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Treatment of Reactive Black 5 by combined electrocoagulation–granular activated carbon adsorption–microwave regeneration process

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ABSTRACT

Treatment of an azo dye, Reactive Black 5 (RB5) by combined electrocoagulation-activated carbon adsorption–microwave regeneration process was evaluated. The toxicity was also monitored by the *Vibrio fischeri* light inhibition test. GAC of 100 g L^{-1} sorbed 82% of RB5 (100 mg L^{-1}) within 4 h. RB5-loaded GAC was not effectively regenerated by microwave irradiation (800 W, 30 s). Electrocoagulation showed high decolorization of RB5 within 8 min at pH_0 of 7, current density of 277 A m^{-2}, and NaCl of 1 g L^{-1}. However, 61% COD residue remained after treatment and toxicity was high (100% light inhibition). GAC of 20 g L^{-1} effectively removed COD and toxicity of electrocoagulation-treated solution within 4 h. Microwave irradiation effectively regenerated intermediate-loaded GAC within 30 s at power of 800 W, GAC/water ratio of 20 g L^{-1}, and pH of 7.8. The adsorption capacity of GAC for COD removal from the electrocoagulation-treated solution did not significantly decrease at the first 7 cycles of adsorption/regeneration. The adsorption capacity of GAC for removal of both A_{265} (benzene-related groups) and toxicity slightly decreased after the 6th cycle.

1. Introduction

Textile wastewater is a major water pollution source in developing countries and often contains high concentrations of unfixed dyes (about 20%). Azo dyes are of great concern because of their widespread use, toxic aromatic amine intermediates, and recalcitrance for aerobic wastewater treatment [1]. Several techniques have been applied to remove dyes from wastewater, including adsorption, chemical oxidation, electrochemical degradation, and advanced oxidation processes. However, their low removal abilities or high costs often limit their application [2].

Electrocoagulation (EC) is a simple and cost-effective approach for wastewater treatment [3,4]. According to recent reports, electrocoagulation can treat dye and actual textile wastewater effectively and rapidly [4–7]. EC usually utilizes aluminum or iron as sacrificial anodes to produce metallic hydroxide coagulants, which can remove dyes from wastewater through precipitation and adsorption [5]. Chloride is often used as supporting electrolyte. The important factors influencing the effectiveness of dye and dyehouse effluent treatment with EC are nature of dye, electrode material, current density, solution pH, and electrolyte concentration and type [4,7–10]. Emamjomeh and Sivakumar [4] reviewed the fundamental theories of electrocoagulation and its application on dye/textile and organic and inorganic pollutants removal. Chatzisymeon et al. [11] utilized electrocoagulation to treat textile dyes and actual dyehouse effluents. They reported that the performance of electrocoagulation increased with increasing current intensity and salinity and decreasing solution pH.

During EC, chloride is anodically converted to active chlorine, which can oxidize the dye, leading to decolorization [4,10,12]. Even though EC can effectively decolorize dye wastewater, effluents may contain high concentrations of COD, residual chlorine/hypochlorite, and toxic intermediates. These may pose risks to environmental health. Both the chlorine and intermediates should be removed before discharge. However, the studies on removal of toxic EC-treated dye solution are limited.

Granular activated carbon (GAC) with extended porous surface area and surface activity can effectively adsorb various classes of dyes [13]. However, because of its high cost, the exhausted GAC needs to be regenerated for reuse. The common techniques for GAC regeneration include thermal, chemical, and biological regeneration [14]. Their high-energy consumption, long regeneration time, and adsorption capacity loss often limit their application. Microwave (MW)-assisted granular activated carbon

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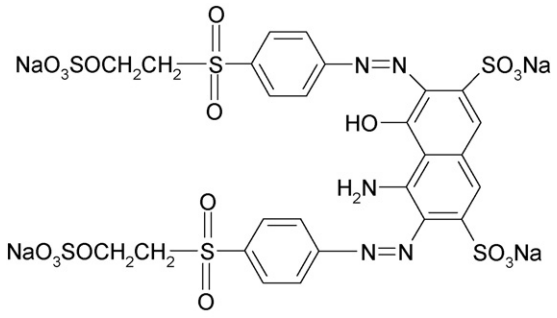

Fig. 1. Molecular structure of C.I. Reactive Black 5 (RB5, azo dye), λ_{max} = 597 nm.

(GAC) regeneration recently attracted attention because it has the advantages of short reaction time, energy savings, and high degradation [15]. The factors influencing MW regeneration performance are activated carbon property, nature of dye, oxygen supply, MW power, and irradiation time [15–17]. MW regeneration has been used on GAC exhausted by dye [14,17,15], pharmaceuticals [18], and phenolic compounds [16,19,20]. However, the studies on MW generation of dye intermediate-loaded GAC are limited.

Bioassays provide valuable information to reflect the toxicity of mixed solution on living organisms. *Vibrio fischeri*, a marine luminescent bacterium, can rapidly and sensitively detect a variety of toxic substrates. The toxic chemicals can interfere with the respiratory electron transfer system in *V. fischeri* and inhibit its light production. *V. fischeri* bioassay can be used as a warning for biotoxicity, because structural determinants associated with *V. fischeri* are similar to those associated with mammals and fish [21]. *V. fischeri* light inhibition test is often used to evaluate the biotoxicity of effluents. The *V. fishcheri* light inhibition test has been used to evaluate the toxicity of dye and textile wastewater during different treatment processes [11,22–25]. For example, Girotti et al. [24] reported that bioluminescent bacteria can be used to monitor industrial wastewater during treatment. Wang et al. [22] found that RB5 intermediates generated during ozonation are toxic to *V. fischeri*. Chatzisymeon et al. [11] found that the toxicity of textile effluents increased sharply after electrochemical oxidation. In our previous study, we also reported that the toxicity of C.I. Acid Black 1 solution treated by Fenton oxidation is higher than that by Fe^0/air treatment [25].

In this study, an azo dye, I.C. Reactive Black 5 (RB5), was selected as the model dye. RB5 is a common di-azo reactive dye used for dying cotton and other cellulose fibers [10]. Several studies have reported that RB5 and its degradative intermediates are biotoxic [22,23,26]. RB5 above 100 mg L^{-1} is 100% toxic to *Daphnia magna* [26]. The RB5 intermediates generated during ozonation and electrochlorination are toxic to *V. fischeri* [22,23]. The aims of the study are to investigate (1) the feasibility of combined electrocoagulation–GAC adsorption to treat RB5, (2) the effectiveness of microwave irradiation on GAC regeneration, and (3) the toxicity evolution of dye solution during treatments.

2. Materials and methods

2.1. Chemicals

The RB5 (C.I. No. 20505; $C_{26}H_{21}Na_4N_5O_{19}S_6$, M.W. = 991.8 g mol^{-1}, 55% purity, Fig. 1) was purchased from Sigma–Aldrich and was used as received. $Na_2S_2O_3{\cdot}5H_2O$ was obtained from Osaka (analytic grade, Japan). Sodium chloride was obtained from Panreac (analytic grade, purity 99%, Spain).

2.2. Electrocoagulation experiment

EC experiment was conducted in a 600 mL beaker containing 500 mL of RB5. If not mentioned otherwise, the RB5 concentration used in this study was 100 mg L^{-1}. The anode and cathode material was cast iron. The immerged area of the electrode was 4 cm × 7 cm, and the gap between cathode and anode was 1 cm. The electrodes were rinsed in 30% HNO_3 and washed with distilled water before the experiment. The EC experiment was conducted under galvanostatic conditions using a regulated DC power supply (GPC-3030D, Taiwan). The solution was continuously mixed by a magnetic stirrer. The initial solution pH was adjusted with diluted sodium hydroxide or diluted hydrochloric acid and measured by pH meter (Cyberscan 510, Taiwan).

The UV–visible spectrum during the RB5 degradation was measured at 200–800 nm using a UV–visible spectrophotometer (Shimadzu, UV-mini 1240, Japan). The maximum absorption wavelength for RB5 is 597 nm at pH 7. The concentration of the EC-treated RB5 solution was measured based on the constructed calibration curves at absorption wavelength of 597 nm. A 5-point calibration was carried out. The apparent molar extinction coefficient (ε) of the RB5 observed at 597 nm was 45,500 M^{-1} cm^{-1}. The sample was diluted with distilled water if the absorbance exceeded the range of calibration curve. COD was determined according to standard method for examination of water and wastewater [27].

2.3. GAC adsorption experiments

A commercial coconut-based granular activated carbon (GAC, 4.76 mm diameter, 10 mm length, Hong-Yu, Taiwan) was used as received. The surface area of GAC was measured by BET (Brunauer–Emmett–Teller-method). BET surface area was measured at 77 K on a BET Specific Surface Area Analyzer (Micromeritics Gemini 2370C). N_2 adsorption–desorption on the surface was used to determine textural properties. The specific surface area of GAC was 763 m^2 g^{-1}. The pH_{zpc} of GAC was measured by Zeta-Meter 3.0+ (Zeta-Meter Inc., USA). The pH_{zpc} of the GAC was 5.5.

For GAC adsorption experiment, known amounts of GAC ash were added to a 300 mL flask containing 100 mL of either untreated RB5 or EC-treated RB5 solution. The initial solution pH was adjusted by addition of 0.1 M of either NaOH or HCl. The flask was sealed with parafilm and shaken in a water bath (20 °C, 50 rpm). At pre-set time intervals, 3 mL samples were taken, filtered by Whatman GF/A, and analyzed by UV–vis spectrophotometer (Shimadzu, UV-mini 1240, Japan). COD was used to determine the organic content of RB5 and intermediates in the solution. The adsorption capacity of GAC was calculated according to the difference of COD amounts before and after GAC adsorption.

2.4. Microwave regeneration of GAC experiment

Distilled-deionized water was used for all microwave regeneration cycles. The operating conditions for MW regeneration of exhausted GAC were 20 g of GAC in 1 L of distilled-deionized water. The solution pH was adjusted to 7 by diluted NaOH and HNO_3. A domestic MW oven (2450 MHz, 800 W, Panasonic-NEV27, Taiwan) was used. After MW irradiation treatment, the solution was withdrawn, centrifuged, and analyzed for COD, UV–vis spectrum, and biotoxicity. The regenerated GAC was added into EC-treated RB5 solutions (pH 7.8) to evaluate its adsorption capacity.

2.5. V. fischeri light inhibition test

The marine luminescent bacteria *V. fischeri* (NRRL B-11117), obtained from DSMZ (Germany), was employed to evaluate the

biotoxicity of dye solution during treatments. The cultivation of luminescent bacteria and toxicity evaluation procedure were according to ISO 11348-1 standard protocol. The solution sample was adjusted to pH 7.0 ± 0.2. *V. fischeri* was exposed to the solution samples for 5 min as determined by a luminometer at 15 °C. Phenol was used as the positive control with EC_{50} ranging from 13 to 26 mg L^{-1}. Toxicity was expressed as the light inhibition ratio and was calculated as follows [28]:

$$\text{inhibition ratio } (\%) = \frac{I_0 \times f_k - I_f}{I_0 \times f_k} \times 100\%,$$

where f_k was the correction factor at t = 5 min, and $f_k = I_{kc}/I_{0c}$. I_{0c} and I_{kc} were the luminescence intensity of the control sample at t = 0 and 5 min, respectively. I_0 and I_f were the luminescence intensity of the sample at t = 0 and 5 min, respectively. The bioluminescence intensity of *V. fischeri* may decrease with exposure time. The correcting factor f_k is used to correct the luminescence intensity of the test sample at t = 0 min. Therefore, in this study, the inhibition ratio (percentage) was used to represent the biotoxicity of pollutants instead of inhibition percentage of the bioluminescence.

3. Results and discussion

3.1. GAC adsorption of RB5 and MW regeneration of exhausted GAC

Adsorption of RB5 onto GAC was evaluated at solution pH of 5.6. As expected, RB5 removal increased with an increase in the GAC dose (Fig. 2a). GAC of 100 g L^{-1} removed 82% of COD after 4 h adsorption. Since GAC is costly, the regeneration of exhausted GAC by MW was evaluated and the operating conditions were pH of 5.6, GAC/distilled-deionized water ratio of 20 g L^{-1}, and irradiation time of 30 s. After microwave irradiation, the regenerated GAC was again added into the 100 mg L^{-1} of untreated RB5 solution to evaluate its adsorption capacity. Fig. 2b indicates that the MW-regenerated GAC only removed 36% COD from the untreated RB5 solution. It is possible that the short irradiation time could not effectively regenerate the exhausted GAC.

3.2. RB5 treatment by electrocoagulation

Treatment of RB5 solution by EC was investigated. Fig. 3a depicts the influences of current density (CD) on RB5 decolorization at the operating conditions: initial solution pH of 7 and NaCl of 1 g L^{-1}. An increase in current density enhanced decolorization. This is because the high CD enhanced the generation of iron hydroxide coagulant (Eqs. (1) and (2)) [8] and active chlorine (Eqs. (3) and (4)) [10,29]. The active chlorine also can enhance the production of iron hydroxide coagulants (Eq. (5)) and directly decolorize dye (Eq. (6)) [4,10,12], resulting in enhancement of decolorization

$$\text{anode}: \quad Fe_{(s)} \rightarrow Fe^{2+} + 2e^- \tag{1}$$

$$\text{solution}: \quad Fe^{2+} + O_2 + H_2O \rightarrow Fe(OH)_3 + H^+ \tag{2}$$

$$\text{anode}: \quad 2Cl^- \rightarrow Cl_2 + 2e^- \tag{3}$$

$$\text{solution}: \quad Cl_2 + H_2O \rightarrow HOCl + HCl \tag{4}$$

$$\text{solution}: \quad HOCl + 2Fe^{2+} \rightarrow 2Fe^{3+} + Cl^- + OH^- \tag{5}$$

$$\text{solution}: \quad \text{dye} + Cl_2 \rightarrow \text{oxidizeddye} + 2Cl^- \tag{6}$$

Energy consumption is an important concern for dye treatment. In this study, the energy consumptions for RB5 decolorization at CD of 277 and 544 A m^{-2} were 0.017 and 0.034 kWh g^{-1}, respectively. Therefore, CD of 277 A m^{-2} was selected for sequential study.

The effect of NaCl on RB5 decolorization was evaluated. An increase in the NaCl dose enhanced decolorization. A high chloride concentration can enhance decolorization because (1) it increases solution conductivity, thus reducing the energy consumption [10], and (2) it increases the active chlorine production [10,12,29]. The effect of initial solution pH on decolorization by EC was also evaluated. The operating conditions were CD of 277 A m^{-2} and NaCl of 1 g L^{-1}. Fig. 3c indicates that the initial solution pH did not obviously affect RB5 decolorization. On the other hand, solution pH can influence (1) the oxidation kinetics of Fe^{2+} to Fe^{3+} [10], (2) the surface charge of coagulating particles [8,10], (3) the ratio of hypochlorous acid (E^0 = 1.49 V) and hypochlorite ion (E^0 = 0.94 V) in solution. The phenomenon that there was no difference in decolorization between pH 4 and 9 was also was observed by Şengil and Özacar [10].

The changes of solution pH during electrocoagulation at different initial solution pH (5, 7, and 9) were monitored. Fig. 3d indicates the solution pH increased with increased time. The pH of these three solutions reached 9.5–9.6 at 6 min, and after that the solution pH changed slightly. The solution pH most probably increased for all studied initial pH's as a consequence of cathodic OH^- formation (Eq. (7))[7].

$$\text{cathode}: \quad 2H_2O_{(aq)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)} \tag{7}$$

Fig. 3e shows the influence of RB5 concentrations on decolorization. The EC conditions were pH of 7, CD of 277 A m^{-2}, and NaCl of 1 g L^{-1}. The increase in RB5 concentration reduced the decolorization. For example, EC completely decolorized RB5 of 50 mg L^{-1} within 4 min. In contrast, when RB 5 concentration increased to 200 mg L^{-1}, 91% color removal was obtained after 10 min. It is probable that the adsorption capacity of metallic hydroxide flocs was not enough for dye adsorption at RB5 of 200 mg L^{-1} [30]. COD removal and toxicity are also important parameters for effluent quality. Fig. 3f indicates that even though 99% of RB5 was decolorized at 8 min, only 39% of COD removal was achieved.

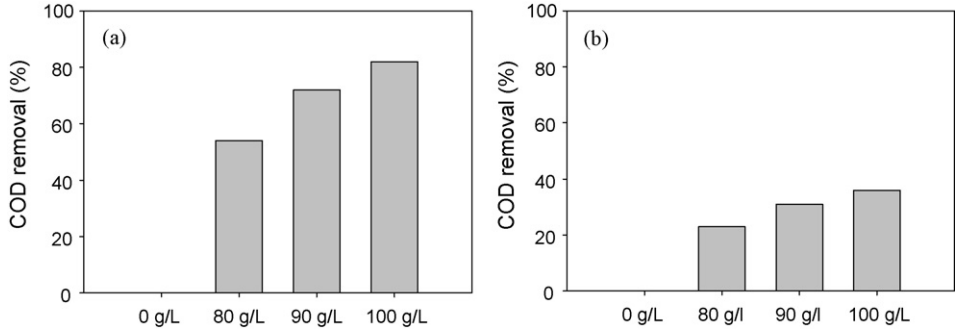

Fig. 2. GAC adsorption of Reactive Black 5: initial and after regenerated by microwave irradiation; (a) GAC adsorption of RB5 (100 mg L^{-1}), pH_0 of 5.6, adsorption time of 4 h, and (b) RB5-loaded GAC regenerated by microwave, GAC/water of 20 g L^{-1}, pH_0 of 5.6, microwave power 800 W, irradiation time of 30 s.

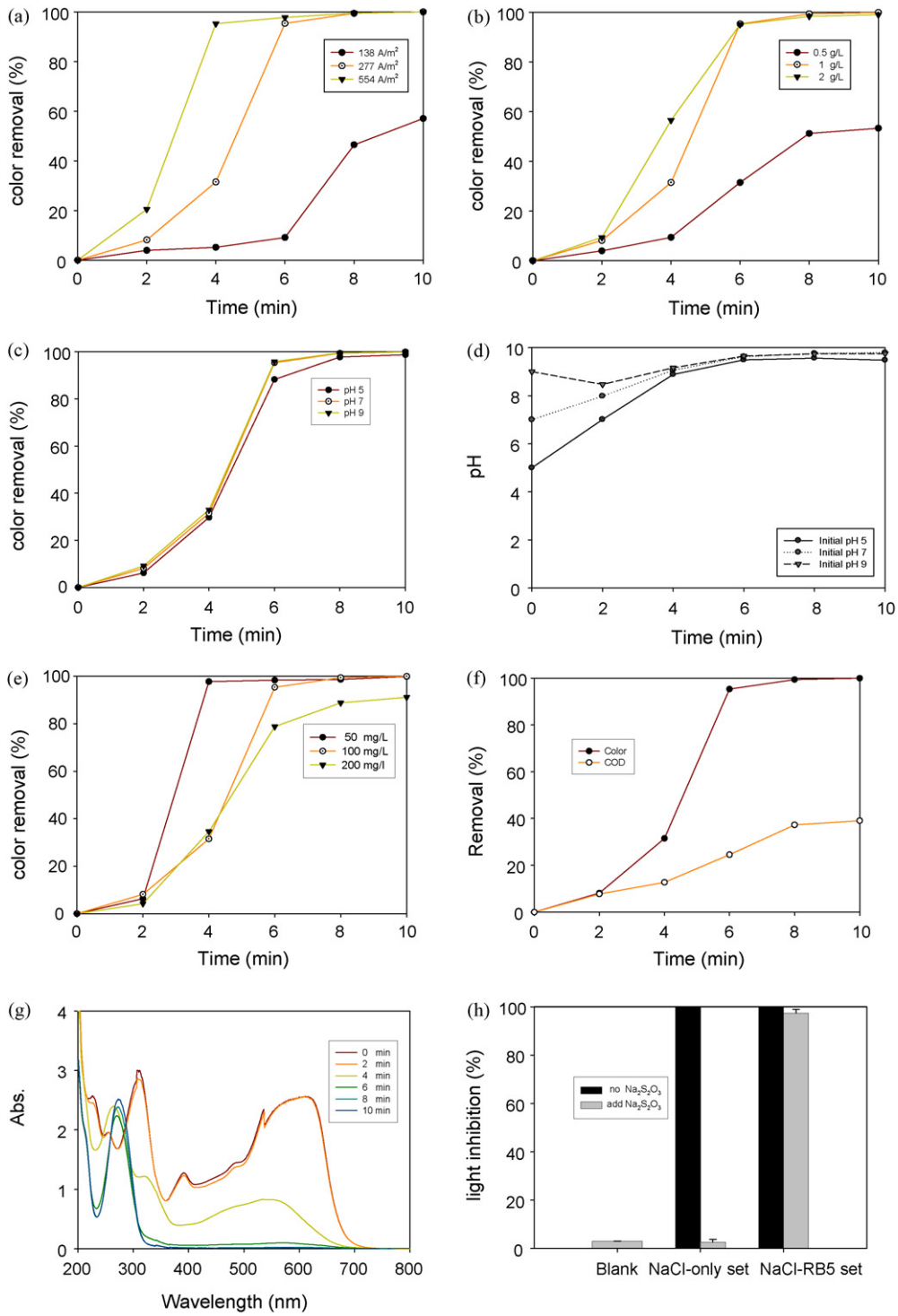

Fig. 3. Electrocoagulation (EC) treatment of Reactive Black 5. If not mentioned, RB5 of 100 mg L^{-1}, pH_0 of 7, current density of 277 A m^{-2}, and NaCl of 1 g L^{-1}; I: color removal influenced by (a) applied current density, (b) NaCl, and (c) initial solution pH. (d) Changes of solution pH during EC. (e) Color removal influenced by RB5 concentration; II: (f) color and COD removal by EC; III: (g) UV–vis spectrum change during EC; IV: (h) *Vibrio fischeri* light inhibition of EC-treated NaCl-only and RB5 sets before and after 20 g L^{-1} $Na_2S_2O_3$ addition, EC treatment time of 8 min.

COD removal did not increase obviously with a prolongation of the EC time. Also, EC and active chlorine did not further remove RB5 intermediates. When operating conditions were current density of 277 A m^{-2}, NaCl of 1 g L^{-1}, initial solution pH of 7, and electrocoagulation time of 10 min, the weight loss of anode was 0.091 g and 0.316 kg of solids produced per cubic meter of treated effluent resulting from the metallic hydroxides formation and dye removal.

The UV–vis spectrum change of RB5 solution during EC was also investigated. For RB5, the adsorption peaks at wavelength 597 and 310 nm are attributed to azo bond and naphthalene components, respectively [8]. Fig. 3g illustrates that the UV–vis band absorption at 320–700 nm completely diminished after 8 min. However, there still was a UV-band absorption peak at about 265 nm. Libra et al. [31] reported that the RB5 anchor group metabolite *p*-aminobenzene-2-hydroxyethylsulfonic acid (*p*-ABHES) has an

absorption peak at 265 nm. The A_{265} of the electrocoagulation-treated RB5 solution should be attributed to benzene-related intermediates. Chemical identification was not conducted in this study to identify the intermediates. Prolongation of EC time to 10 min did not further diminish the UV-bands at 200–320 nm. This implies that EC and active chlorine did not effectively remove the A_{266}-related intermediates.

EC with chloride as supporting electrolyte can generate toxic products such as chlorine/hypochlorite and dye-byproducts. The *V. fischeri* light inhibition test was used to monitor the toxicity changes in solution. The NaCl-only set (NaCl of 1 g L^{-1}, CD of 277 A m^{-2}, pH_0 of 7 and 8 min treatment) was evaluated before and after $Na_2S_2O_3$ addition. First, the background toxicity of $Na_2S_2O_3$ to *V. fischeri* was evaluated. Fig. 3h indicates that 20 g L^{-1} only had a slight influence on *V. fishcheri* (3% light inhibition). The NaCl-only set exhibited high toxicity (100% light inhibition) before $Na_2S_2O_3$ addition. $Na_2S_2O_3$ of 20 g L^{-1} effectively reduced the toxicity of chlorine/hypochlorite generated during EC. Therefore, 20 g L^{-1} of $Na_2S_2O_3$ was used to remove the toxicity of chlorine/hypochlorite in the subsequent study. The toxicity of EC-treated RB5 solution (ECTS, RB5 of 100 mg L^{-1}, NaCl of 1 g L^{-1}, CA of 277 A m^{-2}, pH_0 of 7 and 8 min treatment) was also investigated. Fig. 3h shows that toxicity of the ECTS was high (100% light inhibition) before $Na_2S_2O_3$ addition. After addition of $Na_2S_2O_3$, the toxicity of ECTS was still high (97% light inhibition). This suggests that RB5 intermediates were also a major toxicity source of the ECTS. Even though EC rapidly decolorized RB5, only 39% COD removal was achieved and the ECTS was highly toxic. The COD residue and toxicity should be mitigated before discharge.

3.3. GAC adsorption of EC-treated RB5 solution

The effect of GAC addition on the COD removal of ECTS was investigated (Fig. 4a). GAC adsorbed most RB5 intermediates from ECTS, and 20 g L^{-1} of GAC significantly decreased COD/COD_0 from 61% to 7% after 4 h adsorption. However, an increase in the GAC dose to 40 g L^{-1} did not further reduce COD. This suggests that a slight amount of intermediates present in the ECST was not effectively removed by GAC. Fig. 4b shows the spectrum change of ECTS by GAC adsorption. The A_{266} decreased from 2.61 to 0.04 by 20 g L^{-1} of GAC after 4 h. This suggests that GAC effectively sorbed aromatic RB5 intermediates.

The effects of GAC addition on toxicity mitigation of the NaCl-set and ECST were also assessed. Fig. 4c illustrates that 20 g L^{-1} of GAC completely removed the toxicity of the NaCl-only set (<1%) after 4 h contact. This is because GAC can act as catalyst to chemically reduce strong oxidants to nontoxic products, e.g. chlorine/hypochlorite can be reduced to chloride [32]. The influence of GAC on toxicity mitigation of ECST was also evaluated. Fig. 4d illustrates toxicity evolution of ECST by GAC before and after $Na_2S_2O_3$ addition. GAC effectively reduced the toxicity of ECST within 4 h, whether $Na_2S_2O_3$ was added or not. This implies that GAC not only catalytically reduced chlorine/hypochlorite to chloride but also adsorbed toxic RB5 intermediates. Fig. 4b and d indicates that the trends of A_{266} and the intermediates toxicity were similar. This implies that the toxicity of RB5 intermediates may relate to A_{266}-related byproducts in the ECTS.

Because there are strong oxidants in the ECST, the effect of MW irradiation on COD removal of ECST was assessed. Fig. 5a and b indicates that the microwave irradiation (800 W, 30 s) had only a slight effect on COD removal and spectrum change of ECTS. This suggests that microwave irradiation could not enhance the removal of RB5 intermediates while strong oxidants are present in the ECTS. To conclude, GAC effectively removed COD and toxicity from ECTS. However, because GAC is costly, regeneration of exhausted GAC is needed for economical feasibility.

3.4. Microwave regeneration of spent GAC

The adsorption capacity of MW regenerated GAC was used to evaluate the effectiveness of MW regeneration. First, the RB5 intermediate-exhausted GAC was irradiated in distilled-deionized

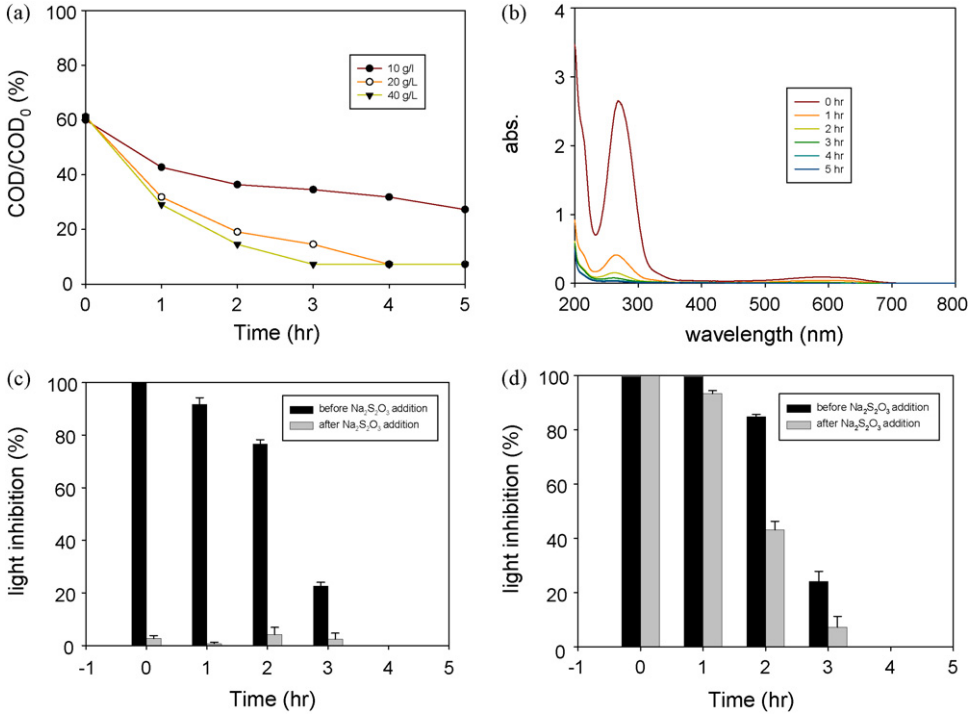

Fig. 4. GAC adsorption of electrocoagulation (EC)-treated RB 5 solution. EC conditions were RB5 of 100 mg L^{-1}, current density of 277 A m^{-2}, NaCl of 1 g L^{-1}, pH_0 of 7 and 8 min treatment. If not mentioned, experimental conditions for GAC adsorption were GAC of 20 g L^{-1} and pH_0 of 7.8. (I): (a) effect of GAC dose, (b) UV–vis spectrum change; (II) *Vibrio fischeri* light inhibition of NaCl-only set (c) and RB5 set (d) before and after 20 g L^{-1} of $Na_2S_2O_3$ addition.

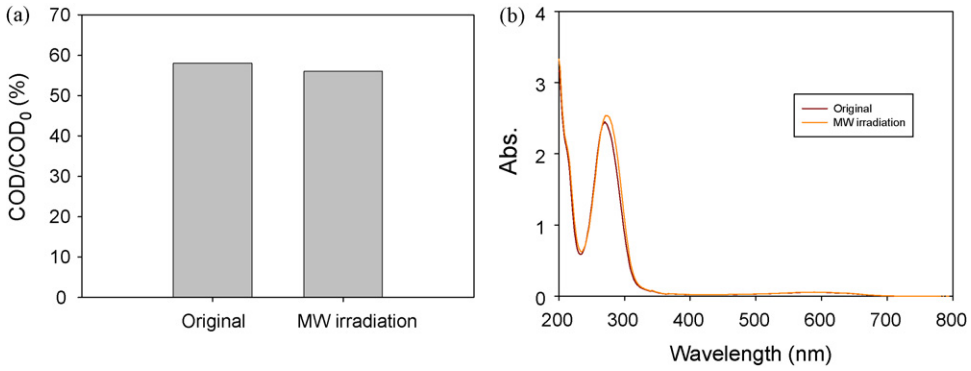

Fig. 5. Effect of microwave irradiation on electrocoagulation-treated RB 5 solution. EC conditions were RB5 of 100 mg L^{-1}, current density of 277 A m^{-2}, NaCl of 1 g L^{-1}, pH_0 of 7 and 8 min treatment. Microwave power of 800 W and irradiation time of 30 s: (a) COD removal and (b) UV–vis spectrum change.

water by microwave. Then, the regenerated GAC was reused for adsorption of ECST. The effect of MW irradiation time on MW regeneration was evaluated. The operating conditions were MW power of 800 W, GAC/water ratio of 20 g L^{-1}, and pH_0 of 7.8. Fig. 6a indicates that an increase in MW irradiation time enhanced GAC regeneration. When 30 s of MW regeneration was applied, the adsorption capacity of the regenerated GAC was similar to that of virgin GAC (Fig. 4a) and decreased the remaining COD percentage (COD/COD_0) of ECTS from 61% to 7% within 4 h adsorption. The effect of GAC/water ratio on GAC regeneration was also investigated. Fig. 6b shows that when the GAC/water ratio increased from 1:50 to 1:25, the adsorption capacity of regenerated GAC slightly decreased. The effect of the pH of the water on GAC regeneration was assessed. Fig. 6c indicates that the initial water pH, ranging from 5.2 to 9.2, did not significantly affect GAC regeneration. After MW regeneration, COD and toxicity of the water were 14 mg L^{-1} and 11% light inhibition, respectively, and it can be discharged directly or channeled to a wastewater treatment plant.

Because of its dielectric property, GAC can absorb microwave energy and convert it to heat due to space-charge polarization [33]. Several studies have reported that mechanisms responsible for MW regeneration of GAC are catalysis [15,17,20], free radicals [34], and high-energy plasma [17,35]. Zhang et al. [15] suggested that the uneven surface of GAC can sorb microwave energy and form a large number of hot spots that can oxidize organic pollutants. Quan et al. [34] used salicylic acid as molecular probe to detect hydroxyl radicals. They reported hydroxyl radicals can be generated by activated carbon powder under microwave irradiation. Dawson et al. [35] observed the plasma phenomenon, which is induced by microwave irradiation in a granular activated carbon fluidized bed.

In this study, only a short MW time was needed (30 s) to regenerate GAC. This is because the COD loaded on GAC was low (3.36 mg g^{-1}). Because the water temperature only increased from 25 °C to 59 °C after GAC regeneration, the loss of RB5 intermediates due to vaporization to air seems to be insignificant. Besides, the short irradiation time benefited the preservation of the microporosity of GAC despite the heat during GAC regeneration [16,36]. In

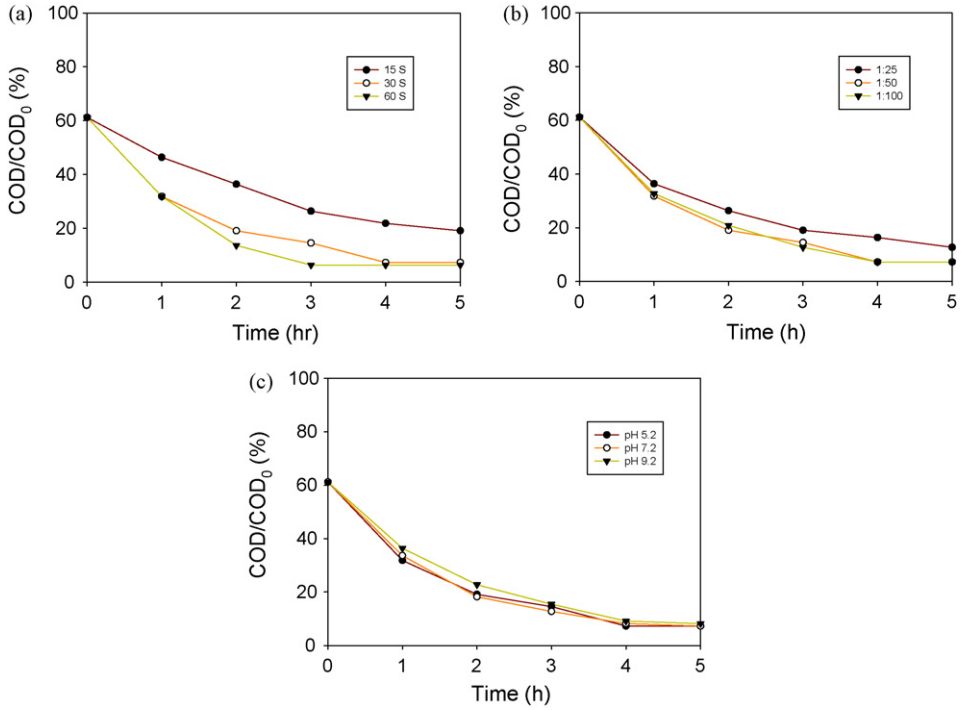

Fig. 6. Adsorption capacity of microwave-regenerated GAC for electrocoagulation-treated RB5 solution. Adsorption conditions were 20 g L^{-1} of GAC and pH_0 of 7.8. If not mentioned, the experimental conditions for GAC regeneration were 800 W, pH_0 of 7.8, and GAC/water ratio of 20 g L^{-1}; (a) effect of MW irradiation time, (b) effects of GAC/water ratio, and (c) effect initial water pH.

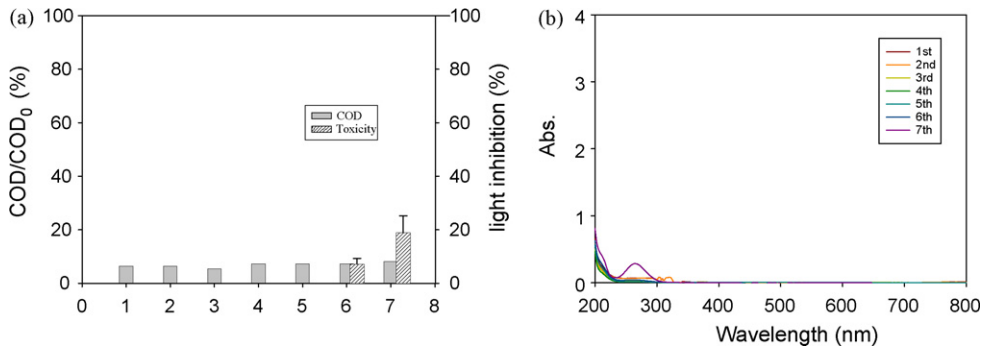

Fig. 7. Influences of adsorption/regeneration cycles on GAC adsorption capacity of electrocoagulation-treated solution. Adsorption conditions were 20 g L^{-1} of GAC, pH_0 of 7.8, and adsorption time of 4 h. MW regeneration conditions were 800 W, pH_0 of 7, GAC/water ratio of 20 g L^{-1}, and irradiation time of 30 s; (a) COD/COD_0 and toxicity and (b) spectrum change of EC-treated RB5 solution after adsorption.

this study, we only evaluated the effectiveness of microwave irradiation on regeneration of the RB5 intermediate-exhausted GAC. The surface of the treated GAC was not analyzed. MW irradiation may change the physicochemical surface properties of GAC, including the amount of catalyst surface area, total pore volume, pore size distribution, and surface chemistry [15–18]. The changes of physicochemical surface properties of GAC will influence the adsorption efficiency and rate. Further study on the surface of the treated GAC (exhausted and regenerated) is suggested.

Oxygen acts as an electron acceptor for organic oxidation during MW regeneration [17,20,34]. In this study, no oxygen was provided except for that dissolved in the water (DO of 6.4 mg L^{-1}). Compared to solution at GAC/water ratio of 1:50, the solution at GAC/water ratio of 1:25 contained less oxygen, which may have been insufficient for organic oxidation during MW regeneration of GAC. After MW regeneration of GAC, the water contained 0.014 mg L^{-1} COD; this is because the microwave dielectric heating enhanced desorption of RB5 intermediates from GAC [37,38]. However, the toxicity of water was slight (light inhibition of 11%).

3.5. *Effect of cycles of adsorption/regeneration on GAC adsorption capacity*

The effect of adsorption/regeneration cycles on GAC regeneration was investigated, and the adsorption capacity of GAC for ECTS was used as the index. The operating conditions for MW regeneration were GAC/water of 20 g L^{-1}, pH_0 of 7.8, and irradiation time of 30 s. As can be seen in Fig. 7a, the adsorption capacity of GAC for COD removal from ECTS did not significantly decrease at the first 7 cycles of adsorption/regeneration. However, the adsorption capacity of GAC for removal of both toxicity (Fig. 7a) and A_{266} (Fig. 7b) slightly decreased after the 6th cycle.

Two mechanisms may be responsible for the decrease in the adsorption capacity of GAC for toxicity and A_{266} removal: (1) The GAC loss during adsorption/MW regeneration cycles [16]. In this study, the GAC mass loss after 7 cycles of adsorption/regeneration was 3.5% compared to the virgin GAC. (2) Reduction of adsorption ability of GAC by MW irradiation [36]. In this study, an experiment was also conducted to investigate effects of MW irradiation-only on GAC. GAC was subjected to 30-s MW irradiation treatment for 7 cycles. Then, the MW-irradiated GAC was used for adsorption of ECTS. Spectrum result indicated that $A_{266} = 0.108$ remained in the ECST after MW-irradiated GAC adsorption (data not shown).

Even though the regenerated GAC maintained its COD removal capacities after 7 cycles of adsorption/MW regeneration, the removal ability of the GAC for toxicity and A_{266} slightly decreased. A small amount of new GAC is suggested to replenish the GAC ability for toxicity and A_{266}-related intermediate removal after the 6th cycle of adsorption/MW regeneration.

4. Conclusions

Even though EC rapidly decolorized RB5 solution at 1 g L^{-1} of NaCl, current density of 277 A m^{-2}, and pH_0 of 7, the EC-treated RB5 solution still contained 61% of COD and was highly toxic (100% light inhibition). Both the strong oxidants and intermediates generated during EC were responsible for solution toxicity. The addition of 100 g L^{-1} GAC removed 82% of RB5 after 4 h adsorption. However, the adsorption capacity of regenerated GAC for RB5 removal obviously decreased after 30-s microwave irradiation (800 W). GAC of 20 g L^{-1} effectively removed COD and toxicity of ECTS after 4 h adsorption. RB intermediate-loaded GAC was effectively regenerated by MW irradiation at MW power of 800 W, GAC/water of 20 g L^{-1}, and irradiation time of 30 s. Both irradiation time and GAC/water ratio were important factors for MW regeneration of exhausted GAC. The adsorption capacity of GAC for COD removal from EC-treated solution did not significantly decrease at the first 7 cycles of adsorption/regeneration. The adsorption capacity of GAC for removal of both A_{266} and toxicity slightly decreased after the 6th cycle.

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