Carbon aerogel materials promoted catalytic ozonation of residual dyes in waste effluents from cotton dyeing

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Abstract

Reactive dyeing of cotton generates large volume of wastewater containing residue dye contaminants. In order to reduce adverse impacts to the environment, the waste effluents must be reclaimed through appropriate processes before charging to the natural water bodies. In this study, carbon aerogel materials, including pure carbon aerogel and its supported metal oxides, was reported in catalytic ozonation of residue dyes in wastewater. The commercially available reactive dye, namely C.I Reactive Blue 19, was used as the probe contaminant. Dye degradation in catalytic ozonation processes was estimated in terms of color and COD removal. The results demonstrated that the catalysts rarely involved in color removal, but displayed promising potentials in facilitating COD removal in dyeing effluents, in which COD removal was significantly promoted comparing to ozonation alone without catalysts. In the specific conditions, especially for the supported metal oxides, COD removal could attain 80% after 3 h treatment, whereas it was only 45% in ozonation alone. In addition, effects of conditional parameters on catalytic ozonation efficiency as well as the reusability of catalysts were also investigated. The results suggested that the catalyst materials exerted outstanding catalytic stability during repeated use, and increasing catalyst dosage, ozone concentration and pH would promote dye degradation especially for COD removal.

Keywords: Textile dyeing effluent, catalytic ozonation, carbon aerogel, color removal, COD removal.

Introduction

Cotton is the most important substrate in textile dyeing industry. It would be generally dyed with dyes or pigments for aesthetic consideration. Within the available colorants, reactive dyes are the most critical dye class for coloration of cotton, due to their excellent application features. Although reactive dyes have been developed drastically to fulfill the requirements during their service in daily life, the relative low dye fixation is still an undeniable issue in the cellulosic dyeing industry. It has been estimated that the discharged dyes not fixed onto fabric could be as high as 60% of the initial dye dosage [**1**]. Furthermore, water consumption in conventional dyeing could be as high as 150 L/kg of cotton [**2**]. Residual dyes will be discharged with the dyeing bath to form a great volume of highly contaminative color wastewater. If the wastewater discharged inappropriately without sufficient reclamation, serious adverse impacts would occur, accounting for not only environmental pollution but also threats to human health [**3**]. As a result, degradation of contaminants in reactive dyeing wastewater is a necessity for the cellulosic coloration industry.

However, problematic issues still exist in dyeing wastewater treatment. Because of the low biodegradability of reactive dyes, the most frequently used biological technology is generally rarely efficient. In addition, over the past decades, regulations on environmental protection are getting stricter than ever before. New regulations are putting into practice, which impose great pressure on the textile dyeing industries around the world. For an instance, the COD discharging limit in China was 100 g/L before 2015, it was however restricted to 60 m/L since 2016. As a result, more direct and effective technologies should be developed to encounter the severe situation. Some novel technologies were developed to tackle this problem, especially the advanced oxidation processes [**4**, **5**]. Wherein, ozonation technology is thought to be one of the potential alternatives for textile wastewater treatment in addition to biological technology. This is because the oxidation potential of ozone, which is as high as 2.07 mV, is extremely strong and is capable to degrade organics rapidly and highly efficiently. Furthermore, merits of no by-products from self-decomposition and easy application of ozone without additional light or thermal energy also supported ozonation to be a promising approach. More

importantly, in the aid of specific catalysts, the degradation capability of ozone towards organic contaminants could be further enhanced strikingly.

The catalytic ozonation is a more efficient process, which has been developed for degradation of the organic contaminants in aqueous solution, so as to improve the water quality, such as reducing COD of wastewater. The catalysts presented could act as a radical promoter and support to yield mineralization and help ozone in improving its efficiency in oxidation conversion of the organic pollutants into inorganics, without any additional operational conditions such as light and thermal energy. In ozonation, it is widely accepted in theory that there are two ozonation routes in aqueous solution, namely the direct and indirect reaction pathways. In the direct oxidation reaction, molecular ozone is the dominant participator in oxidation of organics, conversely in the indirect reaction, the highly reactive hydroxyl radicals deriving from molecular ozone decomposition will predominantly react with organic pollutants [**6**]. In most of catalytic ozonation, the production of hydroxyl radicals from molecular ozone would be substantially promoted, leading to improved oxidation efficiency in ozonation as the hydroxyl radicals have even higher oxidation potential (2.8 mV) than ozone itself. Transition oxides such as titanium oxide [**7**], cobalt oxide [**8**], manganese oxide [**9**], nickel oxide [**10**, **11**] and copper oxide [**12**] and non-metal materials such as carbon were frequently utilized as ozonation catalysts.

Carbon aerogel (CA), which is a new carbon material possessing excellent three-dimensional porous structure, has been adopted in various applications. More specifically, it has been used in dye removal for wastewater treatment, including used as electrodes in electrochemical reactor [**13**], photocatalysts [**14**], and catalysts for ozonation [**15**] pursuing dye degradation, and absorbents to remove color [**16**]. More importantly, depending on the varied applications, structural and physicochemical properties of CA materials can be facilely adapted by adjusting the synthesis parameters, particularly reactant molar ratios, making the catalyst materials more versatile. The present study discusses the application of catalytic ozonation in the presence of CA materials for degradation of residual dyes for reclamation of dyeing effluent. Pure CA, CA supported copper oxide (CuO-Cu_2O/CA), and CA supported cobalt oxide (Co_3O_4/CA) would be used as catalysts during catalytic ozonation of simulated dyeing effluent containing the typical reactive dye, namely C.I. Reactive Blue 19 (RB19), which is persisted to chemical oxidation.

The combination of the metal oxides and CA were expected to synergistically exert effective and durable influence in promoting production of hydroxyl radicals in the catalytic ozonation. In addition, the application of CA support tends to be a feasible method to prevent the problem in separation of catalyst powders from the hydraulic flow after the ozonation [**17**].

The catalysts would be added into an ozonation reactor filled with dye solution for the assessment of their catalytic performance, which was measured by color and COD removal in the simulated wastewater. As operational parameters such as catalyst dosage, ozone concentration and pH might affect the catalytic activity, these variables would be studied to understand the effects on the catalytic performance of catalysts in dye degradation. Furthermore, the reusability of the catalysts also would be evaluated to confirm whether these catalysts are of reliability.

On the basis of literature surveys, this is probably the first attempt to study the role of carbon aerogel materials in promoted degradation of persist textile dye through catalytic ozonation.

Experimental

Materials and chemicals

Reactive dyes, RB19, was provided by Longsheng Group (China) and used without further purification. Other chemicals were of analytic grade and commercially available.

Preparation of catalysts

The preparation procedure of CA has been described elsewhere [**16**]. CuO-Cu_2O/CA and Co_3O_4/CA were prepared with the impregnation method [**18**]. The entire preparation procedure has been illustrated in **Fig. 1**. The structural characteristics of catalysts had been confirmed elsewhere [**15**, **19**].

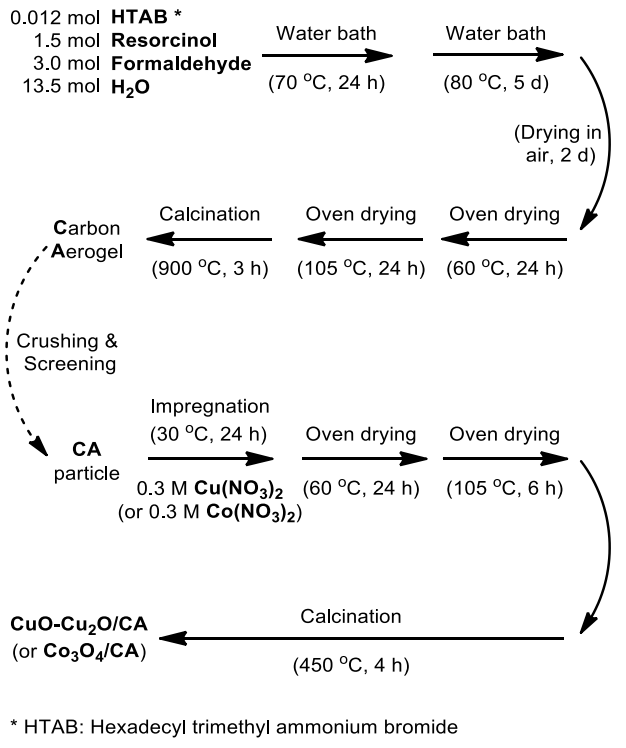

Fig. 1. Schematic procedure for preparation of CA and CA supported metal oxides.

Experimental set-up and procedure

Ozonation was conducted in a cylinder reactor (1000 mL) which was prefilled with dye solution (750 mL), of which

the temperature was maintain at 45 °C. Ozone gas was produced by an ozone generator (*Medozons BM*-02, Russia). Depending on the demand, granular catalysts may be added into the reactor before the treatment. During ozonation, ozone gas which mixed with oxygen was injected into the reactor at a constant flow rate (0.5 L/min), through a porous gas diffuser at the bottom of the glass cylinder. By bubbling of the liquids continuously, residual dyes in the liquor would be gradually oxidized by ozone which transferred from gas stream into aqueous phase. For a determined time interval, 3 mL of the liquor was sampled for color and COD determination after filtered through 0.45 µm syringe filter (Millex-HV, Millipore).

Determination of color and COD removal

Color was determined by the UV-vis absorbance on a UV-Vis spectrophotometer (Perkin-Elmer, Lambda 18), at the wavelength of 595 nm, at which BR19 solution has the maximum absorbance; while COD was tested on a colorimeter (Model DR 900, HACH) according to Hach Method 8000 [**20**]. The removal was calculated using Eq. 1:

$$\text{Removal (\%)} = (C_i - C_t) / C_i \times 100\% \quad \text{Eq. 1}$$

Wherein, C_i is the initial color absorbance or initial COD before ozonation; C_t is the color absorbance or COD after ozonation for time duration of *t*.

Results and discussion

The performance of catalysts in promoting dye degradation

In order to determine the performance of CA materials in promoting dye degradation, color and COD removal in seven different processes are compared in **Fig. 2**.

According to **Fig. 2(a)**, color removal in catalytic ozonation processes and ozonation alone process was almost identical. These processes all attained about 98% in color removal after 3 hour. However, COD removal in these processes in **Fig. 2(b)** was quite dissimilar. Especially for ozonation processes with catalysts of CA supported metal oxides, COD removal of 70% was obtained; while in ozonation without any catalysts the removal was only 45% after 3 h. This demonstrated CA materials rarely participated in color removal when comparing to COD removal, of which the efficiency in catalytic processes was much better than that in ozonation alone process.

It could ascribed to the fact that color removal in ozonation only involved cleavage of chromophore in dye molecular structure, which was easy to realize by molecular ozone due to its high oxidation capacity [**21**]. Whereas in COD removal, more complicated multistage oxidative reactions were provoked towards conversion of organics into inorganics. Catalysts participated substantially in the multistage oxidations by generating hydroxyl radicals, which have even higher oxidation capacity, to enhance degradation of residual dyes. According to a previous study, it has been found that carbon materials could participate in the ozone decomposition through the radical chain reactions with ozone, hydroxyl ion, water medium, hydroxyl groups on CA surface and π electrons of basic carbon substrate **[22]**. A serial of reactions were provoked during ozonation, producing hydroxyl radicals for highly efficient oxidation of dyes and dye intermediates. Thus the COD in the aqueous solution dropped substantially when catalysts added.

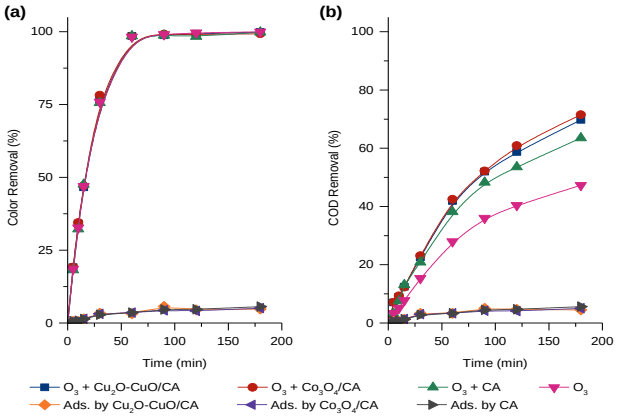

Fig. 2. Comparison of color (a) and COD (b) removal of RB19 (Dye concentration, 0.8 g/L; Catalyst, 1.0 g; Ozone concentration, 5.0 mg/min; pH 5.6).

The process using pure CA catalyst could have 60% in COD removal, which was higher than that of ozonation alone without any catalysts. However, comparing the processes using CuO-Cu_2O/CA and Co_3O_4/CA with that using CA, it was evident from **Fig. 2** that the supported catalysts were of a little higher efficiency. This could be attributed that the multi-valance of the oxidation status of copper (Cu^+ & Cu^{2+}) or cobalt (Co^{2+} & Co^{3+}) facilitated electrons transfer over the catalyst surface, which played a majority in oxidation reactions [**23**]. In addition, the removal arising from adsorption by catalysts was only about 5%, indicating the improved removal in catalytic processes can be ascribed to chemical oxidations rather than physical adsorptions.

Influence of operational parameters on dye degradation

Effect of catalyst amount

The effect of CuO-Cu_2O/CA catalyst dosage in dye degradation was compared in **Fig. 3**. Color removal observed in **Fig. 3(a)** was almost identical in the four processes regardless of catalyst amount, which proved the likelihood that the oxidation of dye molecules by molecular ozone dominated decolorization while the catalyst rarely involved. However, the amount of the catalyst was significant to COD removal, which was drastically improved with increased catalyst amount.

According to **Fig. 3(b)**, the COD removal rate of the process involving 3.0 g catalyst was as high as 80%; while for other processes with less or without the catalyst, the removal rates were much lower. It could be explained that in catalytic ozonation, the

production of hydroxyl radicals were rapidly improved when more catalyst presented [**24**], which accelerated dye oxidation and accounted for efficient COD reduction. In addition, another possible reason for the enhanced degradation may originate in the enhanced ozone mass transfer into aqueous solution due to increased catalyst amount [**25**].

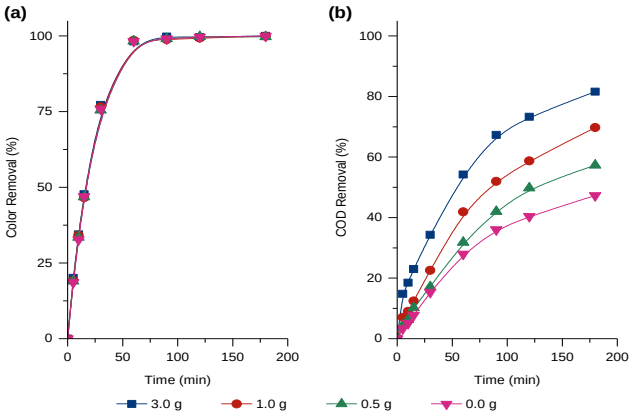

Fig. 3. Effect of catalyst dosage on color (a) and COD (b) removal (Dye concentration, 0.8 g/L; Catalyst type, CuO-Cu_2O/CA; Ozone concentration, 5.0 mg/min; pH 5.6).

Effect of ozone concentration

Fig. 4 corresponds to the effect of applied ozone concentration on dye degradation. The ozone concentration was set to 8.0 g/L, 5.0 g/L, 2.0 g/L and 0.5 g/L for comparison.

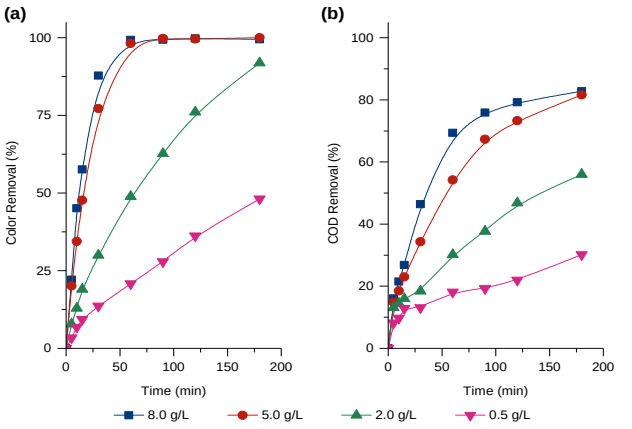

Fig. 4. Effect of ozone concentration on color (a) and COD (b) removal (Dye concentration, 0.8 g/L; Catalyst type, CuO-Cu_2O/CA; Catalyst dosage, 3.0 g; pH 5.6).

It was noticed that color removal in the processes using higher applied ozone concentration, 8.0 g/L and 5.0 g/L, was much rapider than other processes. Color removal could be as high as 98% after 1 hour. While color removal in processes applied with 2.0 g/L and 0.5 g/L ozone gas mixture were only 31% and 22% as shown in **Fig. 4(a)**. For COD removal presents in **Fig. 4(b)**, only 18% of COD were removed after 1 hour when the reactor provided with only 0.5 g/L ozone gas mixture, but the removal rate was dramatically enhanced to 70% when the ozone concentration increased to 8 g/L.

This could be attributed to the fact that by increasing the concentration of ozone in the gas stream, mass transfer of molecular ozone into aqueous solution was promoted accordingly. The degradation was therefore more pronounced when higher concentration of ozone gas mixture applied. This is similar to the findings obtained from a previous study [**26**]. Comparing **Fig. 4** to **Fig. 3**, it was evident that color removal promoted substantially as a result of increased ozone concentration, demonstrating the effect of ozone concentration was dissimilar to that of catalyst dosage. This reinforced the presumption that, in color removal, the cleavage of dye chromophore by molecular ozone predominantly governed the decolorization process; whereas decolorization induced by hydroxyl radicals, which were produced from molecular ozone, was presumably minimal comparing to the overall color removal rate.

Because of the promoted mass transfer of molecular ozone in aqueous solution, the production capacity of hydroxyl radicals was also improved accordingly, which led to a better removal of COD. This phenomenon has also been reported in a study regarding catalytic ozonation of C.I. Basic Blue 9 [**27**].

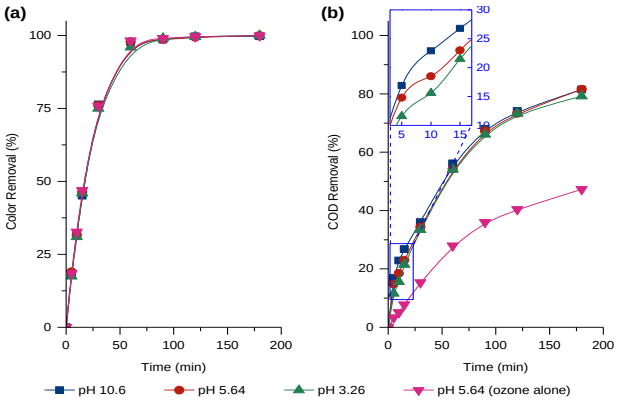

Fig. 5. Effect of pH on color (a) and COD (b) removal (Dye concentration, 0.8 g/L; Catalyst type, CuO-Cu_2O/CA; Catalyst, 3.0 g; Ozone concentration, 5.0 mg/min).

Effect of pH

Among the operational parameters, pH was believed to be the most vital factor influencing the degradation. Some studies revealed that the decomposition of ozone would be remarkably increased when the solution pH getting higher [**28**]. As a result, the effect of solution pH on color and COD removal was studied accordingly. Three different pH values were applied, wherein pH 5.64 was the original pH of dye solution, and the other two pH values were adjusted by 0.1 M NaOH or HCl solution. The removal under different pH conditions is compared in **Fig. 5**.

According to **Fig. 5(a)**, color removal in catalytic ozonation or ozonation alone was rarely different. Decolorization of dye solution in the absence of catalyst possessed similar removal, indicating molecular ozone was majorly responsible for color removal. As shown in **Fig. 5(b),** COD removal was much higher in processes with catalyst, which could be ascribed to the enhanced

generation of hydroxyl radicals in the presence of the catalysts. However, by comparing the three catalytic ozonation with different pH conditions, the COD removal were appreciably similar, notwithstanding the initial pH in different processes were significantly distinct, and the phenomenon observed was contradicted with the findings reported previously [**15**].

To explain this disconformity, it might be assumed that, system pH probably varied along with catalytic ozonation progressed. Therefore, pH evolution was monitored and illustrated in **Table 1**. It was found pH decreased gradually with ozonation time, especially in alkaline condition. The drop was more drastic when dye solution set at pH 10.6. Because of the generation and accumulation of acid byproducts from dye degradation in catalytic ozonation, solution pH declined progressively until sustaining at pH 3.2 steadily after 30 min. Consequently, only at the first beginning higher initial pH was beneficial to COD removal according to **Fig. 5 (b)** (inset). The 10 min COD removal was 23%, 19% and 16% for processes of which the solution pH was 10.6, 5.64 and 3.26 respectively. Thereafter, COD removal was minimally dissimilar after 30 min as pH in different processes was barely different.

Table 1. Evolution of solution pH during catalytic ozonation.

Time (min)	pH		
0	10.6	5.60	3.26
5	7.26	4.51	3.28
10	5.35	3.88	3.24
15	4.18	3.52	3.26
30	3.41	3.34	3.20
60	3.21	3.17	3.12
120	3.08	3.04	3.05
180	2.95	2.89	2.85

(Dye concentration, 0.8 g/L; Catalyst type, CuO-Cu_2O/CA; Catalyst, 3.0 g; Ozone concentration, 5.0 mg/min)

Some studies used buffered solution to maintain the solution pH steady so as to ascertain the treatment efficiency. Nonetheless, it was worth noting that it is not easy to maintain the pH because of dynamically accumulated acidic byproducts in aqueous solution. In addition, the buffering reagents used may lead to adverse impact on degradation. This is because phosphates, which are most frequently used for the majority of buffering system, are the strong Lewis bases. Their presence in the solution would decrease the concentration of surface hydroxyl groups on catalysts, leading to a decreased activity of catalysts [**29**].

Reusability of the catalyst

The catalytic activity of an ideal catalyst should not only be intense in the one-time use, but also should be stable in subsequent repeated utilizations. Some catalysts may have excellent activities, but could not be used for long period. Replacement may be inevitable to sustain the reclamation efficiency. Thus, excellent reusability is extremely critical to CA catalysts especially in continuous real wastewater treatment.

The evolution of COD removal in 21 runs of catalytic ozonation with the same catalyst is demonstrated in **Fig. 6**. COD removal in catalytic ozonation with CuO-Cu_2O/CA and Co_3O_4/CA was around 42%, and it was 38% when only pure CA participated in the reaction for the first cycle of 1 hour process.

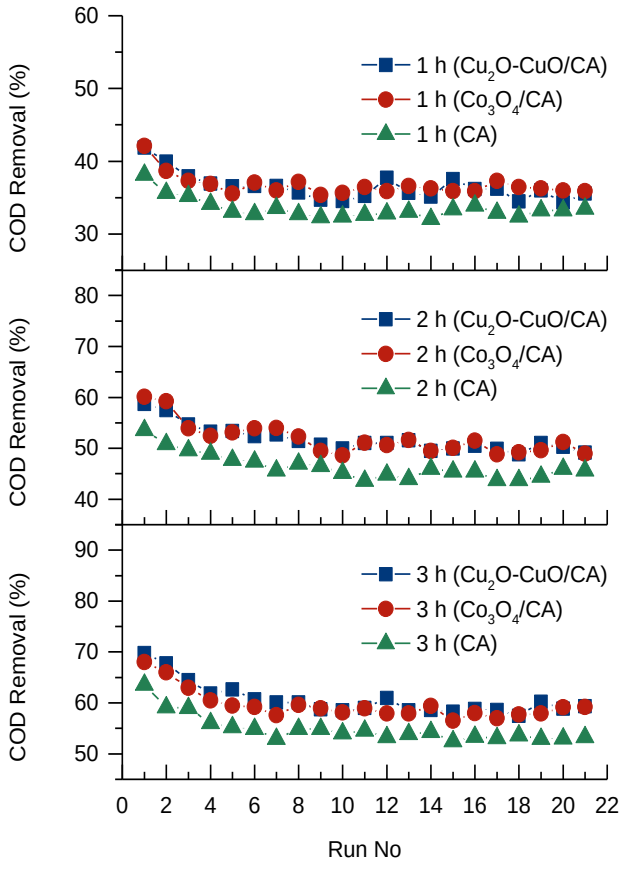

Fig. 6. Reusability of the novel catalyst (Dye concentration, 0.8 g/L; Catalyst type, CuO-Cu_2O/CA; Catalyst, 1.0 g; Ozone concentration, 5.0 mg/min; pH 5.6).

After that, the COD removal rate was slightly dropped until the fourth cycle and maintained almost steady in the subsequent runs. The reusability tendency of the 2 h process and 3 h process were both similar to the 1h process. For the majority of catalytic ozonation, the undeniable slight drops in COD removal could be attributed to the surface oxidation of catalysts during ozonation, which decreased basic groups accounting for production of hydroxyl radicals [**30**]. In turn, degradation efficiency was slightly declined. After the preliminary reuse trials, the performance of the catalysts were sustained steadily, suggesting carbon aerogel materials were of outstanding reusability.

Conclusion

This study provides an insight into the potentials of CA catalysts in catalytic ozonation for degrading residual dyes in dyeing wastewater. The results suggested that in

catalytic ozonation with CA materials, the color removal of RB 19 in aqueous solution was similar comparing to the ozonation alone without any catalysts; however, the result suggested compelling evidence that the COD removal was notably promoted in the presence of catalysts, especially for CuO-Cu_2O/CA and Co_3O_4/CA. This leads to a conclusion that CA supported metal oxides were highly efficient catalysts for degradation of residual reactive dyes by ozonation. In the study on experiment variables, it showed that increasing the catalyst dosage could effectively lead to enhanced COD removal but exert little improvements on color removal; while enhancing the ozone dosage could promote both COD and color removal. Concise controlling of pH may be necessary to sustain high degradation of dyes in aqueous solution, as the system pH may be reduced. It also showed that CA materials had excellent reusability. The catalytic activities were stable during repeated utilization, which was the most outstanding advantage of the catalysts when comparing to other materials in the view of practical utilization.

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