Mesoporous SiO_2 Particles Combined with Fe Oxide Nanoparticles as a Regenerative Methylene Blue Adsorbent

Yul Hong,†,§ Byeong Jun Cha,†,§ Young Dok Kim,*‡§ and Hyun Ook Seo*†,‡

†Department of Chemical and Energy Engineering, Sangmyung University, Seoul 03016, Republic of Korea
‡Department of Chemistry, Sungkyunkwan University, Suwon 16419, Republic of Korea

Supporting Information

ABSTRACT: Mesoporous SiO_2 adsorbents were combined with Fe oxide nanoparticles (~10 nm) that can catalyze thermal oxidation of organic compounds at low temperatures. Fe oxide nanoparticle (~10 nm)-incorporated SiO_2 adsorbents were prepared via a temperature-regulated chemical vapor deposition method followed by a thermal annealing process. The removal efficiency and reusability of Fe oxide/SiO_2 particles were examined and compared to those of bare SiO_2. Upon deposition of Fe oxide nanoparticles, not only the equilibrium adsorption capacity of mesoporous SiO_2 for methylene blue (MB) was improved but also the reusability of SiO_2 adsorbent was increased significantly. The adsorption ability of fresh Fe oxide/SiO_2 particles can be almost fully recovered by simple thermal annealing at atmospheric conditions (400 °C), whereas that of bare SiO_2 reduced significantly under same conditions. In addition, full recovery of initial MB adsorption ability of Fe oxide/SiO_2 can be achieved by a 100 °C annealing process. Fourier transform infrared, thermogravimetric analysis, and X-ray photoelectron spectroscopy analyses indicated that Fe oxide nanoparticles catalyzed thermal degradation of adsorbed MB molecules, resulting in the improved reusability of the Fe oxide/SiO_2 adsorbent. In addition to reusability, the equilibrium adsorption capacity of mesoporous SiO_2 particles for various cationic dye molecules, such as MB, malachite green, and rhodamine B, can be improved by combining Fe oxide nanoparticles.

1. INTRODUCTION

Rapid industrialization in the past decades has caused water pollution and it has become one of the greatest environmental concerns in the recent years. Many industries have utilized various synthetic dyes to color their products, e.g., textile, paper, food, cosmetics, and plastics.⁵−⁶ Most of the synthetic dyes are complex organic molecules and they are not easily biodegraded when discharged into the water.⁶−¹⁰ These dyes can cause serious environmental problems even in their low quantities. For instance, a small amount of dyes can readily change the color of water, resulting in the reduction of sunlight penetration into the water, which, in turn, inhibits the growth of aquatic bacteria.⁵,⁶ Besides, some of the synthetic dyes are carcinogenic or mutagenic in various aquatic organisms.⁷,⁵,¹¹,¹²

Many different methods such as adsorption, coagulation, advanced oxidation, and membrane separation can be utilized for the removal of synthetic dyes from the wastewater.⁵,⁶,¹³−¹⁹ Each technique has its own advantages and disadvantages,¹⁵ however, among various methods, removal of dyes using adsorbents has been considered as the most viable solution due to its simplicity, cheapness, and effectiveness.⁵,¹³,²⁰−²² The main drawback of the adsorption method is that it only converts the phase of dye molecules from aqueous to adsorbed phase but does not decompose them into harmless species. That is to say, an additional treatment is required to decompose the adsorbed dyes (often thermal annealing is utilized), otherwise the used adsorbents are needed to be carefully disposed as waste. After the additional treatments, the regenerated adsorbents can be reused for the removal of dyes from wastewater; however, the loss of their initial adsorption efficiencies often occurs. It has been demonstrated that the regeneration of spent adsorbent can be achieved using various techniques, such as solvent extraction,²³ microwave radiation-assisted desorption,²⁴ chemical decomposition,²⁵ biological degradation,²⁶ and thermal degradation of adsorbates.²⁷−²⁹ Among them, the thermal treatment has been considered as one of the most viable methods due to its simplicity and cost-effectiveness and it has been already utilized to reactivate the granular activated carbon.²⁷−²⁹

Owing to its excellent stability and ease of separation from aqueous phase together with large abundance, SiO_2-based materials has been extensively used as adsorbents for organic pollutants and supporting materials of heterogeneous catalysts.³⁰−³³ Recently, the fabrication pathway of mesoporous SiO_2 nanoparticles has been also investigated³¹,³² and SiO_2 nanoparticle-based organic−inorganic hybrid materials as heterogeneous catalysts have been investigated.³³

Recently, we successfully synthesized small Fe oxide nanoparticles embedded into mesoporous substrates using a temperature-regulated chemical vapor deposition (TR-CVD) followed by a thermal annealing process.³⁴ Our previous results demonstrated that these Fe oxide nanoparticles exhibited high...
catalytic activity toward thermal degradation of carbon-based compounds in their gas phases (CO, acetaldehyde, and toluene).34–36 In this work, Fe oxide nanoparticles were combined with mesoporous SiO2 based on the aforementioned methods34–36 and, for the first time, we demonstrated the utilization of the Fe oxide/SiO2 sample in the removal of organic dyes from the aqueous phase. The performance of Fe oxide/SiO2 as an adsorbent for the removal of organic dyes from aqueous phase, and its efficiency was compared to that of bare SiO2 not only in terms of its adsorption ability but also reusability after the simple thermal annealing process at atmospheric conditions ($\leq 400^\circ$C).

2. RESULTS AND DISCUSSION

2.1. Characterization of Fe Oxide/SiO2. Figure 1 shows cross-sectional energy dispersive spectroscopy (EDS) mapping images of a TR-CVD-prepared Fe oxide/SiO2 particle before the postannealing process. The elemental EDS mapping image of Fe indicates that both inner and outer surfaces of mesoporous SiO2 particles were covered by evenly distributed Fe oxide nanoparticles. After 8 h of postannealing (at 750 °C, 30 sccm of dry air flow), the Fe oxide/SiO2 sample was further analyzed by high-resolution transmission electron microscopy (HR-TEM) (Figure 2a). The lattice structure of small Fe oxide nanoparticles can be identified from the amorphous SiO2 in the HR-TEM image, which allowed us to determine the size of Fe oxide nanoparticles (diameter of $\sim$10 nm) formed by the TR-CVD and a subsequent annealing process. The lattice parameter of Fe oxide nanoparticles obtained from HR-TEM corresponded to the (311) plane of Fe oxide ($\alpha$-Fe$_2$O$_3$ or Fe$_3$O$_4$).37,38

Figure 2b shows X-ray diffraction (XRD) patterns of bare SiO2 and Fe oxide/SiO2 annealed at 750 °C after the TR-CVD process. The bare SiO2 sample did not show any feature in the XRD pattern because of its amorphous nature. For the Fe oxide/SiO2 sample, one can notice the appearance of peaks at 36 and 63°, which can be attributed to (311) and (440) planes, respectively, of Fe oxide ($\alpha$-Fe$_2$O$_3$ or Fe$_3$O$_4$)37,38 and these results are in line with those of the HR-TEM image. However, one cannot discriminate two different phases of Fe oxide ($\alpha$-Fe$_2$O$_3$ or Fe$_3$O$_4$) based on the results of TEM and XRD analyses since both phases of Fe-oxides ($\alpha$-Fe$_2$O$_3$ and Fe$_3$O$_4$) exhibit almost the same lattice constants.37,38 That is to say, Fe oxide/SiO2 consists of either $\alpha$-Fe$_2$O$_3$, Fe$_3$O$_4$, or their mixture.

Figure 2c shows Fe 2p$_{3/2}$ core-level XPS spectrum of the postannealed Fe oxide/SiO2 particles. A broad peak extended from 716 to 706 eV was found in the binding energy region of the Fe 2p$_{3/2}$ core-level. The central position of the binding energy of the Fe 2p$_{3/2}$ core-level peak ($\sim$710 eV) was closer to Fe$_3$O$_4$ states ($\sim$710.4 eV) rather than $\alpha$-Fe$_2$O$_3$ states ($\sim$710.9 eV).39 However, one should note that many elements resulting from final state effects were contributed to the Fe 2p$_{3/2}$ XPS peak;40–42 the Fe 2p$_{3/2}$ peak of Fe oxide can be fitted using six components arising from final state relaxation effects (Figure S1).40–42 Considering this complexity and broadness of the Fe 2p core-level peak resulted from the final state effect, we cannot exclude the possibility of coexistence of Fe$_3$O$_4$ and $\alpha$-Fe$_2$O$_3$ states.

The geometrical structure of Fe oxide-loaded mesoporous SiO2 particles after postannealing was further analyzed by obtaining a nitrogen adsorption–desorption isotherm. The nitrogen isotherms of bare SiO2 samples without and with the annealing process (750 °C, 8 h, at a constant dry air flow of 30 sccm) were also measured. The pore size distributions of bare SiO2 and Fe oxide/SiO2 particles were obtained using Barrett–Joyner–Halenda (BJH) methods with each nitrogen isotherm (Figure 3). Pore volumes with a specified size ($\sim$11 nm) decreased, whereas those of other sizes did not undergo noticeable change upon the deposition of Fe oxide nanoparticles ($\sim$10 nm). It implied that Fe oxide nanoparticles ($\sim$10 nm) were mostly formed into the pores of SiO2 with a pore volume of $\sim$11 nm, although the formation of Fe oxide...
nanoparticles on exterior surface of mesoporous SiO₂ cannot be completely ruled out.

The surface area and average pore diameter of three samples were estimated using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively, based on each nitrogen isotherm, and the results are summarized in Table 1. Original mesoporous SiO₂ particles exhibit a specific surface area of 302.6 m²/g and an average pore size of 13.1 nm. These values remained almost the same after the annealing process at 750 °C, indicating that the mesoporous structure of SiO₂ is highly stable even at the elevated temperature. On the other hand, upon deposition of Fe oxide on SiO₂ particles and subsequent annealing at 750 °C, the specific surface area decreased to 224.3 m²/g, whereas the mean pore size slightly increased to 14.8 nm. This can be attributed to the formation of Fe oxide nanoparticles (~10 nm) whose size is less than the average pore size (13 nm) of the SiO₂ substrate. The pores of the substrates smaller than the average pore size were occupied by Fe oxide nanoparticles (Figure 3), increasing the average pore size and decreasing the specific surface area. However, it is also possible that the Fe oxide nanoparticles induced rupturing of porous structures of the SiO₂ substrate especially upon the annealing process at such a high temperature (750 °C). The amount of Fe loading of Fe oxide/SiO₂ was determined to be ~8.3 wt % by the inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis (Table 1).

Table 1. Specific Surface Area (m²/g) and Average Pore Diameter (nm) of Three Samples (Bare SiO₂ before and after Postannealing and the Postannealed Fe Oxide/SiO₂ Particles) Are Summarized with the Amount of Fe Loading (wt %) of the Postannealed Fe Oxide/SiO₂ Particles

|                  | specific surface area (m²/g) | average pore diameter (nm) | Fe loading (wt %) |
|------------------|-----------------------------|---------------------------|-------------------|
| bare SiO₂        | 302.6                       | 13.1                      |                  |
| 750 °C-annealed bare SiO₂ | 297.8                       | 14.2                      |                  |
| 750 °C-annealed Fe oxide/SiO₂ | 224.3                       | 14.8                      | 8.3               |

The specific surface area and average pore diameter were determined by BET and BJH methods, respectively, based on the respective nitrogen adsorption–desorption isotherm results, whereas the amount of Fe loading was determined by the ICP-OES analysis.

surface area of 302.6 m²/g and an average pore size of 13.1 nm. These values remained almost the same after the annealing process at 750 °C, indicating that the mesoporous structure of SiO₂ is highly stable even at the elevated temperature. On the other hand, upon deposition of Fe oxide on SiO₂ particles and subsequent annealing at 750 °C, the specific surface area decreased to 224.3 m²/g, whereas the mean pore size slightly increased to 14.8 nm. This can be attributed to the formation of Fe oxide nanoparticles (~10 nm) whose size is less than the average pore size (13 nm) of the SiO₂ substrate. The pores of the substrates smaller than the average pore size were occupied by Fe oxide nanoparticles (Figure 3), increasing the average pore size and decreasing the specific surface area. However, it is also possible that the Fe oxide nanoparticles induced rupturing of porous structures of the SiO₂ substrate especially upon the annealing process at such a high temperature (750 °C). The amount of Fe loading of Fe oxide/SiO₂ was determined to be ~8.3 wt % by the inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis (Table 1).

2.2. Methylene Blue (MB) Adsorption (Regeneration of Adsorbents and Repeated MB Adsorption). SiO₂ particles loaded with Fe oxide nanoparticles via TR-CVD and subsequent annealing (750 °C, 8 h) were tested as an adsorbent for MB removal from solution, and hereafter, they are referred as Fe oxide/SiO₂. MB adsorption experiments were repeatedly performed using two adsorbents (bare SiO₂ and Fe oxide/SiO₂) for 3 h at room temperature under dark conditions. Figure 4a schematically shows the sequence of the experiments including the MB adsorption and annealing processes conducted before each MB adsorption test. Prior to the 1st MB adsorption experiment, each adsorbent was annealed at 400 °C for 3 h under atmospheric air conditions. After the 1st MB adsorption test, each adsorbent was collected from MB solution and annealed at 400 °C for 3 h under atmospheric air conditions, referred as regeneration process in Figure 4a. Then, MB adsorption experiments were performed again using each regenerated adsorbent under the same experimental conditions as the 1st MB adsorption test.

UV/vis absorbance spectrum of MB solution was measured every 20 min for the 2 h, and 1 h after that, the absorbance spectrum was obtained again to follow the concentration change of MB solution due to the adsorption of MB molecules on each adsorbent. A characteristic MB absorbance peak with a maximum peak height at 664 nm was observed in the range of 450–750 nm. For all cases of MB adsorption experiments, decreases of the characteristic MB peak intensities were found with increasing the reaction time, whereas the position and shape of the MB absorbance peaks remained the same, indicating that the adsorption of MB molecules on each adsorbent took place.

MB adsorption behaviors during the 1st and 2nd MB adsorption experiments with each sample (bare SiO₂ and Fe oxide/SiO₂) are shown in Figure 4b,c. The MB absorbance peak heights at 664 nm (Abs. at λmax) were measured after background subtraction and plotted as a function of reaction time during the 2 h of the 1st and 2nd MB adsorption experiments (Figures 4b and 3c). Gradual decreases of MB absorbance at 664 nm due to MB adsorption were observed as a function of reaction time for all cases of experiments. Bare SiO₂ exhibited a slightly better MB adsorption ability than Fe oxide/SiO₂ during the 1st MB adsorption test; the MB absorbance peak intensity at 664 nm decreased by ~44% after 2 h of the 1st MB adsorption test, whereas it decreased by ~36% when Fe oxide/SiO₂ was used as an adsorbent under same experimental conditions. However, the MB adsorption ability of bare SiO₂ was significantly reduced when it was reused (the 2nd MB adsorption) after 3 h of the 1st MB adsorption test and the regeneration process (Figure 4b). On the other hand, Fe oxide/SiO₂ exhibited almost the same MB adsorption behaviors when the 2nd MB adsorption experiment was repeatedly performed after the regeneration process under the same conditions (Figure 4c).

The MB adsorption abilities of bare SiO₂ and Fe oxide adsorbents at the 1st and 2nd MB adsorption experiments are compared with their removal efficiency (%) (Figure 4d). The removal efficiency (%) is defined as follows

\[
\text{removal efficiency (\%) } = \frac{C_0 - C}{C_0} \times 100(\%)
\]

where \(C_0\) is the concentration of MB solution at time zero (without any adsorbent) and \(C\) is the concentration of MB solution after 3 h of each adsorption experiment. The concentration of MB solution (\(C\)) was calculated by converting the absorbance of the MB peak at 664 nm measured after 3 h of each MB adsorption experiment to the respective MB

Figure 3. Pore size distributions (BJH plots) of bare SiO₂ and Fe oxide/SiO₂ particles.
concentration based on a linear relationship between the MB concentration and absorbance peak height at 664 nm (data are not shown).

Figure 4d clearly shows different behaviors of bare SiO₂ and Fe oxide/SiO₂ adsorbents when each adsorbent was reused after the regeneration process. The removal efficiency of bare SiO₂ (∼54%) was slightly higher than that of Fe oxide/SiO₂ (∼47%) for the case of the 1st MB adsorption test where each of the fresh sample was used. When each adsorbent was reused (the 2nd MB adsorption test) after the regeneration process (thermal annealing at 400 °C for 3 h), the removal efficiency of bare SiO₂ decreased to 33 from 54%, whereas the efficiency of Fe oxide/SiO₂ was only slightly reduced (from 47 to 42%). For the case of Fe oxide/SiO₂ particles, the MB adsorption experiments were further performed repeatedly using the same experimental procedures (regeneration by 3 h of annealing at 400 °C and repeated MB adsorption test) and the removal efficiency at each repeated adsorption test is calculated (denoted as the 3rd and 4th in Figure 4d). The removal efficiency values obtained from four repeated MB adsorption experiments with Fe oxide/SiO₂ particles are very similar, indicating that the MB adsorption ability of Fe oxide/SiO₂ particles can be almost fully recovered by a simple annealing process (at 400 °C, 3 h, under atmospheric air conditions), whereas that of bare SiO₂ cannot be fully recovered by the same annealing process.

Additional experiments were conducted with Fe oxide/SiO₂ particles using lower temperatures (200 and 100 °C) of thermal annealing as the regeneration process. Prior to the regeneration process at lower temperatures (200 and 100 °C), the collected samples were dried at 60 °C for 4 h to remove remaining water molecules absorbed by Fe oxide/SiO₂ particles. Other experimental conditions were the same as aforementioned cases except for the regeneration process.

There were no noticeable differences in MB adsorption behaviors of Fe oxide/SiO₂ before and after the regeneration
process at each lower temperature (at 200 and 100 °C) (Figure S2). The removal efficiency (%) of each case of study after 3 h of the MB adsorption experiment was calculated and compared in Figure 4e. The removal efficiency of Fe oxide/SiO₂ particles was almost fully recovered upon 3 h of annealing at lower temperatures (200 and 100 °C) under atmospheric air conditions. The additional experiments were performed with decreasing time duration (3 → 2 → 1 h) of 100 and 400 °C annealing to study the influence of annealing temperature on the regeneration rate of the spent Fe oxide/SiO₂ particles (please see Supporting Information, Figure S3). The equilibrium adsorption capacity of Fe oxide/SiO₂ particles was almost fully recovered irrelevant to the time duration (1 or 2 h) of 100 and 400 °C annealing, implying that the regeneration rate of Fe oxide/SiO₂ was not significantly influenced by the annealing temperature under our experimental conditions (Figure S3).

Furthermore, we analyzed the surface of bare SiO₂ and Fe oxide/SiO₂ before and after the regeneration process by means of Fourier transform infrared (FT-IR) spectroscopy to understand the origin of the improved recoverability of MB adsorption ability of Fe oxide/SiO₂ compared to that of bare SiO₂ (Figure S2). The removal efficiency of Fe oxide/SiO₂ particles was almost fully recovered upon 3 h of annealing at lower temperatures (200 and 100 °C) under atmospheric air conditions. The additional experiments were performed with decreasing time duration (3 → 2 → 1 h) of 100 and 400 °C annealing to study the influence of annealing temperature on the regeneration rate of the spent Fe oxide/SiO₂ particles (please see Supporting Information, Figure S3). The equilibrium adsorption capacity of Fe oxide/SiO₂ particles was almost fully recovered irrelevant to the time duration (1 or 2 h) of 100 and 400 °C annealing, implying that the regeneration rate of Fe oxide/SiO₂ was not significantly influenced by the annealing temperature under our experimental conditions (Figure S3).

Figure 5 shows FT-IR spectra of bare SiO₂ and Fe oxide/SiO₂ measured after MB adsorption and regeneration processes in two wavenumber ranges of 1900–1400 and 4000–2500 cm⁻¹. After MB adsorption (before the regeneration process), MB-related IR peaks were observed both on two samples (bare SiO₂ and Fe oxide/SiO₂). The pronounced peak at ~1630 cm⁻¹ corresponds to vibrations of the dimethyl amino group (C≡N+(CH₃)₂) of MB molecules, and the lower-intensity peak at 1602 cm⁻¹ corresponds to C≡C and C≡N heterocyclic vibrations. The intense and broad band of vibration of OH groups extended from 3600 to 3100 cm⁻¹ is also observed after MB adsorption. This broad band can be associated with a complex set of bonded OH groups included in interacting with various forms of MB molecules in solution (monomer, dimer, and H-aggregates) through the nitrogen atoms of MB heterocycle or dimethyl amino group.

In the case of bare SiO₂ (Figure 5a,c), marginal intensity decreases of MB-related IR bands were observed after the regeneration process (400 °C annealing for 3 h under atmospheric air conditions). On the other hand, the MB-related IR bands underwent much dramatic changes on the surface of Fe oxide/SiO₂ upon the same regeneration process. In the wavenumber regime of 1900–1400 cm⁻¹ (Figure 5b), the intensity of the characteristic MB peaks (C≡N+(CH₃)₂) centered at ~1630 cm⁻¹ decreased by more than 50%, whereas observed in the wavenumber range of 1400–500 cm⁻¹, and intensity of each IR spectrum was normalized by the respective intensity of the Si–O–Si stretching peak at 1056 cm⁻¹.

Figure 5. (a, c) FT-IR spectra of bare SiO₂ particles measured after the 1st MB adsorption experiment (before the regeneration) and after the regeneration process. (b, d) FT-IR spectra of Fe oxide/SiO₂ particles measured after the 1st MB adsorption experiment (before the regeneration) and after the regeneration process. The spectra measured after the 1st MB adsorption experiments are denoted as dotted lines, while those measured after the regeneration process are marked as solid lines.
two additional peaks at 1477 and 1456 cm\(^{-1}\) appeared upon regeneration, which can be attributed to the C–H bending vibrations of \(-\text{CH}_3\) groups. Similar changes were also observed in the other wavelength range (4000–2500 cm\(^{-1}\)), as shown in Figure 5d. The broad vibration band of bonded \(-\text{OH}\) groups relating to the various forms of MB molecule complexes almost disappeared upon regeneration, whereas new peaks relating to asymmetric and symmetric stretching of \(-\text{CH}_3\) groups appeared in the wavenumber range of 2910–2858 cm\(^{-1}\).

Our experimental observations imply that, in the presence of Fe oxide nanoparticles, thermal decomposition of MB molecules adsorbed on SiO\(_2\) particles took place during the regeneration process (400 °C annealing for 3 h under ambient air conditions). These results indicate that Fe oxide nanoparticles loaded on the SiO\(_2\) adsorbents acted as a catalytic active center for the thermal degradation of MB molecules under our experimental conditions. It is worth mentioning that Fe oxide nanoparticles synthesized on mesoporous substrates via similar processes used in this work (TR-CVD and postannealing processes) have been previously proved to exhibit high catalytic activities for thermal degradation of organic compounds (CO, acetaldehyde, and toluene).\(^{34-36}\)

One might already notice the appearance of the characteristic IR peak of molecular water at high wavenumber range (>3600 cm\(^{-1}\)) upon the regeneration of Fe oxide/SiO\(_2\) adsorbent (Figure 5d), and this can be associated to the formation of molecular water\(^{45}\) during the oxidation of MB molecules adsorbed on the Fe oxide/SiO\(_2\) surface. Please note that the total oxidation of organic compounds produces CO\(_2\) and H\(_2\)O as final products. Thus, it seems that total oxidation of adsorbed MB molecules on Fe oxide/SiO\(_2\) also took place during the regeneration process, although some of them underwent partial oxidation leaving intermediates mostly consisting of CH\(_3\) bonds. Based solely on the results of IR analyses, however, one cannot determine the exact products or intermediates of the oxidation of adsorbed MB molecules upon the regeneration of Fe oxide/SiO\(_2\) adsorbents. Further investigations, e.g., surface analysis during the regeneration process using operando FT-IR, are ongoing to understand the detailed mechanism of MB degradation on Fe oxide/SiO\(_2\) particles.

Nevertheless, these findings can already explain the reason behind the higher recoverability of MB adsorption capacity of Fe oxide/SiO\(_2\) than that of bare SiO\(_2\) upon the same thermal annealing process. Most of the adsorbed MB molecules did not undergo the thermal degradation on the surface of bare SiO\(_2\) during the regeneration process. They occupied the adsorption sites of SiO\(_2\) adsorbents after regeneration, resulting in the decrease of the MB adsorption ability as bare SiO\(_2\) was reused for MB adsorption. However, in the case of Fe oxide/SiO\(_2\), Fe oxide nanoparticles catalyzed thermal degradation of adsorbed MB molecules, regenerating the adsorption sites on the surface of adsorbents either by total oxidation or by partial oxidation of adsorbed MB molecules. Some of the MB molecules were partially oxidized, leaving some intermediate carbon species on the Fe oxide/SiO\(_2\) surface; however, these smaller species did not disturb MB molecules to be adsorbed on Fe oxide/SiO\(_2\) when Fe oxide/SiO\(_2\) was reused for MB adsorption. Therefore, the MB adsorption ability of Fe oxide/SiO\(_2\) particles can be almost fully recovered by the regeneration process (400 °C thermal annealing for 3 h under atmospheric air conditions).

### 2.3. Further Analysis of the Regeneration Process (TGA and XPS Analyses)

Regeneration processes on both SiO\(_2\) particles (bare SiO\(_2\) and Fe oxide/SiO\(_2\)) were further studied by means of thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS). To increase the MB-related signal on both analyses, the MB concentration was doubled (5 to 10 mg/L) and the solution was agitated using a shaker at a constant speed (300 rpm). More details on sample preparation for TGA and XPS analyses are provided in the Materials and Methods section.

Figure 6a,b shows TGA results of MB-adsorbed two SiO\(_2\) particles (bare SiO\(_2\) and Fe oxide/SiO\(_2\)), and those of the fresh sample are also shown in Figure 6c,d for comparison. Weight loss below 200 °C was attributed to the desorption of water molecules, and it was pronounced on MB-adsorbed SiO\(_2\) particles than MB-adsorbed Fe oxide/SiO\(_2\) particles, indicating that a higher amount of water molecules remained on the bare SiO\(_2\) particles. Both MB-adsorbed samples exhibited gradual weight loss after 200 °C with the increasing temperature. The amount of weight loss after 200 °C for both cases of SiO\(_2\) particles (MB-adsorbed bare SiO\(_2\) and MB-adsorbed Fe oxide/SiO\(_2\)) was larger than that for the respective fresh sample, which can be attributed to the degradation of adsorbed MB molecules. Figure 6e shows the TG spectrum of each MB-adsorbed SiO\(_2\) particle (SiO\(_2\) or Fe oxide/SiO\(_2\)) subtracted by the respective TG spectrum of the as-prepared sample.
the amount of adsorbed MB molecules on both SiO2 particles was very similar, which implies that the thermal degradation of MB molecules can facilitate on mesoporous SiO2 in the presence of Fe oxide nanoparticles.

Figure 7 shows the result of differential scanning calorimetry (DSC) of each MB-adsorbed SiO2 particle together with that of each of the as-prepared sample. Various processes can take place simultaneously during the thermal treatment of DSC analysis, such as evaporation of weakly bound species (endothermic), bond breaking (endothermic), oxidation (endothermic), and combustion of surface carbon (exothermic), which resulted in a very broad feature especially in the temperature range of 200−600 °C (Figure 7).

Moreover, these make it very difficult to assign each broad peak to a specific thermal process. Nevertheless, we observed the difference in DSC spectra measured with each of SiO2 before and after MB adsorption, which was much pronounced in the case of Fe oxide/SiO2 than that of bare SiO2. These results are in line with other analysis results (FT-IR and TGA), indicating the pronounced thermal processes relating to the decomposition of adsorbed MB on the surface of Fe oxide/SiO2 (e.g., formation of −CH3 species by partial oxidation of MB and combustion of −CH3 species) than the bare SiO2 surface.

Figure 8 shows the Fe 2p core-level XPS spectrum of Fe oxide/SiO2 particles regenerated at 400 °C for 3 h following the MB adsorption experiments using a shaker (experimental details can be found in the Materials and Methods section).

Figure 8. Fe 2p core-level XPS spectra of as-prepared and regenerated Fe oxide/SiO2 particles (denoted as-prepared and after regeneration, respectively).

For comparison, the Fe 2p core-level XPS spectrum of as-prepared Fe oxide/SiO2 particles is also displayed in Figure 8. The extension of the Fe 2p XPS peak to a lower binding energy region was observed after the regeneration process; the Fe 2p3/2 peak extended to a lower binding energy region (<710 eV) upon the regeneration process. The extension of lower binding energy can be attributed to the formation of metallic Fe of which the Fe 2p3/2 peak is located at ~707 eV. By adding an additional component centered at 707 eV (metallic Fe states) to the Fe 2p3/2 peak of as-prepared Fe oxide/SiO2, the shape of the Fe 2p3/2 peak of regenerated Fe oxide/SiO2 can be well fitted (Figure S1); the Fe 2p3/2 peak of regenerated Fe oxide/SiO2 was well fitted by adding an component at 707 eV (metallic Fe states) to six components (oxidized Fe states), which were used for peak fitting of the as-prepared sample case. Our XPS analysis results imply that some of Fe oxide were reduced into metallic Fe states during the regeneration process at 400 °C, whereas the remaining Fe oxide did not undergo significant changes in their oxidation states, i.e., between Fe(II) and Fe(III) states.

It had been demonstrated that the metal−support interaction can play a role on catalytic performance of Fe oxide nanoparticles;36,40 however, further investigations utilizing an operando technique are required to understand the origin of catalytic activity of Fe oxide nanoparticles and determine the exact oxidation states of Fe oxide nanoparticles responsible for the catalytic activity for MB degradation.

2.4. Equilibrium Adsorption Capacity for Various Organic Dyes. The equilibrium adsorption capacity of Fe oxide/SiO2 particles for three different cationic organic dyes (methylene blue (MB), malachite green (MG), and rhodamine B (Rhb)) were examined and compared to that of bare SiO2 particles. Organic dye adsorption experiments were performed with 30 mL of each organic dye solution (10 ppm) and 0.03 g of each SiO2 particle (bare SiO2 or Fe oxide/SiO2). After 3 h of agitation (at 300 rpm and 20 °C) of each dye solution containing the adsorbent, no obvious decrease of concentration was found for all cases, implying that the dye adsorption reached its equilibrium states within 3 h.

Figure 9 shows the equilibrium removal efficiency (%) of bare SiO2 and Fe oxide/SiO2 for three organic dyes (MB, MG, and RhB) obtained from 3 h of adsorption experiments using a shaker. For all three cationic organic dyes, the equilibrium removal efficiency (%) of mesoporous SiO2 was improved upon incorporation of Fe oxide nanoparticles into the pore.
Fe oxide/SiO2 can be further improved by reducing the surface of Fe oxide nanoparticles seems to exhibit higher affinity for cationic dye adsorption than that of the bare SiO2 surface. We would like to mention that both bare SiO2 and Fe oxide/SiO2 particles did not exhibit noticeable adsorption ability toward methyl orange, which is an anionic organic dye molecule, implying that the electrostatic interaction between the adsorbent and organic dyes might come into play. Further investigations are now ongoing to derive kinetic and thermodynamic parameters that can give a deeper understanding of the organic dye adsorption process on mesoporous SiO2 with and without Fe oxide nanoparticles in the aqueous phase.

Furthermore, we studied the effect of the amount of Fe oxide on mesoporous SiO2 on the equilibrium adsorption capacity of Fe oxide/SiO2. Three Fe oxide/SiO2 samples with different amounts of Fe loadings (1.4, 7.23, and 8.3 wt %) were prepared, and their equilibrium adsorption capacities for MB molecules were examined. Details on sample preparation and MB adsorption experiments can be found in the Supporting Information section.

Figure 9 shows that the equilibrium removal efficiencies of Fe oxide/SiO2 can be further improved by reducing the amount of Fe loading on mesoporous SiO2 particles, although the surface of Fe oxide has higher affinity for MB adsorption than that of SiO2 surface. This is mainly because of the increase of the surface area of Fe oxide/SiO2 with the decreasing Fe loading. Please note that the trend of equilibrium removal efficiency (%) change upon the variation of Fe loading is well matched with that of BET surface area (m²/g) (Figure 10). It is worth mentioning that the adsorption capacity of the Fe oxide/SiO2 sample with a Fe loading of 1.4 wt % can be also fully recovered by the regeneration process.

3. CONCLUSIONS

Fe oxide nanoparticles (~10 nm) were synthesized by a TR-CVD method followed by a thermal annealing process (at 750 °C, 8 h, a constant dry air flow of 30 sccm) on mesoporous SiO2 particles. The formation of Fe oxide nanoparticles with a size of ~10 nm into the porous structure of SiO2 was evidenced by HR-TEM, XRD, and N2 isotherm analyses. The performances of mesoporous SiO2 with and without Fe oxide nanoparticles toward MB removal from an aqueous phase were examined. The adsorption ability of fresh Fe oxide/SiO2 was maintained even after further repeated MB adsorption following each regeneration process (for four times of repeated MB adsorption tests) and its MB adsorption ability was almost fully recovered by annealing at low temperatures (200, 100 °C). The regeneration process of Fe oxide/SiO2 particles was further studied by means of FT-IR, TGA, and XPS analyses, and the results indicated that Fe oxide nanoparticles can catalyze the thermal degradation of adsorbed MB molecules, reproducing the adsorption sites. In addition, it was found that the equilibrium capacity of mesoporous SiO2 for the cation organic dye (MB, MG, RhB) adsorption can be further improved by the formation of Fe oxide nanoparticles in the porous structure of the SiO2 adsorbent. Our experimental observations demonstrate the potential application of the combined structure of Fe oxide nanoparticles and mesoporous adsorbents in a water purification system.

4. MATERIALS AND METHODS

4.1. Sample Preparation. The Fe oxide/SiO2 particles were prepared by a TR-CVD method and a subsequent postannealing process, which were previously introduced.34 Commercially available mesoporous SiO2 particles bought from Sigma Aldrich (a particle size of 250−500 μm (35−60 mesh) and a mean pore size of 15 nm) were used as a substrate. Bis(cyclopentadienyl) iron (Fe(Cp)2, Aldrich) was used as a metal precursor, whereas oxygen and water originally existing in the reactor served as oxidizing agents during TR-CVD of the iron oxide on SiO2 particles. More details on the reactor setup can be found in the Supporting Information. TR-CVD of iron oxide on SiO2 particles was preceded via two steps. First, the temperature of the chamber was increased to 60 °C and then maintained for 2 h. During this first step, solid Fe(Cp)2 precursors were vaporized and the vaporized precursor molecules were diffused into the internal porous structure of SiO2 particles, probably adsorbed on both outer and inner surfaces of mesoporous SiO2 particles. As a
second step, the temperature of the chamber was further increased to 200 °C and maintained for 12 h. At this higher temperature, oxygen or water already existing in the reactor now reacted with adsorbed Fe(Cp)_2 on SiO_2 particles, converting it to iron oxides. After TR-CVD of iron oxides on SiO_2 particles, the particles were further annealed at 750 °C for 8 h using a furnace at a constant dry air flow (30 sccm) condition (Figure S4). The sample (1.3 g) was put on a quartz boat, and the boat was place on the center of a quartz reactor. Dry air flow was controlled by a mass flowmeter controller (MFC), and the temperature of the reactor was monitored and controlled using a furnace equipped with a K-type thermocouple. Two Fe oxide/SiO_2 samples with lower amounts of Fe loading (1.4 and 7.2 wt %) were prepared using a furnace (PMF-3, U1TECH). Ferrocene powder samples (0.5 and 2.5 g) were mixed with 10.0 g of SiO_2 particles and placed in a quartz crucible (100 mL), and the crucible was placed in the furnace. The temperature was regulated as aforementioned (60 °C for 2 h and 120 °C for 12 h), and 1.3 g of samples were taken and annealed at 750 °C for 8 h at dry air flow (30 sccm).

4.2. Sample Characterization. After the TR-CVD process for Fe oxide deposition on mesoporous SiO_2 particles, the particles were mechanically fractured and the element distribution of the cutting planes was analyzed using scanning electron microscopy (SEM, JEOL, JSM-7100F) equipped with EDS. After the postannealing process (at 750 °C for 8 h under a dry air flow), the geometrical structure of Fe oxide/SiO_2 particles was analyzed by HR-TEM (JEOL, JEM ARM 200F). Prior to TEM measurements, samples were grounded. Crystallinity of Fe oxide/SiO_2 samples was analyzed by obtaining XRD patterns by an X-ray diffractometer (Rigaku, Ultima IV) using Cu Kα radiation (40 kV, 30 mA, λ = 1.54 Å) with a scanning rate of 4°/min. For comparison, the XRD pattern of bare SiO_2 was also gathered under the same conditions. More information about the internal structure of Fe oxide/SiO_2 particles was obtained by determining the surface area and average pore diameter of Fe oxide/SiO_2 particles by BET and BJH methods, respectively, based on N_2 adsorption−desorption isotherms (3Flex, Micromeritics), and the results of BET and BJH plots were compared to the respective data of bare SiO_2 without and with annealing. The amount of Fe loading on the Fe oxide/SiO_2 sample was determined using ICP-OES. XPS spectra of the as-prepared and regenerated Fe oxide/SiO_2 sample were obtained at room temperature using an Mg Kα line and a concentric hemispherical analyzer (CHA, PHOIBOS-Has 2500, SPECS). TGA and DSC analyses were performed at a constant heating rate (10 °C/min) under atmospheric air conditions using a thermogravimetric analyzer (SDT Q600, TA Instruments). FT-IR spectra (4000−400 cm⁻¹) were obtained in an ATR mode by accumulating signals of 64 scans using an FT-IR spectrometer (optics-vertex 70, Bruker). Each IR spectrum (4000−400 cm⁻¹) was obtained by accumulating signals of 64 scans measured at a scanning velocity of 1.6 kHz under room temperature.

4.3. MB Adsorption Test. The MB adsorption tests on bare SiO_2 and Fe oxide/SiO_2 were proceeded by placing 0.05 g of each sample on the bottom of a glass beaker (250 mL) containing 70 mL of MB solution with an MB concentration of 5 ppm (5 mg/L). Prior to the MB adsorption experiments, each sample was annealed at 400 °C for 3 h under atmospheric air conditions. During the adsorption experiments, MB solution was agitated using a magnetic stirrer (spinning speed of 120 rpm) placed at the center of the beaker bottom. The magnetic stirrer was physically separated from SiO_2 particles (bare SiO_2 or Fe oxide/SiO_2) by a glass dish to prevent particles from possible cracking induced by a physical collision with the spinning stirrer. MB adsorption experiments were conducted for 3 h at room temperature under dark conditions. To follow the change of MB concentration due to the adsorption on SiO_2 particles (bare SiO_2 or Fe oxide/SiO_2), a 4 mL aliquot was collected and its UV−vis absorbance in the wavelength range of 400−900 nm was measured using a UV−vis spectrometer (Thermo Fisher, Genesys 10S UV−vis spectrometer). After the measurement, the aliquot was rein fused into the beaker containing MB solution and SiO_2 particles. The UV−vis absorbance measurement was carried out every 20 min for the first 2 h of MB adsorption experiments, and then, the absorbance was again measured after 1 h (total 3 h of MB adsorption experiments). The pH values of MB solution before and after the MB adsorption experiments were measured using a pH meter (Seven Compact S210, Mettler Toledo), and there were no changes of solution pH upon MB adsorption experiments for all cases of study (pH = 7).

4.4. Regeneration of the Adsorbent and the Repeated MB Adsorption Test. After 3 h of MB adsorption experiments, SiO_2 particles (bare SiO_2 or Fe oxide/SiO_2) were collected and annealed at 400 °C for 3 h under ambient conditions using a furnace. During this annealing process, collected samples were put on a quartz boat and the boat was placed at the central part of a quartz tube. The setup used for this annealing process was the same as the one shown in Figure S5, except for, in this case, both sides of the quartz reactor were opened to the ambient air. After the regeneration process via thermal annealing, MB adsorption experiments were performed with each sample (0.05 g) under the same experimental conditions mentioned above.

4.5. Examination of the Equilibrium Adsorption Capacity for Organic Dyes. Each SiO_2 particle (0.03 g) (bare SiO_2 or Fe oxide/SiO_2) preannealed at 400 °C for 3 h was placed at the bottom of a glass vial containing 30 mL of organic dye solutions (MB, MG, RhB, and MO) with a concentration of 10 ppm (10 mg/L). The upper part of vials was covered with a Teflon cap, and the vials were agitated at a constant shaking speed (300 rpm) using a shaker (IST-4075R, JEIO TECH) for 3 h. At a certain time-interval, the shaker was turned off and a 4 mL aliquot of the solution was taken from the vial for the measurement of UV−vis absorbance. After the absorbance measurements, the aliquot was rein fused into the vial containing MB solution and SiO_2 particles and the vial was covered again by the cap. Then, the agitation was restarted using the shaker to continue the MB adsorption on SiO_2 particles. After 3 h of MB adsorption experiments, collected bare SiO_2 and Fe oxide/SiO_2 particles were dried at 60 °C for 3 h at ambient air conditions and then samples were analyzed by TGA. Fe oxide/SiO_2 particles collected from the solution after 3 h of MB adsorption experiment were annealed at 400 °C for 3 h at ambient air conditions prior to XPS analysis. The ground Fe oxide/SiO_2 particles were pelletized for XPS analysis.

4.6. Examination of Equilibrium Adsorption Capacity of Fe Oxide/SiO_2 with Different Fe Loading Amounts. Equilibrium adsorption capacities of three Fe oxide/SiO_2 samples with various amounts of Fe loading (1.4, 7.23, and
8.3 wt %) were examined using 30 mL of MB solution with a concentration of 20 ppm (20 mg/L) for 3 h. MB solution (30 mL) and 0.03 g of each sample were placed in a glass vial, and the vial was sealed by a Teflon cap. The vial was agitated for 3 h at 300 rpm using a shaker, and then, 4 mL of the aliquot was taken for UV−vis measurements.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00726.

Fitted Fe $2P_{3/2}$ spectra of as-prepared and regenerated Fe oxide/SiO$_2$ particles (Figure S1); absorbance changes of MB peaks as a function of reaction time during 2 h before and after regeneration at 200 and 100 °C with bare SiO$_2$ and Fe oxide/SiO$_2$ (Figure S2); equilibrium removal efficiency of Fe oxide/SiO$_2$ (Fe loading 8.3 wt %) measured after regeneration by thermal annealing at two different temperatures (100 and 400 °C) for decreased time durations (1 and 2 h) (Figure S3); and schematic description of cross section of the reactor used for TR-CVD (Figure S4) and the quartz used for sample annealing (Figure S5) (PDF)

AUTHOR INFORMATION

Corresponding Authors
*E-mail: ydkim91@skku.edu (Y.D.K.).
*E-mail: hyun.okk.seo@smu.ac.kr (H.O.S.).

ORCID

Young Dok Kim: 0000-0003-1138-5455
Hyun Ook Seo: 0000-0002-8957-171X

Author Contributions

$Y$.H. and B.J.C. contributed equally.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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