Modeling of Sulfonamide Antibiotic Removal by TiO₂/High-Silica Zeolite HSZ-385 Composite

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ABSTRACT

TiO₂/high-silica zeolite composite synthesized by a sol-gel method was applied to the removal of sulfamethazine (SMT) antibiotic from water, and simple models including both adsorption and photocatalytic decomposition were developed. In this study, two types of model were constructed: a synergistic model that included the interaction between the zeolite and TiO₂ in the composite, and an individual model, which did not include the interaction. We obtained rate constants for adsorption, desorption and photocatalytic decomposition experimentally, and compared them with the results calculated using the synergistic and individual models. The individual model predicted that ca. 55% of SMT would be removed from the system after 6 hours of treatment; however, our experiments showed that 80% of the SMT was removed, suggesting the existence of another reaction pathway. Therefore, a synergistic model was constructed, in which part of the SMT adsorbed onto the zeolite within the composite, desorbed from the zeolite and migrated to the TiO₂, and was then photocatalytically decomposed. Experiments were carried out with varying amounts of the TiO₂-zeolite composite, and the synergistic model was validated. We estimated that 10% of the desorbed SMT was photocatalytically decomposed without being released into the water. When TiO₂-zeolite composite concentrations were 0.04, 0.12 and 0.20 g/L, and the treatment time was 6 hours, the proportions of the total decomposition of SMT that occurred via this synergistic reaction pathway were calculated as 52.2, 58.6 and 66.7%, respectively. In other words, over half the SMT was decomposed through the synergistic reaction, which played a very significant role in overall removal of SMT (the remainder of the SMT was decomposed through simple photocatalysis on the TiO₂).

Keywords: photocatalyst; adsorbent; composite; modeling; synergistic reaction

Nomenclature

C	concentration of sulfamethazine in the aqueous phase (mg/L)
C'	concentration of sulfamethazine after desorption (mg/L)
C_0	initial concentration of sulfamethazine (mg/L)
C_c	concentration of TiO ₂ -zeolite composite (g/L)
C_e	equilibrium concentration of sulfamethazine (mol/L)
C_{P25}	concentration of P25 (g/L)
k_{ad}	rate constant of adsorption of sulfamethazine (L/mg/min)
k_{de}	rate constant of desorption of sulfamethazine (1/min)
k_{p1}	pseudo-first-order rate constant of photocatalytic decomposition (1/min)
k_{p2}	rate constant of decomposition of sulfamethazine desorbed from zeolite within TiO ₂ -zeolite composite (1/min)
k_{c-SMT}	pseudo-first-order rate constant of photocatalytic decomposition of sulfamethazine treated by TiO ₂ -zeolite composite (1/min)
k_{c-SA}	pseudo-first-order rate constant of photocatalytic decomposition of sulfanilic acid treated by TiO ₂ -zeolite composite (1/min)
$k_{P25-SMT}$	pseudo-first-order rate constant of photocatalytic decomposition of sulfamethazine treated by P25 (1/min)
k_{P25-SA}	pseudo-first-order rate constant of photocatalytic decomposition of sulfanilic acid treated by P25 (1/min)
K_L	Langmuir constant (L/mg)

m_{p1}	amount of sulfamethazine decomposed through R_{p1} per minute (mg/g)
m_{p2}	amount of sulfamethazine decomposed through R_{p2} per minute (mg/g)
M_w	amount of sulfamethazine remaining in water (mg)
M_c	amount of sulfamethazine remaining in TiO ₂ -zeolite composite (mg)
M_s	amount of sulfamethazine remaining in system (mg)
q	amount of adsorbate on the adsorbent (mg/g)
q_e	amount of sulfamethazine adsorbed onto zeolite or TiO ₂ -zeolite composite after reaching adsorption equilibrium (mg/g)
q_m	maximum adsorption capacity (mg/g)
R_{ad}	adsorption of sulfamethazine onto TiO ₂ -zeolite composite
R_{de}	desorption of sulfamethazine from TiO ₂ -zeolite composite
R_{de}'	simple transfer of sulfamethazine from TiO ₂ -zeolite composite to aqueous phase after desorption
R_{p1}	photocatalytic decomposition of sulfamethazine on TiO ₂ -zeolite composite
R_{p2}	photocatalytic decomposition of sulfamethazine desorbed from zeolite onto TiO ₂ in TiO ₂ -zeolite composite
S	the sum of the squares of the differences between experimental and calculated results for the removal of sulfamethazine using TiO ₂ -zeolite composite (mg ²)
V	volume of the sulfamethazine solution (L)
v_{ad}	adsorption rate of sulfamethazine on TiO ₂ -zeolite composite (mg/g/min)
v_{de}	desorption rate of sulfamethazine from TiO ₂ -zeolite composite (mg/g/min)
v_{de}'	simple transfer rate of sulfamethazine from TiO ₂ -zeolite composite to aqueous phase after desorption (mg/g/min)

v_{p1}	photocatalytic decomposition rate on TiO ₂ -zeolite composite (mg/L/min)
v_{p2}	photocatalytic decomposition rate of sulfamethazine which has been transferred to the surface of TiO ₂ particles on the composite (mg/g/min)
w	amount of the adsorbent (g)

1. Introduction

Pharmaceuticals and compounds derived from personal care products are increasingly found in the environment and have attracted much attention [1-4]. The concentration of pharmaceuticals detected in the environment is quite low (ng/L– μ g/L); however, ecotoxicity of pharmaceuticals at μ g/L levels has been reported [5]. For the sustainable use of water, suitable treatment methods for the removal of discharged pharmaceuticals are required, and research on water purification methods is currently being conducted in scientific and industrial circles [6, 7].

Recently, the removal of pharmaceuticals using photocatalysts and adsorbents such as zeolites and activated carbons has been investigated [8-11]. We tested high-silica Y-type zeolite, a relatively hydrophobic zeolite, for adsorption of sulfonamide antibiotics, and revealed that the pH of the sulfonamide solution greatly affected the removal efficiencies [12]. In addition, high-silica Y-type zeolite could quickly and selectively remove sulfonamides, even if coexisting materials were present at high concentrations [13]; however, it cannot adsorb sulfonamides after reaching saturation. Conversely, TiO_2 photocatalyst has high oxidizing power, and can decompose recalcitrant organic compounds under ultraviolet (UV) irradiation, although it typically takes a few hours to photocatalytically remove pollutants from water [9-11]. To overcome the disadvantages of each material, the synthesis of photocatalyst/adsorbent composites and their application to removal of pharmaceuticals or chemicals in water have been reported [14-17]. We have also reported the synthesis of TiO_2 -zeolite composites and applied them to remove sulfonamide antibiotics from secondary effluent [18]. The composites could remove sulfonamide from secondary effluent more effectively than TiO_2 alone. However, the mechanism of the interaction between the

photocatalyst and adsorbent has not yet been thoroughly examined.

In this study, we applied the TiO_2 -zeolite composite to the removal of sulfamethazine (SMT), which is one of sulfonamide antibiotics, and its analogue. Sulfonamide antibiotic are popular active antimicrobial agents used in animal food production due to their relatively low cost [19, 20]. However, some of sulfonamide antibiotics are not completely removed by conventional wastewater treatment systems, such as activated sludge processes, due to their high resistance to biodegradation and detected in natural river or effluent of wastewater treatment plant [21]. We quantitatively determined the rate constants for adsorption, desorption and photocatalytic decomposition. Based on these parameters, we constructed simple models containing adsorption, photocatalytic decomposition and photocatalytic decomposition after desorption, and evaluated the contributions of each reaction to the removal of SMT. The details of our models are described in next chapter.

2. Development of TiO_2 -zeolite composite model

Two simple models were constructed in this study, one is the individual model in which there is no interaction between the TiO_2 and zeolite, and adsorption (R_{ad}), desorption (R_{de}) and photocatalytic decomposition (R_{pl}) of SMT occur (Fig. 1 (a)). In this work, we use “adsorption” to mean adsorption of SMT onto zeolite in the composite, and are not referring to any short-term adsorption onto the surface of TiO_2 . Another is the synergistic model, in which part of the SMT adsorbed on the zeolite transfers to the surface of the TiO_2 , and is subsequently photocatalytic decomposed (Fig. 1 (b)). As well as R_{ad} , R_{de} and R_{pl} , two reactions after R_{de} are suggested: photocatalytic decomposition of SMT that has transferred to the surface of the TiO_2 particles within

the composite (R_{p2}) and simple transfer of SMT from the TiO₂-zeolite composite to the aqueous phase after desorption (R_{de}'). For simplicity of the model, only the behavior of SMT in water with TiO₂-zeolite composite was treated in this study.

In our previous studies, kinetic parameters for adsorption of sulfonamides onto high-silica zeolite and photocatalytic decomposition using TiO₂ were investigated and it was clarified that these reactions could be expressed as a Langmuir model and pseudo-first-order model, respectively [10, 12]. To construct a synergistic model, we first determined experimental rate constants for R_{ad} , R_{de} and R_{p1} when SMT was treated by TiO₂-zeolite composite. The SMT solution was mixed with the composite under dark conditions, and adsorption and desorption rate constants (k_{ad} , k_{de}) were measured. On the other hand, it is impossible to determine the rate constant for R_{p1} directly because adsorption (desorption) and photocatalytic decomposition occur simultaneously. Therefore, an analogue compound of SMT (sulfanilic acid: SA), which is not adsorbed by HSZ-385 zeolite was treated by TiO₂-zeolite composite and the rate constant (k_{c-SA}) was determined. Similarly, SMT and SA solutions were treated by TiO₂ powder (P25) and the pseudo-first-order rate constants for each reaction ($k_{P25-SMT}$, k_{P25-SA}) were determined. From the value of k_{c-SA} and the ratio of $k_{P25-SMT}/k_{P25-SA}$, the rate constant for R_{p1} (k_{c-SMT}) was estimated ($k_{P25-SMT}/k_{P25-SA} = k_{c-SMT}/k_{c-SA}$). Then, the individual model was constructed using k_{ad} , k_{de} and k_{c-SMT} and the calculated results were compared to the experimental results. We assumed that the difference between the results of the individual model and experiments was because of the synergistic reaction (R_{p2}), and the rate constant R_{p2} was set so as to minimize the difference.

3. Experimental

3.1. Chemicals

High-silica Y-type zeolite (HSZ-385, mean particle size 4 μm , $\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$) was purchased from TOSOH Ltd., Japan. TiO_2 powder (P25, surface area 50 m^2/g) was kindly provided by Nippon AEROSIL Ltd. SMT (purity > 99%) was purchased from Aldrich and SA (purity > 99%) and titanium tetraisopropoxide were purchased from Kanto Chemicals, respectively. The details of other chemicals used in this study are given in the Appendice.

3.2. Synthesis of TiO_2 -zeolite composite

TiO_2 -zeolite composite was synthesized as follows: 22.5 mL of 2-propanol was added to 2.5 mL of titanium tetraisopropoxide. Subsequently, 2.5 mL of an aqueous high-silica zeolite suspension containing 670 mg of high-silica zeolite was added to the titanium tetraisopropoxide solution. After stirring for 1 h, the precipitates were recovered by filtration, washed with distilled water, dried at 105 $^\circ\text{C}$, and then calcined at 700 $^\circ\text{C}$ for 3 h. The ratio of TiO_2 to zeolite in the composite was 1:1. TiO_2 powder was prepared in a similar manner. Characterization of the TiO_2 -zeolite composite was performed by scanning electron microscopy (SEM: JSM-5510LV, JEOL, Ltd.), energy dispersive X-ray spectroscopy (EDX: Genesis, EDAX) and X-ray diffraction (XRD, Ultima IV, Rigaku Co. Ltd.). The SEM and EDX images and XRD patterns are shown in our previous study [18]. The surface areas of high-silica zeolite and TiO_2 -zeolite composite were measured by BET adsorption method (BELSORP-mini, BEL Japan, Inc.).

3.3. Quantitative analyses

The concentrations of SMT and SA were measured by ultra performance liquid chromatography (UPLC: ACQUITY, Waters). The UPLC analysis was performed using a BEH C18 column (2.1×150 mm; Waters) with a linear gradient from 10% acetonitrile in 0.05% formic acid (isocratic for 0.5 min) to 90% (0.5–7 min) at a constant flow rate of 0.3 mL/min. A photodiode array detector was placed after the analytical column and the wavelength was set to 254 nm. The coefficient of variance for the LC analysis was <5% based on three measurements.

3.4. Adsorption experiment

The adsorption rate was evaluated by changing the amount of TiO₂-zeolite composite (dosages 2, 4, 6, 8, 10 mg; concentrations 0.04, 0.08, 0.12, 0.16, 0.20 g/L) added to SMT solution (10 mg/L, 50 mL) under dark condition. The pH was adjusted to 7 using sodium hydroxide. After addition of TiO₂-zeolite composite powder into the reaction vessel, aliquots (1 mL) were taken at designated times, filtered through a membrane filter (DISMIC; pore size, 0.20 µm; ADVANTEC, Ltd.) and subjected to UPLC.

After stirring for 24 h, SMT concentrations were measured and an adsorption isotherm was constructed. Each adsorption experiment was repeated three times, and the error bars represent the standard deviation.

3.5. Photocatalytic decomposition of SMT and SMT analogue (SA)

To evaluate the photocatalytic activity of TiO₂-zeolite composite, an SMT analogue which was not adsorbed by the composite was used as the target compound. SA solution (10 mg/L, 50 mL) and TiO₂-zeolite composite (dosages 2, 4, 6, or 10 mg, concentrations

0.04, 0.08, 0.12, or 0.20 g/L) were placed in a glass vessel. pH and temperature were adjusted to 7.0 and 25 °C. The solution was stirred and irradiated with a UV lamp (maximum wavelength 365 nm; UV intensity 1.0 mW/cm²). After UV irradiation, a filtered aliquot was subjected to UPLC. Similarly, 10 mg/L of SMT or SA were treated by TiO₂ powder and the pseudo-first-order rate constant for photocatalytic decomposition of SMT by TiO₂-zeolite composite was estimated. As a control, the rate constants of photocatalytic decomposition of SMT and SA by P25 (a commercial TiO₂ powder) were obtained.

3.6. Photocatalytic and adsorptive removal of SMT using TiO₂-zeolite composite

The SMT solution (10 mg/L, 50 mL) was poured into a glass vessel. TiO₂-zeolite composite (dosages 2, 6, or 10 mg, concentrations 0.04, 0.12, or 0.20 g/L, respectively) was placed into the reaction vessel, and the pH was adjusted to 7.0. The solution was stirred at 25 °C and irradiated with a UV lamp set to 1.0 mW/cm².

After UV irradiation, a designated aliquot that had been membrane filtered was subjected to UPLC, and the SMT concentration in the aqueous phase (*C*) was quantified. In addition, we measured the amount of SMT contained in the composite. We had previously reported that the adsorption of SMT onto high-silica zeolite was reversible, and that no adsorption of SMT occurred at a pH above 10 [12]. The pH of a designated aliquot of SMT-TiO₂-zeolite suspension was adjusted to greater than 10 and the SMT adsorbed onto the composite desorbed. After desorption of SMT, TiO₂-zeolite composite was removed by filtration, and the concentration of SMT in the supernatant (*C'*) was measured using UPLC.

The amounts of SMT in the water M_w (mg), the whole system M_s (mg) and on the

TiO₂-zeolite composite M_c (mg) were calculated as follows:

$$M_w = C \cdot V \quad (1)$$

$$M_s = C' \cdot V \quad (2)$$

$$M_c = M_s - M_w \quad (3)$$

V (L) is the solution volume.

4. Results and discussion

4.1. Adsorption of SMT on TiO₂-zeolite composite

Figure 2 shows the time course of concentration of SMT solutions treated by different amounts of TiO₂-zeolite composite under dark conditions. We had confirmed that our synthesized TiO₂ could not adsorb SMT (Fig. A2) and adsorbed SMT was released under alkaline condition and all of adsorbed SMT could be recovered [18]; therefore, the decrease in SMT concentrations must be attributed to adsorption on the composite. Rapid adsorption occurred, with the solutions reaching equilibrium within 30 min, which is quite a bit faster than that observed for activated carbon [7]. In our previous study, we found that adsorption behavior of sulfonamide antibiotics on high-silica zeolite HSZ-385 could be expressed by a Langmuir model:

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (4)$$

where q_e (mg/g), q_m (mg/g), K_L (L/mg) and C_e (mg/L) are the amount of SMT adsorbed onto the TiO₂-zeolite composite at equilibrium, the maximum adsorption capacity, the Langmuir constant and the equilibrium concentration of the SMT, respectively. Therefore, a Langmuir adsorption isotherm was constructed using the experimental data: after 24h stirring, SMT concentrations were 5.9, 2.7, 1.7, 1.1 and 0.8 mg/L when

the concentrations of TiO₂-zeolite composite were 0.04, 0.08, 0.12, 0.16 and 0.20 g/L, respectively (Fig. 3). The values of q_m , K_L and the coefficient of determination (R^2) for the Langmuir plot were 141 mg/g, 0.59 L/mg and 0.994, respectively. The q_m value for the TiO₂-zeolite composite was about half that reported in our previous study for high silica zeolite HSZ-385 [12]. The BET surface areas of high-silica zeolite and TiO₂-zeolite composite were 424, 222 m²/g, respectively. The zeolite content of the composite was ca. 50%; this measured q_m value is plausible and the adsorption capacity of zeolite does not seem to decrease when the zeolite is incorporated into a composite with TiO₂. We have already reported the value of K_L for the adsorption of SMT on high-silica zeolite in our previous study (0.62 L/mg) [12]. It is similar to the value of K_L for the adsorption of SMT on the composite (0.59 L/mg), indicating adsorption rate of SMT on zeolite is close to that on the composite.

In a Langmuir model, the adsorption rate v_{ad} (mg/g/min) and desorption rate v_{de} (mg/g/min) are expressed as follows:

$$v_{ad} = k_{ad} C (q_m - q) \quad (5)$$

$$v_{de} = k_{de} q \quad (6)$$

where k_{ad} (L/mg/min) and k_{de} (1/min) are rate constants of adsorption and desorption, and C (mg/L) and q (mg/g) are adsorbate concentration and the amount of adsorbate on the adsorbent (TiO₂-zeolite composite). The variation in q can be expressed as a function of v_{ad} and v_{de} :

$$\frac{dq}{dt} = v_{ad} - v_{de} = k_{ad} C (q_m - q) - k_{de} q \quad (7)$$

During the adsorption process, the amount of adsorbate removed from solution is equal to that adsorbed on the adsorbent:

$$-V \cdot \frac{dC}{dt} = w \cdot \frac{dq}{dt} \quad (8)$$

$$\frac{dC}{dt} = -\frac{w}{V} \cdot \frac{dq}{dt} = -\frac{w}{V} [k_{ad} C (q_m - q) - k_{de} q] \quad (9)$$

V (L) and w (g) are the volume of solution and mass of composite adsorbent. The values of k_{ad} and k_{de} can be expressed using Langmuir constant K_L :

$$K_L = \frac{k_{ad}}{k_{de}} \quad (10)$$

We selected the values of k_{ad} and k_{de} to minimize the sum of the squares of the differences between experimental and calculated results. The values of k_{ad} and k_{de} obtained in this study were 3.00×10^{-2} and 5.20×10^{-2} 1/min, respectively, and calculated results are shown as solid lines in Fig. 2.

4.2. Photocatalytic decomposition of SMT and SMT analogue

In our previous study, sulfonamides were adsorbed onto high-silica zeolite through hydrophobic interaction, therefore, we used SMT analogue which had similar structure but was not adsorbed onto the composite to determine rate constant for photocatalytic decomposition. SA was selected as SMT analogue because SA has sulfo group and has negative charge under all pH range. We checked adsorption behavior of SA onto TiO₂-zeolite composite and confirmed SA was not adsorbed (Fig. A3).

The time courses of the concentrations of SA solutions treated with irradiation in the presence of TiO₂-zeolite composite, and SMT and SA solutions irradiated in the presence of P25 and the relationship between $\ln(C/C_0)$ and UV irradiation time (where C_0 and C are the concentrations of SMT or SA at times 0 and t , respectively) are shown

in Fig. 4 and Fig. A4. We have confirmed that no adsorption of SA or SMT on P25 or synthesized TiO₂ occurred (Fig. A2). A linear relationship between $\ln(C/C_0)$ and UV irradiation time was confirmed (Fig. A4). Hence, a pseudo-first-order reaction model expressed as $\ln(C/C_0) = -kt$ (where k (1/min) is the pseudo-first-order rate constant) was suitable to describe the photodegradation of SMT and SA. In addition, the relationships between the rate constants k_{c-SA} , $k_{P25-SMT}$ and k_{P25-SA} and the concentrations of either composite or P25, are shown in Fig. 5. The expected value of k_{c-SMT} is also given, as a function of composite concentration. The values of k_{c-SA} , $k_{P25-SMT}$ and k_{P25-SA} increased logarithmically rather than linearly with both concentrations of composite and P25. This is because of light scattering caused by the TiO₂ particles; similar results were obtained in our previous study [10]. The values of k_{c-SA} , $k_{P25-SMT}$ and k_{P25-SA} (1/min) can be expressed as:

$$k_{c-SA} = 0.52 \times 10^{-2} \times \ln C_{P25} + 1.87 \times 10^{-2} \quad (11)$$

$$k_{P25-SMT} = 1.62 \times 10^{-2} \times \ln C_{P25} + 7.64 \times 10^{-2} \quad (12)$$

$$k_{P25-SA} = 0.63 \times 10^{-2} \times \ln C_c + 2.69 \times 10^{-2} \quad (13)$$

C_c and C_{P25} (g/L) are concentrations of TiO₂-zeolite composite or P25. The calculated ratio of $k_{P25-SMT}$ to k_{P25-SA} ($0.04 < C_{P25} < 0.20$) obtained using eqs. (12) and (13) was 3.17 ± 0.18 ; thus, we estimated k_{c-SMT} :

$$k_{c-SMT} = 3.17 \times k_{c-SA} = 3.17 (0.52 \times 10^{-2} \times \ln C_c + 1.87 \times 10^{-2}) \quad (14)$$

4.3. Adsorption and photocatalytic decomposition of SMT by TiO₂-zeolite composite

Fig. 6 shows the removal of SMT by TiO₂-zeolite composite at different composite concentrations. In all conditions, the amount of adsorbed SMT drastically increased in the initial stage of treatment, and then decreased quickly. Without UV irradiation, adsorbed SMT was retained [18]; therefore, the decrease is due to photocatalytic decomposition. When P25 was used, it still took a few hours to photocatalytically remove SMT from water. Such quick removal of SMT when the composite was used is the greatest advantage of our composite for water purification. In addition, the amounts of SMT adsorbed onto the composite gradually decreased as a result of photocatalysis and 52%, 59% and 73% of the SMT was decomposed after 3-hours treatment when the TiO₂-zeolite composite concentrations were 0.04, 0.12 and 0.20 g/L, respectively. Therefore, the composite was regenerated, and could adsorb SMT continuously without reaching adsorption equilibrium.

To model the adsorption and photocatalytic decomposition of SMT, we first suggested an ‘individual model’, in which there was no interaction between TiO₂ and zeolite, and the reactions that occurred were: adsorption (R_{ad}), desorption (R_{de}) and photocatalytic decomposition (R_{pl}) of SMT (Fig. 1 (a)). The concentrations of TiO₂-zeolite composite were set as 0.04, 0.12 and 0.20 g/L (TiO₂-zeolite composite dosages of 2, 6 and 10 mg per 50 mL of SMT solution, respectively). The rates of R_{ad} (v_{ad}) and R_{de} (v_{de}) are already defined in eqs. (5) and (6). The rate of R_{pl} is defined as v_{pl} and expressed as follows:

$$v_{pl} = k_{c-SMT} C \quad (15)$$

From eqs. (7) and (9), the variation of C and q in the individual model can be expressed as:

$$\frac{dq}{dt} = v_{ad} - v_{de} = k_{ad} C (q_m - q) - k_{de} q \quad (16)$$

$$\frac{dC}{dt} = -\frac{w}{V} [v_{ad} - v_{de}] - v_{p1} = -\frac{w}{V} [k_{ad} C (q_m - q) - k_{de} q] - k_{c-SMT} C \quad (17)$$

The calculated results are shown in Fig. 6. The overall trends in M_w , M_c and M_s are similar to those of the experimental results; however, the values of M_c and M_s were different. After 6-h treatment, M_s obtained by calculation was much larger than the experimental M_s , indicating that there must be another decomposition mechanism. Therefore, we suggested a ‘synergistic model’, in which a portion of the SMT adsorbed on the composite transfers to the surface of the TiO_2 . As well as R_{ad} , R_{de} and R_{p1} , two reactions after R_{de} were suggested: photocatalytic decomposition of SMT that has transferred onto the surface of the TiO_2 particles in the composite (R_{p2}) and simple transfer to the aqueous phase (R_{de}') (Fig. 1 (b)). The rates of R_{p2} and R_{de}' are defined as v_{p2} and v_{de}' , and expressed as follows:

$$v_{p2} = k_{p2} q \quad (18)$$

$$v_{de}' = v_{de} - v_{p2} = (k_{de} - k_{p2}) q \quad (19)$$

where k_{p2} (1/min) is the rate constant for reactions R_{p2} . The variation in C and q during treatment using TiO_2 -zeolite composite can be expressed as:

$$\begin{aligned} \frac{dC}{dt} &= -\frac{w}{V} [v_{ad} - v_{de}'] - v_{p1} \\ &= -\frac{w}{V} [k_{ad} C (q_m - q) - (k_{de} - k_{p2}) q] - k_{c-SMT} C \end{aligned} \quad (20)$$

$$\begin{aligned} \frac{dq}{dt} &= v_{ad} - v_{de} \\ &= k_{ad} C (q_m - q) - k_{de} q \end{aligned} \quad (21)$$

The values of k_{ad} , k_{de} and k_{c-SMT} are calculated in previous sections. We simulated C and q in the presence of different amounts of TiO₂-zeolite composite ($w = 2, 6, 10$ mg, $C_c = 0.04, 0.12, 0.20$ g/L). The values of k_{c-SMT} obtained using eq. (14) when the concentrations of TiO₂-zeolite composite were 0.04, 0.12, and 0.20 g/L were 0.57×10^{-2} , 2.23×10^{-2} and 3.00×10^{-2} 1/min, respectively. The value of k_{p2} which minimized the sum of the squares of the differences between experimental and calculated results (S) was determined ($k_{p2} = 0.48 \times 10^{-2}$, see Fig. A5). The experimental and calculated results are shown in Fig. 7 (a)–(c). By comparing the values of k_{p2} and k_{de} (5.20×10^{-2} 1/min), we can determine that ca. 10% of desorbed SMT was photocatalytically decomposed through R_{p2} .

4.4. Contribution of synergistic effect to overall decomposition of SMT

To quantitatively evaluate the synergistic effect between TiO₂ and zeolite in the composite, we compared the amounts of SMT decomposed through R_{p1} (m_{p1} (mg/min)) and R_{p2} (m_{p2} (mg/min)) per minute using the synergistic model. m_{p1} and m_{p2} are defined based on v_{p1} and v_{p2} :

$$m_{p1} = v_{p1} V = k_{c-SMT} C V \quad (22)$$

$$m_{p2} = v_{p2} w = k_{p2} q w \quad (23)$$

From eqs. (22) and (23), the cumulative amounts of SMT decomposed through R_{p1} and R_{p2} when the concentrations of TiO₂-zeolite composite were 0.04, 0.12 and 0.20 g/L were calculated (Fig. 8). In the initial stage ($t < 5$ min), where the concentrations of SMT in aqueous media were relatively high, SMT was mainly decomposed through R_{p1} . Then, the contribution of R_{p2} became higher as the concentrations of SMT in the aqueous media were lowered through adsorption onto the zeolite in the composite. The

proportions of the amounts of SMT decomposed through R_{p2} to the total of SMT decomposed after 6-h treatment when TiO₂-zeolite composite concentrations were 0.04, 0.12 and 0.20 g/L were 52.2, 58.6 and 66.7%, respectively, indicating adsorption-photocatalytic decomposition played a substantial role in total removal of SMT.

In previous studies [15-18], though advantages of photocatalyst-adsorbent composites were reported, the mechanism of the interaction between the photocatalyst and adsorbent was not thoroughly discussed. Therefore, in this work we have measured and deduced the reaction rate of each reaction, and quantitatively evaluated the contribution of the synergistic reaction to the total decomposition of SMT. For the modeling of photocatalytic reaction, photon absorption, irradiance and reactor geometry also affect the rate constant therefore Grčić et al. constructed promising model with considering them [22]. In this study, empirical equations were used for explaining the effect of composite concentration and photon adsorption was not included in our proposed model. In our future plan, the model that includes the factor of UV intensity or photon absorption will be developed. Photocatalyst-adsorbent composites can be widely applied to other pollutants by choosing the appropriate adsorbent, and our analytical approach should be useful for understanding other composite-pollutant systems.

5. Conclusion

A model of removal of SMT from solutions using TiO₂-zeolite composite was constructed based on measured rate constants of adsorption and desorption of SMT onto zeolite and photocatalytic decomposition of SMT on TiO₂. The experimental results differed from those calculated using our “individual model”, indicating that there must

be another decomposition mechanism in addition to simple photocatalytic decomposition. Thus, we proposed a synergistic model, in which a portion of the adsorbed SMT transfers to the surface of the TiO_2 in the composite and is subsequently photocatalytically decomposed. The good agreement between the results calculated using the synergistic model and our experimental data implies that there is a synergistic effect between the TiO_2 and the zeolite in our composite.

Acknowledgment

This research was financially supported by the Core Research for Evolutional Science and Technology (CREST) program of the Japan Science and Technology Agency.

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Figure Captions

Fig. 1 Proposed decomposition mechanisms of SMT on TiO₂-zeolite composite; individual (a) and synergistic model (b).

Fig. 2 Adsorption of SMT on TiO₂-zeolite composite as a function of contact time. Composite concentrations: 0.04 (diamonds), 0.08 (squares), 0.12 (triangles), 0.16 (crosses) and 0.20 g/L (circles).

Fig. 3 Langmuir isotherm of SMT on TiO₂-zeolite composite.

Fig. 4 Time courses (under UV irradiation) of (a) SMT and (b) SA concentrations during treatment with P25; (c) SA concentration during treatment with TiO₂-zeolite composite. P25 or composite concentrations: 0.04 (diamonds), 0.08 (squares), 0.12 (triangles) and 0.20 g/L (crosses).

Fig. 5 Relationships between (a) P25 concentration and reaction rate constants $k_{P25-SMT}$ (diamonds) and k_{P25-SA} (crosses); (b) TiO₂-zeolite composite concentration and k_{c-SA} (triangles). Dashed line shows the expected value of k_{c-SMT} .

Fig. 6 Time courses of amounts of SMT in water (M_w , blue squares), TiO₂-zeolite composite (M_c , red diamonds) and total system (M_s , green triangles) obtained experimentally with composite concentrations of (a) 0.04, (b) 0.12 and (c) 0.20 g/L. Lines show the calculated results obtained using the individual model with the same composite concentration.

Fig. 7 Time courses of amounts of SMT in water (M_w , blue squares), TiO₂-zeolite composite (M_c , red diamonds) and total system (M_s , green triangles) obtained experimentally with composite concentrations of (a) 0.04, (b) 0.12 and (c) 0.20 g/L. Lines show the calculated results obtained using the synergistic model with the same composite concentration.

Fig. 8 Cumulative amounts of SMT decomposed through R_{p1} (blue) and R_{p2} (red), as calculated using the synergistic model.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8