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A hybrid electrochemical advanced oxidation/microfiltration system using BDD/Ti anode for acid yellow 36 dye wastewater treatment

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ABSTRACT

Conductive diamond is an excellent electrode material due to its resistance to corrosion, wide potential window, and mechanical stability. Diamond doped with boron (BDD) as the anode in electrooxidation (EO) reactor to degrade trace but refractory pollutants from wastewater has received enormous attention recently. In this study, an innovative BDD/Ti electrooxidation–microfiltration (EO/MF) hybrid system was designed and tested for simultaneous removal of refractory organics and particles in dye wastewater. The system was fabricated in a tubular fashion with BDD/Ti as the anode, stainless steel (SS) as the cathode, and a ceramic membrane in between for filtration practice. The synthetic dye wastewater contained acid yellow 36 (AY-36) as the model organic pollutant while kaolin was added to make up the particles in the suspension. The experiments were operated in a continuous up-flow mode at pH 3 with a current density of 30 mA/cm^2. A complete COD removal and more than 90% removals of color and turbidity from the dye wastewater were achieved, suggesting that particles can be removed via MF would not hinder the performance of EO. In conclusion, the single stage hybrid system of BDD/Ti–EO/MF can be a potent treatment process for dye wastewater.

1. Introduction

Chemical precipitation with alum or ferrous sulphate has been used commonly in treating textile wastewater containing dyestuffs; however, it suffers from such drawbacks as generation of large volume of sludge leading to disposal problem and the contamination of residual chemicals in the treated effluent. Physicochemical treatments such as filtration, coagulation, adsorption, flocculation, and chemical oxidations by means of oxidizing agents such as chlorine, ozone, hydrogen peroxide or even wet-air oxidation (WAO) are other popular options the wastewater treatment, but they are not reliable in removing all pollutants [1–3].

The new favorable alternative is advanced oxidation processes (AOPs). They are generally defined as the aqueous phase oxidation primarily relying on the mechanism of destruction of the target pollutant by the intermediacy of highly reactive species such as hydroxyl radicals (·OH) [4]. This physicochemical method has been successfully tested in eliminating a variety of compounds from wastewater. Currently, many methods are available to generate hydroxyl radicals such as H_2O_2/UV, UV/O_3, H_2O_2/O_3, TiO_2 photocatalysis, Fenton's reaction, photo-Fenton/ultrasound, and wet-air oxidation, which can be further enhanced by processes including ionizing radiation, microwaves, pulsed plasma and ferrate reagent [4,5]. Electrochemical advanced oxidation process (EAOP) is one among them, in which the reactive oxidizing hydroxyl radical is generated by electrooxidation (EO). By applying the potential above the thermodynamic stability of the anode [6], namely, 1.23 V/SHE, the water molecules can be activated and electrolyzed to produce hydroxyl radicals. The strong reactivity of ·OH can mineralize organic pollutants into carbon dioxide along with water and inorganic anions. Hence, EAOP is superior to any other physicochemical degradation due to its environmental compatibility, versatility and high energy efficiency, amenable to automation, and safe to operate under mild conditions.

The efficiency of electrochemical process is determined by the electrode material and parameters such as pollutants concentration, pH, current density, and supporting electrolyte [7]. Previous research has also suggested that the key to effective oxidation is electrode materials which dictate the reaction mechanism in electrochemical oxidation and the degradation pathway of pollutants [8]. Conductive diamond such as BDD is an excellent material for the electrode due to its high resistance to corrosion, wide potential window of approximately 3.0 V, and strong mechanical stability [9]. A review on the oxidation of synthetic dye compounds by electrochemical treatment processes using BDD anode has indicated that it is superior to Ti/Sb_2O_5—SnO_2, Pt/Ti, TiRuO_2, or PbO_2 anode with respect to its high stability, high oxidative ability and low cost

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[7]. Satisfactory color and COD removals (ranging from 80% to 100%) by EO using BDD anode in wastewaters containing 3,4,5-trihydroxybenzoic acid, remazol brilliant blue, acid yellow 1, o-toluidine, basic blue 3, crystal violet, acid black 210, orange II, and Alizarin Red S have been reported [7].

To manufacture a high performance BDD electrode, the first step is to select a suitable substrate. It is true that BDD film can be successfully deposited on Si substrate to form the BDD/Si electrode via chemical vapor deposition (CVD). Unfortunately, its application in the treatment of industrial wastewater has been limited by the brittleness and low conductivity of silicate substrate. Researchers have tried other substrate materials such as Nb, Ta, Ti, and W to enhance the conductivity and compatibility. Among them, Nb, Ta and W are too expensive to use in wastewater treatment [10]. Reasonable cost and high conductivity of Ti substrate renders BDD/Ti electrode acceptable in the electrochemical application.

To treat dye wastewater, special design is needed to concurrently remove organic pollutants and particles. A study on dye wastewater treatment by ceramic membrane microfiltration in a cross-flow mode has failed to reduce the absorbance of 2,3-acidic wastewater and DSD acidic wastewater completely [11]. To enhance the treatment efficiency, a two-stage operation, electrochemical process using BDD plus filtration, has been studied by Joao et al. [12]. They employed a combined electrochemical/reverse osmosis (EO/RO) to remove phenol and electrochemical/nanofiltration (EO/NF) to degrade AO7 dye. Even though the COD removals in both cases were more than 95%, the combined process only targeted at soluble organic pollutants and not particle suspension. Another combined electrochemical oxidation and membrane process was studied by Chen et al. [13] to treat wastewater from textile dyehouse. A single cell electrochemical reactor with PbO_2 anode and arc-shaped transfer-flow membrane module was set up in alternating sequence. The electrooxidation and membrane filtration process complemented each other. While the former effectively removed the color, the latter nearly completely removed the TSS (total suspended solids) content. Masid et al. [14] combined electrooxidation and RO membrane process to treat high-strength chemical industry wastewater. The result showed that electrooxidation prior to RO membrane process increased membrane performance by the degradation of organics and hence the removal of TDS (total dissolved solids) content. Researchers have also found the formation of polymeric intermediates during anodic oxidation of orange II at Ti/B-diamond electrode [9,10]. As a result, the solution became more turbid due to the generation of impurities. This phenomenon gives more merit to supplement the EO process with MF, which may prevent the escape of the side products from the treatment system.

The objective of this study was to develop a single reactor combining the electrooxidation using BDD/Ti anode and ceramic membrane microfiltration to simultaneously remove soluble organic matters modeled by AY-36 azo dye, and particulate matters, simulated by kaolin from wastewater.

2. Materials and methods

2.1. Chemicals

20 mg/L of azo-dye in 2 L of aqueous solution was prepared by dissolving commercial acid yellow 36 (AY-36) powders (Alpha Aesar, UK). AY-36 is an azo dye having chemical formula $C_{18}H_{14}N_3NaO_3S$ and chemical structure as shown in Fig. 1. 5 mg/L of kaolin (Riedel-de Haën, Germany) was also applied to simulate suspended particles. To set the solution at pH 3, $HClO_4$ was added. 10 mL of 3 M potassium chloride standard solution (Fluka Analytical) was introduced as a background electrolyte. All

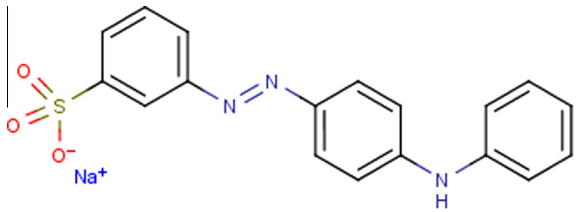


Fig. 1. AY-36 chemical formula.

chemical reagents used are in analytical quality. Deionized water (18.3 MΩ cm, Milli-Q) was used in the experiments.

2.2. BDD/Ti electrode

The BDD/Ti anode was prepared using CVD method provided by Creating Nano Technologies, Inc., Taiwan. The deposition of BDD film was carried out in a hot-filament CVD (HFCVD) reactor, shown in Fig. 2. The system consisted of a process chamber equipped with a tungsten filament to activate the gas-phase reaction and a substrate stage to control the substrate temperature. The Ti substrate was pre-treated in an ultrasonic bath of toluene containing 0.6 μm diamond powders for 60 min to enhance the nucleation density. The gas mixture of CH_4 (5%), H_2, and $B(OCH_3)_3$ (0.3%) was pumped into the gas chamber for the deposition of BDD film, with the substrate temperature at 800–850 °C and the chamber pressure at 5 torr. The thickness of the BDD film deposited on Ti was about 2 μm.

To verify the morphology and crystal structure of BDD/Ti electrode, HR-SEM (Hitachi S-4700I cold cathode FE-SEM with energy dispersive spectrometer) and XRD/TF (thin film X-ray diffractometer, RU-H3R Rigaku, Japan) were used, respectively. The diamond and graphitic phases in the deposited films were characterized by a micro-Raman spectrometer (Dilor XY-100) using an Ar laser of 514.5 nm wavelength with a resolution of 1.8 cm^{-1}. Also, the potential window was determined by cyclic voltammogram (CV) performed in conventional three-electrode cell by Autolab potenstat/galvanostat 302 N run by Nova 1.9 software. Applying 2 mV/s scan rate, Pt plate was used as counter electrode, Ag/AgCl as reference and 0.5 M H_2SO_4 as supporting electrolyte.

2.3. EO/MF hybrid system

The EO/MF hybrid system is shown in Fig. 3. The reactor module is consisted of a tubular ceramic membrane and electrodes. The pore size of the membrane was 1.4 μm, which was encased in a stainless steel (SS 304) tube also served as the cathode. The BDD/Ti electrode at the center, with a surface area of 9.4 cm^2, was the anode. The diameters of SS housing and BDD/Ti anode were 11.0 mm and 2.0 mm, respectively. The gap between anode and cathode was approximately 4.5 mm. The EO/MF experiments were carried out in an up-flow mode.

2.4. Experimental condition and analytical method

All the experiments were conducted under controlled current of 30 mA/cm^2 with the same initial pH of 3. The filtrate was sampled periodically for the determination of UV/Visible absorbance, chemical oxygen demand (COD) and turbidity. COD was determined by using the COD Reactor Digestion Method and the calibration procedure described in the User-Entered Programs section of the DR/4000 Spectrophotometer. The UV/Visible absorbance was analyzed by Hitachi U3010 Spectrophotometer with a 1-cm quartz cell. A wavelength scan was conducted in 1 nm step ranging from 200 to 700 nm to determine pronounced peaks during the reaction.

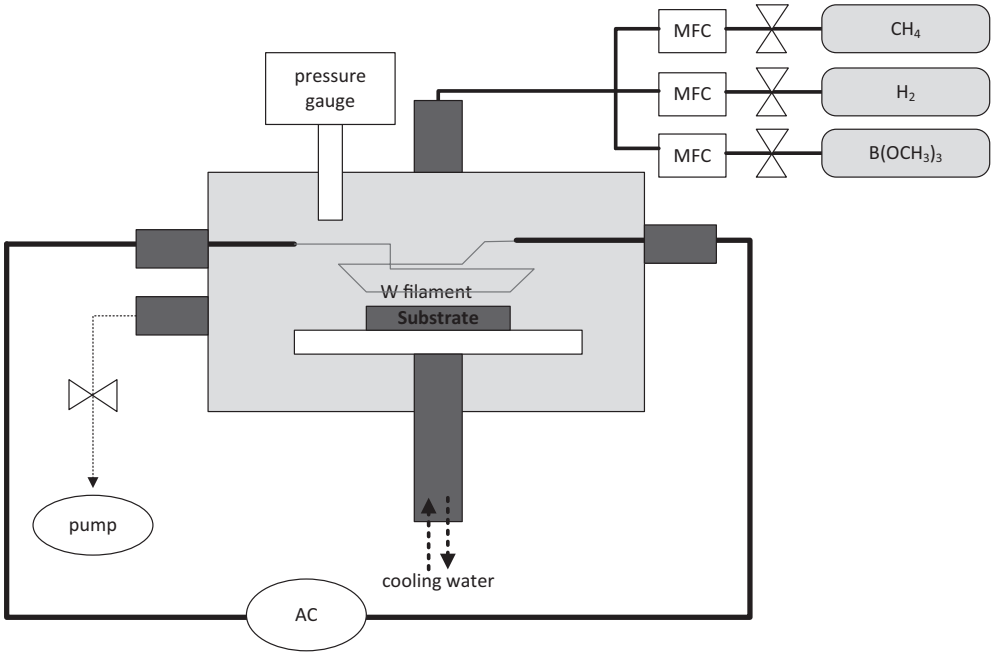


Fig. 2. Hot-filament CVD system.

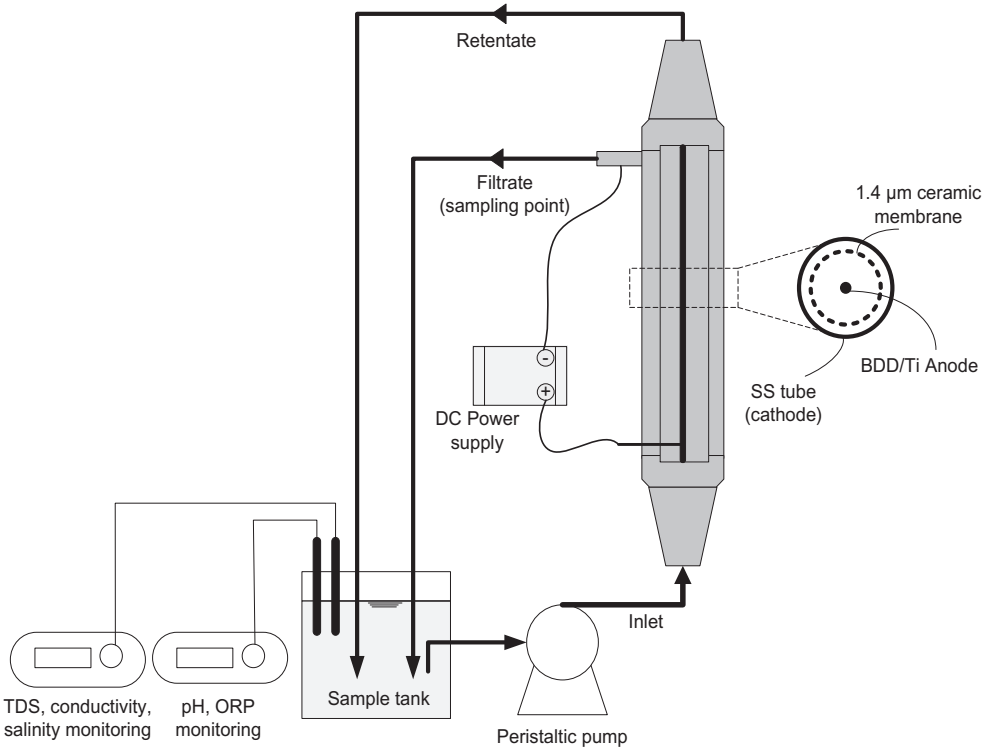


Fig. 3. Schematic of BDD/Ti electrochemical–microfiltration (EO/MF) hybrid system.

To analyze the formation of intermediate products, absorbance was measured at wavelength of 280, 256, and 230 nm for phenol group, benzene ring, and carboxyl group, respectively. To determine the degradation of azo bond (N=N) in AY-36, absorbance at 434 nm was detected. The WTW turb 555 Laboratory Turbidimeter was applied for measuring turbidity of water sample.

3. Results and discussion

3.1. Surface and electrochemical analysis of BDD/Ti anode

The SEM image of the BDD/Ti electrode is displayed in Fig. 4. The BDD film of 2 μm thickness was evenly coated on the surface

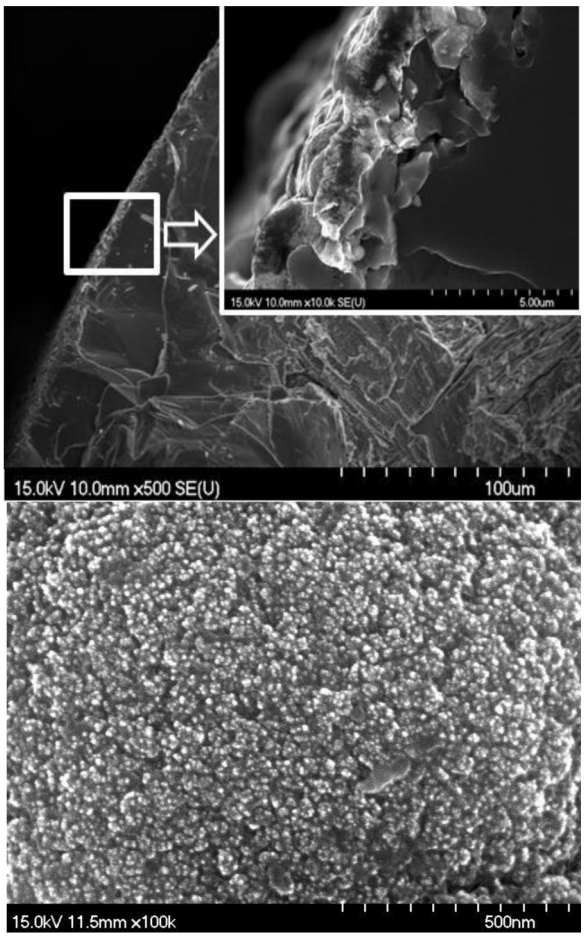


Fig. 4. SEM cross section and top-view image of BDD/Ti electrode.

of Ti substrate. The smoothness of the coating can be attributed to the doping by boron, which induces the secondary nucleation and decreases the grain size of the diamond [15]. It also shows the BDD films are well arranged nanocrystalline diamond, which is uniform and dense grain without cracks or holes. The XRD pattern of the BDD/Ti electrode, shown in Fig. 5, confirmed the formation of diamond on the surface of Ti by the distinctive diamond (1 1 1) peak at 44°. The intensive TiC peaks at 36° and 41° indicated the presence of a TiC layer between the diamond film and Ti substrate. The Raman characteristic band of diamond structure at 1332 cm^{-1} was significantly shown, while the peak at 1140 cm^{-1} was barely visible (Fig. 6). Many studies have indicated that 1140 and 1470 cm^{-1} bands in Raman spectra are characteristics of diamond nanocrystallites [16–20], due to the effect of reduced size or the disruption of a tetrahedral carbon network [16]. A band around 1590 cm^{-1} was probably due to the amorphous or graphitic sp^2 carbon impurities.

The cyclic voltammogram (CV) of BDD/Ti (Fig. 7) shows a wide potential window ranged from −0.75 to 2.3 V with very low background current. In the inset figure can be viewed clearly this low background current value (near 0.5 mA/cm^2) and that the onset of oxygen evolution reaction is 2.3 V. For O_2 evolution, the potential sifted toward more positive direction for oxidizing organic compounds in the wastewater. Higher overpotential of O_2 evolution due to water discharge can enhance the current efficiency and lower the energy consumption of electricity.

3.2. EO/MF operation

To test the performance of EO/MF hybrid system in removing organic pollutant and particles, 20 mg/L AY-36 dye solutions with 5 mg/L of kaolin were used. The removals of COD, turbidity and color by the BDD/MF hybrid system at a current density of 30 mA/cm^2 were monitored for a period of 6 h, which are shown in Fig. 8. Satisfactory result was achieved in an hour. The inset in Fig. 8 compares the performances of the system in treating the dye solution with and without kaolin after 6 h of operation. The result also reveals that COD is not detectable while the color measurement still shows a slight peak. It is due to the detection sensitivity of COD measurement is relative low as COD values under 3 mg/L.

All blank experiments (in the absence of electricity; data not shown) showed that there was no significant change in COD concentration and color of the solution, indicating that no appreciable oxidation of AY-36 occurred without the electrooxidation process.

To understand the electrolysis operating regime of this study, the instantaneous current efficiency (ICE) was calculated from COD value using following equation [21]:

$$\mathrm{ICE} = \frac{(\mathrm{COD}_t - \mathrm{COD}_{t+\Delta t})}{8I\Delta t}FV$$

where COD_t and $\mathrm{COD}_{t+\Delta t}$ are the chemical oxygen demands at times t and $t + \Delta t$, (in g O_2/L) respectively; I is the current (A); F is Faraday's constant (96,500 C/mol); and V is the volume of the electrolyte (L).

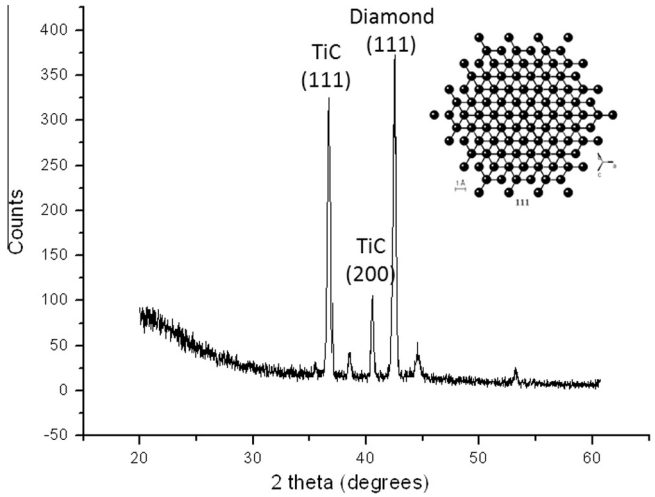


Fig. 5. XRD pattern of the BDD/Ti electrode.

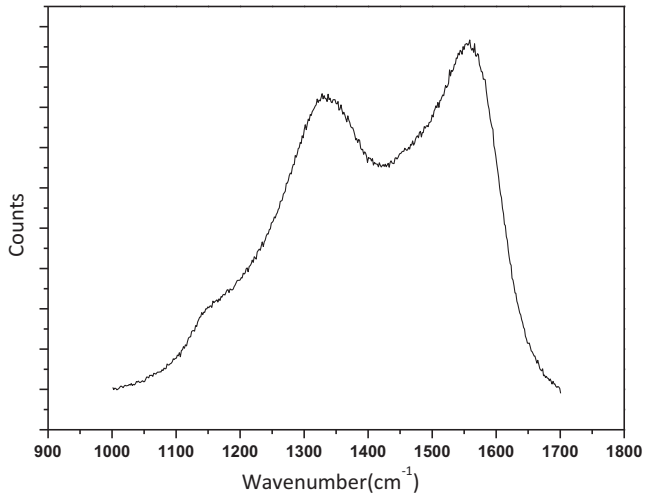


Fig. 6. Raman spectra of BDD/Ti electrode.

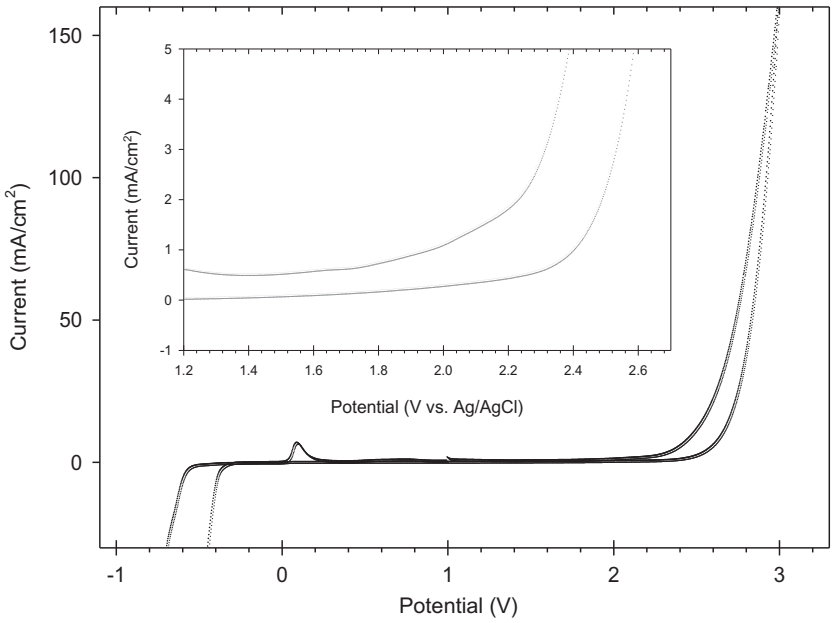
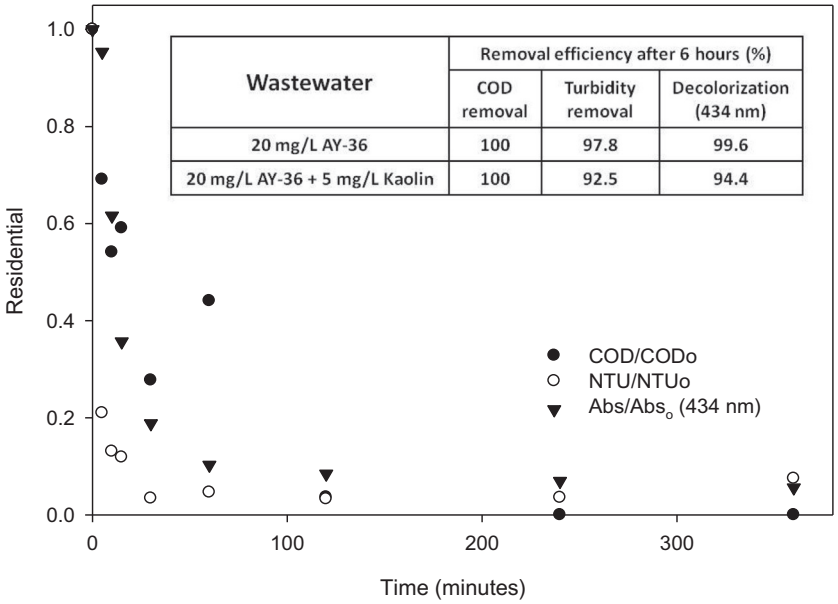


Fig. 7. The cyclic voltammetric curves of BDD/Ti electrode in 0.5 M H_2SO_4. Inset figure is the zoom in image on oxygen evolution potential range.



Wastewater	Removal efficiency after 6 hours (%)		
	COD removal	Turbidity removal	Decolorization (434 nm)
20 mg/L AY-36	100	97.8	99.6
20 mg/L AY-36 + 5 mg/L Kaolin	100	92.5	94.4

Fig. 8. Performance of BDD/Ti electrochemical–microfiltration hybrid system for COD reduction, turbidity removal and discolouration of 20 mg/L AY-36 dye solution with 5 mg/L of kaolin during 6 h reaction time. The inset table is the comparison of COD, color, and particles removal of 20 mg/L AY-36 dye solution with and without 5 mg/L of kaolin.

The determination of ICE using COD technique in this experiment was more reliable than OFR (oxygen flow rate) method due to the application of KCl as the support medium. The Cl^- present could evolve into Cl_2 and interfere the OFR measurement [22]. The maximum of 90% ICE was obtained during the first 15 min of operation, resulting in 33% of COD removal. Afterwards, the ICE kept dropping to around 1% by 6 h of operation caused by the decrease of COD in the system [10]. The low current efficiency at high charge loading (longer operation time under controlled current) indicates that the operation of the system was limited by mass transfer [1,9]. Aside from the strong oxidation capability of hydroxyl radical generated, the presence of active chlorine in the solution arisen from KCl (as the supporting electrolyte here) solution might also contribute to some COD removal via indirect oxidation. Whilst hydroxyl radicals can only present very close to the anode surface and has very short lifetime, the active chlorine can be existed in the bulk solution and have a role in oxidizing organic that present far from the anode surface. The presence of active chlorine, however, poses a risk of the formation of undesired toxic chloro-organic and electrogeneration of chlorine–oxygen byproducts such as ClO_2^-, ClO_3^- and ClO_4^- which have health risk [6]. But, by setting the pH to acidic (under pH 4), or at pH 3 in this study, the formation of such byproducts is not expected.

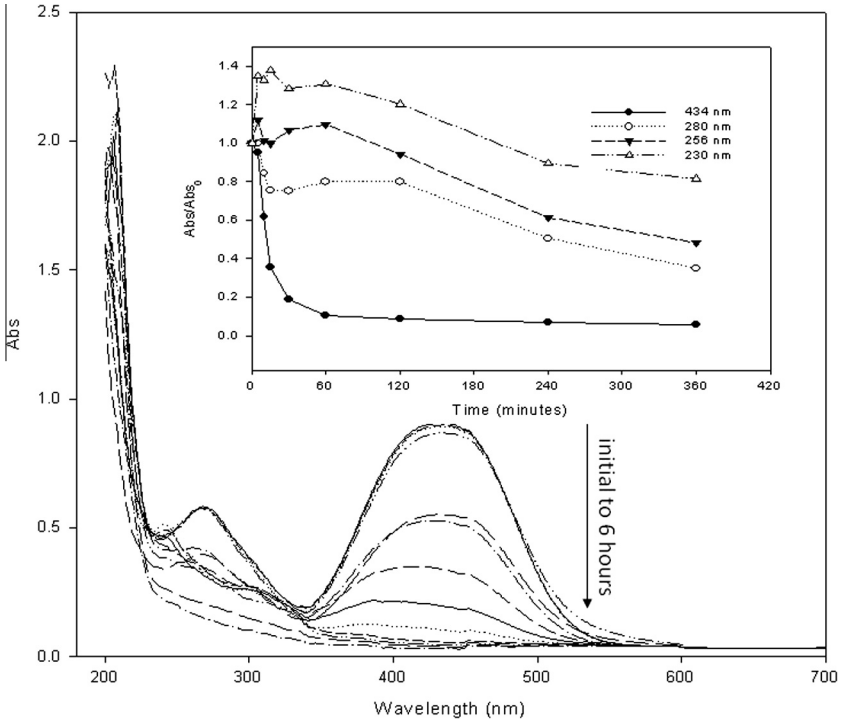


Fig. 9. The removal of color with an initial concentration of 20 mg/L performed with BDD/Ti EO/MF system. Current density: 30 mA/cm^2; pH 3 by adding $HClO_4$; electrolyte: 5 mL/L KCl. The inset figure displays the degradation rate of AY-36 azo bond (434 nm), phenol (280 nm), benzene (256 nm) and carboxyl (230 nm) in 6 h operation time.

Fig. 9 shows the UV/Visible wavelength scan of AY-36 degradation within 6 h of operation, and the individual measurement at 434, 280, 256 and 230 nm wavelengths (inset). The UV/Visible spectrum in this figure reveals one main peak in the visible light region and several peaks in the UV region. Their intensities declined continuously along the process. Inset figure shows the variations of these peaks (Abs/Abs_0). Mohamad et al. [23] described the pathway of the degradation of metanil yellow (AY-36) by hydroxyl radical in a photocatalysis process. He pointed out that intermediates including phenols, benzenes and carboxyls formed before the complete mineralization of AY-36. The intensified absorbance of some wavelengths in the UV region during the first hour indicates the formation of phenol (280 nm), benzene (256 nm) and carboxyl (230 nm) as intermediates, which were further degraded at longer operation time. The faster decline of 434 nm peak compared to others suggested that color reduction as the N=N of the AY-36 were broken is much easier to achieve than the breaking of the aromatic ring. The latter may require several steps and longer reaction time.

4. Conclusions

The well prepared BDD/Ti electrode shows a low background current and a wide potential window. Also, by observing the capability of this system to remove COD, turbidity and color, the potential applicability of BDD/Ti electrooxidation/microfiltration (EO/MF) hybrid system for simultaneous removal of soluble organic dye and particle suspension from wastewater has been verified. Undetected presence of COD and almost total discolouration for relative low initial concentration (20 mg/L) after treatment suggests that the setup in this study for wastewater treatment cannot merely allow effluent quality comply with discharge limits, but is able to reduce organics to trace level for the purpose of wastewater reuse.

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