo order	15.378	0.544	2.199	1.922
	Elovich model	117.217	0.839	3.570	14.652
	Intraparticle diffusion	3.157	0.970	5.366	0.395
Average		21.454	0.661	1.752	
Standard deviation		25.091	0.212	1.937	
Coefficient of variation (%)		116.953	32.040	110.594	

The values of RMSE range from 0.351 to 14.652. These results from statistical evaluation indicate that Elovich model is unfit for colour removal from MO and colour removal from textile wastewater would fit well into intraparticle diffusion model. These results indicate that Elovich should not be used for modelling colour removal typical wastewaters. In addition with the least error from intraparticle diffusion model of colour removal from textile wastewater indicates that the model could be used for modelling colour removal from textile wastewater. Based on the statistical evaluation and from Figures 2 and 3 it can be said that the mechanism of colour removal electrochemically follows two-steps, namely pore diffusion and intraparticle transport.

4. Conclusions

Based on the study it can be concluded that colour removal:

i. from MO, MB, SB, textile and paint wastewaters fitted well into Pseudo first and second, Elovich and intraparticle models respectively.

ii. Models for textile and paint wastewater should be intraparticle diffusion because of its higher CD and MSC values and lower total error and RMSE.

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SYMBOLS

q_e the electrochemical capacity at equilibrium(col./v)

$$= 0.600\frac{(C_0 - C_t)}{V_t}$$

q_{e1} the electrochemical capacity at equilibrium of pseudo first-order process (col./v)

q_{e2} the electrochemical capacity at equilibrium of pseudo second-order process (col./v)

q_t the electrochemical capacity at time t (col./v),

k_i the rate constant of pseudo first-order process.

k_2 the rate constant of pseudo second-order process.

α the initial electrochemical rate

β the discharging constant during any one experiment.

R the per cent pollutant removed (%)

t the contact time (h)

a the gradient of linear plots

k_{id} the intraparticle diffusion rate constant (/h)

V volume of the sample used (600ml) = 0.6L

C_o initial colour

V_t potential difference (volts)

C_t final colour

A Estimated colour of the diluted samples

B volume of the samples used (ml)

D dilution factor

Col Colour unit

v volts

p and n number of parameter = 1 and number of data points = 8 respectively

R' ($C_{14}H_{14}N_3NaO_3S$,), $C_{37}H_{27}N_3Na_2O_9S_3$, and $C_{20}H_{12}N_3NaO_7S$ for SB, MB and Mo respectively

EDTA ethylenediaminetetraacetic acid