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Decomposition of Methylene Blue Adsorbed on Zeolite by Dielectric Barrier Discharge

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In this study, dielectric barrier discharge (DBD) was used to decompose methylene blue (MB) adsorbed on pellet-shaped zeolite, and zeolite was reused as an adsorbent. The DBD treatment was performed in air under atmospheric pressure. The effect of plasma treatment on the zeolite structure was investigated. The effect of DBD treatment was evaluated by the amount of MB adsorbed on the zeolite and the Total organic carbon (TOC) of the solution in the repeated adsorption test. When the plasma-treated zeolite was added to pure water, some substances desorbed from the zeolite, and as a result of NMR analysis, it was found that the substance does not have a benzene ring structure. The results showed that the methylene blue adsorbed on the zeolite was decomposed into a low molecule without a benzene ring by the DBD treatment, and it was desorbed during the next adsorption cycle, so that the adsorption site was recovered while maintaining the structure of the zeolite.

本研究では、ペレット状ゼオライトに吸着したメチレンブルー (MB) を誘電体バリア放電 (DBD) で分解し、ゼオライトを吸着剤として再利用した。DBD 処理は、大気圧下の空气中で実行された。プラズマ処理がゼオライト構造に及ぼす効果を調査した。DBD 処理の効果は、繰り返し吸着テストでゼオライトに吸着された MB の量と溶液の全有機体炭素 (TOC) によって評価された。プラズマ処理したゼオライトを純水に加えると、ゼオライトからいくつかの物質が脱離した。NMR 分析の結果、その物質はベンゼン環構造を持たないことが示された。その結果、ゼオライトに吸着したメチレンブルーは DBD 処理によりベンゼン環のない低分子に分解され、次の吸着サイクルで脱着し、ゼオライトの構造を維持したまま吸着部位が回復したことが明らかになった。

Key Words

Dielectric barrier discharge plasma, Zeolite, Adsorption, Water treatment

1. Introduction

In recent years, the problem of colored wastewater has been raised because of a growing interest in environmental issues. Many of the dyes contained in colored wastewater are carcinogenic and affect aquatic organisms^{1) 2)}. Many textile dyes have high brightness brilliance and intensity of colors and are highly visible even in a very low concentration³⁾. In Japan drainage standards are set by Water Pollution Control Law; however, no items in it are related to chromaticity. Therefore, the colored components of wastewater discharged from the textile-dyeing industry are often untreated. Current major wastewater treatment methods comprise biological treatment methods using

microorganisms and bacteria and coagulation sedimentation methods with the addition of flocculants, which are widely used in Japan. However, dye wastewater discharged from dyeing factories contains persistent organic substances and cannot be sufficiently treated via biological treatments. In addition, water-soluble dyes are difficult to treat using coagulation precipitation methods and sludge is generated.

Various methods have been proposed to remove harmful dyes from colored wastewater. In the advanced oxidation process using ozone, hydrogen peroxide, and ultraviolet rays, harmful substances are decomposed by generating highly reactive OH radicals^{4)~6)}. Decomposition of dyes by various forms of plasma has also been reported^{7)~9)}. These methods are often effective even for persistent dyes, but have the problems that hydrogen peroxide is expensive and that the cost of plasma power and equipment is too large.

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Adsorption is one of the simple and cheap methods^{10) 11)}. Activated carbon has excellent performance as an adsorbent, but its high cost has hindered its use^{12) ~ 14)}. For this reason, zeolite has been taken up in many studies as a low-cost adsorbent^{15) 16)}. In addition, efforts have been made to improve the performance of zeolite¹⁷⁾. Most of the zeolites used as adsorbents reported in the literature are in powder form. The powder state has a large surface area and has the advantage that many dyes can be adsorbed in a short time, but handling becomes complicated. Handling is easier if pelletized zeolite is used, but the adsorption performance is inferior to powdered zeolite. For the reuse of zeolite after adsorption, desorption with alcohol has been proposed, but the need for large amounts of alcohol is a cost disadvantage. In this study, the adsorbed zeolite was regenerated using low temperature plasma. Since the dye is concentrated on the surface of zeolite and it is not necessary to use energy to raise the water temperature, efficient decomposition can be expected. By using a large amount of pellet type zeolite and regenerating it at low cost, it is considered that it will be a new method that is excellent in both the overall adsorption rate and the cost of the system.

2. Experimental Procedures

MB is a kind of basic dye and is a stable substance having a phenothiazine structure. Due to its stability and low toxicity, it has been used by many researchers for degradation evaluation. For the above reasons, MB was used as the dye model in this study. A ϕ 1.5 mm pellet type 4A zeolite (TOSOH) was used as the adsorbent.

Methylene blue adsorption experiments were performed at room temperature. A dye solution of concentration 400 mg/L was prepared by making up 0.4 g of methylene blue to 1 L with deionized water. Dye concentration was determined by obtaining absorbance using a UV-vis spectrophotometer. The initial concentration and volume of MB solution were set to 400 mg/L and 150 mL. 15 g of zeolite was charged into the MB solution and adsorbed for 20 hours while stirring with a magnetic

stirrer. The zeolite was removed from the solution and the absorbance and TOC of the solution were analyzed. The zeolite taken out of the solution was put into a dryer and dried at 80 °C for more than 6 h. The dried zeolite was treated by DBD plasma for 5 or 20 minutes. Schematics of the experimental apparatuses are shown in Fig. 1. DBD plasma was generated by a pulse power supply (SUEMATSU PPM100S). The pulse power supply was operated under the following conditions: peak voltage: 25 kV, polarity: positive, pulse repetition rate: 1000 pps. Zeolite was placed on an acrylic plate, and an aluminum plate was placed on top of the zeolite. The size of the acrylic plate was thickness 2 mm $\times$ width 180 mm $\times$ length 245 mm. The size of the aluminum plate was thickness 1 mm $\times$ width 110 mm $\times$ length 180 mm. There is a gap of about 2 mm between the zeolite and the aluminum plate.

The plasma-untreated or plasma-treated zeolite was re-introduced into the 400 mg/L methylene blue solution and the above process was repeated.

UV-vis absorption spectra of the MB solution after the adsorption of methylene blue by zeolite were measured using a spectrophotometer in the wavelength range of 200–800 nm. The concentration of MB in the solution was determined from the absorption maximum at 668 nm, which was also employed for the calibration curves.

The adsorption rate was calculated as

$$\text{conv (\%)} = \frac{C_0 - C}{C_0} \times 100$$

where C_0 was the initial concentration and C was the final concentration.

X-ray diffraction (XRD) patterns of the samples were obtained on an Ultima IV diffractometer with Cu K α radiation at a scan rate of 2° min⁻¹ with a step size of 0.02°. The total organic carbon (TOC) in the aqueous solution was measured by using a TOC-VCPH (Shimadzu, Japan) analyzer, which works on combustion method. ¹H NMR measurement was measured by using an AVANCE III 500 (BRUKER), and heavy water (D₂O) was used as the measurement solvent.

Fig. 1 Schematics of the experimental apparatuses

3. Results and Discussion

The XRD patterns of the original zeolite and the zeolite treated with plasma for 15 minutes are shown in Fig. 2. These XRD patterns are almost the same, and the peak peculiar to 4A zeolite can be confirmed. Since the gas temperature of DBD is low, it is considered that the zeolite structure is maintained even if plasma treatment is performed.

The effect of contact time on the adsorption rate of MB on the original zeolite is shown in Fig. 3. The adsorption rate of MB reached 40% in 1 hour and then gradually increased to 97% until 20 h. Even if the contact

Fig. 2 The XRD patterns of (a) the original zeolite and (b) the zeolite treated with plasma for 15 minutes

Fig. 3 Adsorption percentage with adsorption time for methylene blue onto original zeolite

time was further increased, the change in adsorption rate of MB was very small, so the adsorption time for one cycle was set to 20 h in this study.

The effect of adsorption performance by plasma treatment in successive adsorption cycles was investigated. As shown in Fig. 4, methylene blue was continuously accumulated in the zeolite by successive adsorption cycles. The amount of adsorbed MB increases with each cycle, but the amount of adsorbed MB per cycle rapidly decreases in the case (c) where plasma treatment is not performed between cycles. Zeolites treated with plasma between cycles suppressed the decrease of adsorption amount per cycle. The total amounts of adsorbed MB using 4 repetitions were 12.5, 14.2 and 15.4 mg/g for (c) no plasma treatment, (b) plasma treatment 5 minutes and (a) plasma treatment 20 minutes, respectively.

The effect of the number of repetitions on the TOC of the solution is shown in Fig. 5. In the second repetition, the TOC of the solution was the smallest when plasma treatment was not performed. However, as shown in Fig. 4, the amount of methylene blue adsorbed on the zeolite is the smallest when the plasma treatment was not performed. It is considered that this is because the methylene blue adsorbed on the zeolite at the first repetition is decomposed by the plasma, and changes into a molecule shape that is difficult to be adsorbed on the zeolite. These substances are desorbed when it is put into the solution at the second repetition. Depending on the type of dye, there are cationic, anionic and nonionic dyes. Zeolite has a negatively charged crystal skeleton and is effective for adsorbing the methylene blue, which is a cationic dye, but it is very difficult to adsorb anionic and nonionic dyes. It is possible that methylene blue was decomposed by plasma, and a substance that does not become a cation was generated in the process. As a result,

Fig. 4 The effect of the number of repetitions on the amount of adsorbed MB per gram of the zeolites. (a) Plasma treatment 20 minutes, (b) Plasma treatment 5 minutes and (c) No plasma treatment

Fig. 5 The effect of the number of repetitions on the TOC of the solution

it is considered that the electrostatic bond with the zeolite weakened and it was desorbed from the zeolite. After the second repetition, the amount of increase in TOC in the untreated plasma is larger than that in the treated plasma. In the case of no plasma treatment, the zeolite adsorption sites fill up as the number of repetitions increases, and finally the TOC value becomes the amount of carbon contained in the initial concentration of MB. On the other hand, in

the case of plasma treatment, the substances that have not been decomposed into carbon dioxide, methane, and other gaseous substances are only desorbed in the solution, and it is considered that the TOC value is suppressed.

After the methylene blue-adsorbed zeolite was treated with plasma, it was put into pure water and stirred for 20 hours. NMR spectra of methylene blue aqueous solution and experimental solution is shown in Fig. 6. The large peak around 4.7 ppm is derived from H of DOH contained in D₂O. The peak a around 3.2 ppm in the spectrum of the methylene blue solution is due to four -CH₃ in the side chain -N(CH₃)₂, and the three peaks b - d around 7.0 to 7.5 ppm are due to the conjugated system of the basic skeleton. In (2) and (3), which contain the substances desorbed from the zeolite, all peaks from a - d disappeared. This means not only the dissociation of CH₃, which is the bond with the lowest bond dissociation energy, but also the decomposition progresses until the destruction of the conjugated system, and it is desorbed in pure water. A new peak is generated due to the desorbed substance. Since there is no peak near b - d, it is considered that the benzene ring is also destroyed.

4. Conclusion

When the pellet type 4A zeolite was irradiated with a dielectric barrier discharge, there was no change in the XRD patterns. In the successive adsorption cycles of MB,

Fig. 6 NMR spectra of methylene blue aqueous solution and experimental solution. (1) Methylene blue aqueous solution 40 ppm, (2) Plasma treatment 5 min, (3) Plasma treatment 20 min

the adsorption performance was maintained by treating with plasma between the cycles. The total amounts of adsorbed MB using 4 repetitions were 12.5, 14.2 and 15.4 mg/g for no plasma treatment, plasma treatment 5 minutes and plasma treatment 20 minutes, respectively. MB adsorbed on zeolite is decomposed by plasma. However, not all MB is gasified, and a part of the decomposed product is desorbed from the zeolite in the next adsorption cycle and flows out into the solution.

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