Development of Actual Dyestuff Wastewater Treatment by Ozone with Carbonaceous Materials Produced from Waste Fiber

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Abstract: The methylene blue and dyestuff removal efficiency in a textile factory by ozonation and/or carbonaceous material treatment was investigated. Three kinds of carbonaceous materials were prepared from wool (WL), polyester (PET), and cotton (CT) discharged from the textile factory. The physical properties of the carbonaceous materials were very different. The specific surface area and pore volume of WL were the lowest, while those of CT were the highest. The dyestuff removal efficiency from actual dyestuff water was the highest when using the carbonaceous material (CT) prepared from cotton waste fiber. The decreases in the chromaticity, turbidity, COD, and TOC of the actual dyestuff wastewater depended upon the mean pore diameter of the carbonaceous material. The COD and TOC of the actual dyestuff wastewater were only slightly decreased by ozonation. The ozonation with CT would be useful for the removal of the dyestuff from actual textile wastewater. These results indicated that the waste cotton fiber could be converted into a carbonaceous material as an adsorbent for the removal of dyestuff from actual wastewater.

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1. Introduction

The annual volume of fiber waste discharge has reached some two million tons in Japan, and the product life cycle has been substantially shortened. In 2008, the amounts of WL, CT, and PET used in Japan were 15,862, 115,481, and 11,146 tons, respectively. With the exception of synthetic fiber, CT is the most widely used. Approximately 10% of all waste fiber products is recycled, while the remaining 90% is incinerated or used for land reclamation [1]. Other methods of recycling include the chemical decomposition and regeneration of polyester fiber, and the reuse of cotton as an automotive insulation material. The use of these products as reinforcing materials in walls and other applications have also been reported [2-4]. In recent years, in an effort to expand clothing recycling, corporations have been asked to exercise social responsibility in their pursuit of profits. However, the fiber product recycling ratios have not increased, largely because of consumer resistance to the use of recycled products and the cost of recycling.

In Japan, water pollution due to wastewater from textile factories or industries is controlled by the regulations of the Water Pollution Control Act, which provides environmental standards for the protection of human

health. The environmental water-quality standard in the public water areas of irrigation areas had an achievement rate of 87.6% in 2009 in Japan. However, the environment quality standard for organic pollution, that is, the biochemical oxygen demand (BOD) or chemical oxygen demand (COD), in rivers, lakes, and seawater only had achievement rates of 92.3%, 50.0%, and 79.2%, respectively [5]. In particular, the achievement rate for lake water has been lower than those for river water and seawater.

Recently, trihalomethanes, which have generated serious concerns about the safety of tap water, have been shown to be carcinogenic substances [6, 7]. They are formed during the process of chlorine sterilization and disinfection processing by reactions with organic compounds, for example, dyestuff or humic acid in nature [7-9]. The wastewater in the textile industry contains not only hazardous materials but also a high concentration of dyestuff and nitrogenous substances. Colored wastewater from the textile industry is becoming a problem around the world [10, 11]. Ozone and/or activated carbon have been used to remove dyestuff in water treatment plants [12, 13]. Advanced oxidation is one of the most efficient methods for the decolorization of textile wastewater [14]. An advanced oxidation process such as ozone treatment [15] is an emerging technology aimed at the degradation of pollutants in wastewater [16]. The dyestuff is decom-

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posed by ozonization and adsorbed on the activated carbon [17]. Many kinds of dyestuffs and chemical substances are used in the textile industry. The wastewater discharged from the textile industry contains various dyestuffs. The removal of a specific dyestuff has been examined using ozone decomposition or adsorption on various kinds of adsorbents. The removal of Reactive Blue 19 [18-22], Acid Red 1 [23], Methylene Blue or Orange II [24], and Indigocarmine [25] has been reported. The dyestuff removal ability of an adsorbent has to be evaluated using actual wastewater from a textile factory.

In this study, the ozone degradation and dyestuff removal abilities of carbonaceous materials produced from wool, polyester, and cotton were evaluated using actual wastewater discharged from a textile factory.

2. Experimental

2.1 Production of carbonaceous materials

The carbonaceous materials were essentially produced as follows: wool (WL), polyester (PET), or cotton (CT) was placed in a magnetic furnace under flowing nitrogen gas at 1 L/min with the temperature increased over 2 h to a final temperature of 1273 K. The material was then held at this temperature for 2 h before being naturally cooled.

2.2 Physical properties of carbonaceous materials

The specific surface area was measured from the adsorption isotherm at the temperature of liquid nitrogen (-195.8°C) with high-purity nitrogen gas (99.999%) as the adsorption gas by using NOVA4200e (Quantachrome, FL, USA). It was calculated by fitting the Brunauer-Emmett-Teller (BET) equation to the nitrogen adsorption isotherm in a relative pressure range of 0.05–0.30 [26]. The pore size distribution and pore volume were similarly measured from the adsorption isotherm in a relative pressure of 0.025–0.99 and the desorption isotherm in a relative pressure of 0.1–0.99 at the temperature of liquid nitrogen, and calculated using the Dollimore-Heal method [27]. The pores were assumed to be cylindrical, and the average pore diameter (D) was calculated from the specific surface area (S) and pore volume (P) by using Eq. (1) [28].

$$D = \frac{4P}{S} \quad (1)$$

2.3 Amount of methylene blue adsorbed onto carbonaceous materials

The amount of methylene blue adsorbed was measured by using the following method: 0.05-g samples of the carbonaceous materials were added to

50-ml quantities of a methylene blue solution at different initial concentrations, and the mixtures were shaken for 24 h at 298 K. Each mixture was then filtered through a membrane filter with a pore size of 0.45 μm . The optical absorbance of the filtrate was measured using a spectrophotometer (U-1100, Hitachi, Ltd.) to determine the equilibrium concentration. The absorption wavelength used for methylene blue was 665 nm. The amount adsorbed onto the carbonaceous material was calculated using Eq. (2):

$$V = \frac{(C_o - C)}{W} \times \frac{50}{1000} \quad (2)$$

where C_o (mg/L) is the initial concentration, C (mg/L) is the equilibrium concentration, W (g) is the weight of the carbonaceous material, and V (mg/g) is the amount of methylene blue absorbed on the carbonaceous material.

2.4 Carbonaceous material treatment of actual dyestuff wastewater

Actual dyestuff wastewater was obtained from a textile factory in Tokushima prefecture. The carbonaceous material (0.1 g) was added to 50 mL of the actual dyestuff wastewater, the mixture was shaken for 24 h at 298 K, and then the chromaticity (390 nm) and turbidity (870 nm), TOC, and pH were measured using a digital chromaticity and turbidity meter WA-PT-4DG (Kyoritsu Chemical-Check Lab., Japan), TOC500 (Shimadzu, Japan), and digital pH meter (Mettler Toledo, Japan), respectively. COD was measured by using the acidic high-temperature permanganate method. Briefly, 7.5 mL of a 30% AgNO_3 solution, 5 mL of a 30% H_2SO_4 solution, and 5.0 mL of a 0.005 mol/L KMnO_4 were accurately added to a 50-mL specimen, which was heated in a water bath. The specimen was then decolorized with a 0.0125-mmol/L $\text{Na}_2\text{C}_2\text{O}_4$ solution and titrated with a 0.005-mol/L KMnO_4 solution. A titer of the 0.005-mol/L KMnO_4 solution obtained for the titration was labeled “ a .” A similar volume obtained as a blank experiment was labeled “ b .” The titer of the 0.005-mol/L KMnO_4 solution was labeled “ f .” COD was calculated by using the following:

$$\text{COD} = 0.2 \times (a - b) \times f \times \frac{1000}{V_L} \quad (3)$$

where V_L (mL) is the amount of wastewater.

2.5 Ozone and carbonaceous material treatments of actual dyestuff wastewater

Ozone was generated from oxygen gas (flow rate, $1.8 \times 10^{-3} \text{ m}^3/\text{hr}$) using an A-27 ozone generator (Okano Works, Japan). The ozone generation ability of the A-27 is more than 1%, and the amount of ozone generated was approximately 40 mg/min. The amount of ozone gener-

ated was determined by titration with $\text{Na}_2\text{S}_2\text{O}_3$ using a starch solution as an indicator after adsorbing ozone into a potassium iodine solution. 200 mL of the actual dyestuff wastewater and 1.0 g of the carbonaceous material were placed in an Ichinose-type gas washing bottle of the ozonation apparatus, and treated with air, ozone, or oxygen gas for 1 h with stirring. The chromaticity, turbidity, TOC, COD, and pH were measured before and after the treatments.

2.6 Ozone and carbonaceous material treatments of actual dyestuff wastewater in four reactors

There are four treatment tanks for the decolorization of dyestuffs in a textile factory located in Tokushima Prefecture. A small-scale setup of the actual textile water treatment plants in Tokushima Prefecture was constructed. The apparatus consisted of four reactors and is shown in Fig. 1. The ozone flow rate was $1.8 \times 10^{-3} \text{ m}^3/\text{h}$. 200 mL of the actual dyestuff wastewater and 1.0 g of carbonaceous material were added to each reactor, and treated with ozone or both ozone and carbonaceous materials for 1 h. The chromaticity, turbidity, TOC, COD, and pH were measured before and after treatments.

3. Results and discussion

3.1 Physical properties of carbonaceous materials

The specific surface area and pore size distribution

Fig. 1 Ozone and/or carbonaceous material treatment apparatus.

of the carbonaceous materials are listed in Table 1. Those of CT were the highest because there were structure spaces called “lumen” in the cotton fiber [29], along with a micro-fibril structure [30]. Moreover, in the case of the carbonaceous material produced from wool fiber, the pore volume was not significantly increased by carbonization. Activated carbon may generally be classified by its pore diameter, such as microporous ($5 < r \leq 20 \text{ \AA}$), mesoporous ($20 < r \leq 500 \text{ \AA}$), or macroporous ($500 \text{ \AA} < r$). The specific surface area generally increases with increasing micropore formation [28], and this tendency was observed in the carbonaceous materials. The specific surface area of PET was $1019 \text{ m}^2/\text{g}$, but the total pore volume did not increase. This result indicated that the macropores ($500 \text{ \AA} < r$) of PET were larger than those of WL and CT. The mean pore diameter of the carbonaceous materials was greater in the order of PET, WL, and CT. Carbonaceous materials with different pore structures could be produced from fiber wastes by carbonization.

The SEM micrographs in Fig. 2 showed that the original wool and polyester fibers lost their fibrous form and underwent pore formation. Polyester, which is produced by the condensation polymerization of dicarboxylic acid and a diol and has a melting point of approximately 240°C , appeared to enter a molten state at 400°C . On the other hand, CT retained its fibrous structure, and SEM images showed no discernable change owing to carbonization. Because cotton fiber is derived from plants, its main component is cellulose. Therefore, cotton fiber may retain its fibrous structure after carbonization, whereas polyester fiber might melt owing to carbonization. Because fibrous activated carbon has been reported to exhibit higher adsorption rates than the particle form [24], it may be possible to use carbonized cotton as a carbonaceous material for various applications.

3.2 Amount of methylene blue adsorbed onto carbonaceous materials

Methylene blue can burn the eyes, causing permanent injury to the eyes of humans and animals. Upon inhalation, it can produce short periods of rapid or

Table 1 Physical properties of carbonaceous materials.

Materials	Specific surface area (m^2/g)	Pore volume (mL/g)			Mean pore diameter ($\text{\AA}$)
		$r \leq 20 \text{ \AA}$	$20 < r \leq 500 \text{ \AA}$	Total	
WL	133	0.01	0.00	0.01	4.3
PET	1019	0.02	0.01	0.04	1.4
CT	1253	0.16	0.15	0.32	10.2

The specific surface area on WL, PET, and CT before carbonization was $0 \text{ m}^2/\text{g}$.

Fig. 2 SEM images of carbonaceous materials produced from WL, PET, and CT at 1273K.

difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion, painful micturition, and methemoglobinemia [31, 32]. The adsorption isotherms of methylene blue onto WL, PET, and CT are shown in Fig. 3. The amounts of methylene blue adsorbed onto WL, PET, and CT increased in the order of WL, PET, and CT. The dyestuff adsorption mechanism onto the adsorbent would have been caused by its porosity [25, 33]. These results indicated that the amount of methylene blue adsorbed onto the carbonaceous materials depended upon their specific surface areas. The PET and CT obtained from the polyester and cotton fibers may be useful as adsorbents for the quantitative removal of methylene blue from an aqueous solution.

3.3 Actual wastewater treatment by carbonaceous materials

The decreasing chromaticity, turbidity, and COD by the wastewater treatment have become indices for the efficiency of the wastewater treatment in a textile factory. Moreover, TOC indicates the quantity of carbon contained as an organic substance in water. TOC can be used as an index of organic compounds. The changes in the chromaticity, turbidity, TOC, COD, and pH in the actual dyestuff wastewater by the carbonaceous material treatments are listed in Table 2. The chromaticity, TOC,

Fig. 3 Adsorption isotherms of methylene blue onto carbonaceous materials produced from WL, PET, and CT at 1273K.

and COD decreased by the carbonaceous material treatment, while the pH of the solution did not change. The chromaticity in the actual dyestuff wastewater was lower in the order of PET, WL, and CT. Its turbidity was increased by the WL and PET treatments, while it was decreased by the CT treatment. WL and PET might be broken into fragments by carbonization. However, the structure of CT was fibrous and porous, and the dyestuff may be easily adsorbed onto the cotton fiber. In spite of the specific surface area of PET being greater than that of WL, the chromaticity and turbidity in the actual dyestuff wastewater after the PET treatment were higher than those after the WL treatment. The TOC and COD in the actual dyestuff wastewater after the PET and WL treatments were similar. These results indicated that the amount of dyestuff adsorbed onto the carbonaceous materials in the actual dyestuff wastewater was not directly proportional to the specific surface areas and pore volumes of the carbonaceous materials.

The relationships between the chromaticity, turbidity, TOC, and COD and the mean pore diameter are shown in Fig. 4. They decreased with the decreasing mean pore diameter. The smaller pore diameter of some of the carbonaceous materials would be an important factor for

Table 2 The chromaticity, turbidity, TOC, and pH of actual dyestuff wastewater by carbonaceous material treatment.

Materials	Chromaticity (degree)	Turbidity (degree)	TOC (mg/L)	COD (mg/L)	pH
Blank	338	2.6	76	166	7.4
WL	120	5.4	41	86	7.3
PET	240	8.2	42	90	7.2
CT	6	0.4	7	0	7.4

the decreasing chromaticity, turbidity, TOC, or COD. These results indicated that CT would be suitable for the treatment of actual dyestuff wastewater. The mean pore diameter could be used to estimate the removal efficiency of the dyestuff from actual wastewater using carbonaceous materials.

Fig. 4 Relationship between chromaticity, turbidity, TOC or COD and mean pore diameter.

The chromaticity, turbidity, TOC, and pH in the actual dyestuff wastewater by oxygen, ozone, and/or carbonaceous material treatments are listed in Table 3. The chromaticity in the actual dyestuff wastewater was not changed by the oxygen treatment but was decreased by the ozone treatment. Moreover, it decreased by the oxygen and ozone treatments with CT. These results indicated that the contact frequency of the dyestuff and CT was increased by the circulation of the actual wastewater in a reactor with the oxygen and/or ozone treatments. The TOC was not decreased by the oxygen and/or ozone treatments, but was decreased by approximately 38% by the CT treatment. The pH of the solution changed to basic. The turbidity of the actual

dyestuff wastewater was increased by the CT treatment, because the CT may be decomposed during the ozone treatment. Many kinds of organic acidic and low molecular materials have been produced by the ozone treatment of organic compounds [34]. These are easily adsorbed onto the pores of carbonaceous materials. The dyestuff would be converted to low molecular materials by the ozone treatment with CT, and the dyestuff removal ability would be increased by using this method.

3.4 Application of ozonation along with carbonaceous material treatment to dyestuff wastewater

The use of ozonation, along with carbonaceous material treatment, could be useful for the removal of dyestuff in actual wastewater. The chromaticity, turbidity, TOC, COD, and pH in the actual dyestuff wastewater discharged from a textile factory with a series of four reactors after carbonaceous material treatments are listed in Table 4. The results in each of the four reactors were similar, because the amount of ozone in reactor 1 was the largest. The chromaticity and COD in reactor 1 were the largest among those of all the reactors.

The removal percentages for the chromaticity, TOC, and COD in the actual dyestuff wastewater by the ozone and/or CT treatments from the data in Table 3 are listed in Table 5. The chromaticity, TOC, and COD after the ozone treatment without CT were smaller than those after the ozone treatment with CT. The turbidity after ozone treatment with CT was greater than that after the ozone treatment without CT. The fact that the COD reduction was low may reflect the decomposition of the dye molecules into small organic substances via the ozone treatment process [35], and the lower COD removal compared to the color removal can be explained by the incomplete oxidation of the organic materials [36]. On the other hand, the lower TOC removal rate under the experimental conditions can be explained by the

Table 3 The chromaticity, turbidity, TOC, and pH of actual dyestuff wastewater by oxygen, ozone, and/or CT treatments.

Treatments	Chromaticity (degree)	Turbidity (degree)	TOC (mg/L)	COD (mg/L)	pH
Blank	379	6.8	80	183	7.6
Oxygen	379	7.0	77	183	8.4
Oxygen with CT	120	9.4	50	73	8.4
Ozone	139	3.8	75	149	8.2
Ozone with CT	59	9.2	50	73	8.1

Table 4 The chromaticity, turbidity, TOC, and pH of actual dyestuff wastewater by oxygen, ozone, and/or CT treatments in four series reactors.

Treatments	Number of reactors	Chromaticity (degree)	Turbidity (degree)	TOC (mg/L)	COD (mg/L)	pH
Blank	—	340	5.6	70	192	7.8
Oxygen with CT	1	220	4.5	69	142	8.1
	2	241	4.7	69	150	8.1
	3	270	4.8	68	152	8.2
	4	280	4.9	68	159	8.1
Ozone with CT	1	70	10.2	43	82	8.1
	2	99	10.1	43	82	8.1
	3	130	10.4	45	93	8.0
	4	130	9.3	40	92	8.0

Table 5 The removal percentage of chromaticity, turbidity, and TOC of actual dyestuff wastewater by ozone and/or CT treatments.

Treatments	Removal percentage (%)			
	Chromaticity	Turbidity	TOC	COD
Ozone	63.3	44.1	6	18.6
Ozone with CT	84.4	-35.3	37.5	60.1

resistance of the aromatic structures to cleavage and the production of small organic molecular fragments not being completely mineralized under the prevailing oxidative conditions [37]. The ozone treatment with CT of the actual dyestuff wastewater in a textile factory could be a better method than the use of only the ozone treatment. This result indicated that the ozone treatment with CT would be useful for the removal of the dyestuff from textile wastewater.

4. Conclusion

The chromaticity, TOC, and COD in the actual dyestuff decreased after all the carbonaceous material treatments. In particular, they were the lowest after the CT treatment. Moreover, the turbidity of the actual dyestuff wastewater in a textile factory with a series of four reactors after ozone treatment with CT increased compared to the use of only the ozone or CT treatment. The mean pore diameter of the carbonaceous material was an important factor in estimating the removal efficiency of a dyestuff from actual wastewater. This result indicated that the carbonaceous material produced from cotton

waste fiber discharged from a textile factory could be utilized for wastewater treatment in a textile plant.

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