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FIXED BED SYSTEM PACKED WITH POROUS MATERIALS FOR REMOVAL OF ORGANIC DYE FROM WASTEWATER

Fixed beds were adopted for removal of organic dye from water by photocatalytic decomposition or adsorption. To this end, macroporous titania or silica micro-particles were synthesized from emulsions as micro-reactors and packed in the bed. During feeding aqueous methylene blue solution, UV light was irradiated for generation of active radicals for removal of dye by photocatalytic decomposition. Porous silica particles were also used as adsorbents in the bed for continuous adsorption of organic dye. For regeneration of the porous titania or silica particles, rinsing with fresh water was carried out before repeated cycles.

Keywords: porous particles; photocatalyst; adsorbent; fixed bed

1. Introduction

Low-cost processes using adsorbents can be a strong candidate for water purification [1]. Because photocatalytic decomposition of organics is efficient for reduction of chromacity, the development of convenient photo-reactors is also important in environmental technology [2]. Though CSTR (Continuously Stirred Tank Reactor) or rotating cylinders have been studied as reaction systems, tubular reactor as continuous manner can be another candidate, because the amount of packing material may be adjusted by controlling the length of the reactor [3].

Thus far, porous particles for laboratory-scale experiments have been employed in slurry-type batch reactors or adsorbents for removal of dyes, toxic chemicals, or polymeric materials in water due to facile nature of batch experiments [4-6]. Significant set-ups for continuous operation have been also conducted using fluidized bed or tubular reactors [7,8]. However, such researches are mainly limited to gas-phase reactions for removal of VOCs or NO_x [9,10]. In particular, fixed bed photocatalytic reactors have been developed by combined design of light source and photocatalytic particles as packing material in fixed bed reactors [11,12]. However, such systems have been studied using photocatalytic pellets composed of supporting pellets coated with TiO₂ nanoparticles with thin layer, which is not advantageous to photocatalytic reactions. Thus, it is still important to develop continuous system using fixed bed packed with porous catalysts

for water purification using macroporous particles with high porosity and photocatalytic activity without using any inactive supporting materials.

In this study, organic contaminant in water was removed by fixed bed reactor or adsorbent. For adsorption or decomposition of methylene blue, porous silica or titania particles were packed inside the tubular system, respectively. Packing materials were synthesized from emulsions as micro-reactors with liquid precursors of SiO₂ or TiO₂. Continuous operation was carried out by feeding waste water to the reactor, while outlet stream was collected for measurement of dye concentration. Recycle of the packing materials was also tested by repeated uses of the particles. The removal efficiency was maintained for a few cycles, implying that industrial application of the tubular system is possible after scale-up. The purpose of this paper is to confirm the possibility of macroporous particles without inert core or supporting materials as packing material for removal of organic dye using fixed bed reactor or adsorbent.

2. Experimental

For synthesis of macroporous particles, polystyrene (PS) nanospheres were synthesized by dispersion polymerization [13]. Macroporous titania and silica micro-particles were synthesized from emulsions as micro-reactors using PS nanospheres

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as templates [14]. When PS nanospheres were not included in emulsions, gelation of silicic acid in the droplets were induced by heating to form surface-wrinkled silica micro-particles [15]. Porous titania particles were packed in tubular reactor made of glass (ID = 6 mm), and aqueous solution of methylene blue (MB) was fed using syringe pump. For photocatalytic decomposition, 4 UV lamps (F10T8 BLB, 10W, peak wavelength at 352 and 369 nm, Black light Blue, Sankyo Denki) were used and concentration of the dye was measured from outlet stream by UV-visible spectrometer. Though excellent photocatalytic packed bed reactor has been developed using visible light LEDs, the photocatalytic nanomaterials were coated on PS beads as supporting material [16]. Because there are no inert cores in our macroporous particles, more strong photocatalytic activity can be expected. Additionally, mass transfer inside our photocatalytic particles can be enhanced through macropores, which allow the diffusion and convectional transfer of reactant inside the particles [17].

Porous silica particles were packed in the bed for adsorption of MB, and the recycle of packing materials was conducted by heating using box furnace at 500°C for 5 hours or rinsing with fresh water. The morphologies of porous particles were observed using FE-SEM. Crystallinity of the titania was analyzed by XRD.

3. Results and discussion

When PS nanospheres were not used as templates, gelation of silicic acid inside shrinking emulsions resulted in formation of surface-wrinkled silica particles, as presented in Fig. 1a. When PS nanospheres were used, the composite particles formed after heating the droplets were calcined to fabricate macroporous particles, as shown in Fig. 1b. Tetraethylorthosilicate (TEOS) or silicic acid can be adopted as silica precursor, whereas titanium diisopropoxide bisacetylacetonate (TDIP) was chosen as titania source. When aqueous solution containing organic dye is fed to

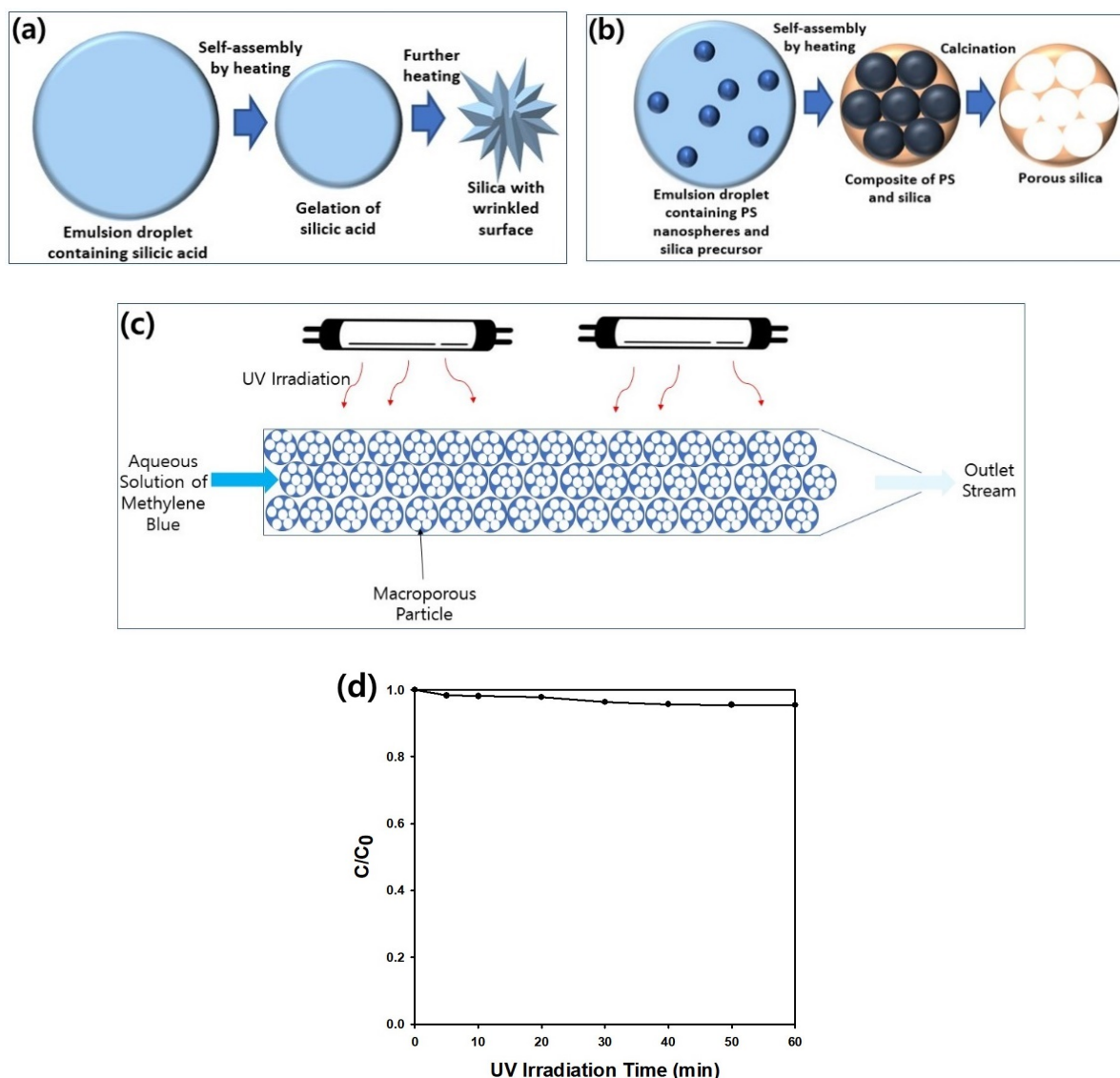


Fig. 1. Schematic figure of the synthesis of porous silica particles from emulsion droplets without (a) or with (b) PS nanospheres as sacrificial templates. (c) Schematic figure for wastewater treatment system using continuous tubular reactor packed with porous particles with or without photocatalytic activity. (d) Photolysis of methylene blue (MB) as a function of UV irradiation time

the bed, contaminant can be removed by photocatalytic decomposition or adsorption, causing decrease of the dye concentration in outlet stream, as displayed in Fig. 1c. It is beneficial to use our porous particles in packed bed, because the increased surface to volume ratio of the particles. Because the concentration of MB decreased very slightly under UV illumination without any photocatalytic materials, photolysis were ignored and photocatalytic decomposition was considered as the only mechanism for removal of the dye under UV light, as presented in Fig. 1d.

Fig. 2a contains SEM image of macroporous titania particles synthesized from emulsions. Because the macropores were generated from PS nanospheres with 400 nm in diameter as templates, a few spherical cavities could be formed in each particle. Since the original emulsions were polydisperse spheres, the overall morphologies of the particles were also spherical. Powder XRD result is included as inset image, presenting anatase crystallinity, which is useful for photocatalytic decomposition of organics. Fig. 2b contains the change of the concentration of MB as a function of UV irradiation time. Feed rate of MB solution (q_0) was maintained as 0.3 ml/min, and concentration of MB from inlet flow (C_0) was chosen from various values ranging from 0.0000025 to 0.0000075 g/ml. When C_0 was relatively small (0.0000025 to 0.000005 g/ml), the reactant concentration

decreased rapidly in the initial stage of operation. However, it required about 40 minutes to stabilize the packed bed, because temporary rise of the concentration observed. When C_0 increased to 0.0000075 g/ml, outlet concentration increased to higher value compared to the results from lower C_0 . Because the concentration of radicals generated from titania is finite, it is difficult to decompose all organics from concentrated inlet stream, causing high reactant concentration in outlet. Thus, C_0 should be determined as moderately low value for sufficient removal of organics, and q_0 was also adjusted from 100 to 300 $\mu\text{l}/\text{min}$, as presented in Fig. 2c. While C_0 was kept as 0.0000025 g/ml, the change of the concentration in outlet stream was monitored as a function of UV irradiation time. Under the moderate feed rate condition from 0.1 to 0.45 ml/min, reactant concentration in outlet stream decreased to about 0.0000005 g/ml after short stabilizing period. However, the outlet concentration increased drastically at higher q_0 like 0.6 ml/min, because high value of q_0 decreased retention time of the reactant, causing insufficient reaction time. Thus, q_0 can be chosen from 0.1 to 0.45 ml/min. Several cycles of continuous operation were conducted to check the possibility of repeated uses of the packed bed. Though heat treatment at 500°C was applied to all cycles for regeneration of the photocatalyst, temporary rise of the reactant concentration was observed in the

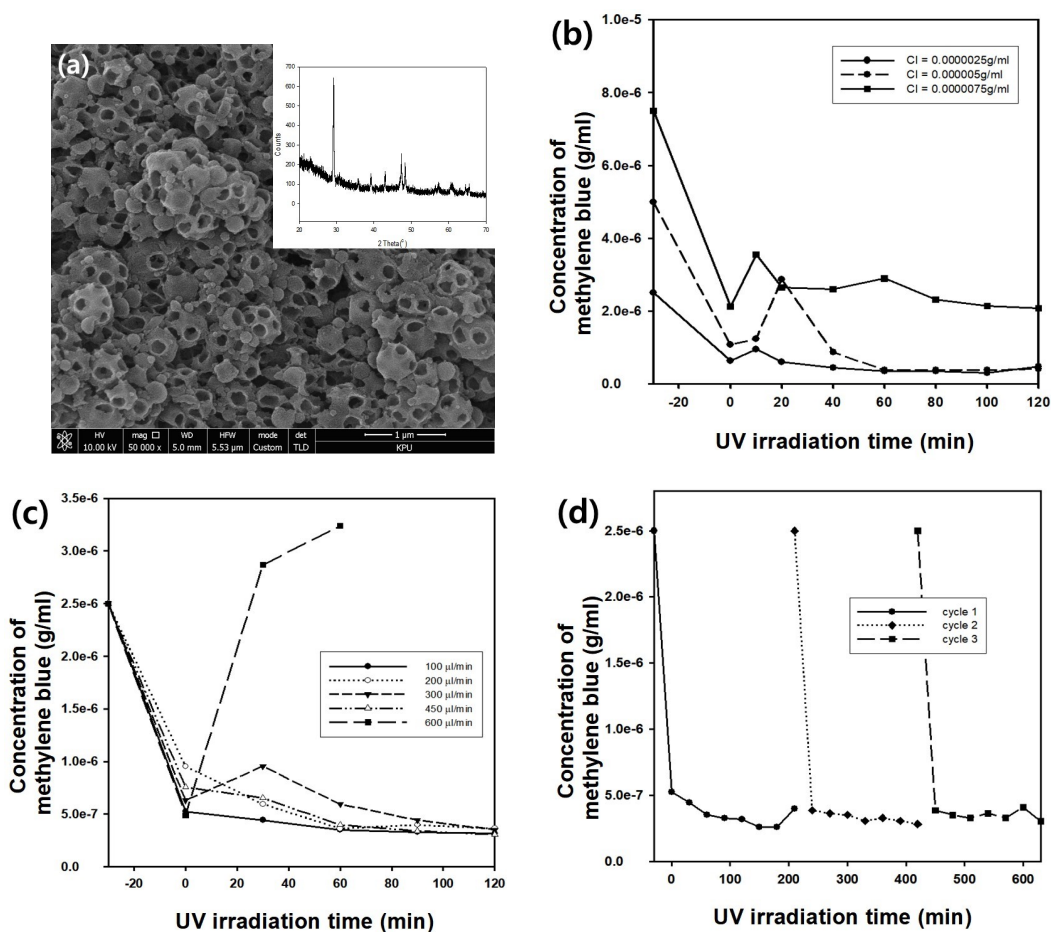


Fig. 2. (a) SEM image of macroporous titania micro-particles. The inset image contains XRD result. (b) Change of MB concentration as a function of UV irradiation time for various dye concentrations in inlet stream (C_0). Feed rate (q_0) was 0.3 ml/min. (c) Change of MB concentration as a function of UV irradiation time for various q_0 values. C_0 was 0.0000025 g/ml. (d) Change of MB concentration as a function of UV irradiation time in packed bed for repeated cycles. Packing materials were regenerated by rinsing with fresh water. q_0 was 0.1 ml/min

initial stage of the third cycle, implying that remnant carbons or organics may remain on the surface of the porous titania after heat treatment, causing decrease of photocatalytic activity from the third cycle. Thus, rinsing of the packing materials using distilled water was conducted, and the results are presented in Fig. 2d. During three repeated cycles, consistent decrease of the concentration was observed without unstable change of dye concentration, implying that rinsing is more effective than heating for removal of undecomposed reactants. Although the results were not reproduced here, the rate constant for each cycle was estimated from semi-log plot, assuming the first order kinetics. The evaluated values were 2.231×10^{-3} , 1.626×10^{-3} , and

$3.954 \times 10^{-3} \text{ min}^{-1}$ for the 1st, 2nd, and 3rd cycle, indicating that rinsing of the photocatalytic particles can be adopted for reuse of the porous particles, though the variation of rate constants can be observed due to insufficient removal of all contaminants adsorbed on the photocatalytic particles.

Adsorption of MB was also conducted using four different porous silica particles in the fixed bed. Fig. 3a contains SEM image of macroporous silica particles synthesized from emulsions using sodium silicate as raw material purified by anion exchange resin. Because PS nanospheres with 510 nm in diameter were used as templates, a number of voids covered with thin shell can be observed from each particle. When PS nanospheres were not

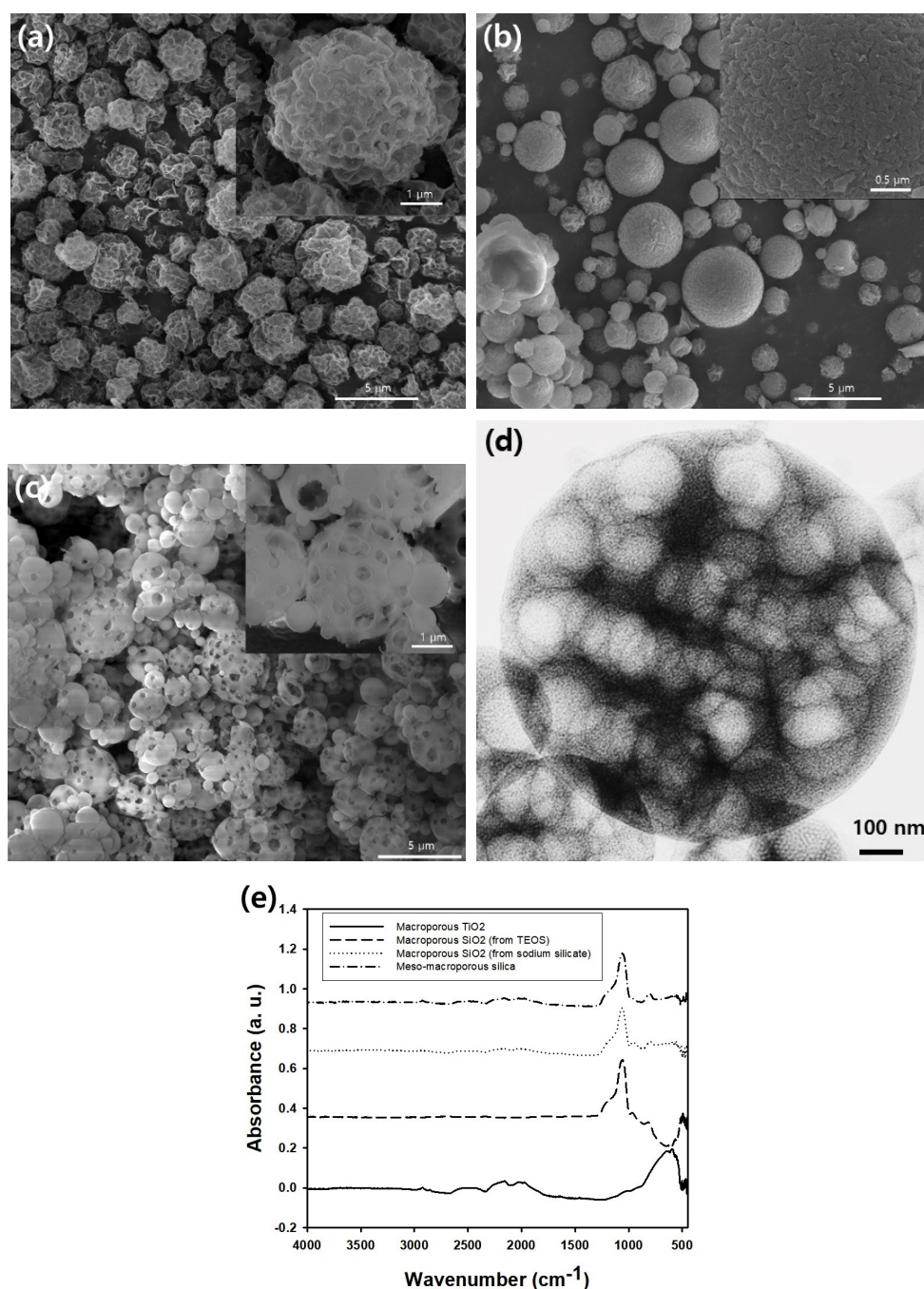


Fig. 3. SEM image of (a) macroporous silica micro-particles synthesized from sodium silicate, (b) surface-wrinkled silica particles, (c) macroporous silica micro-particles synthesized using TEOS, and (d) meso-macroporous silica micro-particles. (e) FT-IR spectra of porous materials used in this study

included in emulsions, droplets containing silicic acid resulted in surface-wrinkled silica micro-particles, as shown in Fig. 3b, in which rough surface can be observed from magnified inset SEM image. For comparison, TEOS was adopted as raw material to synthesize macroporous silica micro-particles from emulsions, as presented in Fig. 3c. Macropores could be formed by removing PS nanospheres with 370 nm in diameter, as included in inset magnified image. Similarly, meso-macroporous silica particles could be synthesized using PS nanospheres and Pluronic F127 as dual templates, as shown in Fig. 3d. In addition to morphologies of the porous particles, FT-IR spectra of the porous particles were measured, as displayed in Fig. 3e. For porous titania and silica particles, characteristic peaks appeared near 690 and $1,080\text{ cm}^{-1}$, respectively, indicating that compositional homogeneity could be confirmed by optical measurements [18,19].

In Fig. 4a, the concentration of MB from outlet stream was monitored as a function of adsorption time by fixing q_0 as 0.3 ml/min to compare the results from various silica particles in Fig. 3. For most adsorbents, the concentration decreased within 40 minutes to form transparent outlet streams, except the result from surface-wrinkled silica particles. Since there are no macropores in the surface wrinkled particles, unadsorbed dye can be accumulated inside the bed, causing gradual rise of the

concentration after short decreasing period in the initial stage, as displayed in Fig. 4a. In Fig. 4b, the change of MB concentration is plotted as a function of adsorption time for different values of C_0 . Most contaminants could be removed by adsorption onto the silica micro-particles, implying that 0.3 ml/min is slow enough for sufficient adsorption. Fig. 4c contains the change of MB concentration as a function of adsorption time for various q_0 . When q_0 was from 300 to $600\text{ }\mu\text{l/min}$, most contaminant could be removed, implying that electrostatic attraction between MB and silica surface was strong enough to capture the dye molecules by physisorption. Fig. 4d contains the change of MB concentration during 5 repeated cycles, when q_0 was 0.3 ml/min . The concentration in outlet stream decreased rapidly with adsorption time, indicating that adsorption capacity of the porous particles could be maintained by rinsing with water.

4. Conclusions

Fixed bed was adopted for removal of methylene blue from water. Macroporous titania microparticles synthesized from emulsions as micro-reactor were packed in tubular reactor for photocatalytic decomposition of the organic dye. Porous silica

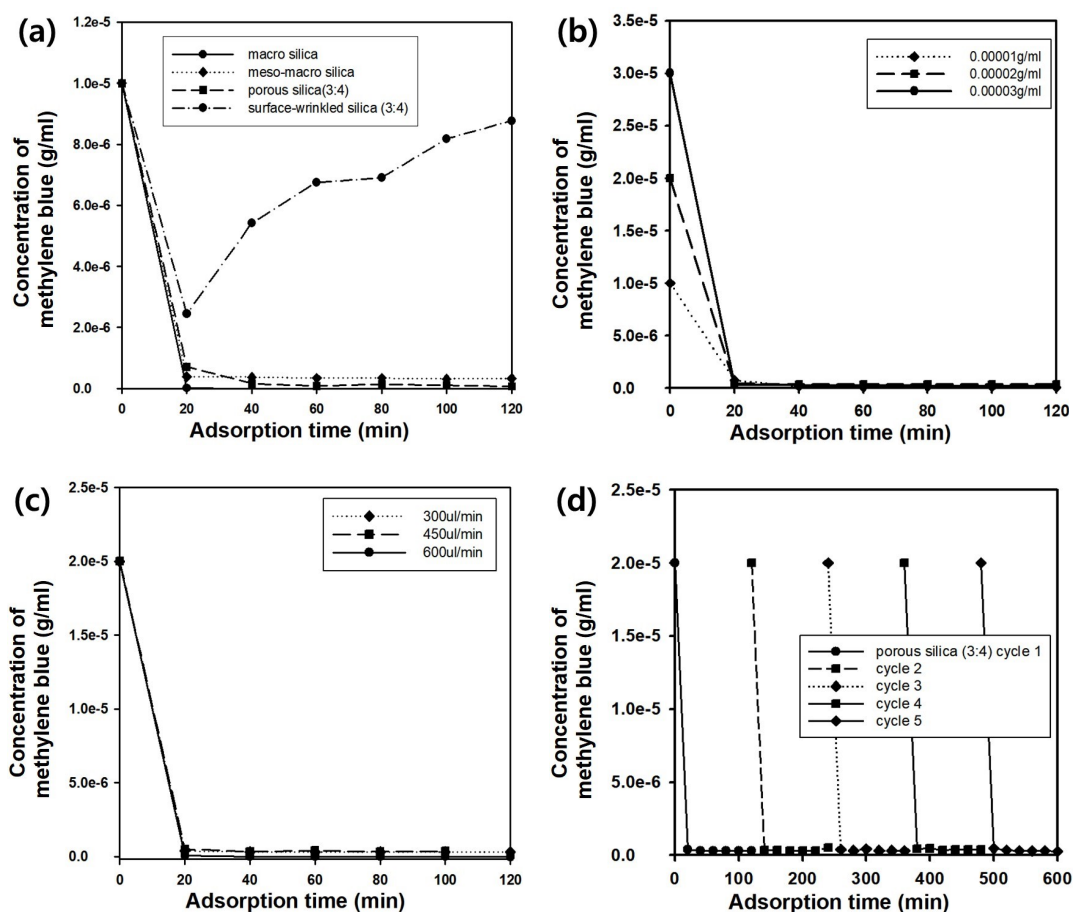


Fig. 4. (a) Change of MB concentration as a function of adsorption time for various kinds of adsorbents. q_0 was 0.3 ml/min . (b) Change of MB concentration as a function of adsorption time for different values of C_0 . q_0 was 0.3 ml/min . (c) Change of MB concentration as a function of adsorption time for different values of q_0 (300 to $600\text{ }\mu\text{l/min}$). C_0 was fixed as 0.00002 g/ml . (d) Change of MB concentration as a function of adsorption time for repeated cycles. q_0 was 0.3 ml/min . Before each cycle, packing materials was rinsed using fresh water. Macroporous silica particles synthesized using sodium silicate were adopted as adsorbents in (b) to (d)

micro-particles were packed in the bed for adsorption. During repeated operations in continuous manner, adsorption efficiency could be recovered by rinsing the porous particles. By adjusting dye concentration and feed rate, stable operation conditions could be determined in both photocatalytic and adsorption systems. During continuous operation, initial concentration of the organic dye affected the removal efficiency of the photocatalytic decomposition. For concentrated inlet stream, the removal of methylene blue was not effective due to insufficient retention time. In adsorption system, type of adsorbents was important, because the concentration in exit stream increased rapidly for packing materials of silica micro-particles without macropores.

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