Research Article

Solution Plasma-Assisted Green Synthesis of MnO$_2$ Adsorbent and Removal of Cationic Pollutant

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In this study, we proposed the solution plasma- (SP-) assisted green synthesis method using plants extracts, i.e., glucose, with the expectation of acting as a reducing agent and promotor for the formation of powder state of nanostructured MnO$_2$. MnO$_2$ was simply and rapidly synthesized within 10 min by the SP-assisted method. The structural features and morphology of as-synthesized MnO$_2$ were characterized by XRD, Raman, FE-SEM, and TEM analyses. For potential application of as-synthesized MnO$_2$, cationic dye, i.e., methylene blue (MB), removal performance was investigated by batch experiment at an initial concentration of $C_0 \sim 100$ mg L$^{-1}$. The obtained MnO$_2$ exhibited effective dye removal ability given high $C_0$, and simultaneously applied plasma discharging further enhanced removal efficiency. These contributions therefore open a new window not only on a powerful and environmentally benign synthesis route for efficient adsorbents but also on supporting multiple removal mechanism.

1. Introduction

Advances in scientific technology have made human life more comfortable but also these amenities are usually accompanied with environmental load. Especially, water pollution is a serious problem of all over the world. One of the main contributions of water pollution was organic pollutants derived from industrial waste. Therefore, diverse wastewater treatment techniques have been extensively studied, and these can be largely categorized as physical, chemical, and biological approach and can serve as an example of physical adsorption, oxidative degradation, coagulation, photo degradation, etc., concretely [1–3]. Among them, removal of synthetic organic dye by adsorption has been widely applied as the most economical method due to its cost-effectiveness and simple and efficient solid adsorbents [4, 5].

As the representative adsorbents, there are carbon-based inorganic adsorbent, transition metal oxide, hybrid composite and so on. In particular, nanostructured manganese dioxide (MnO$_2$) has been considered as attractive and promising green material because of not only its low cost, earth abundance [6, 7], and nontoxicity but also its structural flexibility combined with outstanding physicochemical properties for applications in various fields such as environmental applications (e.g., decomposition of organic dye and oxidation of volatile organic compounds), electrode materials for sustainable energy system (e.g., metal-air battery, lithium secondary battery, and fuel cell), and photocatalyst [8–10]. Notably, MnO$_2$ presented multifunctional properties which are the physical adsorption, catalytic oxidation with hydrogen peroxide (H$_2$O$_2$), and photocatalytic oxidation due to different crystallographic polymorphs of MnO$_2$ (i.e., $\alpha$, $\beta$, $\gamma$, $\delta$, and $\lambda$-type). Of which, birnessite-MnO$_2$ ($\delta$-MnO$_2$) is known as the most reactive type [11]. The highest negative-charge density of birnessite makes it a potential candidate for removal of cationic pollutants. However, it still exhibited not enough removal capability without additional agents. To overcome this problem, design and synthesis of nanostructured MnO$_2$ are essential for improving adsorption capability through the expanding interfacial area. Although various synthesis techniques such as hydrothermal,
microwave irradiation, template-assist method, coprecipitation, and microemulsion method are utilized for preparation, they required toxic chemical agents or longer process time and higher temperature [12–15]. Thus, a significant current focus in the advancement of green synthesis is satisfying both ecofriendly and energy-saving. In this regard, plasma in liquid named solution plasma (SP) has great potential for the green approach [16]. Since the electron temperature ($T_e \sim 104$ K) is much higher than that of heavy particles such as ions or neutrons ($T_i, T_n \sim 300$ K), the thermal motion of heavy particles can be ignored, and thus, the solution temperature is kept close to ambient temperature or slightly high during plasma discharge [17, 18]. Therefore, these unique characteristics of SP opened up the new route for synthesizing the specific materials.

In our previous work, we successfully synthesized colloidal MnO₂ nanosheets in the KMnO₄ aqueous solution by one-pot SP process without additional chemical reagents and verified possible reaction mechanism [19]. Since the colloidal state adsorbents are difficult to recover due to easy aggregation with solid absorbents in the aqueous solution [20], we have tried to synthesize the powder state of MnO₂ by the SP-assisted green synthesis method using sugar, i.e., glucose. We expected that glucose acts as the reducing agent and promotor for the formation of powder state MnO₂. Furthermore, the SP was utilized as an assistant for decomposition of organic pollutants. Recently, plasma-assisted water treatments, including thermal/nonthermal plasma, microwave plasma, or arc plasma [21–23], have been demonstrated to be the effective way for remediation of waste water. Plasma-based techniques could oxidize and decompose the toxic organic molecules to less toxic or nontoxic small by-products. Although the above techniques are highly efficient under low-level pollutants, they do not present sufficient capability under high-level pollutants. Hence, we focused on the simultaneous adsorption and degradation reactions for enhancing removal ability through highly reactive species including electrons, radicals (H⁺, H₂, O₂⁻, and OH⁻), and ions generated from decomposition of water molecules. To verify the potential application of as-synthesized MnO₂ by the SP-assisted method, removal capability of cationic pollutant, i.e., methylene blue (MB), was examined.

2. Materials and Methods

2.1. Synthesis of MnO₂ by SP. The MnO₂ was successfully synthesized by SP process in the sugar (i.e., glucose) added potassium permanganate (KMnO₄) aqueous solution. KMnO₄ was selected as the MnO₂ source, and glucose was utilized as a promoter for powder form of MnO₂. All chemicals were obtained from Wako Pure Chemical Industries Ltd., Japan, and used without further purification. The precursor was prepared by following steps: 1.0 g of KMnO₄ was mixed sufficiently by magnetic stirring in 100 ml volume of DI water, and then, 0.15 g of glucose was put in this solution. Figure 1 shows the experimental setup of the SP system. As-prepared precursor was moved to a glass reactor for SP treatment. To generate the plasma in solution, bipolar pulse power supply (Kurita, Japan) was utilized and discharge conditions of frequency and pulse width were adjusted at 20 kHz and 2.0 μs, respectively. After SPP for 10 min, powder form of MnO₂ was synthesized and sample was obtained by filtration and oven-dry procedures. The as-obtained MnO₂ was used as the adsorbent material.

2.2. Characterizations. The structural properties of as-prepared MnO₂ were evaluated by using an X-ray diffractometer (XRD, Rigaku Ultima IV, Rigaku Corp., Japan) and Raman spectroscopy with 532.5 nm laser wavelength (NRS-1000, JASCO corp., Japan). The morphology was observed by field emission scanning electron microscopy (FE-SEM, S-4800, HITACHI High-Technologies Co., Ltd., Japan) and transmission electron microscopy (TEM, JEM-2500SE, Japan). Optical emission spectroscopy (OES, Ocean optics Inc., USB4000+) was carried out to investigate the reactive species during plasma discharging. Ultraviolet-visible spectroscopy (UV-vis, Shimadzu UV-3600, Japan) was used to observe the dye removal performance.

2.3. Batch Experiment for Cationic Dye Removal. To determine the cationic dye removal or degradation capability, methylene blue (MB, C₁₆H₁₈ClN₃S₄·nH₂O) was utilized as typical cationic dye. The dye removal capability of adsorbent (MO), plasma (SP), and adsorbent/plasma (MO+SP) system were observed under following conditions. Firstly, the initial concentration ($C_0$) of MB aqueous solution was fixed at 100 mg L⁻¹ because dye removal capability in low contaminant concentration is difficult to verify the effect of each system due to the rapid adsorption or degradation in the first few minutes. All of the batch tests were carried out under natural pH (6.5–6.8) and temperature (298 K), and details were as follows: (i) adsorbent system (MO): 0.06 g of MO was put into the 100 ml volume of MB stock solution,
and UV-vis spectrum was measured after 30 min of contact time; (ii) plasma system (SP): the plasma was generated in MB solution using bipolar DC pulse power supply (frequency: 20 kHz, pulse width: 1.5 μm) for 30 min; (iii) adsorbent/plasma system (MO + SP): the plasma was generated in MB solution including 0.06 g of MO for 30 min.

The dye removal efficiency (equation (1)) and adsorption capacity (equation (2)) of the adsorbents (MO) were determined by the following equations:

\[
\text{removal efficiency (\%)} = \left(1 - \frac{C_t}{C_0}\right) \times 100, \\
\text{adsorption capacity (mg/g)} = \frac{(C_0 - C_t)V}{W},
\]

where \(C_0\) and \(C_t\) (mg L\(^{-1}\)) are the initial and the absorbed dye concentration at contact time, respectively. \(V\) (L) is the volume of dye stock solution and \(W\) (mg) is the amount of dosage.

### 3. Results and Discussion

#### 3.1. Plasma-Assisted Synthesis of MnO\(_2\).

The glucose is classified as reducing sugars since it can reduce metal ions (M\(^{n+}\) to M\(^0\)) owing to its free aldehyde groups in the molecular structure [24]. Therefore, MnO\(_4^-\) could be reduced to MnO\(_2\) by glucose in the KMnO\(_4\) aqueous solution. However, this reduction process is a very sluggish chemical reaction without reactive agents, which was determined in our preliminary study. It took more than 12 hours to form powder state MnO\(_2\) completely. Hence, the SP was introduced to accelerate chemical reaction. Reduction mechanism of MnO\(_4^-\) to MnO\(_2\) in the presence of plasma was already proposed in our previous work [19]. Briefly, highly reactive species are generated from decomposition of water molecules during plasma discharging in aqueous solution, which promote rapid reduction reaction from MnO\(_4^-\) to MnO\(_2\). Since these reactive species are very active, reactions occur with multiplicity. The main chemical reaction could be suggested by the following equations:

\[
\text{H}_2\text{O} \longrightarrow \text{H}^+ + \text{OH}^- \text{ (in the plasma zone)} \tag{3}
\]

\[
\text{MnO}_4^- \text{ (VII)} + 3\text{H}^+ \longrightarrow \text{MnO}_2 \text{ (IV)} + \text{OH}^- + \text{H}_2\text{O} \text{ (chemical reduction)} \tag{4}
\]

Especially in liquid phase where molecules are closely packed, a remarkably high reaction rate could be achieved [16]. As a result, we obtained MnO\(_2\) powders within 10 min. The effect of SP was verified by the OES spectrum that was measured during plasma discharge in aqueous solution in Section 3.4.

#### 3.2. Structure and Morphology Analysis.

Structure features were observed by XRD and Raman analysis. As can be seen in Figure 2(a), the observed peaks (marked with ▽) at 2\(\theta\) = 12.37°, 24.97°, 37.18°, and 66.21° correspond with the birnessite-type potassium manganese oxide hydrate (JCPDS No. 52-0556). It is layered MnO\(_2\) composed of edge-sharing [MnO\(_6\)] octahedral with K\(^+\) ions and water molecules in the interlayer (~0.7 nm) [25]. For further information of structural properties, Raman spectroscopy measurements were performed. As shown in Figure 2(b), the predominant three peaks marked with \(\nu_1\) (~637 cm\(^{-1}\)), \(\nu_2\) (~566 cm\(^{-1}\)), and \(\nu_3\) (~501 cm\(^{-1}\)), respectively, well correspond with the major vibration peaks of the birnessite-type MnO\(_2\): \(\nu_1\) indicates symmetric stretching vibration of Mn–O in the [MnO\(_6\)] octahedral, and \(\nu_3\) indicates stretching vibration mode of Mn–O in the [MnO\(_6\)] octahedral layers [26]. Figure 2(c) shows the XPS survey spectra. As expected, Mn 2p, O 1s, and K 2s peaks were detected, and narrow-scan spectra for Mn 2p shows a clear peak splitting at 653.76 and 642.02 eV, corresponding to the Mn 2p\(_{3/2}\) and Mn 2p\(_{1/2}\). This peak separation value (11.74 eV) is consistent with the literature of birnessite-type MnO\(_2\) [27]. The FE-SEM and TEM images are shown in Figure 3. The FE-SEM image revealed that MnO\(_2\) has spherical aggregated nanoparticles with 20–100 nm size (Figure 3(a)). This nanoporous structure might have an advantage in pollutants removal due to frequent contact between MnO\(_2\) and pollutant. The nanostructure was further evidenced in the TEM image (Figure 3(b)). Meanwhile, the selected area electron diffraction (SAED) pattern showed that MnO\(_2\) has amorphous crystalline structure (Figure 3(b) inset) and it is in good agreement with broad and weak XRD pattern.

#### 3.3. Cationic Dye Removal Test.

To confirm the cationic dye removal capability of adsorbent (MO), plasma (SP), and adsorbent/plasma (MO + SP) systems, batch experiments were performed under natural pH, ambient temperature, adsorbent dosage of 0.06 g L\(^{-1}\), and contacting or treatment time of 30 min. Preliminary experiments to find out equilibrium contact time demonstrated about 30 min. In addition, when the plasma discharge was performed more than 30 min in MB stock solution, solution temperature increased. Considering these points, we set the treatment time for 30 min to compare the dye removal capability by each system excluding other external factors.

Figure 4(a) shows the UV-vis spectra of MB solution before and after treatment. The predominant three peaks at 665, 611, and 292 nm represent monomer, dimer, and aromatic ring of MB molecules, respectively [28]. The removal capability of MB was determined by measuring the intensity of absorbance spectra at 665 nm after treatment. After 30 min, the absorption intensities of all systems diminished and dye removal capability is of the following order: adsorbent/plasma (MO + SP) > adsorbent (MO) > plasma (SP). The calculated values of removal efficiency (left side, gray bar) and capacity (right side, ■ ■ ■ ■) using equations (1) and (2) based on the UV-vis results are presented in Figure 4(b). Notably, the adsorbent/plasma system (MO + SP) showed higher capability for dye removal than the adsorbent (MO) and plasma (SP) systems. This result demonstrated that the dual-treatment system with plasma and adsorbent is the effective method for dye removal.
3.4. SP-Assisted Pollutants Removal Mechanism. To clarify the effects of SP on pollutant removal, the OES spectrum was measured during plasma discharging in an aqueous solution. As shown in Figure 5(a), hydrogen ($H_\alpha$; 665 nm and $H_\beta$; 486 nm), oxygen (O I; 777 and 845 nm) and hydroxyl (OH; 309 nm) radicals were detected. It is believed that reactive species generated from decomposition of water molecules by plasma discharging. The formation of plasma in the aqueous solution can be described as follows. When the voltage is applied between submerged electrodes, water evaporation and microbubbles are generated by Joule heating. After applied voltage is high enough to reach the breakdown voltage, discharge is initiated [29]. During the plasma discharging, energetic electrons and ions could contribute to degradation of organic molecules, i.e., MB molecules. In fact, the SP process has been used for organic compound decomposition, and it efficiently destroyed aromatic ring structure [30]. Therefore, as can be seen in Figure 5(b), an
Figure 4: (a) UV-vis spectra for MB solution before and after treatment using adsorbent (MO), plasma (SP), and adsorbent/plasma (SP + MO) systems, respectively. (b) MB removal efficiency (gray bar) and capacity (---■---) of each approach (C₀ = 100 mg L⁻¹, 297 K, contact or treatment time = 30 min).

Figure 5: (a) OES spectrum collected during plasma discharging in aqueous solution, and (b) schematic presentation of the adsorbent/plasma system for pollutant removal in aqueous solution.
adsorption and chemical degradation simultaneously occurred. Moreover, chemical degradation could be classified to three types of mechanisms. First, since the generated O and OH radicals have higher oxidation potential [21, 31], which mainly contribute to degradation of MB molecules. Moreover, repetitive generation of abundant OH radicals during discharging (equation (3)) could continuously affect the MB degradation. And also, the SP provides UV radiation effect and strong electric fields that are composed of energetic electrons, which could support degradation [32–34]. Note that the small plasma zone and weaker radiation energy than the solar simulator limited a radiation range and power, respectively, and thus, we assume that a UV radiation effect plays a subsidiary role in this system. On the basis of the above discussion, we believe that these multiple reaction mechanisms could be enhancing removal efficiency under high-level pollutants.

4. Conclusions

In this study, we have investigated a SP for both synthesis and pollutant removal as a prospective green route. SP-assisted synthesis significantly reduces process time without toxic reactive agents through reactive species (energetic electrons, radicals, and ions) generated during plasma discharging. Successfully synthesized MnO2 nanoparticles presented a removal efficiency of 72.4% for C0 = 100 mg L−1 within 30 min. In addition, simultaneously applying plasma discharge increased a removal efficiency to 81.5% due to the generated O and OH radicals with UV radiation and electric fields. These findings will be useful for designing an innovative green approach for MnO2 absorbent and understanding multiple reaction mechanisms for cationic pollutant removal.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

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