

Electrochemical Oxidation of Acid Brown 98 using Ti/Ru_{0.3}Ti_{0.7}O₂ Composite Anode

Shakeel Zeb^{1,2}, Sajjad Hussain^{2,*}, Hammad Amjad Khan², Zarshad Ali¹, Nadeem Khan², Khurram Imran Khan², Farman Ali¹, Sabir Khan³, Maria del Pilar Taboada Sotomayor³, Saima Gul⁴

¹ Department of Chemistry, Hazara University, Mansehra, KPK, Pakistan

² Faculty of Materials and Chemical Engineering, GIK Institute of Engineering Sciences and Technology 23460, Topi, KPK, Pakistan

³ Department of Analytical Chemistry, Institute of Chemistry, State University of São Paulo (UNESP), 14801-970 Araraquara, SP, Brazil

⁴ Department of Chemistry, Islamia College Peshawar, Pakistan

*E-mail: sajjad.hussain@giki.edu.pk

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Textile and leather industries effluent containing dyes are one of the major concern to flora and fauna. The electrochemical oxidation of a synthetic wastewater containing, acid brown 98 (AB 98) was investigated in a laboratory scale reactor containing Ti/Ru_{0.3}Ti_{0.7}O₂ composite anode. The degradation experiments were carried out at ambient temperature and pressure under different influential parameters such pH, different electrolytes, current density. The dye concentration and extent of mineralization were observed using UV-Visible Spectroscopy and Total Organic Carbon (TOC) analysis. The anode was characterized in the dye wastewater containing the appropriate amount of NaCl and Na₂SO₄ salts using cyclic voltammetry. The result demonstrate that the electrochemical oxidation of the synthetic dye solution increases with the decrease in pH and increase in the concentration of chlorine ions and current density (5-20 mAcm⁻²). It is also further determined that 67% TOC was removed using a 0.1 M, NaCl as an electrolyte and a 20mAcm⁻² current density, under 60 minutes of electrolysis. The energy consumption (kWhm⁻³) of the degradation is minimum at low current densities and high NaCl concentrations.. The kinetic study reveals that AB 98 degradation followed pseudo 1st order kinetics.

Keywords: decontamination, electrochemical degradation, dyes, wastewater

1. INTRODUCTION

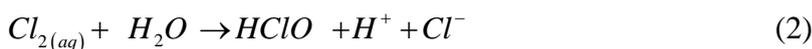
Textile owns a large share and an important one in the industrial landscape of the developing countries. In textile processes large volumes of water are consumed for washing and dying purposes

[1]. In consequence, the textile factories pollute the water bodies with effluents containing dyes which are used at different stages of the textile manufacturing process. The effluents which have dye are well known to negatively affect the water bodies in which gas solubility also plays a key role [2]. Wastewater from the textile industry characteristically inherits a mixture of suspended particles, chemical oxygen demand (COD), acidity and color [3]. It has been reported that insoluble dyes causes residual color which is highly resistive to biological action [4].

Methods used to treat wastewater include physical, chemical, and biological processes. Each method has distinct advantages and disadvantages. Biological degradation is prone to being less effective on Azo dyes due to the dyes resistive properties [5][6] [7]. Traditionally, treatment begins with the chemical coagulation of the wastewater using, but not limited to, chemicals such as ferrous, lime and poly-electrolytes, followed by the biological treatment and, adsorption using activated carbon. Coagulation in this method produces large amounts of sludge which is a significant drawback of this method. For the complete removal of color from the wastewater, researchers combine chemical coagulation, electrochemical oxidation and activated sludge or ion exchange processes [8] [9]. The use of sacrificial iron electrodes in the electrochemical technology generates iron sludge which is again a problem.

Recently, scientific community has found different oxidation methods, such as ozonation, photocatalytic oxidation, and electrochemical oxidation, to be effective against textile effluent. Literature has instances of the photocatalytic oxidation method used for the removal of some textile dyes like acid orange 7, acid blue 80, reactive orange 16 and brilliant orange K-R [10], [11], [12][13]. Nevertheless, this method produces low degradation rates at low pH levels of 6.3. The process as described contains positively charged TiO_2 particles in low pH environment that gets attacked by Cl^- ions, the TiO_2 adsorbing Cl^- ions due to the ionic forces. This results in the low rates of formation of the hydroxyl ions which decreases the photocatalytic activity and results in the presence of chloride ions in the effluent. Other researches have combined the electrochemical and photochemical oxidation process to enhance the removal efficiency of textile wastewater [14]. Similarly, ozonation is also used to eliminate more effectively the color and less effectively the Chemical oxygen demand (COD) [15] [16]. Presently, electrochemical oxidation processes have showed highly promising consequences to eradicate these contaminants in short period of times when compared to conventional oxidation processes. Electrochemical oxidation is a green technology which is used for the degradation of organic and inorganic compounds in wastewater. In electrochemical treatment, direct or indirect oxidation may be applied for the destruction of organic pollutant. In the direct oxidation method, the pollutant is initially adsorbed on the anode and then oxidization is done by the transference of the anodic electron. However, in indirect oxidation the pollutant is oxidized by the strong oxidant such hydroxyl radical, chlorine/hypochlorite ion in bulk of solution.

The efficacy of the indirect electrochemical treatment of pollutants in aqueous medium govern by some parameters such as the presence of ions which act as mediators. The most frequently studied electrogenerated oxidant is active chlorine, a term that encompasses free chlorine and HClO/ClO^- [17]. During this process the chlorides is electrochemically converted into to chlorine, hypochlorous acid, and/or hypochlorite (reactions 1 to 4), which can oxidize the organics near the anode and/or in the bulk.



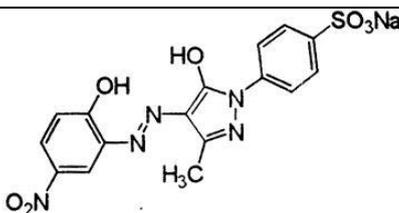
The electro-chemical oxidation method is extensively used for the depletion of dyes and other contaminants from industrial or domestic wastewater. The electrochemical decontamination of dyes like Chromotrope 2R Xiaoming *et al.* [18], amaranth Fajardo *et al.* [19], methylene blue Samia *et al.* [20], Indigo Carmine Lazhar *et al.* [21], Acid yellow Zaira *et al.* [22], Acid Blue and Basic Brown Awad *et al.* [23] has been previously investigated using BDD, Ti/Pt-SnSb, PbO₂, Ti/RuSnO₂, Ti/RuO₂, Ir-Sn-Sb oxide and Pb/PbO₂ anode respectively. Based on the existing literature, several studies have been performed to remove synthetic dyes from water by electrochemical process through different electrodes. In this study, an electrochemical degradation was applied on acid brown 98 a common leather industry dyes using Ti/Ru_{0.3}Ti_{0.7}O₂ anode and stainless steel as cathode under and different influential factors, like current density, nature of electrolyte, electrolyte concentration, and initial pH. Furthermore the kinetic and energy consumption were also evaluated. The concentration of dye was determined by UV visible spectrophotometer and total organic carbon was analyzed us TOC analyser.

2. EXPERIMENTAL

2.1. Materials Used

All the required chemicals such as NaCl, H₂SO₄, NaOH and Na₂SO₄ were obtained from Sigma-Aldrich and were utilized as received. However, the Acid brown 98 dye was acquired from Chemdyes Corporation Ltd. Pakistan and the composite anode have a composition of Ti/Ru_{0.3}Ti_{0.7}O₂ was supplied by De Nora Brazil. The Table 1 shows the characteristic of acid brown 98 dye.

Table 1. Chemical structure and characteristic of acid brown 98

Molecular structure	
Molecular formula	C ₁₆ H ₁₂ N ₅ NaO ₇ S
molecular weight	441.35 g mol ⁻¹
CI number	18840:2
Application	Textile and leather industry
Color	Yellow light brown

Similarly, electrolytes and the synthetic discharge solution were prepared in deionized water.

2.2. Electrochemical cell and experiments

Electrochemical oxidation was performed in an undivided lab scale glass reactor having a capacity of 600 mL. Each experiment electrolyzed 500 mL of synthetic dyes wastewater. The constant current was maintained using DC power supply (GW Instek, Taiwan). The working and counter electrodes, immersed vertically, expose a 14 cm² area to the solution while maintaining an inter electrode distance of 2 cm. pH of wastewater was maintained by a dilute sodium hydroxide (NaOH)/dilute sulfuric acid (H₂SO₄) solution and measured by a pH meter (Milwaukee, United States). The magnetic stirrer constantly stirred the sample solutions at ~400 rpm to enhance the mass transport rate of electrolyte. The concentration of acid brown 98 was determined by a spectrophotometer (ZUZI 4201/20).

2.3. Total Organic Carbon (TOC) Analysis

The TOC analyzer (Shimadzu TOC-VCP, Japan) is used to detect the mineralization of the acid brown 98 wastewater. At constant flow of oxygen, the samples are injected under varying temperature ranging from 650 °C - 900 °C. TOC analysis values were calculated by the difference of total oxidisable and non oxidisable carbon.

2.4. Cyclic Voltammetry

A wide used electroanalytical technique used to find the redox reactions at the electrode surface in the presence of a suitable electrolyte. Three different types of electrodes are used in cyclic voltammetry analysis, for instance, stainless plate cathode, Ti/Ru_{0.3}Ti_{0.7}O₂ composite anode and calomel reference electrode. The experiments are performed in a 0.003 M Na₂SO₄ and 0.1 M NaCl electrolytes. The cyclic voltammograms (10 cycles at the scan rate of 50 mV s⁻¹) were recorded using 500 ml solution in cell containing three electrodes.

3. RESULT AND DISCUSSION

3.1. Electrochemical characterization of composite anode

Cyclic voltammetry is a useful technique to investigate the reactions occurring on the interference of electrode [24]. In the present study in situ characterization of oxide composite anode like Ti/Ru_{0.3}Ti_{0.7}O₂ is done by the CV method and absence of Acid Brown 98 dye in the presence of supporting electrolytes like Na₂SO₄. The black line in **Fig. 1** characterizes Na₂SO₄ electrolyte without the Acid Brown 98 dye. It is evident that no change in current potential occurs when in the region between 0.4 to 1.2 vs calomel reference electrode (CRE). When the potential overtakes 1.2 V vs CRE, a rapid increase in the current is seen as oxygen evolution reaction begins (OER) initiates. Potential range of OER region decreases in the presence of dye voltammograms.

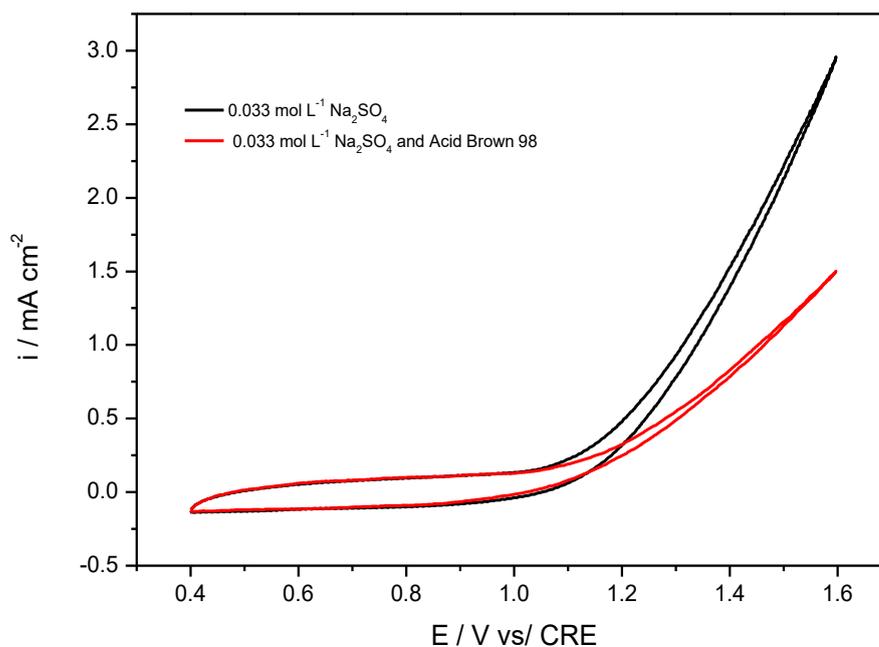


Figure 1. Cyclic voltammetry profile using a commercial $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ and supporting electrolytes containing $0.033 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$, in the absence (black line) and presence (red and blue line) of 180 mg L^{-1} Acid black 234 and 180 mg L^{-1} Acid brown 98 respectively.

3.2. Electrochemical behavior of in the presence of NaCl electrolyte

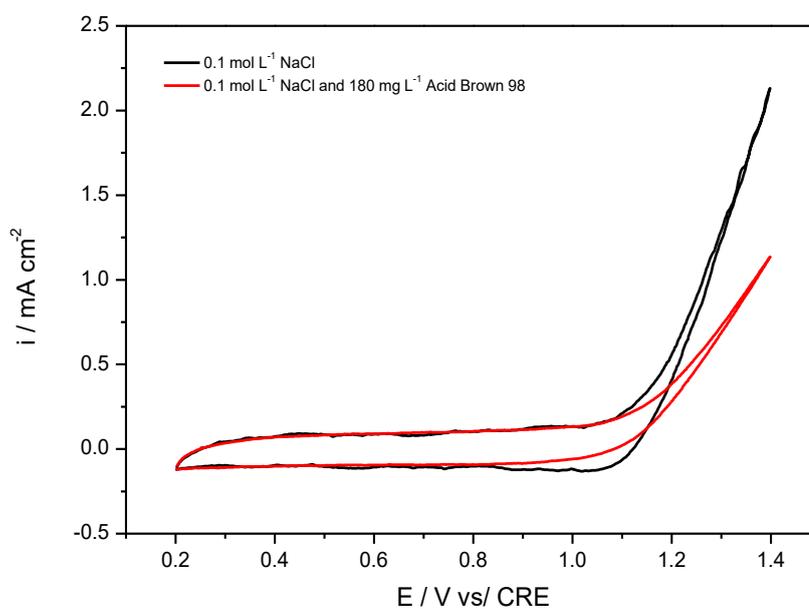


Figure 2. Cyclic voltammetry profile using a commercial $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ anode and supporting electrolytes containing $0.10 \text{ mol L}^{-1} \text{ NaCl}$ in distilled water (black line) and presence (red and blue line) of 180 mg L^{-1} Acid black 234 and 180 mg L^{-1} Acid brown 98 respectively.

In situ characterization of the anode in the presence of NaCl electrolyte is presented in the **Fig. 2**. The cyclic voltammograms is recorded from + 0.2 to +1.4 V vs CRE. The black line shows NaCl electrolyte contained in distilled water without dye which has no changes in the current when E/V vs CRE is from + 0.2 to +1.1 V. As current raised to 1.1 V against CRE, an oxygen evolution reaction (OER) starts. If the contaminate solution contain NaCl electrolyte the potential of OER is lowered and may generate Cl₂ gas at the anode surface and may lead to chlorine evolution reaction (CER) as current is raised above potential 1.1 V against CRE [27].

3.3. Influence of various supporting electrolytes on treatment of AB98

The removal of Acid Brown 98 takes place under supporting electrolytes with a constant current of 20 mA cm⁻². In Fig. 3, it obvious that sulfate ions are unable to completely degrade the Acid Brown 98 dye under 35 min of electrolysis. The oxidant species generated by the sulfate ions degrade only 10 % in Na₂SO₄ and 18 % in H₂SO₄ solutions, with a rate that was slower than that of NaCl. The electro chemical degradation is performed using an active anode like Ti/Ru_{0.3}Ti_{0.7}O₂. The oxidation pathway of active anode in presence of sulfate ion is given below. Sulfate ion splits the water and forms the ·OH free radical which interacts with anode surface and helps create a promotion of the electrode to a higher oxide state MO_{x+1} which may not cause enough degradation because it is not strong oxidant species $MO_{x+1} + R \rightarrow RO + MO_x$.

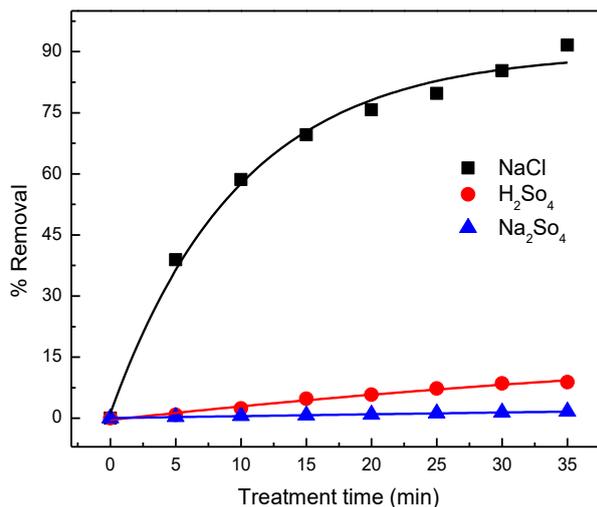


Figure 3. Effect of supporting electrolytes on degradation of 180 mg L⁻¹ Acid Brown 98 dye at 20 mA cm⁻².

In the presence of NaCl electrolyte, the removal of dye is attained by indirect oxidation as chlorine/hypochlorite oxidant species are produced on the anode surface. The following oxidation reaction (1-4) was proposed by Panniza et al. [25]. The profile in Fig. 1 shows 90% degradation was achieved in presence of NaCl electrolyte. The results of H₂SO₄ and Na₂SO₄ are similar to the study of Hussain et al. who reported that Ti/Ru_{0.3}Ti_{0.7}O₂ anode with H₂SO₄ or Na₂SO₄ is not a suitable

electrolyte for the degradation of antibiotic sulfmethaxazole [26]. Similarly, the work by Malpass et al. shows that small amounts of atrazine can be degraded in 120 min in the presence of H_2SO_4 , Na_2SO_4 and NaNO_3 as supporting electrolytes and with NaCl , complete degradation can take place in under 60 min of electrolysis [27].

3.4. Influence of sodium chloride on treatment of AB98

The Fig. 4 illustrates the color removal efficiency (%) of acid brown 98 at various NaCl concentrations and constant ionic strength of 0.1 mol L^{-1} . The ionic strength was maintained by adding Na_2SO_4 . At lower concentrations of NaCl as supporting electrolyte, i.e., 0.02 to 0.04 mol L^{-1} , larger degradation rate of the dye with nearly 44% and 65% occurs within 35 min. In the presence of 0.1 mol L^{-1} , NaCl , degradation extent of the dye was 90% in 35 min; because at higher concentration of NaCl more Cl^- ions are available which act as a stronger oxidant species to degrade dye. When the amount of NaCl electrolyte increases it generates more chlorine/hypochlorite species which speed the degradation of the dye. This behavior is in completely agreement with the reported literature of the degradation of organic compounds being enhance with the NaCl concentration [28] [29].

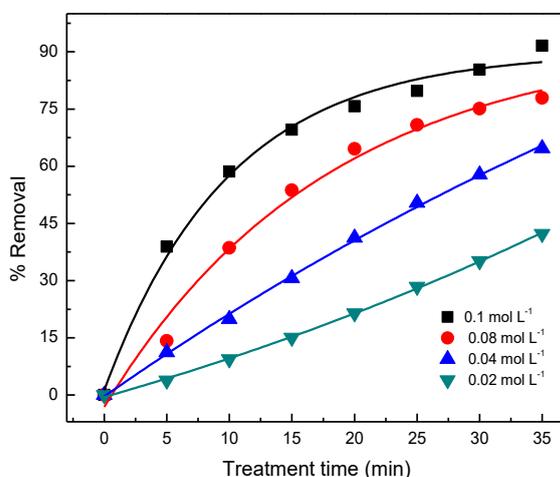


Figure 4. Effect of NaCl concentration on degradation of 180 mg L^{-1} Acid Brown 98 dye at 20 mA cm^{-2} .

3.4.1. Kinetic of treatment process using different NaCl concentration

Degradation of Acid Brown 98 in the presence of electrolytes having various concentrations of Cl^- ions exposed a linear relationship between the natural logarithm of the variation in dye concentration and treatment time. The kinetic profile for the removal of the dye is presented in Fig. 5 which clearly shows that the dye degradation followed the pseudo-first-order kinetics. The rate constant (k) is obtained from equation (i) and the reaction half-life is calculated from equation (ii) [30]. C and C_0 are the final and initial concentrations of the dye. Concentrations of dye is expressed in mg L^{-1} and rate constant k in min^{-1} respectively.

$$\ln(C/C_0) = -k.t \quad (\text{i})$$

$$t_{1/2} = 0.693/k \quad (\text{ii})$$

With increase in the concentration of Cl^- , rate constant k (min^{-1}) is also enhanced while the half-life ($t_{1/2}$) of the electro-chemical reaction decreases.

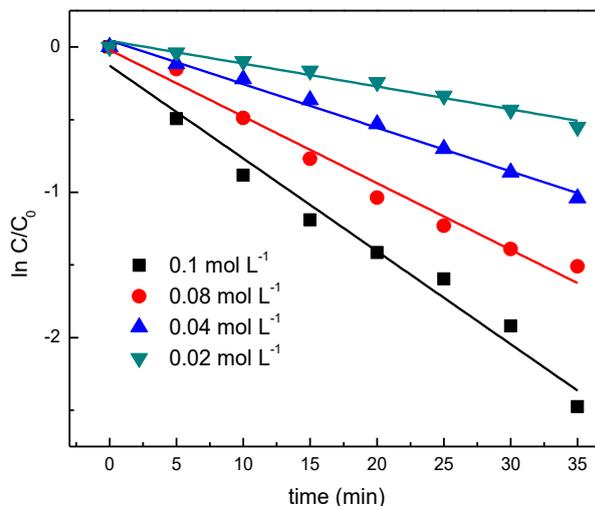


Figure 5. Pseudo 1st order plot of Acid Brown 98 degradation in the presence of different NaCl concentration

3.5. Degradation of AB98 under the influence of various current density

It is evident to maintain a constant current density for the maximum degradation of the dye. The degradation of dye was tested with different current densities from 5 to 20 mAcm^{-2} as presented in Fig. 6. The degradation of dye increases with increase in current density from 5 to 20 mAcm^{-2} . The maximum degradation 89% is achieved at 20 mAcm^{-2} under 35 min. The electrochemical degradation of the dye at various current densities shows the pseudo-first-order kinetic. Table 2 presents the values of rate constant and half life time. The rate constant (k) increases with the increase of the current density. Increasing current density produces Cl_2/OCl^- species which results in high degradation [26]. The large internal surface area of the $\text{Ti}/\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ composite anode favors active chlorine species generation. Similarly the results agree with costa et al [31]; depletion of acid black 210 dye at BDD anode and enhanced reduction of the dye as current density increased from 25 to 100 mAcm^{-2} . Similarly, Awad et. al., [23] confirmed the increasing depletion of basic brown and acid blue dye with increasing current density on the Pb/PbO_2 electrode in the range from 0 - 45 mAcm^{-2} . For the lowest expenditure of energy and the maximum reduction of dye, the present study concludes the current density of 20 mAcm^{-2} to be the best option.

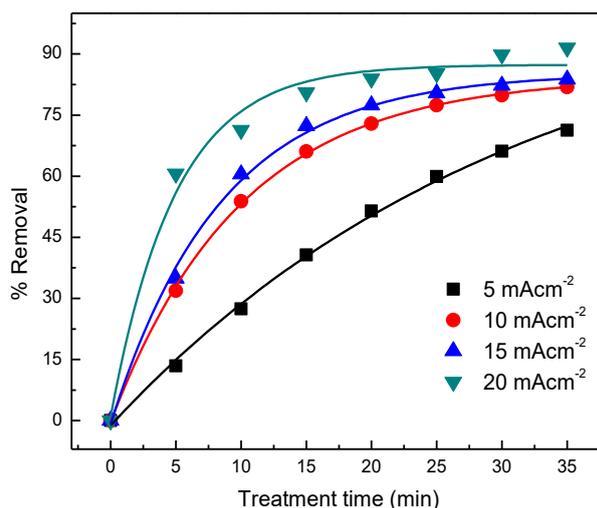


Figure 6. Effect of current density on degradation of 180 mg L⁻¹ Acid Brown 98 dye using 0.1 M NaCl as electrolyte.

3.6. pH study on degradation of AB98 dye

Table 2. Pseudo-first-order rate constants, half-life and energy consumption parameters for the decontamination of acid brown 98 synthetic effluent along with the corresponding square of the correlation coefficient (R²)

Parameters	K (min ⁻¹)	t _{1/2} (min)	Energy consumption (kWh m ⁻³)	Average Voltage	R ²	
Current Density (mA cm ⁻²)	5	0.036	19.25	0.249	3.06	0.998
	10	0.048	14.23	0.621	3.81	0.939
	15	0.051	13.58	1.672	4.54	0.894
	20	0.062	11.17	2.040	5.05	0.900
Electrolytes	Na ₂ SO ₄	0.0004	1732.5	1.475	4.52	0.992
	H ₂ SO ₄	0.0029	238.96	0.982	2.79	0.977
	NaCl	0.063	11	0.894	3.81	0.976
NaCl (mol L ⁻¹)	0.02	0.015	46.2	1.465	4.49	0.973
	0.04	0.030	23.1	1.456	4.46	0.991
	0.08	0.045	15.4	1.335	4.09	0.978
	0.1	0.063	11	1.243	3.81	0.976

To see the effect of pH on the electro oxidation of Acid Brown 98 various pH variations (i.e., 3, 6 and 10) were performed. The oxidation of dye decreases with increasing pH. Fig.7 displays the

oxidation of the dye increases as pH decreases. 90% degradation of the dye is attained with pH 3 within 35 min. At a low pH, the dye solution contains chlorine ions in the form of HOCl which has a high oxidation potential (1.49 v). The solution also contains increased OCl^- ions that shows dominance which has low oxidation potential (0.94 v) and cause low degradation at higher pH [32] The present result shows similar behavior with [33] [34] who investigated the degradation of real textile water and concluded that 70% degradation can be attained at pH: 4 in 120 min. Similarly another study conducted by Hussain et. al, in which the SMX was completely removed at acid pH.[26]

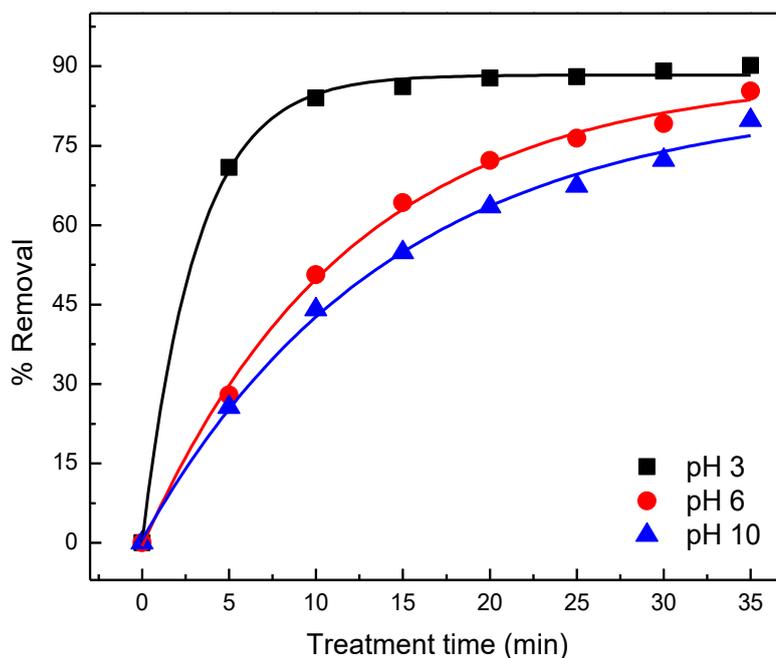


Figure 7. Effect of pH on electrolysis of 180 mgL^{-1} Acid Brown 98 dye solution at current density of 20 mA cm^{-1} and 0.1 M NaCl as electrolyte.

3.7. Organic content removal of AB98

The profile of TOC displays in Fig. 8 and reveals that at different treatment time of the waste and current density of 20 mA cm^{-2} , TOC removal efficiency was 67%. It can be seen that 67% TOC is removed in 60 min while almost 90% reduction of dye is achieved in 35 min. The color of the dye is due to chromophores which easily breaks down. Compared to the chromophore group, aromatic intermediates and acyclic compounds demonstrates the highest stability against the strong oxidant species which it takes a long time for the degradation and a low TOC removal was attained [29].

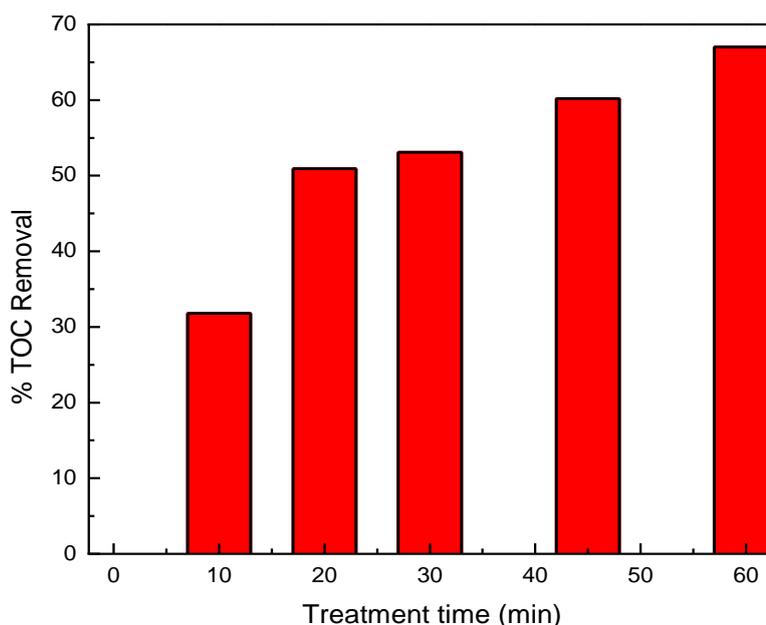


Figure 8. TOC removal during the electrochemical degradation of 180 mg L^{-1} Acid Brown 98, current density 20 mA cm^{-2} and 0.1 M NaCl .

3.8. Energy requirement for AB98 degradation using electrochemical process

As the energy consumption is an important parameters in any electrochemical process, so we demonstrated in Table 2 the energy consumption date related to decontamination of Acid Brown 98 dye. Equation (iii) was utilized to calculate the energy consumption for the degradation of Acid Brown 98 [29].

$$\text{Energy consumption (KWhm}^{-3}\text{)} = I \times V \times t / V_s \quad (\text{iii})$$

Where V represents the average voltage, V_s is the volume of the glass reactor 500 ml, I shows average applied current and t is depletion time (h).

When the electro-oxidation of dye thrives as current density increases from 5 to 20 mA cm^{-2} , the energy consumption also expands from 0.25 to $\sim 2.0 \text{ kWh m}^{-3}$. Moreover, the energy cost is also low at 5 mA cm^{-2} compared to 20 mA cm^{-2} . At low current density the degradation takes a long time while at high current density the degradation occurs much faster which leads to an overall lower energy cost. Thus, for the maximum color removal and for low energy cost, 20 mA cm^{-2} is best applied current density due to short time.

3.9. Comparison of degradation methods

Different process like photo-Fenton, Photo-catalysis, anodic oxidation used for degradation of acid brown dye. Herein we demonstrate some processes along with materials used for the as Photocatalyst or as anode for acid brown dye. The Table 3 shows that about 70-80% acid brown 14 was removed using $\text{CuFe}_2\text{O}_4\text{-TiO}_2$ and $\text{CuFe}_2\text{O}_4\text{-TiO}_2\text{-Ag}$ as Photocatalyst. Similarly anodic

oxidation proved good degradation efficiency toward acid brown 14 dye. The current work was a good agreement toward electrochemical oxidation using composite anode $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ and removed acid brown 98 about 90%.

Table 3. Comparison of different methods and materials for the degradation of acid brown dye

S.No	Process or Materials used	Type of Dye	% Removal	Reference
1	Photo-catalysis using $\text{CuFe}_2\text{O}_4\text{-TiO}_2$	Acid brown 14	70	Shamin et al [35]
2	Photo-catalysis using $\text{CuFe}_2\text{O}_4\text{-TiO}_2\text{-Ag}$	Acid brown 14	80	Shamin et al [36]
3	Anodic oxidation using graphite anode	Acid brown 14	98	Bassyouni et al [37]
4	Photo-electro-oxidation assisted peroxy monosulfate	Acid brown 14	97	Nemat et al [38]
5	Photo-catalysis using TiO_2 and ZnO	Acid brown 83	90-95	Sandoval et al [39]
7	Electrochemical process using $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ Composite anode	Acid brown 98	90%	This work

4. CONCLUSION

The metal oxide composite anode ($\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$) demonstrated minute production of physical adsorbed species $\text{M}(\bullet\text{OH})$, but a good ability to generate strong oxidative chlorine species like (HClO and Cl^-) using NaCl as electrolyte. 90% degradation of acid brown 98 solution containing 0.1 M NaCl was observed at pH 3 and 20 mA cm^{-2} , however 67% of TOC removed, because the generated intermediate is somewhat more recalcitrant than the parent dye molecule due to the TOC removal. The measured absorbance and their corresponding concentration drop obeyed a pseudo first-order kinetics with high value of rate constant at higher electrolyte concentration. The energy consumption parameters reveals that usage of NaCl as supporting electrolyte is economically feasible for the degradation of acid brown 98 dyes. The energy consumption was least at low current density however we need longer electrolysis time, therefore an optimum current density is essential to treat dye wastewater.

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