



Influence of physico-chemical treatment of coconut shell-based carbon electrode on the inceneration of antraquinone dye

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ABSTRACT

Physico-chemically activated coconut shell-based carbon electrode was fabricated to treat anthraquinone dye. Electrode was moulded using specific solvent according to following formula : 54% activated carbon (100 or 200 mesh), 43.3% water, and 2.7% polyvinyl alcohol. Performance of electrode was investigated based on UV-Vis spectra data of RB19 dye degradation on varied carbon particle size (100 and 200 mesh), type and concentration of electrolyte (NaCl and Na₂SO₄), applied potential (5, 6, 7 V), and electrode doping (PbO₂ and B). The absorbance peak at λ_{590} and λ_{226} was decreased for 67-75% and 38-42%, respectively, using fabricated electrode. Type and concentration of electrolyte as well as applied potentials were not related to the increasing of efficiency of degradation process. PbO₂ and Boron doping showed conflicting behaviors; boron-doping was able to increase the performance of electrode, but on the other hand, PbO₂ doping shows no effect.

Keywords: Carbon electrode, Coconut shell, Antraquinone, Electrodegradation

INTRODUCTION

Nowadays, electrochemical technologies have gained a great interest due to their effectivity as a solution to environmental problems related to industries[1,2], especially wastewater contamination. In view of this, electrochemical method has the advantages of environmentally compatible, highly efficient and compact [3] compared to conventional chemical technologies, which will produce subproduct and incur removal cost.[4,5]

Electronic conductor (electrode) is the main and important material in electrochemical system, aside from ionic conductor (electrolyte solution).[6] It must thus have superior characteristics, such as, physicochemically stable and robust (resistant to corrosion and passivation), selective, has a high oxidative capacity, electrical conductivity and oxygen overpotential, and low cost/life ratio.[7,8] Carbon is a much cheaper electrode material compared to metal or metal oxide, like Pt, Au, PbO₂, SnO₂, and boron-doped diamond (BDD).

Carbon has a conductive characteristic with a fruitful porosity and has been widely used as electrode.[9,10] Guohua [3] reported that phenol removal efficiency of carbon electrode was about 70% with 5 months duration of robustness. In addition, the high carbon content of coconut shell (97%) obtained by pyrolysis was reported by previous study [11], despite the drawbacks of having high resistivity, high energy consumption, and low intensity.[12] Yamada [13] mentioned that physical-chemical activation and moulding process might enhance the activation of carbon electrode related to nanoporous formation (less than 100 nm). Metal or metal oxide deposition will further improve the electroactivity properties of electrode.[14] Doped graphite electrode is becoming an interesting field of research due to their applicability as fuel cell by methanol oxidation.[15]

In this work, the anodic oxidation of remazol brilliant blue r (anthraquinone dye) has been investigated using coconut shell-based carbon electrode in salt electrolyte (NaCl and Na₂SO₄). UV-Vis spectroscopy was used to investigate the activity of carbon electrode on oxidation process under different experimental conditions.

EXPERIMENTAL SECTION

2.1. Materials and instrumentation

Carbon electrodes were prepared using coconut shell carbon char (physical-chemically activated), polyvinyl alcohol (Merck), Pb(NO₃)₂ (Merck), HNO₃ (Merck), NaF (Merck), H₃BO₃ (Merck), and distilled water. Remazol Brilliant Blue R (Sigma) was used for preparing synthetic dye wastewater. NaCl (Merck), Na₂SO₄ (Merck) and distilled water were prepared to investigate the electrodegradation capability of fabricated electrode.

Studies of dye electrodegradation were executed with both cathode and anode of by coconut shell-based carbon electrode and Ti electrode (commercial plate), at a distance of 2.0 cm between themselves. The experiment was performed with a power supply of dc current (GW INSTEK sps-3610). Spectrophotometer UV-Vis double beam (Shimadzu UV-1800) was used to evaluate the efficiency of treatment.

2.2. Procedure

2.2.1. Fabrication of carbon electrode

Carbon electrodes were fabricated by using specific solvent. A 0.25 g of polyvinyl alcohol (PVA) was dissolved into 4 mL of distilled water at 80°C and stirred for 30 – 40 min. Then, 5 g of carbon powder (activated following procedure described by Aris et.al [16]) was promptly added using rotator drivestry to ensure homogeneity and subsequently dried at room temperature overnight. The sample was further prepared in a cylindrical mould (6 mm diameter) using 10 ton of one way compression force in a TarnoGrocki. Moulded carbon char was then dried at room temperature for 24 h and followed by oven drying at 110°C for 4 h.

Carbon electrode doping with PbO₂ was executed by electrodeposition process using 0.12 M Pb(NO₃)₂, 0.886 M HNO₃ and 0.02 M NaF. It was done at potential of 3.5 V for 3.5 h using dc power supply (GW INSTEK sps-3610). Afterwards, PbO₂-doped carbon electrode was rinsed and soaked in distilled water into neutral pH. It was then doped by boron by adding 0.5 g H₃BO₄ to precursor mixture of PVA, carbon and distilled water before the moulding process.

2.2.2. Electrodegradation of anthraquinone dye

Electrodegradation was done with a single electrolysis cell (see Fig.1) with 50 mL working volume. Anode (coconut shell-based carbon electrode) with 5.65 cm² active surface area was placed vertically in pair with the cathode (Ti plate) at a distance of 2.0 cm. Remazol brilliant blue r (anthraquinone dye) with molecular formula of C₂₂H₁₆N₂Na₂O₁₁S₃ and molecular weight of 626,5 g/mol was used as the target of experiment. An investigation of degradation efficiency was carried out on varied carbon particle size (100 and 200 mesh), electrolyte solution (NaCl and Na₂SO₄), electrolyte concentration, potential (5, 6, 7 V), and doping (PbO₂ or Boron).

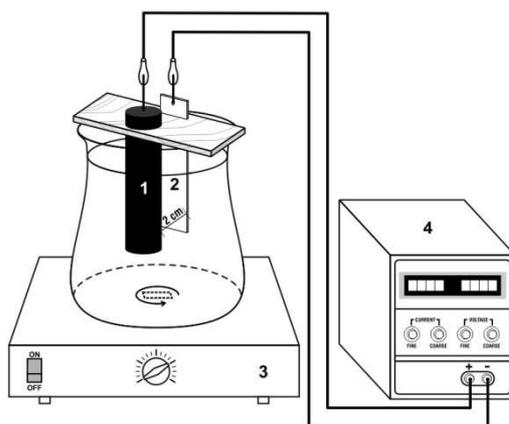


Fig. 1. Electrodegradation cell of Remazol Brilliant Blue R dye; (1) Anode (coconut shell-based carbon electrode), (2) Cathode (Ti), (3) Magnetic Stirrer, and (4) DC power supply

RESULTS AND DISCUSSION

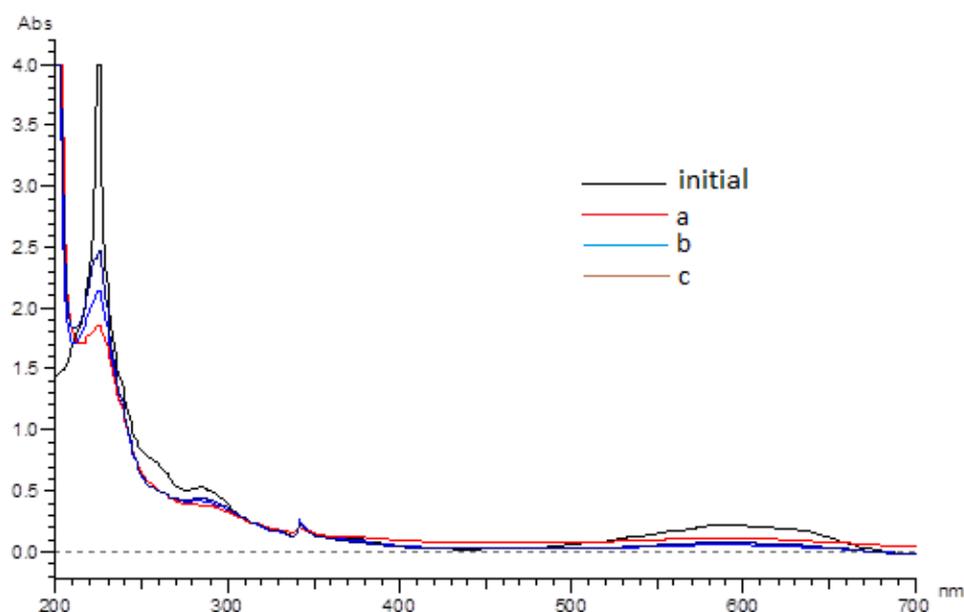


Fig. 2. The UV-Vis spectrum data representing dye degradation using (a) graphite, (b) 200 mesh, and (c) 100 mesh carbon

UV-Vis spectrum data of Remazol Brilliant Blue r degradation shows the effect of electrolysis run, as illustrated in Fig. 2. The occurrence of dye degradation is evident from the decreased intensity of absorbance peaks on visible and UV area, as tabulated in Table 1.

Table1. Absorbance reduction percentage of maximum peaks of RB 19 on varied electrode after electrolysis

No	Wavelength (λ)	Absorbance reduction percentage (%) after electrolysis		
		Graphite	100 mesh carbon	200 mesh carbon
1	590 nm	49	67	75
2	226 nm	54	38	42

Electrodegradation performance of coconut shell-based carbon electrode is quite similar to commercial graphite electrode, especially of 200 mesh carbon, where a higher reduction of intensity on visible wavelength (590 nm) was obtained. This in turn ensures the capability of synthesized electrode on degrading dye and is feasible to be further studied. The 200 mesh carbon electrode shows a higher performance; it is possibly caused by: (1) higher surface area, (2) higher value of electrical conductivity that will facilitate electron transfer and (3) greater stability in respect of rigid form.

It was interesting to note that coconut shell-based carbon electrode shows high performance on dye electrodegradation, thus the optimum design parameters need to be further investigated. Electrolyte solution and potential are two affecting parameters to the performance of electrochemical process. NaCl and Na₂SO₄ solutions were used to study the effect of electrolyte, as shown in Fig. 3.

UV-Vis spectra shows no effect of NaCl concentration on performance of degradation. It is proven that Cl₂, HClO, or ClO⁻ generated by chloride ion (Cl⁻) oxidation are not responsible for dye degradation, possibly because it is carried out by specific oxidator or by direct oxidation process. Several studies mentioned that the degradation of organic compounds occurred at the anode by adsorbed hydroxyl radicals (\cdot OH) or chemisorbed active oxygen at the surface of anode, commonly known as anodic oxidation. [5,15,17] The mechanism of direct oxidation is as follow :



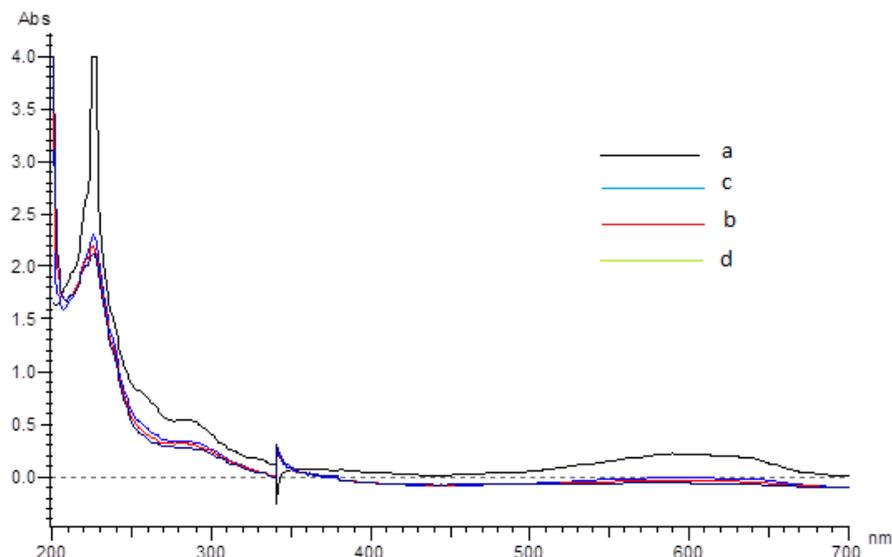


Fig. 3. UV-Vis spectra of RB 19 degradation using coconut shell-based carbon electrode on varied NaCl concentration (a) initial, (b) 2400 mg/L, (c) 3600 mg/L and (d) 4800 mg/L for 60 min

The mechanism explains that pollutant is adsorbed at the surface of anode and degraded by electron transfer reaction.

Similar trend was observed when using Na_2SO_4 electrolyte, as seen in Fig. 4. Higher concentration of Na_2SO_4 do not necessarily lead into reduction of absorbance intensity. This indicates that anion generated by electrolyte has no active role in forming dye oxidator. However, it is known that cation-anion generated solely act as charge carrier between electrodes.

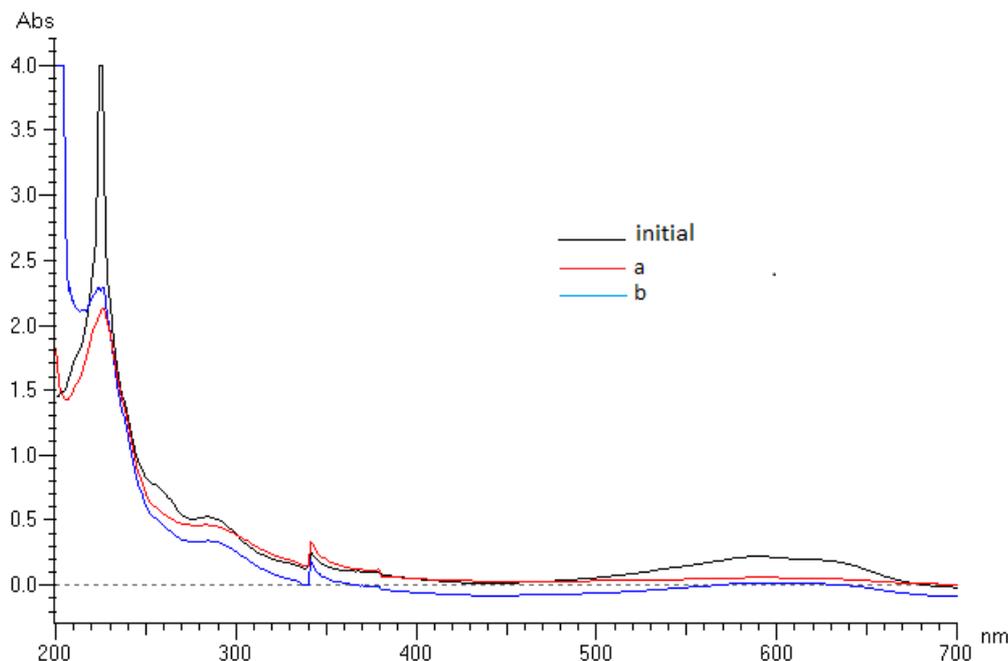
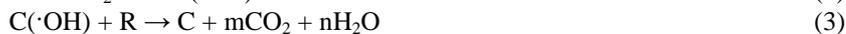
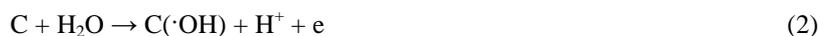


Fig. 4. UV-Vis spectra of RB 19 electrodegradation using 200 mesh carbon electrode and Na_2SO_4 electrolyte of (a) 1000 mg/L and (b) 2000 mg/L

Degradation mechanism by forming hydroxide radical ($\cdot\text{OH}$) is as follows :



Based on those reactions, it is obvious that hydroxide radicals are generated from water molecule as solvent. Peralta-Hernandez[18], reported another reaction of oxygen evolution of $\text{C}(\cdot\text{OH})$, as follows:



However, some researchers reported that pollutants were completely mineralized by generated $\cdot\text{OH}$ species on the incineration process by carbon anode at high potential.[19]

The effect of potential on the performance of dye electrodegradation was evaluated using measured applied potentials (5, 6, and 7 V). The observed effect is shown in UV-Vis spectra in Fig. 5

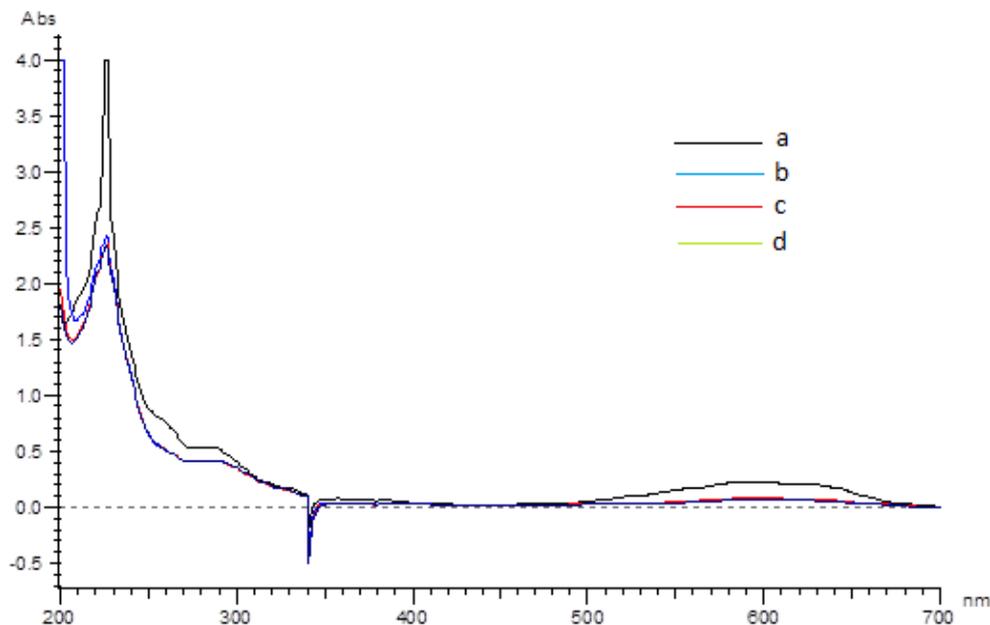


Fig. 5. UV-Vis spectra of RB 19 degradation using fabricated carbon electrode and Na_2SO_4 electrolyte at varied applied potential: (a) initial, (b) 5 V, (c) 6 V and (d) 7 V for 60 min

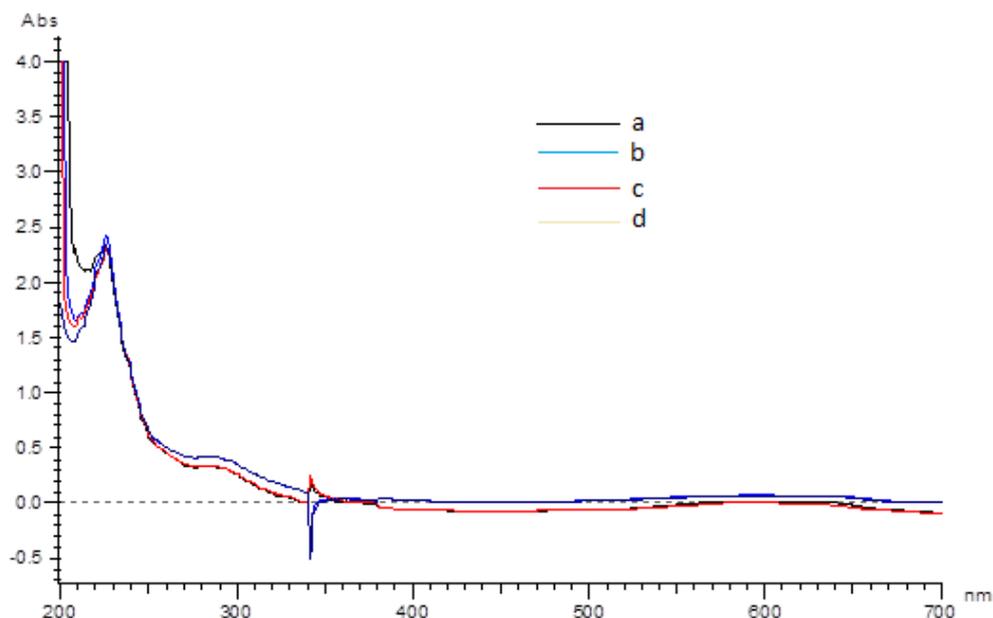


Fig. 6. UV-Vis spectra of RB 19 electrodegradation using fabricated carbon electrode in (a) NaCl 2400 mg/L at 5 V, (b) Na_2SO_4 2000 mg/L at 5 V, (c) NaCl 2400 at 7 V, and (d) Na_2SO_4 2000 mg/L at 7 V

The increase of potential from 5 to 6 and 7 V was clearly not linked to the improvement of performance of electrodegradation. Hence, applied potential of 5 V is, more or less, sufficient in order for the electrode reaction to proceed. Based on the observation that increasing applied potential will not enhance oxidation, therefore, it can be concluded that the limiting parameter of electrode reaction of electrochemical system is highly dependent on the surface area of electrode, instead of applied potential. This conclusion is supported by spectra data detailed in Fig. 6. The increase of applied potential and type of electrolyte show no significant impact on the decrease of absorbance.

This trend corroborates that (1) surface area of electrode is the limiting electrode reaction, (2) electrolyte only has a main role as charge carrier.

The performance of carbon electrode was expected to be enhanced by doping active material into electrode.

PbO₂ and boron, as highly electroactive and cheap materials, were doped into carbon electrode by applying Pb²⁺ electrodeposition method. Fig. 7 shows the performance of aforementioned doped carbon electrode.

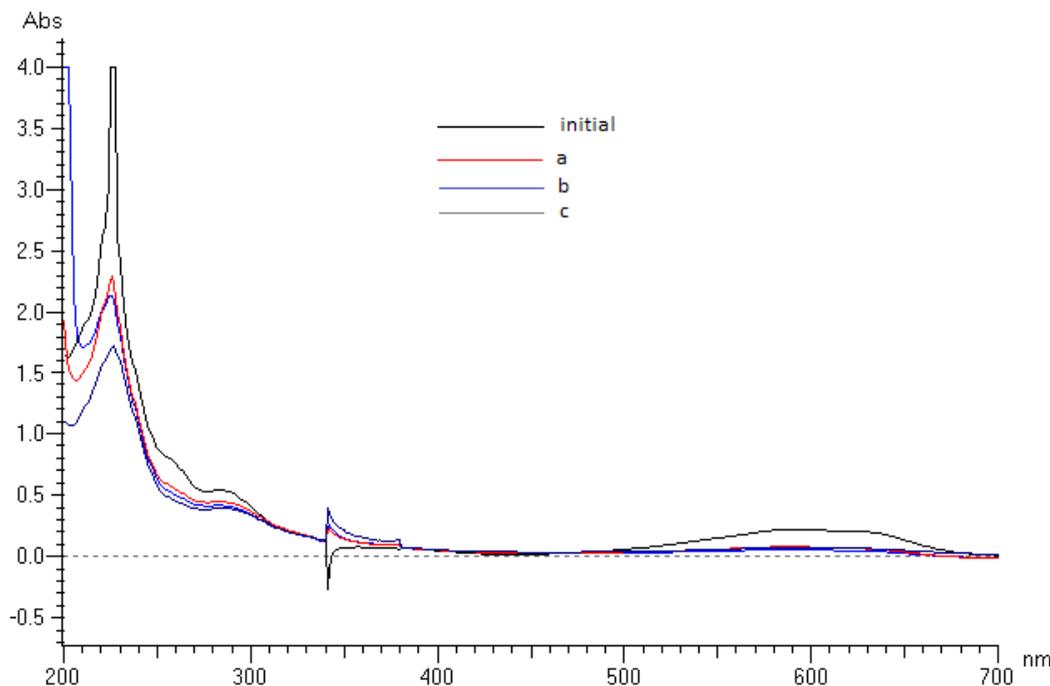


Fig. 7. UV-Vis spectra of dye electrodegradation using (a) 100 mesh carbon, (b) PbO₂ doped carbon, and (c) Boron doped carbon electrodes

PbO₂-doped carbon electrode was evidently not able to increase the performance of dye electrodegradation, as seen in Fig. 7. On the contrary, it shows negative effects, such as: (1) lower performance, and (2) lower endurance of electrode, which are evident by a higher peak of absorbance at UV region and higher intensity of absorbance at 200 – 220 nm when using doped electrode compared to non-doped electrode.

It should be noted that a different trend was observed when using boron-doped carbon electrode. The performance of electrodegradation was increased significantly, as shown by the absorbance data on UV region (226 nm wavelength). However, it was found that the dissolution of carbon will lead into instability of electrode, which is unfavorable in respect of material. The dissolution can be attributed to the acidic condition due to the solvation or oxidation of boric acid as the main precursor during the electrodegradation process.

CONCLUSION

Coconut shell char is a suitable precursor for the fabrication of carbon electrode. The performance of dye electrodegradation is comparable to those of graphite electrode, with 49% and 75% removal efficiency on UV and visible regions. Pollutants are degraded by direct oxidation and are not affected by either type or concentration of electrolyte and potential. Doping of PbO₂ and boron on electrode shows a conflicting effect on the performance of electrodegradation process.

Acknowledgments

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