Desalination and Water Treatment
www.deswater.com

27 (2011) 237–242
March

1944-3994/1944-3986
doi: 10/5004/dwt.2011.1980

The combination and optimization study on RB29 dye removal from water by peroxy acid and single-wall carbon nanotubes

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Received 1 May 2010; Accepted 22 August 2010

ABSTRACT

The presence of synthetic dyes in aquatic environments poses potential health and ecological risks. Several techniques are available for dyes' removal. In this study the degradation of an anthraquinone dye, Reactive blue 29 (RB29), using an advanced oxidation process followed by single-wall carbon nanotubes (SWCNTs) was investigated. Advanced oxidation process was optimized over a period of 60 min by varying the ratio of acetic acid to hydrogen peroxide, the compounds which form peroxy acid. Reduction of 20.2–56.4% of RB29 was observed when the ratio of hydrogen peroxide/acetic acid/dye changed from 344/344/1 to 344/344/0.08 at different times (60, 120 and 180 min). Hydrogen peroxide served as controls in all advanced oxidation process and demonstrated minimal degradation over the time course study. The optimum ratio of acetic acid/hydrogen peroxide/dye was found to be 344/344/0.16 over 60 min. The resultant then introduced for further removal by SWCNTs as adsorbent. The adsorption of RB29 onto SWCNTs was also solely investigated. The Langmuir, Freundlich and BET isotherms were determined and the result revealed that the adsorption of RB29 onto SWCNTs well explained by BET model and changed to Freundlich isotherm when SWCNTs used after the application of peroxy acid. The maximum adsorption capacity of RB29 by SWCNTs also decreased from 496 mg/g to 472 mg/g when SWCNTs used solely and in sequence with peroxy acid, respectively. The removal of RB29 using an advanced oxidation process prior to the application of SWCNTs was also optimized over a period of 2 h. Color removal obtained over 2 h was 67.8–84.4% depending on the amount of SWCNTs used. Further studies are needed to identify the effects of peroxy acid degradation intermediates and to investigate their effects on SWCNTs.

Keywords: Reactive blue 29; Peroxy acid; Adsorption isotherm; Single-wall carbon; Optimization; Nanotubes

1. Introduction

Disposal of dye-contaminated wastewater is one of the serious environmental problems. Dyes are extensively used in the textile, leather, paper and other industries. The complex aromatic structure of dyes makes them more stable and difficult to be removed from water bodies [1]. Textile manufacturing wastewater characterized by highly fluctuating pH, high chemical oxygen demand (COD), strong color and biotoxicity [2]. It has been estimated that approximately 50% of applied reactive dyes is wasted because of dye hydrolysis in the alkaline dye bath contains dyes at concentration in the range of 10–200 mg/l [3]. It has been documented that residual color is usually due to insoluble dyes which have low biodegradability as Reactive blue 21, direct

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blue 80 and vat violet with COD/BOD ratio of 59.0, 17.7, and 10.8, respectively [4].

Due to the regulations worldwide have grown stricter, the effluent of textile and related industries have to be treated before discharge to the environment. This has resulted in a highly demand for environmentally friendly technologies. Numerous approaches including electrochemical oxidation [5], ozone treatment [6], biological treatment [7], membrane filtration [8], and adsorption [9] have been applied to remove organic compounds. Promising results have been achieved using advanced oxidation processes (AOPs) for effluent from dye industries in recent years [10]. These processes are based on the production of highly reactive radicals, especially hydroxyl reactive radicals which promote destruction of the target pollutant until mineralization [11]. Moreover, adsorption technology with no chemical degradation is attractive due to its unique effectiveness, efficiency and economy [12]. Carbon nanotubes attracting increasing research interest as a new adsorbent. They are an alternative for the removal of organic and inorganic contaminants from water because they have large specific surface area, small size, hollow and layered structure [13]. CNTs have been proven to possess great potential as superior adsorbents for removing many kinds of organic and inorganic contaminants including 1,2-dichlorobenzene [14], trihalomethanes [15], fluoride [17], lead [18], nickel [19] and arsenate [20]. According to the grapheme layer, CNTs can be classified into single-wall CNTs (SWCNTs) and multi-wall CNTs (MWCNTs). Although SWCNTs have much greater specific surface area than MWCNTs, few research have focused on organic pollutants' removal by SWCNTs. In recent years, different studies have tried to increase the efficiency of AOPs by using various methods such as integrated (combined) process. The main purpose of integrating different treatment methods is to enhance the process efficiency as well as to reduce the operating cost. Owing to the high ratio of COD/BOD and non-biodegradability of reactive dyes, RB29 was chosen in this experiment. In this study the oxidative degradation of a reactive anthraquionone dye (RB29) in aqueous solutions using peroxy acid followed by SWCNTs as adsorbent was investigated.

2. Materials and methods

2.1. Materials

Commercial RB29 dye was obtained from Dystar Hoechst Corporation. The formula, molecular weight and maximum wavelength of light absorbed by RB29 were $C_{31}H_{19}O_9N_5S_2Cl_2Na_2$, 788 g/mol and 589 nm, respectively. The structure of RB29 is shown in Fig. 1.

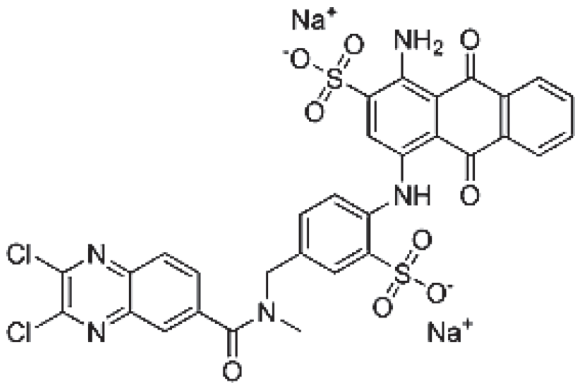

Fig. 1. Structure of RB29.

All solutions were prepared using deionized water and reagent grade chemicals. Glacial acetic acid, hydrogen peroxide and anhydrous sodium sulfite were purchased from Merck company. The SWCNTs were purchased from Iranian Research Institute of Petroleum Industry (RIPI). The solution of RB29 was prepared in 30 mg/l initial concentration for all experiments.

2.2. Characterization of SWCNTs

Single-wall carbon nanotubes were subjected to energy dispersive spectrometer for surface distribution of elemental composition and scanning electron microscopy (SEM). Size and morphology of SWCTs were reported by transmission electron microscopy (TEM). The specific surface area of SWCNTs were measured by BET method. Pictures of SEM of selected SWCNTs is shown in Fig. 2. The outer and inner diameters of SWCNTs were 1–2 nm and 0.8–1.1 nm, respectively. The length of SWCNTs was 10 μm with specific surface area

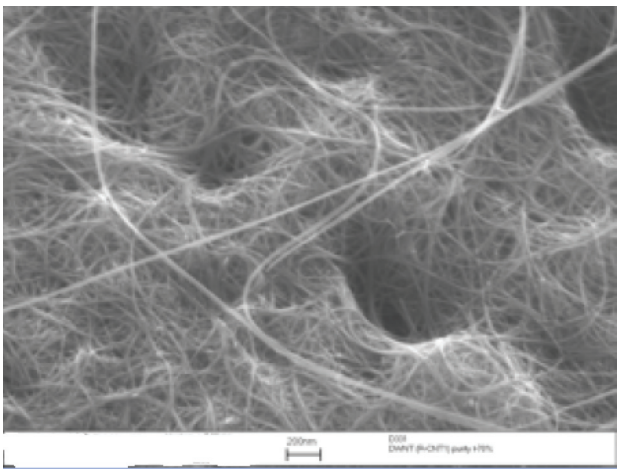

Fig. 2. SEM micrograph of SWCNTs.

of 700 m^2/g. The differential thermal analysis (DTA) and the thermo gravimetric analysis (TGA) was conducted to specify the purity of selected SWCNTs. Based on the result the purity of selected SWCNTs was 95%.

2.3. Methods

2.3.1. Peroxy acid oxidation

Peroxy acid oxidation experiment were conducted using 250 ml pyramid glass bottles with the addition of 100 ml Reactive blue 29 (30 mg/l) solution. Predetermined volumes of acetic acid (50%) and hydrogen peroxide (30%) were added to each bottle in order to keep the mole ratio of hydrogen peroxide/acetic acid/dye in 344/344/1 and lower. Then the samples were put on the illuminated refrigerated incubator shaker (Innova 4340) and shaken at 150 rpm. The temperature kept at 318 K. The samples were shaken for a chosen reaction time after which the reaction quenched by adding 1 ml of sodium sulfite (1 M). The experiments carried out for four different mole ratio of hydrogen peroxide/acetic acid/dye (344/344/1, 344/344/0.3, 344/344/0.16 and 344/344/0.08) and at various times (60, 120 and 180 min). The initial, final concentration and pH of dye was measured by spectrophotometer and pH meter, respectively. Four control groups' experiments were also prepared. Controls did not contain any acetic acid.

2.3.2. Batch adsorption experiment

Batch adsorption experiments were conducted after optimum advanced oxidation process was found. The pH of the solutions then adjusted to 5 by adding NaOH 0.1 N. Different suspensions of SWCNTs (4, 6, 7 and 8 mg) added to each bottle. The solutions put again on shaker and equilibrated at 318 K for 24 h. At the end of the equilibrium period, the suspensions were centrifuged at 4000 rpm for 10 min for analysis of the dye concentration. The adsorption of RB29 dye was detected using a spectrophotometer at 589 nm. Each experiment was performed twice and the results are average values. The amount of adsorbed RB 29 onto SWCNTs was calculated as follows:

$$q = \frac{C_i - C_e}{m}$$

where, C_i and C_e are the initial and equilibrium concentration in mg/l and m is the amount of SWCNTs in mg/l, respectively. In order to conduct adsorption experiment of RB29 solely, reactive blue (30 mg/l) was equilibrated by different suspensions of SWCNTs (0.13, 0.1, 0.08, 0.06, 0.04 and 0.02 g/l) at pH = 5 and temperature of 318 K for 24 h. Then samples taken from each bottle and centrifuged at 4000 rpm. Final concentration of RB29 was measured by spectrophotometer.

3. Results and discussion

3.1. Advanced oxidation process by peroxy acid

It was suggested that peroxy acid oxidation occurs through the formation of hypothesized peroxy acid compounds. Bach et al. [21], demonstrated the epoxidation of alkanes using peroxy acids. This peroxy acid compound will initiate the release of hydroxyl radical or hydroxyl cation. Like in other AOPs the hydroxyl radical or possibly hydroxyl cation oxidizes the contaminant. Acetic acid has been determined to be the preferred organic acid to be used from previous experiment [22]. The effects of different mole ratios of hydrogen peroxide/acetic acid/dye at various times (60, 120 and 180 min) in color removal are shown in Fig. 3. As illustrated by increasing both the mole ratios and time course study the color removal efficiency increased. Although the color removal efficiency increased from 20.2% to 30% after the mole ratio went up from 344/344/1 to 344/344/0.16, it showed no significant difference in decolorization in mole ratio of 344/344/0.08 in 60 min Therefore, the optimum mole ratio was selected as 344/344/0.16 in 60 min. With hydrogen peroxide alone (controls) no significant disappearance of RB29 was observed (data not shown). An assumption can be made that without the hydrogen peroxide catalyst the AOPs process is no more efficient. The final pHs of solutions after advanced oxidation process were 2.5–3 depending on the hydrogen peroxide/acetic acid/dye mole ratio. pH of solutions at the end of the reaction was low because of residual acetic acid that was left in solutions. In study conducted by Belgin et al. [23], some organic and

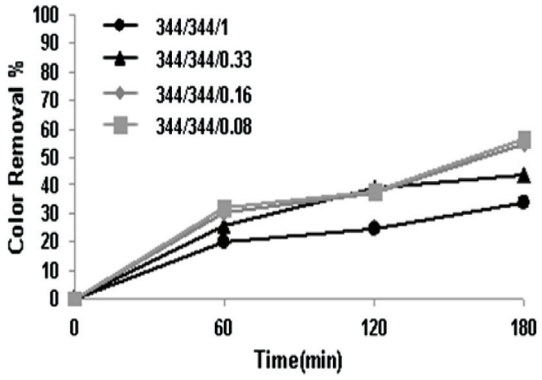

Fig. 3. Color removal due to different mole ratio of hydrogen peroxide/acetic acid/dye within an elapsed time of 180 min.

inorganic intermediates generated during the degradation of RB4 dye. The partial charge showed that OH radical attacked to N position on the RB4 to form three intermediates groups (alkylated chains, long chain alkanes, and minor polymers were found).

3.2. Adsorption isotherm

The $1/q$, $Ln(q)$ and $C_e/(C_s - C_e)q$ are correlated with the isotherm of models of Langmuir, Freundlieh and BET, respectively.

$$\frac{1}{q} = \frac{1}{b} + \frac{1}{abC_e}$$

$$\log\ q = \log k + \frac{1}{n}\ \log C_e$$

$$\frac{C_e}{(C_s - C_e)q} = \frac{1}{A(x_m)} + \frac{A-1}{Ax_m}$$

where C_e is the equilibrium concentration (mg/l); b, the maximum adsorption capacity (mg/mg); a, the Langmuir constant, k and n are the Freundlich constants. x_m and A are the amount of solute adsorbed in forming a complete monolayer (mg/mg), a constant to describe the energy of interaction between the solute and the adsorbent surface in BET model, respectively. The plot of BET models when SWCNTs used solely and Freundlich model after the application of peroxy acid are shown in Figs. 4 and 5, respectively. Tables 1 and 2 summarizes the coefficient of Langmuir, Freundlich and BET isotherms at pH = 5 and temperature of 318 K for both experiments. R^2 values for both models exceeded 0.9. The results indicated that adsorption of RB29 onto SWCNTs first well explained by BET isotherm with R^2 = 0.987 which showed that dye molecules form multilayer on SWCNTs. Freundich isotherm fitted the experimental data better than BET and Langmuir with R^2 = 0.958 when SWCNTs used in sequence with peroxy acid. n in Freundlich equation gives an indication of how favorable the adsorption process is. It is generally stated that values of n in the range of 2–10 represent good, 1–2 moderately difficult, and less than 1 poor adsorption characteristics. The studied material is good adsorbent for RB29 and

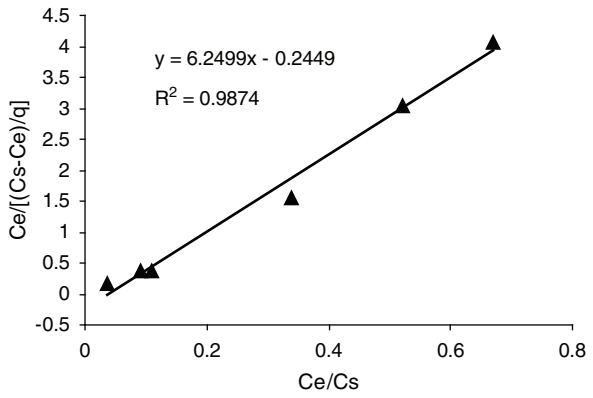

Fig. 4. BET isotherm of RB29.

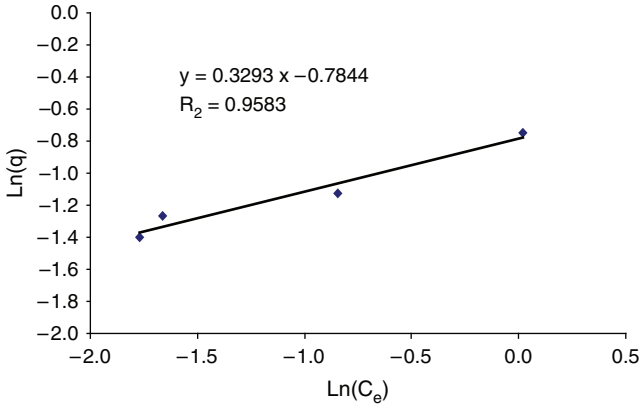

Fig. 5. Freundlich isotherm of RB29 after peroxy acid process.

Table 1
Constant of Freundlich, Langmuir and BET isotherm of RB29

Freundlich isotherm		
K	n	R^2
0.225	4.701	0.808
Langmuir isotherm		
a	b	R^2
1.059	0.4	0.827
BET isotherm		
A	x_m	R^2
24.52	0.166	0.987

Table 2
Constants of Freundlich, Langmuir and BET isotherm of RB29 after peroxy process

Freundlich isotherm		
K	n	R^2
0.456	3.036	0.958
Langmuir isotherm		
a	b	R^2
5.936	0.5	0.908
BET isotherm		
A	x_m	R^2
260.88	0.451	0.956

Table 3
Optimization process of peroxy acid and SWCNTs over a period of 2 h

Optimized concentration of peroxy acid to dye (344/344/0.16) (1 h AOP and 1 h contact with SWCNTs)			
SWCNTs (g/l)	0.1	0.08	0.06
Color removal (%)	72.13	66.35	60.9
Concentration of peroxy acid to dye halved (344/344/0.33). The amount of SWCNT doubled (1 h AOP and 1 h contact with SWCNTs)			
SWCNTs (g/l)	0.2	0.16	0.12
Color removal (%)	84.46	79.13	67.83

might for intermediates (n = 3.036) [24]. The data also showed that maximum color removal by combination of optimized peroxy acid and implication of 0.08 g/l SWCNTs (24 hl) was 99.4%. In view of the fact that the adsorption isotherm changed and maximum adsorption capacity of SWCNTs for RB29 also decreased from 496 to 472 mg/g it can be deducted that degradation intermediates had direct effects on adsorption of RB29 by SWCNTs. Two assumptions can be made: (a) intermediates compete with RB29 for the adsorption onto SWCNTs or (b) intermediates inhibit the adsorption of RB29 onto SWCNTs. Mechanism of SWCNTs towards RB29 and AOPs degradation intermediates may be derived from two reasons. One reason might be based on van der Waals interactions occurring between carbon atoms and aromatic backbones of the dye and intermediates. The other might be due to the electrostatic attraction between the dye and intermediates onto SWCNTs surface. To achieve a cleaner water and healthier environment, more effective and powerful treatment methods are required. The integration of such methods is useful in order to fulfill the environmental regulations. Integration of physical and chemical treatment processes is useful to take advantages of the methods and to minimize the drawback of each methods. Therefore, the integration (combination) study of peroxy acid (as chemical treatment) and SWCNTs (as physical treatment) over the time period of 2 h conducted. Table 3 shows the combination study of peroxy acid and SWCNTs over a period of 2 h. As it was observed before, the optimum concentration of acetic acid/hydrogen peroxide/dye found to be 344/344/0.16. This optimum concentration sequenced with different amounts of SWCNTs for RB29 (30 mg/l) removal in 2 h. In the next step, the optimum concentration of peroxy acid halved and the amounts of SWCNTs doubled. Maximum color removal was 72.13 when 0.1 g/l of SWCNTs used and it increased to 84.46% as the amount of SWCNTs doubled. It is clear that the potential of SWCNTs are greater than peroxy acid for RB29 removal. This result is based on the future design of a decolorization strategy where cost plays a key role.

4. Conclusion

Both AOP process by peroxy acid and adsorption onto SWCNTs have high affinity for RB29 dye removal. The optimum mole ratio of hydrogen peroxide/acetic acid/dye was found to be 344/344/0.16 in 60 min. The disappearance of RB29 by peroxy acid seemed to be dependent on the acetic acid as hydroxyl radical formation catalyst and hydrogen peroxide as hydroxyl radicals source. The use of a more specific AOP like a peroxy acid process to target pollutants may have great utility. However, there are significant environmental implications in adding large amounts of acetic acid to a watery system. These implications range from drastic decrease of the pH of the system to solubilizing unwanted organic compounds. The selected SWCNT was so effective for RB29 and might for intermediates. The Freundlich isotherm with R^2 = 0.958 well fitted to the data obtained from combination experiment. Maximum color removal was 99.4% in combination process by peroxy acid and 0.08 g/l of SWCNTs as adsorbent. The optimization study of peroxy acid and SWCNTs over a period of 2 h revealed that degradation of 84.4% of RB29 could be obtained. BET isotherm with R^2 = 0.987 well fitted to the data obtained from experiments conducted by SWCNTs for RB29 solely. Further research works on testing the effects of intermediates on adsorption of RB29 onto SWCNTs are needed to optimize the application of SWCNTs in water treatment.

Acknowledgments

This study was funded by Tehran University of Medical Sciences, Department of Environmental Health Engineering (2009–2010). The authors would like to thank the laboratory Staff of the Environmental Health Engineering Department for their collaboration in this research.

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