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SYNTHESIS OF SILICA MICROSPHERES CONTAINING IRON OXIDE NANOPARTICLES FOR REMOVAL OF ORGANIC POLLUTANT BY ADSORPTION AND PHOTOCATALYTIC DECOMPOSITION

Iron oxide nanoparticles were incorporated to form composite microspheres of SiO_2 and Fe_2O_3 for magnetic separation of the particles after adsorption or photochemical decomposition. Economic material, sodium silicate, was purified by ion exchange to prepare aqueous silicic acid solution, followed by mixing with iron oxide nanoparticles. Resulting aqueous dispersion was emulsified, and composite microspheres of SiO_2 and Fe_2O_3 was formed from the emulsion droplets as micro-reactors during heating. Removal of methylene blue using the composite microspheres was performed by batch adsorption process. Synthesis of composite microspheres of silica containing Fe_2O_3 and TiO_2 nanoparticles was also possible, the particles could be separated using magnets efficiently after removal of organic dye.

Keywords: Composite Microsphere, Magnetic Nanoparticle, Self-assembly, Adsorption

1. Introduction

Adsorption process has been intensively studied for removal of VOCs (volatile organic compounds) in exhausted gas, decoloration of wastewater from textile industry, and purification of sewage water [1-3]. Although activated carbon is the most popular adsorbent for various contaminants, there exist some drawbacks such as difficulty of separation of used adsorbent particles and their expensive cost. Since activated carbon can be used as particulate form, they should be excluded from purified water for reuse of the adsorbent particles [4]. However, it is difficult to separate activated carbon from wastewater, because gravitational sedimentation or filtering require time-consuming steps. Thus, it is necessary to develop novel adsorbent particles for facile separation from liquid medium by economical manner.

Batch-type adsorber or photocatalytic reactor can be operated using slurries or suspended particles as adsorbent or photocatalytic particles [5]. Though such particles can be separated by centrifugation or sedimentation after purification of liquid medium, magnetic separation can be considered to remove particulate materials [6]. For this purpose, development of synthesis method of composite particles with magnetic property is essential using economic precursors like water glass (sodium silicate).

In this study, iron oxide nanoparticles were adopted to form composite microspheres of SiO_2 and Fe_2O_3 for magnetic separation of the particles after adsorption process. Economical starting material, sodium silicate was purified by ion exchange resin to prepare aqueous silicic acid solution, followed by mixing with iron oxide nanoparticle dispersion. The resulting aqueous dispersion was emulsified by homogenizer using oil as continuous phase, and heating of the complex fluid system was carried out to synthesize composite microspheres of SiO_2 and Fe_2O_3 from the emulsion droplets as micro-reactors. The mixing ratio of silicic acid solution and Fe_2O_3 nanoparticle dispersion was adjusted, and removal of methylene blue using the resultant composite microspheres was performed by batch-mode adsorption process.

2. Experimental

Iron oxide nanoparticle dispersion was added to aqueous silicic acid solution by proper mixing ratio, followed by mechanical homogenization in tetradecane as continuous phase. Then, the complex fluid was heated at 95°C for 1.5 hour. The resulting composite microspheres were washed with hexane several times and dried at room temperature.

Typically, 30 ml of aqueous suspension of adsorbent particles was prepared as the concentration of 0.002 g/ml after mild sonication. Separately, 30 ml of aqueous solution of methylene blue was prepared with various concentration, followed by

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mixing the suspension of adsorbent particles. The resulting mixture was agitated as 110 rpm, and the concentration change of methylene blue was monitored in regular time interval using UV-visible spectrometer. For photocatalytic decomposition of methylene blue, UV lamps were used for light irradiation for batch-type reactor containing composite microspheres of silica containing Fe_2O_3 and TiO_2 nanoparticles.

The morphologies of composite microparticles were observed using field emission scanning electron microscope (FE-SEM, Hitachi-S4700). XRD analysis and FT-IR spectrum of composite microspheres of silica and iron oxide were analyzed using powder X-ray diffractometer (XRD Ultima IV) and FT-IR spectrometer Nicolet), respectively. Concentration of methylene blue in aqueous solution was measured using UV-visible spectrometer (OPTIZEN POP).

3. Results and discussion

In this study, silica microspheres were synthesized from emulsion droplets as micro-reactors using silicic acid as precursor material. For magnetic separation of the microspheres after wastewater treatment by adsorption, iron oxide nanoparticles were included in precursor solution to prepare composite microspheres. For photocatalytic decomposition, titania nanoparticles were added to the precursor solution to prepare silica-Fe_2O_3-TiO_2 composite microspheres, as displayed schematically in Figure 1(a). After formation of droplets by emulsification of aqueous dispersion of precursor mixture, subsequent heating results in shrinkage of droplets and consolidation of composite microspheres by self-assembly.

Figure 1(b) contains SEM image of iron oxide nanoparticle dispersion after drying. Irregular morphologies of the iron oxide nanoparticles can be observed indicating that tiny nanoparticles are difficult to be recognized after self-organization with silicic acid and subsequent gelation inside emulsion droplets. The primary particle size of the nanopowder could be estimated as 43 nm, which is much smaller than composite microspheres of silica containing the nanoparticles. The dispersion of primary particles was aggregated to form secondary particles with 327.6 nm in diameter, as shown in inset histogram of Figure 1(b). Because the size distribution of the particles was bimodal, as shown in the histogram, the size of the particle dispersion showed relatively smaller average size like about 327.6 nm.

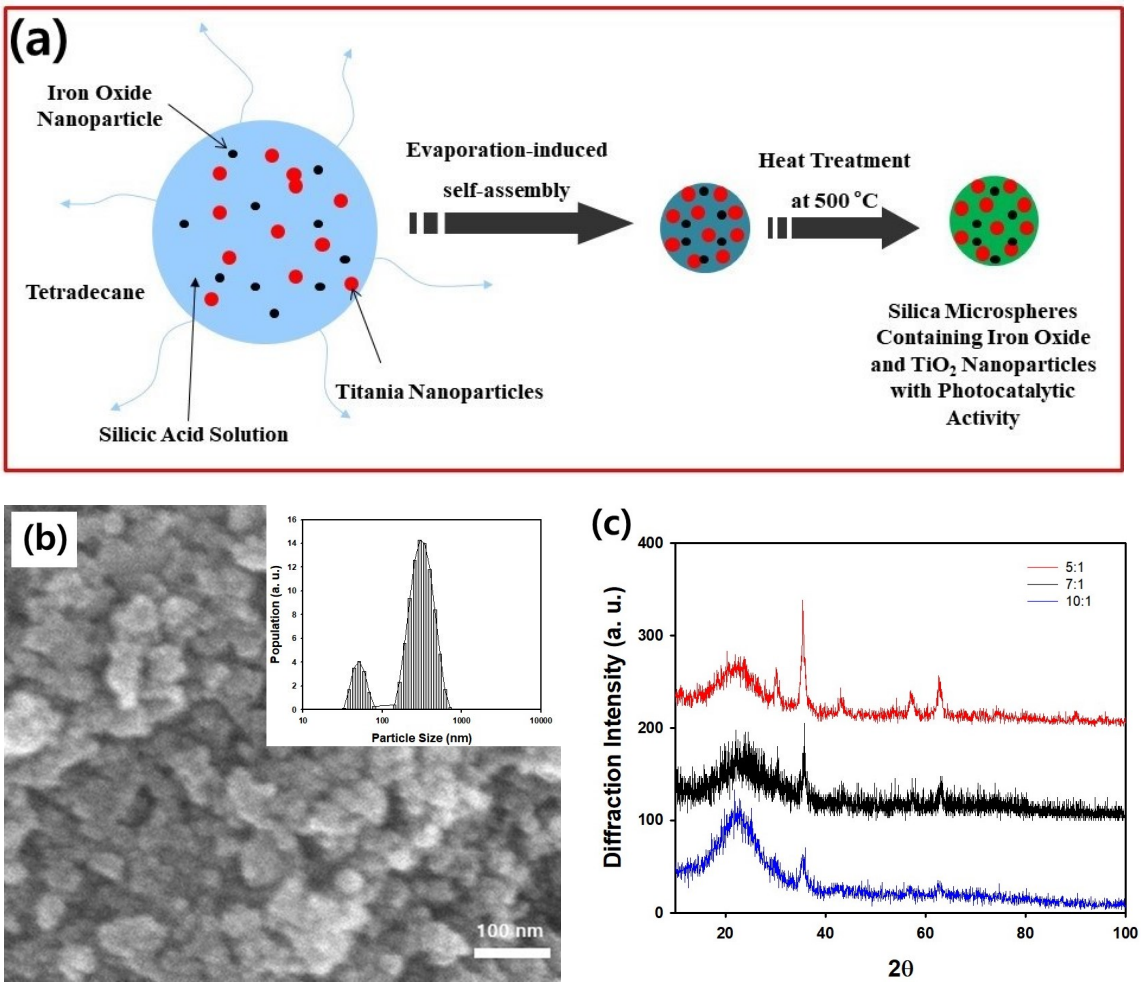

Fig. 1. (a) Schematic figure for the synthesis of composite microspheres of silica containing Fe_2O_3 and TiO_2 nanoparticles. (b) SEM image and size distribution of iron oxide nanoparticles. (c) XRD analysis result of composite microspheres of silica containing Fe_2O_3 nanoparticles. Mixing ratio of silicic acid and iron oxide nanoparticle dispersion was adjusted as 10:1, 7:1, and 5:1, respectively, in precursor mixture

XRD analysis results of the composite microspheres of silica containing Fe_2O_3 nanoparticles were confirmed for samples prepared using silicic acid and iron oxide nanoparticle dispersion as 10:1, 7:1, and 5:1 as mixing ratio, as displayed in Figure 1(c). Because crystalline phase of silica is amorphous, only diffraction peaks from iron oxide were detected, and the diffraction peaks became stronger as the mixing ratio of iron oxide nanoparticle dispersion increased, indicating that magnetic property of the composite microspheres also increased due to the addition of more concentrated Fe_2O_3 nanoparticles.

Figure 2(a) contains SEM image of the composite microspheres of silica containing Fe_2O_3 nanoparticles prepared using silicic acid and nanoparticle dispersion with mixing ratio of 5:1. The entire morphology of the microparticles was spherical with polydisperse size distribution, whereas each particle had wrinkled surfaces, providing adsorption sites of organic dyes like methylene blue due to electrostatic attraction between the dye molecules and particle surface. As shown in Figure 2(b), elemental composition of the microspheres was analyzed from EDS spectrum, and oxygen was detected with metallic elements such as silicon and iron. Although organic materials were removed by washing and calcination, carbon was derived from carbon tape on SEM holder. The existence of iron oxide nanoparticles embedded in the composite microspheres were confirmed by FT-IR spectrum shown in Figure 2(c), since the characteristic peak of OH stretching vibration appeared at about 1,630 cm^{-1}. Iron oxide nanoparticles could be impregnated to the microspheres successfully by emulsion-assisted synthesis, since characteristic peaks below 700 cm^{-1} appeared at 576 cm^{-1} due to stretching vibration of Fe-O from Fe_2O_3 [7]. Since original emulsion droplets produced using homogenizer is polydisperse, the resulting composite microspheres also showed polydisperse nature, as shown in histogram of inset image in Figure 2(c).

In this study, various mixing ratios of silicic acid and iron oxide nanoparticle dispersion in precursor solution were investigated to study resulting morphologies of the composite microspheres, as displayed in SEM image in Figure 3(a) and 3(b). Although the result is not reproduced here, spherical shapes could not be maintained and irregular rod-like particles were produced, when excess amount of the nanoparticle dispersion was used (mixing ratio like 3:4).

For practical application in separation technology, the composite microspheres synthesized using silicic acid and iron

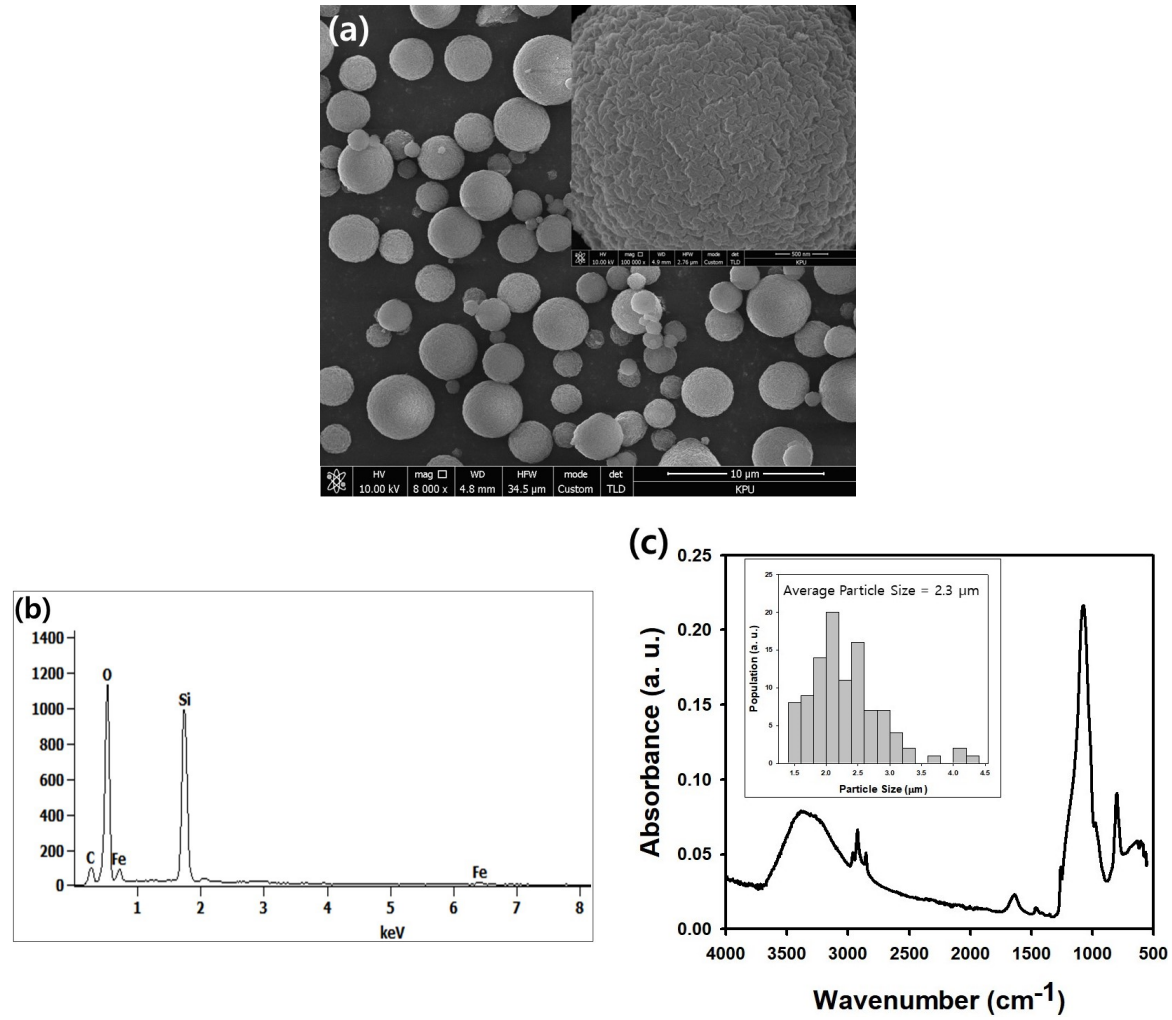

Fig. 2. (a) SEM image, (b) EDS spectrum, and (c) FT-IR spectrum of composite microspheres of silica and iron oxide prepared using silicic acid and iron oxide nanoparticle dispersion as mixing ratio of 5:1. Inset image in Figure 2(a) contains size distribution of the composite microspheres

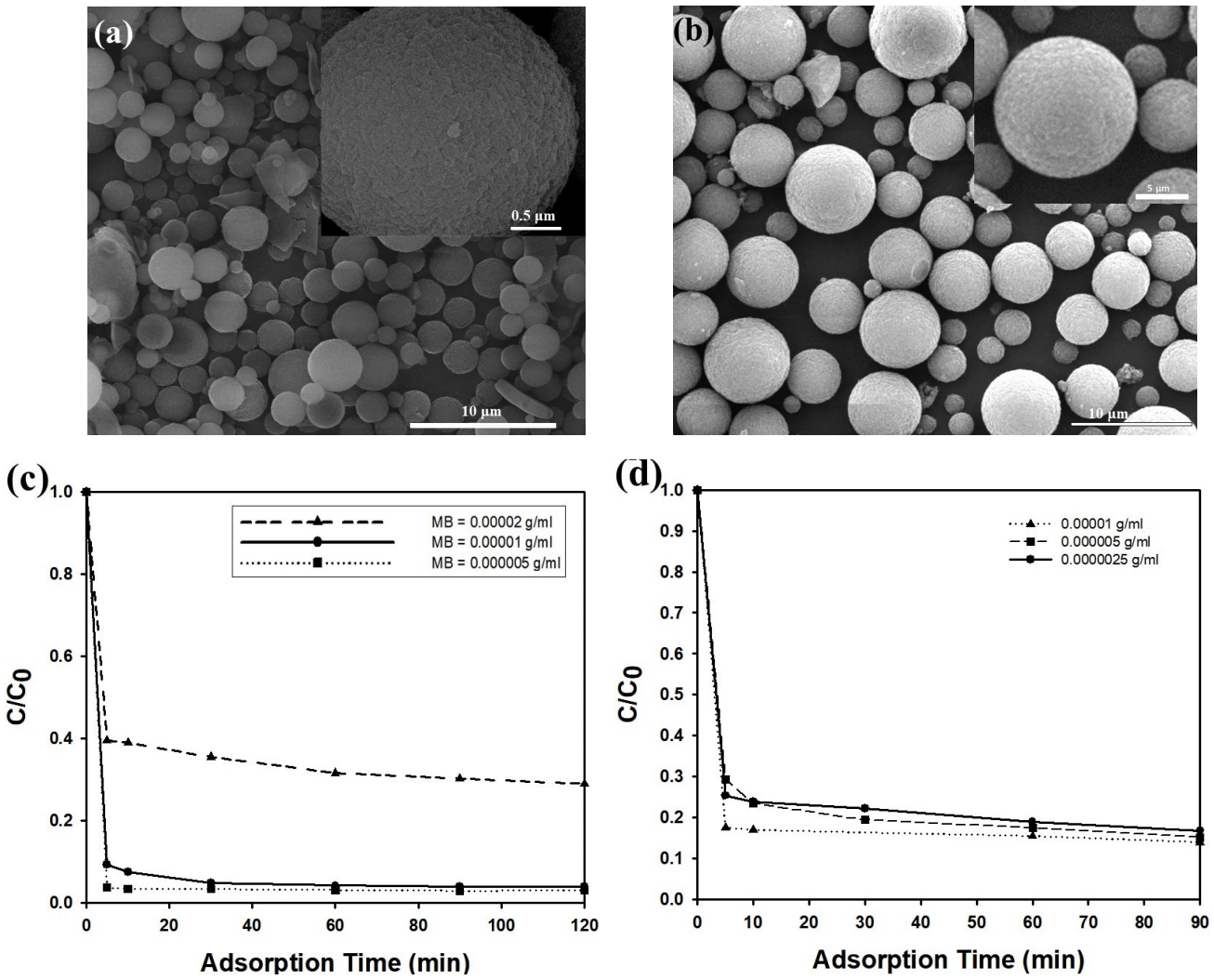

Fig. 3. (a) and (b) SEM image of composite microspheres of silica containing iron oxide nanoparticles prepared using silicic acid and iron oxide nanoparticle dispersion as mixing ratio of 10:1 and 2:1, respectively. (c) and (d) Change of dimensionless concentration of methylene blue as a function of adsorption time for different initial dose (C_I) of methylene blue. The composite microspheres prepared using silicic acid and iron oxide nanoparticle dispersion with 5:1 and 3:1 as mixing ratio, respectively

oxide nanoparticle dispersion with 5:1 of mixing ratio were adopted as adsorbent to remove methylene blue in aqueous medium. Initial dose of methylene blue (C_I) was changed from 0.000005 to 0.00002 g/ml, and change of the dye concentration was monitored as a function of adsorption time. As adsorption time increased, the concentration of methylene blue decreased due to adsorption of the organic dye onto surface of adsorbent particles. However, the smallest value of C/C_0 after 90 minutes of adsorption process was measured as about 80%, when C_0 was 0.00001 g/ml, indicating that small amount of contaminant can be remained by single step adsorption process. As shown in Figure 3(c), most contaminants could be adsorbed after 2 hours, when C_I was 0.000005 and 0.00001 g/ml. However, removal efficiency after 2 hours of adsorption decreased to about 70% when C_I increased to 0.00002 g/ml, implying that adsorption capacity decreased with increasing initial dose of organic dye. When the amount of iron oxide nanoparticles in the composite microspheres increased (mixing ratio = 3:1), adsorption kinetics data of methylene blue is shown in Figure 3(d). In this case, adsorption efficiency was found to be inferior to that of the composite microspheres used in experiments of Figure 3(c), and removal efficiency was smaller than 90 %, indicating that silica is more advantageous than iron oxide for adsorption of cationic dye like methylene blue.

In addition to composite microspheres of silica and iron oxide, silica microspheres containing iron oxide and titania nanoparticles were synthesized by emulsion-assisted self-assembly scheme shown in Figure 1(a) to prepare photocatalytic microparticles with magnetic property. For embedding of iron oxide and titania nanoparticles in silica microspheres, liquid precursor like silicic acid and nanoparticle dispersions of Fe_2O_3 and TiO_2 were mixed, followed by emulsification and heating to form silica microparticles with Fe_2O_3 and TiO_2 nanoparticles by gelation. After washing and heating, magnetic microspheres having photocatalytic ability were synthesized, as displayed in SEM image of Figure 4(a). Since the average particle size is about 1.67 µm, sedimentation of the particles can be expected by gravitational force. Figure 4(b) contains change of dimensionless concentra-

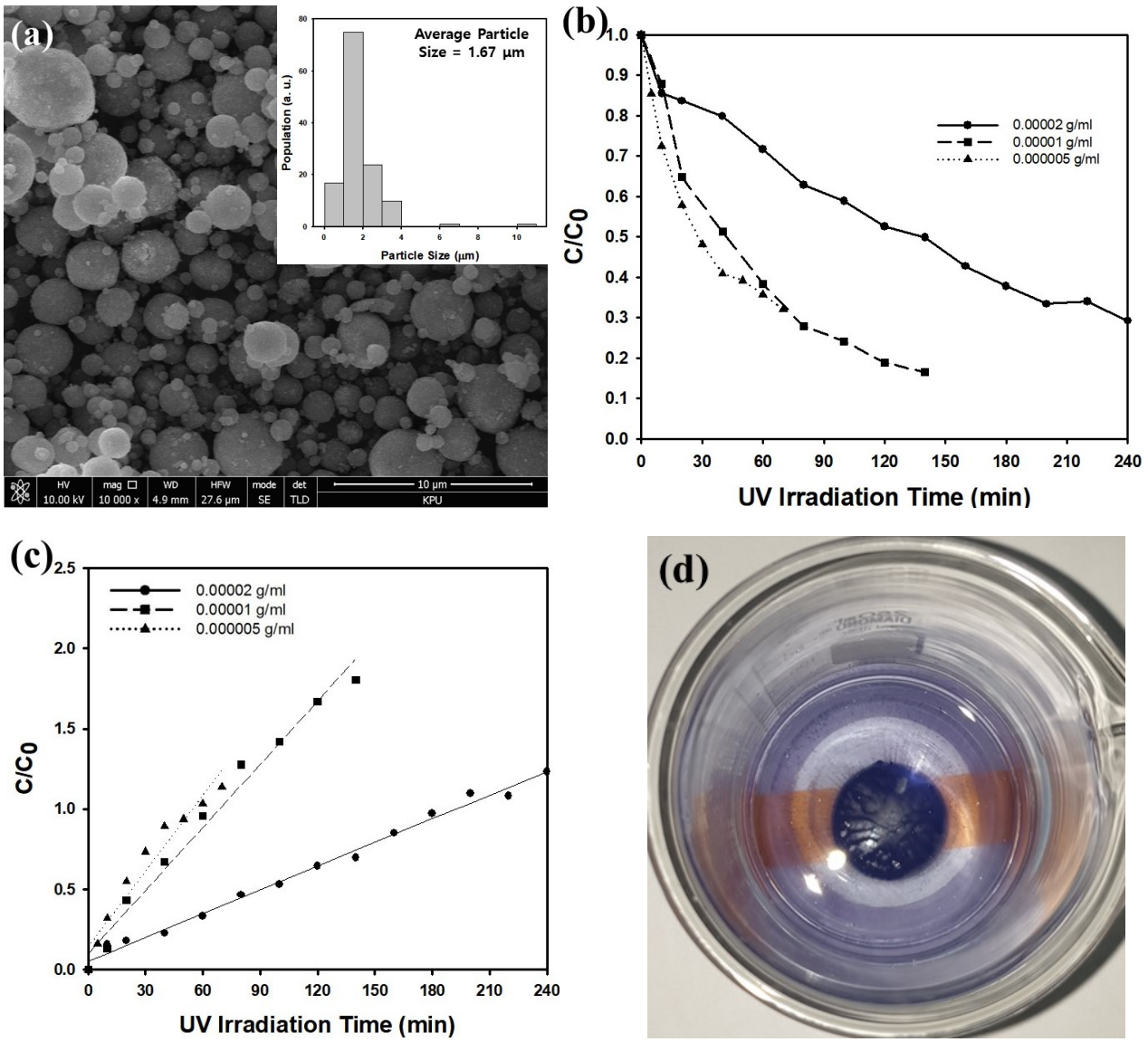

Fig. 4. (a) SEM image of composite microspheres of silica containing Fe_2O_3 and TiO_2 nanoparticles. Inset image shows size distribution of the particles. (b) Change of dimensionless concentration of methylene blue as a function of UV irradiation time. (c) Semi-log plot of Figure 4(b). (d) Photograph of composite microspheres shown in Figure 4(a) after photocatalytic decomposition of methylene blue and magnetic separation of the particles

tion of methylene blue as a function of UV irradiation time for three different initial dose of the dye, C_I = 0.000005, 0.00001, and 0.00002 g/ml. As shown in the semi-log plot of Figure 4(c), decomposition rate of the dye increased with decreasing value of C_I, implying that more prolonged UV irradiation time is required for purification of concentrated dye solution. Assuming the first order kinetics, apparent rate constant could be estimated from the slope of the graph in Figure 4(c), as shown in Table 1. When magnet with circular shape was attached on the bottom of beaker, sedimentation of the particles after photocatalytic decomposition of methylene blue was enhanced, as shown in photograph of Figure 4(d). Thus, our composite microspheres used for slurry-type batch adsorber or photocatalytic reactor can be easily separated by applying magnetic force after removal of organic dyes for 1 or 2 hours. Further purification of remaining water can be carried out, if the first purification step was not completed.

TABLE 1

Rate constant of photocatalytic decomposition of methylene blue for various initial dose of the dye

Initial Dose of Methylene Blue (C_I, g/ml)	Apparent Rate Constant (k_{app}, min^{-1})
0.000005	0.0049
0.00001	0.0131
0.00002	0.0157

4. Conclusions

Composite microspheres of silica containing Fe_2O_3 or TiO_2 nanoparticles were synthesized using emulsion droplets as micro-reactors for removal of organic dye by physical adsorption or photochemical decomposition. Composition of the

microspheres could be adjusted by changing the mixing ratio of raw material, silicic acid, and nanoparticle dispersion. For most synthesis conditions, morphology of the composite particles were microspheres with wrinkled surfaces, which is advantageous to adsorption of cationic dyes. During adsorption or photochemical reaction under UV illumination, most contaminants could be removed within 1 or 2 hours. Our micron-sized composite microspheres in this study were advantageous in that the particles after adsorption or photochemical decomposition process could be separated easily from aqueous medium by natural gravitational sedimentation of the particles after adsorption process. Addition of magnetic nanoparticles like iron oxide in silica microspheres resulted in enhancement of the sedimentation, which is useful in slurry-type reactors.

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