Simultaneous Removal of Dye and Chemical Oxygen Demand from Aqueous Solution by Combination Treatment with Ozone and Carbonaceous Material Produced from Waste Biomass

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This paper shows the efficacy of the combination of ozonation and adsorbent treatment in removing cationic and anionic dyes (methylene blue and acid orange 7, respectively) and chemical oxygen demand (COD) from wastewater. The adsorbent was prepared with coffee ground, rice bran, and soybean bran as sources of waste biomass, and was calcined at 1000°C. We demonstrated three methods, namely, singular ozonation, singular adsorbent treatment, and the combination of the two treatments. The removal percentage of dye and COD by ozonation was greater than that by adsorbent treatment. However, the incomplete removal of dye and COD through ozonation suggested that singular treatment is not sufficient for this purpose. Subsequently, we evaluated the combination treatment; the removal percentage of dye and COD by this treatment was higher than those from the singular treatments, which indicates that the adsorption and degradation capacities were enhanced. In addition, the calcined adsorbent could be used at least four times. These results show the novelty and utility of this treatment for the removal of dye and COD from wastewater containing dye. [DOI: 10.1380/ejssnt.2018.229]

Keywords: Ozonation; Carbonaceous material; Dye; Degradation; Adsorption

I. INTRODUCTION

Dyes are synthetic aromatic compounds used in a range of industries, such as textiles, pharmaceuticals, pulp and paper, paints, plastics, food, and electroplating [1, 2]. More than 700,000 tons of dyes and pigments are produced globally [3]. Effluents from the textile industry contain high concentrations of toxic chemicals, high levels of chemical oxygen demand (COD) and biochemical oxygen demand (BOD), a wide range of pH levels and temperatures, and very strong color [4]. Since most of the dyes are made up of aromatic, they are usually toxic, and non-biodegradable, apart from being carcinogenic and teratogenic [5]. Methylene blue (MB, a cationic dye) is a typical toxic dye, and can cause high blood pressure, mental disorder, nausea, and abdominal pain in individuals exposed to large amounts of it (> 0.7 mg/kg) [6]. In addition, acid orange 7 (AO, an anionic dye) is a synthetic acid dye that is toxic at a concentration of 0.011 mg/mL, based on the acute toxicity test EC50 [7]. Therefore, it is critical to develop practical methods to reduce the content of MB and AO in wastewater before it is discharged into the environment.

Several methods are applied for the treatment of textile effluents, including biological, chemical, and physical methods and their combination [3, 8]. Among them, ozonation is an advanced oxidation process (AOP) used in the effective organic degradation in wastewater. It is also a proven environment-friendly technique for removing different types of pollutants, such as pesticides, dyes, herbicides, and even biorecalcitrant chemical species that resist biological treatment [1]. Recently, catalytic ozonation has been recognized as one of the most promising methods for wastewater treatment [3]. Activated carbon exhibits catalytic activity in the decomposition of ozone and shows a high adsorption capacity as well [1, 9]. The combination of ozone and activated carbon has been identified as an interesting alternative for destruction of organic molecules. It has also been reported that activated carbon acts as an initiator and/or promoter of ozone transformation into OH radicals, thereby increasing the range of applicability of this process. However, activated carbon is expensive and limited the production.

In this study, we first focused on the carbonaceous material produced from waste biomass, which is very cheap and easily available, and studied its characteristics. Secondly, we analyzed the combination of ozonation and adsorbent treatment (using carbonaceous material produced from waste biomass) for the removal of dyes (MB and OA) and COD from wastewater. Finally, the repetitive use of adsorbent in the combination treatment was evaluated.

II. EXPERIMENTAL METHODS

A. Materials

The two dyes, MB (CAS No.: 7220-79-3) and AO (CAS No.: 633-96-5) were purchased from Wako Pure Chemical Industries Ltd., Osaka, Japan and Tokyo Chemical Industry Co. Ltd., Osaka, Japan, respectively.

Coffee ground (CB), rice bran (RB), and soybean bran (SB) were the sources of waste biomass to be used as adsorbent in this experiment. The calcination treatment was performed, as follows. The waste biomass was placed in a muffle furnace and the required temperature (1000°C) was maintained for 2 h to obtain CB1000, RB1000, and SB1000. The specific surface areas of un-calcined and calcined waste biomass were measured using a specific surface area analyzer (NOVA4200e, Yuasa Ionic, Osaka, Osaka, Japan).
Japan). Their morphologies were observed using scanning electron microscopy (SEM; SU1510, Hitachi Ltd., Osaka, Japan).

B. Effect of ozonation on removal of dye and COD

Dye solution (200 mL) with an initial concentration of 100 mg/L was taken in a gas-washing bottle and aerated using an ozone generator (Nihon Ozone Co., Ltd., Kagoshima, Japan) at room temperature (approximately 25°C). The conditions for ozonation were as follows: flow rate of ozone via oxygen gas of 30 mL/min, voltage of 40 V, and ozone concentration of approximately 50 mg/L. The sample solution (1–2 mL) was taken out from the gas-washing bottle at intervals of 5, 15, 30, 50, 70, and 90 min, respectively. The solution was then analyzed using a spectrophotometer (UV-1200, Shimadzu Co., Ltd., Osaka, Japan). The absorption wavelength used for MB and AO were 655 and 485 nm, respectively. The residual percentage of dye was calculated using pre-ozonation and post-ozonation values of the dye concentration.

In addition, the reaction percentage of ozone was calculated using the following method [10]: Potassium iodide solution (200 mL) at 0.1 g/L was taken in a washing bottle, and titrated by sodium thiosulfate at 0.1 mol/L, before and after the ozone treatment. Ozone gas concentration was calculated using Eq. (1);

\[ C = \frac{2400NfT}{V}, \]

where \( C \) is the ozone gas concentration (mg/L), \( N \) is the normality of potassium iodide (N), \( f \) is the factor of potassium iodide, \( T \) is the titer of potassium iodide (mL), and \( V \) is the volume of ozone gas (mL). Thereafter, the reaction percentage of ozone was calculated using values of ozone gas concentration, before and after the reaction.

Finally, the chemical oxygen demand (COD) value was determined to evaluate the removal of organic compounds from aqueous solution [11].

C. Effect of adsorbent treatment on removal of dye and COD

The adsorbent (0.2 g) was added to 200 mL of dye solution (initial concentration 100 mg/L) placed in a gas-washing bottle. The suspension was aerated with oxygen gas (Kouan Sangyo Co., Ltd., Higashi-Osaka, Japan) at room temperature (approximately 25°C). The rate of oxygen gas was maintained at 30 mL/min. The experimental procedures were the same as elaborated in Section II B. The residual percentage of dye, reaction percentage of ozone, and COD were estimated by this method.

In addition, we demonstrated that the adsorbent could be used repeatedly. Firstly, we conducted the combination treatment. Secondly, the used adsorbent was collected, and dried at 50°C for 24 h. Finally, the dried adsorbent was used again for removal of dye and COD. These treatments were conducted four times in a row. Furthermore, the SEM images of the adsorbent after the combination treatment were taken and analyzed in this study.

III. RESULTS AND DISCUSSION

A. Properties of un-calcined and calcined CB, RB, and SB

SEM images of un-calcined and calcined CB, RB, and SB are shown in Fig. 1. It was evident that the pores were produced because of calcination treatment. In addition, the specific surface areas of CB, RB, SB, CB1000, RB1000, and SB1000 measured in m²/g, were recorded as 1.0, 2.4, 3.2, 88.0, 145.6, and 51.0, respectively. These results support the hypothesis that calcination treatment is useful for increasing the specific surface area. Biomass such as CB, RB, and SB is comprised with dietary fiber, saccharide, protein, lipid, etc. Moreover, the surface functional groups onto biomass are existed. The components (organic compounds, etc.) or surface functional groups in biomass are loss by calcination treatment. These phenomena indicate that the carbon element is loss. In addition, previous study reported that the number of acidic functional groups and surface hydroxyl groups onto waste biomass decreased with increasing calcination temperature [12]. The pores of carbonaceous materials produced from biomass are produced by above-mentioned. The general pore size classification of activated carbon is, as follows: macropore (d > 500 Å), mesopore (20 < d < 500 Å), and micropore (d < 20 Å). The specific surface...
area is larger in adsorbent with micropores [13]. However, the presence of mesopores along with micropores in the adsorbent enhances its adsorption, especially that of large adsorbate molecules, such as dye molecules [14].

**B. Removal of dye and COD by ozonation**

Figure 2 shows the changes in parameters with respect to dye and COD, post-ozonation. Residual percentage of MB and AO was 0%, after ozonation at 90 min. The pH of solution shifted to acidic range (5.7 to 3.3 for MB and 6.3 to 3.5 for AO). In addition, the reaction percentage of ozone was in the range 8.3–10.2%. The decolorization of MB was faster than that of AO, which may be due to the difference in their structure. However, in this study, we could not elucidate the degradation mechanism in detail. Further, the removal percentages of COD in the case of MB and AO were 69.2% and 29.3%, respectively, which indicates that while ozonation removes COD, but not completely. This process has been drawing attention for treatment of wastewater containing dyes. There are two modes of reaction of ozone with organic compounds in water: Direct reaction and indirect reaction. In the direct oxidation mode, ozone acts on the double bonds of functional groups or dipolar structure, reducing the color of effluents; however, the drawback is generation of degraded products (by-products) [1, 15], warranting additional treatment to remove them [1]. In the indirect oxidation by ozone, hydroxyl radicals generated in radical chain reactions react with organic compounds. These radicals decompose most of the organic compounds into CO₂ and H₂O [1]. In this study, the chromophore in MB and AO solutions was degraded by ozonation, and thereafter, low molecular weight compounds were produced. Consequently, as the treatment time elapsed, the residual percentage of dye reduced. However, it was difficult to remove low molecular weight compounds formed in the process [3]. Similar results have been reported by several studies [1, 15–17].

**C. Removal of dye and COD by adsorbent treatment**

The impact of contact time on the adsorption of dye and COD using the un-calcined and calcined adsorbent is shown in Figs. 3 and 4, respectively. The use of CB, RB, and SB adsorbents in their un-calcined form yielded residual dye percentages of 66.0, 41.6, and 37.8, respectively in the case of MB. Similarly, the removal percentages of COD were 17.5, 10.7, and 43.2%, respectively. The pH in solution shifted to the basic range (6.6 to 8.1). These results suggest that for the adsorption of dye and COD, SB treatment was the most efficient among all adsorbent treatments studied; however, it was less efficient when compared to singular ozonation. Similar trends were observed for AO. Moreover, it was proved that un-calcined adsorbent treatment is not sufficient for the removal of AO.

The use of calcined adsorbent resulted in higher removal percentages of dye and COD in the case of both MB and AO as compared to that corresponding to the un-calcined adsorbent (exceptions were RB1000 and SB1000 in the case of MB). However, singular adsorbent treatment did not exhibit satisfactory removal of dye and COD in wastewater containing dye. Previous studies reported that the dye adsorption capacity depended on the specific surface area (a physical property) [18–20]. Similar trends were observed in this experiment. In other words, the adsorbent surface is a critical factor in wastewater purification. Moreover, the components in each waste

![FIG. 2. Changes in dye and COD by ozonation.](image)

![FIG. 3. Effect of contact time on the adsorption of dye and COD by un-calcined adsorbent.](image)

![FIG. 4. Effect of contact time on the adsorption of dye and COD by calcined adsorbent.](image)
FIG. 5. Effect of contact time on the removal of dye and COD by combination ozonation and un-calcined adsorbent treatment.


D. Effect of combination of ozonation and adsorbent treatment on removal of dye and COD

The impact of contact time on the removal of dye and organic compounds by means of the combination of ozonation and adsorbent treatment is shown in Figs. 5 and 6. The removal percentage of dye and COD by the combination of ozonation and un-calcined adsorbent treatment was significantly higher as compared to that from singular un-calcined or calcined adsorbent treatments, but lower than that from singular ozonation. On the other hand, the combination of ozonation and calcined adsorbent yielded higher dye removal rates and COD removal percentages than the other treatments. The residual percentage of dye decreased markedly in the first 15 min (especially, CB1000 was found to be most efficient for the removal of dye, among all adsorbents under study.) The COD removal percentages in the case of MB and AO using singular ozonation, ozonation + CB1000, ozonation + RB1000, and ozonation + SB1000 were 68.0, 72.3, 82.0, and 80.1% and 28.9, 52.3, 67.3, and 62.6%, respectively. In addition, the reaction percentage of ozone in the combination treatment was greater than that from singular treatment.

Activated carbon not only has excellent adsorption capacity, but also exhibits high catalytic activity due to its high surface area (physical property) and surface functional groups [25–29]. On combining ozonation and adsorbent treatment, carbonaceous material acted as a catalyst during ozonation; it converted the ozone into highly reactive species that attacked the complex structures, thereby accelerating their degradation [15, 30]. Moreover, on comparing its efficiency with that of the singular treatment, the combination treatment showed a higher efficiency in COD removal [31]. Similar results were reported in other studies [32, 33].

A previous study had reported that the solution pH strongly affects the degradation capacity in ozone treatment. The optimal pH for degradation by means of ozonation process is neutral and basic [34]. In this experiment, it was observed that the solution pH in the case of MB and AO shifted from 5.6 to 7.0 in the combination treatment of ozonation and calcined adsorbent. These results point towards the efficacy of combination treatment in the degradation of dye and removal of COD in wastewater.

E. Application of combination of ozonation and CB1000 adsorbent treatment

Repetitive use of calcined adsorbent, CB1000 in the combination treatment was also evaluated in this study. Figures 7 and 8 show the residual percentages of dye and removal percentages of COD, and the changes in color, respectively. The treatment was found to be useful for the removal of dye and COD on repetitive use of the adsorbent. However, the degradation rate of MB and AO gradually slowed down with the successive use of the adsorbent.
sorbent. In addition, the removal percentages of COD in the 1st, 2nd, 3rd, and 4th turns were 78.7%, 74.3%, 73.5%, and 72.4% for MB and 46.3%, 58.6%, 45.2%, and 64.9% for AO, respectively. These results show that the adsorption and catalytic capacity of CB1000 was sustained in the four rounds of combination treatment. Moreover, the decolorization was evident after each combination treatment (after 90 min). Finally, we studied the SEM images of CB1000 post-treatment (Fig. 9). The CB1000 surface was not damaged by the repeated combination treatment that further suggests that the adsorption and catalytic capacity of CB1000 did not reduce with repetitive use. Previous studies had not reported on the repetitive use of adsorbent, therefore the results obtained in this study are novel and immensely useful for the purpose of purification (degradation and removal) of wastewater containing dye.

F. Comparison of catalytic ozonation treatment

Several studies have been carried out to ascertain the impact of various catalysts or adsorbents on ozonation of dyes (Table I) [35–40]. The removal of dye and COD from the combination of ozonation and CB1000 treatment were reported as 100% and 72% for MB, and 100% and 52% for AO, respectively, which are greater than from any other treatment. The results thereby suggest that the combination of ozonation and CB1000 treatment has great potential for the removal of dye and COD from wastewater containing dye.

IV. CONCLUSION

In this study, we evaluated the removal of dye (MB and AO) and COD by means of ozonation, adsorbent treatment, and the combination treatment. First, we prepared the un-calcined and calcined biomass adsorbents (CB, RB, and SB, and CB1000, RB1000, and SB1000, respectively.) Thereafter, their characteristics were analyzed. The calcination treatment was found to be useful in increasing the specific surface area in biomass adsorbent. Next, the removal of dye and COD from ozonation was found to be greater than that from un-calcined or calcined adsorbent treatment, which indicates that ozonation is effective in the removal of dye and COD from wastewater containing dye. Third, the combination of ozonation and calcined biomass adsorbent treatment was found to be more efficient in the removal of dye and COD, as compared to singular ozonation or adsorbent treatment. These results show that calcined adsorbent can play a very important role in the degradation of dye (chromophore) when combined with ozonation, due to its role in adsorption and catalytic effect on ozonation. Finally, it was shown in the experiment that the adsorbent can be used at least four times, without losing its functionality. This result is novel and very useful for the degradation and removal of dye in wastewater.
## TABLE I. Catlytic ozonation method for removal of dye and COD.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Dyes</th>
<th>Removal of dye (%)</th>
<th>Removal of COD (or TOC) (%)</th>
<th>Treatment time (min)</th>
<th>Solution pH</th>
<th>Catalyst dosage (g/L)</th>
<th>Ozone dosage (mg/min or mL/min)</th>
<th>Initial concentration of dye (mg/L)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified AC</td>
<td>Methylene blue</td>
<td>-</td>
<td>-</td>
<td>120</td>
<td>6</td>
<td>0.8</td>
<td>325</td>
<td>1000</td>
<td>[24]</td>
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<tr>
<td></td>
<td>C.I. reactive red 2</td>
<td>&gt; 90</td>
<td>-</td>
<td>120</td>
<td>-</td>
<td>3</td>
<td>500</td>
<td>40</td>
<td>[25]</td>
</tr>
<tr>
<td></td>
<td>C.I. acid orange 6</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metal oxide</td>
<td>Reactive oxide</td>
<td>99</td>
<td>-</td>
<td>60</td>
<td>7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[26]</td>
</tr>
<tr>
<td>Perfluorooctyl alumina</td>
<td>Real waste water</td>
<td>75.1</td>
<td>40.2 (34.8)</td>
<td>-</td>
<td>10</td>
<td>300</td>
<td>48</td>
<td>-</td>
<td>[27]</td>
</tr>
<tr>
<td>Powdered copper sulphide</td>
<td>Acidic red 151</td>
<td>-</td>
<td>&gt; 90</td>
<td>80</td>
<td>10</td>
<td>0.1</td>
<td>115</td>
<td>100</td>
<td>[28]</td>
</tr>
<tr>
<td>MgFe₂O₄</td>
<td>Acid orange II</td>
<td>&gt; 90</td>
<td>48.1</td>
<td>40</td>
<td>4.6-9.6</td>
<td>0.1</td>
<td>0.5</td>
<td>50</td>
<td>[29]</td>
</tr>
<tr>
<td>CB1000</td>
<td>MB</td>
<td>100</td>
<td>72</td>
<td>90</td>
<td>6.2</td>
<td>0.1</td>
<td>1.5</td>
<td>100</td>
<td>This study</td>
</tr>
<tr>
<td>CB1000</td>
<td>AO</td>
<td>100</td>
<td>52</td>
<td>90</td>
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<td>1.5</td>
<td>100</td>
<td>This study</td>
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