

Removal of crotamiton and its degradation intermediates from secondary effluent using TiO₂-zeolite composites

Qun Xiang, Shuji Fukahori, Youhei Nomura and Taku Fujiwara

ABSTRACT

Crotamiton, a scabicide and antipruritic agent persistent during biological treatment processes, is frequently detected in secondary effluent. In this study, titanium dioxide (TiO₂) and high-silica zeolite (HSZ-385) composites were synthesized and applied for the treatment of crotamiton in secondary effluent. Crotamiton was rapidly adsorbed by HSZ-385, and the adsorption performance of crotamiton in the secondary effluent was quite close to that in the test using ultrapure water. Even though the TiO₂-zeolite composites showed lower adsorption rates than that of HSZ-385, similar crotamiton adsorption capacities were revealed using both test materials. The photocatalytic decomposition of crotamiton was significantly inhibited by the water matrix at low initial concentrations. The TiO₂-zeolite composites rapidly adsorbed crotamiton from secondary effluent, and then the crotamiton was gradually decomposed under ultraviolet irradiation. Importantly, when using TiO₂-zeolite composites, coexisting material in the secondary effluent did not markedly inhibit crotamiton removal at low initial crotamiton concentration. The behaviors of the main intermediates during treatment demonstrated that the main degradation intermediates of crotamiton were also captured by the composites.

Key words | adsorption, crotamiton, decomposition, intermediates, secondary effluent, TiO₂-zeolite composites

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INTRODUCTION

Increasing attention is being paid to the presence of pharmaceuticals and personal care products in the environment around the world, and recent developments in analytical technology have allowed a wide range of pharmaceuticals and personal care products to be detected in environmental water samples (Tamura *et al.* 2017). Some of the pharmaceuticals and personal care products have been reported to cause toxic effects in the environment at concentrations of micrograms per litre and there is concern that the presence of these chemicals in the environment could cause drug-resistant bacteria to develop (Kyzas *et al.* 2015). Many pharmaceuticals used to treat humans and livestock are excreted in urine and feces, and various pharmaceuticals have been found in sewage effluent (Oulton *et al.* 2010). There is therefore an urgent need for advanced sewage treatments to be developed to allow pharmaceuticals to be removed, to protect the aquatic environment and allow water resources to be used in a sustainable way.

In a number of recent studies, TiO₂ photocatalysis has been used to treat pharmaceuticals and personal care products in wastewater (Yang *et al.* 2017). However, the photocatalysis of target compounds can be inhibited by coexisting materials, such as inorganic ions and organic matter in wastewater (Salaeh *et al.* 2016). In addition, toxic intermediates may be produced during photocatalysis, and the effects of pharmaceutical degradation products in the environment are of concern.

Adsorption has been used widely for wastewater purification, and various types of adsorbents have been developed to remove different pollutants (Ji *et al.* 2010; Hasan *et al.* 2013; Cabrera-Lafaurie *et al.* 2014; Kyzas *et al.* 2015; Dordio *et al.* 2016). High-silica Y-type zeolite (HSZ-385), which is a hydrophobic zeolite, has been used to remove sulfonamide antibiotics from livestock urine and selectively remove sulfonamides even in the presence of high concentrations of coexisting materials (Fukahori *et al.* 2013). However, adsorption techniques permanently

transfer the contaminants to the sorbent but do not destroy the contaminants, and saturation of the adsorbent is an important problem.

Attempts have been made to synthesize TiO₂-adsorbent composites that allow both processes to be used to treat pharmaceuticals in wastewater (Yap *et al.* 2012; Khraisheh *et al.* 2014; Kovacic *et al.* 2016). The introduction of MoS₂ in the TiO₂-MoS₂-reduced graphene oxide composite worked as a co-catalyst to reduce electron-hole pairs, and greatly enhanced the photocatalytic activity of TiO₂ for bisphenol A removal (Luo *et al.* 2017). A nitrogen-doped-TiO₂/activated carbon composite was synthesized to regenerate spent powdered activated carbon through solar photocatalysis for cost-effective application in wastewater treatment and the synergistic effects of the adsorption and solar photocatalysis of sulfamethazine as exhibited by the composites were examined (Yap & Lim 2012; Yap *et al.* 2012). A graphene-TiO₂-ZSM-5 composite material showed higher stability, stronger absorption of visible light, and lower band gap value (Hu *et al.* 2016). We have synthesized TiO₂-zeolite composites and used them to treat sulfonamide antibiotics in secondary effluent (Ito *et al.* 2014). Sulfamethazine was removed from secondary effluent more effectively by the composites than by TiO₂ alone; however, the behaviors of degradation intermediates produced during photocatalysis have not yet been studied when treated with TiO₂-zeolite composites in secondary effluent. When applying the TiO₂-zeolite composites for pharmaceutical removal in real wastewater, the behaviors of the degradation intermediates should be taken into consideration from the viewpoint of the control of the toxic intermediates and the possible competition effect on the removal of pharmaceuticals.

Crotamiton is a scabicide and antipruritic agent that has frequently been detected in sewage effluent because of its stable nature and wide consumption. Nakada *et al.* reported that crotamiton concentration in the effluent ranged from 245 to 968 ng/L (Nakada *et al.* 2006). Conventional activated sludge treatment processes showed limited removal efficiencies for crotamiton in Japan (Nakada *et al.* 2006; Okuda *et al.* 2008; Nakada *et al.* 2010), and the persistent property of crotamiton has also been reported in sewage treatment plants located in Switzerland, Singapore and China with similar concentration levels (Kahle *et al.* 2009; Sun *et al.* 2014; Tran & Gin 2017). Therefore, development of a new technology for removal of crotamiton from sewage effluent is urgently required. We previously investigated the TiO₂-catalyzed photocatalysis of crotamiton and proposed a degradation pathway (Fukahori *et al.* 2012). However, the adsorptive removal and TiO₂-photocatalyzed

removal of crotamiton and its degradation intermediates from real wastewater need to be further studied. In addition, we hypothesize that the TiO₂-zeolite composites can not only remove the target pharmaceuticals, but also capture the degradation intermediates before complete mineralization, thus providing a method to mitigate the negative effect of the intermediates in the treated water.

In this study, we synthesized TiO₂-zeolite composites and applied them to treat crotamiton in secondary effluent. Adsorption and photocatalytic decomposition rates by the TiO₂-zeolite composites were compared with those by the zeolite or TiO₂ alone. Inhibitory effects of coexisting materials in the secondary effluent against crotamiton removal were also evaluated. The behaviors of the crotamiton degradation intermediates when using the TiO₂-zeolite composites were clarified to verify our hypothesis that the composites can mitigate the possible impact of the degradation intermediates.

MATERIALS AND METHODS

Materials

The molecular structure and physicochemical properties of crotamiton are shown in Table S1 in the Supplementary Material (available with the online version of this paper). Crotamiton (purity > 97%) was purchased from Sigma-Aldrich (St Louis, MO, USA), and HSZ-385 (surface area 600 m²/g, mean particle size 4 μm, SiO₂/Al₂O₃ ratio 100) was purchased from Tosoh Ltd (Tokyo, Japan). The synthesis method of the TiO₂-zeolite composites was explained in detail in our previous publication (Ito *et al.* 2014). The composites had a TiO₂ to zeolite ratio of 1:1. TiO₂ powder was prepared following a similar method. All other chemicals used were of reagent grade.

Quantitative analyses

The crotamiton concentrations in the aqueous samples were determined using an Acquity UPLC-Xevo TQ ultra-performance liquid chromatography (LC) tandem mass spectrometry (MS/MS) instrument (Waters, Milford, MA, USA). Separation was achieved using a BEH C18 column (2.1 mm i.d., 150 mm long; Waters). A linear mobile phase mixture gradient was used, starting at 10% acetonitrile in 0.05% formic acid (isocratic for 0.5 min) and increasing to 90% acetonitrile in 0.05% formic acid at 7 min, and the constant flow rate was 0.3 mL/min. A photodiode array detector

between the analytical column and the MS/MS instrument was used at a wavelength of 254 nm. The structures of the intermediates were identified from the mass spectral patterns obtained by LC/MS/MS.

The total organic carbon (TOC) concentration was determined using a Sievers 900 Laboratory TOC analyzer (GE Analytical Instruments, Boulder, CO, USA). Ion concentrations were determined using a DX-120 ion chromatography system (Dionex, Sunnyvale, CA, USA). The cation analyses were performed using a CS12A column (4 mm i.d., 250 mm long; Dionex) and a mobile phase of 20 mM methanesulfonic acid at a flow rate of 1 mL/min. The anion analyses were performed using an AS12A anionic column (4 mm i.d., 200 mm long; Dionex) and a 2.7 mM Na₂CO₃ and 0.3 mM NaHCO₃ mobile phase at a flow rate of 1.5 mL/min. The concentration of HCO₃⁻ was calculated from the alkalinity measured using a titration method. The pH was measured using a portable pH meter (D-51, Horiba, Tokyo, Japan).

Secondary effluent and crotamiton solution

The secondary effluent was taken from a sewage treatment plant in Kochi, Japan, on 8 March 2016. The effluent was passed through Whatman GF/B glass fiber filter papers (GE Healthcare Bio-Sciences, Pittsburgh, PA, USA), and the filtrate was stored at 4 °C. The water quality of the secondary effluent after filtration was analyzed and the results are shown in Table 1. The crotamiton concentration in the secondary effluent was below the detection limit. A stock crotamiton solution (100 mg/L) in ultrapure water was prepared, and this stock solution was diluted with ultrapure water and the secondary effluent to prepare the test solutions. The initial crotamiton

Table 1 | Water quality of the secondary effluent

Parameter	Unit	Value
Na ⁺	mg/L	50.9
Mg ²⁺	mg/L	4.13
K ⁺	mg/L	9.37
Ca ²⁺	mg/L	20.7
SO ₄ ²⁻	mg/L	30.1
Cl ⁻	mg/L	63.5
NO ₃ ⁻	mg/L	32.3
HCO ₃ ⁻	mg/L	57.2
TOC ^a	mg C/L	4.98
pH	-	6.92

^aTOC, total organic carbon.

concentration in each test solution was either 10 mg/L or 100 µg/L. We conducted the experiments at high initial concentration of 10 mg/L for the evaluation of the degradation mechanism of crotamiton. The lower initial concentration of 100 µg/L was also prepared to consider the effect of initial concentration on the removal of crotamiton.

Adsorption experiment

Adsorption isotherms were obtained by performing experiments adding different amounts of HSZ-385 or TiO₂-zeolite composites to crotamiton solutions. The adsorption kinetics were studied by adding HSZ-385 (5 mg) or TiO₂-zeolite composites (10 mg) to crotamiton solutions (10 mg/L or 100 µg/L, 50 mL) at 25 °C in glass vessels. Each mixture was stirred well and the pH of the solution was adjusted to pH 7.0 ± 0.1 before an experiment was performed. After a set treatment time, the treated solutions were passed through DISMIC-13HP 0.2-µm membrane filters (Toyo Roshi Kaisha, Tokyo, Japan) to determine the crotamiton concentrations in the aqueous phase (C_t) by LC/MS/MS.

Photocatalytic decomposition of crotamiton by TiO₂

A crotamiton solution (10 mg/L or 100 µg/L, 50 mL) was added to a glass vessel, then TiO₂ (5 mg) was added and the mixture (at 25 °C) was stirred well and the pH of the solution was adjusted to pH 7.0 ± 0.1. The solution was then irradiated using an FL287-BL365 UV lamp (Raytronics, Tokyo, Japan), which had a maximum output wavelength of 365 nm. The UV intensity was controlled at 1,000 µW/cm² using a UV-340C light meter (Custom, Tokyo, Japan). After a set irradiation time, the treated solutions were passed through 0.2-µm membrane filters, and the crotamiton concentrations (C_t) were then determined. The TOC concentration in each treated solution was also determined.

Adsorptive removal and photocatalytic degradation of crotamiton using the TiO₂-zeolite composites

A crotamiton solution (10 mg/L or 100 µg/L, 50 mL) was added to a glass vessel, then TiO₂-zeolite composites (10 mg) were added and the mixture (at 25 °C) was stirred well and the pH of the solution was adjusted to pH 7.0 ± 0.1. The solution was then irradiated with UV at an intensity of 1,000 µW/cm². After a set irradiation time, the treated solutions were passed through 0.2-µm membrane filters, and the crotamiton concentrations were then determined. The TOC concentration in each treated solution was also determined.

To measure the mass of crotamiton adsorbed on the TiO₂-zeolite composites, the treated solution containing the composites was passed through a Whatman GF/B glass fiber filter paper; then the filter paper was placed in 50 mL of 50% methanol to desorb the crotamiton from the composites. The solution was then filtered and analyzed by LC/MS/MS to allow the crotamiton concentration (C_t') to be determined. The recovery rate for desorption was $104 \pm 2\%$ (mean \pm standard deviation, $n = 3$).

The amount of crotamiton in a treated solution ($M_{\text{in water}}$) was calculated using Equation (1), in which V is the solution volume.

$$M_{\text{in water}} = C_t \times V \quad (1)$$

Similarly, the amount of crotamiton adsorbed by the composites was calculated using Equation (2).

$$M_{\text{in composites}} = C_t' \times V \quad (2)$$

The total amount of crotamiton remaining in the system ($M_{\text{in system}}$) was calculated using Equation (3).

$$M_{\text{in system}} = M_{\text{in water}} + M_{\text{in composites}} \quad (3)$$

RESULTS AND DISCUSSION

Adsorption of crotamiton by HSZ-385 and TiO₂-zeolite composites

Plots of the remaining to initial crotamiton concentrations against time for the HSZ-385 and TiO₂-zeolite composite

adsorption experiments without UV irradiation are shown in Figure 1. Crotamiton was rapidly adsorbed by HSZ-385, and adsorption equilibrium was reached within 10 min under all experimental conditions. The TiO₂-zeolite composites showed similar performances to the HSZ-385, but with lower initial removal rates. However, the removal efficiency was close to that achieved using HSZ-385 after 30 min. TiO₂ did not appear to adsorb crotamiton without UV irradiation (Figure S1 in the Supplementary Material, available with the online version of this paper).

It has been reported that the presence of inorganic ions and organic materials affects the adsorption of pharmaceuticals (Bui & Choi 2010). Nevertheless, HSZ-385 showed selective adsorption to sulfonamide antibiotics in secondary effluent and livestock urine, and bisphenol A in landfill leachates (Fukahori *et al.* 2013; Ito *et al.* 2014; Chen *et al.* 2015). In our study, the removal of crotamiton from secondary effluent showed quite similar performances compared with the treatments in ultrapure water (Figure 1(a) and 1(b)), which indicated that the other components of secondary effluent caused little inhibition to the zeolite adsorption of crotamiton.

We previously investigated the mechanism involved in the adsorption of sulfa drugs to HSZ-385 and found that HSZ-385 adsorbed neutral sulfa drugs more effectively than non-neutral sulfa drugs and that hydrophobic interactions played the most important roles in the adsorption process (Fukahori *et al.* 2011). Crotamiton has no ionizable functional groups and is hydrophobic ($\log K_{\text{ow}} = 2.73$); therefore crotamiton may have been rapidly removed by HSZ-385 through hydrophobic interactions.

The pseudo-second-order model shown in Equations (4) and (5) was used to assess the adsorption kinetics. In the equations, k_2 (g/(mol min)) is the adsorption rate constant,

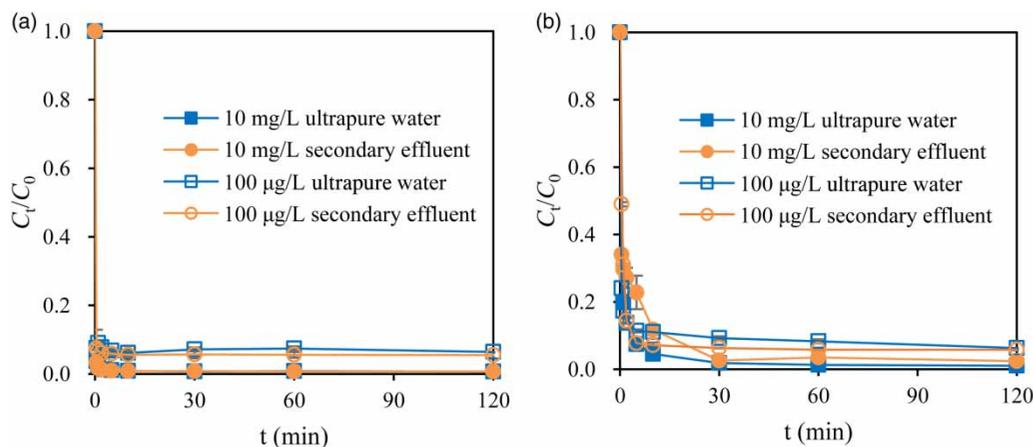


Figure 1 | Adsorption of crotamiton by (a) HSZ-385 and (b) TiO₂-zeolite composites. Results are means \pm standard deviations ($n = 2$).

and q_t (mol/g) and q_e (mol/g) are the amounts of crotamiton adsorbed at time t and after reaching adsorption equilibrium, respectively. The (t/q_t) values were plotted against t (min), then the k_2 and q_e values were calculated.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

The half-life $t_{1/2}$ is often used to evaluate the adsorption rate. The half-life is the time required for half of the q_e to be adsorbed, and was obtained by inserting $t = t_{1/2}$ and $q_t = q_e/2$ into Equation (5). The q_e , k_2 , and $t_{1/2}$ values obtained for different experimental conditions are shown in Table 2.

Table 2 | Pseudo-second-order kinetic parameters for the adsorption of crotamiton

	q_e (mol/g)	k_2 (g)	$t_{1/2}$ (min)
(a) HSZ-385			
Ultrapure water $C_0 = 10$ mg/L	4.87×10^{-4}	9.22×10^4	0.0231
Secondary effluent $C_0 = 10$ mg/L	4.87×10^{-4}	8.64×10^4	0.0248
Ultrapure water $C_0 = 100$ μ g/L	4.90×10^{-6}	1.75×10^6	0.118
Secondary effluent $C_0 = 100$ μ g/L	5.04×10^{-6}	9.34×10^6	0.0234
(b) TiO ₂ -zeolite composites			
Ultrapure water $C_0 = 10$ mg/L	4.87×10^{-4}	9.87×10^5	0.260
Secondary effluent $C_0 = 10$ mg/L	4.82×10^{-4}	2.76×10^5	0.754
Ultrapure water $C_0 = 100$ μ g/L	5.01×10^{-6}	4.80×10^5	0.418
Secondary effluent $C_0 = 100$ μ g/L	5.05×10^{-6}	7.90×10^5	0.252

The $t_{1/2}$ values for HSZ-385 adsorption were clearly lower than that for the TiO₂-zeolite composites, indicating the faster adsorption rate of HSZ-385. However, the values of q_e were at the same order of magnitude for the same crotamiton initial concentration (5×10^{-4} mol/g, $C_0 = 10$ mg/L; 5×10^{-6} mol/g, $C_0 = 100$ μ g/L). This result suggests that the synthesis of the composites did not have a clear effect on the adsorption capacity of the zeolite. The $t_{1/2}$ values were similar when the initial concentrations were 10 mg/L and 100 μ g/L, which indicated that crotamiton was rapidly adsorbed by the HSZ-385 and TiO₂-zeolite composites at a wide range of initial concentrations and is favorable for the application in practical wastewater treatment.

Various isotherm models can be used to process aqueous phase adsorption data, but the Langmuir and Freundlich isotherm models are most commonly used to describe adsorption processes (Rostamian & Behnejad 2016). The Langmuir and Freundlich isotherm models are shown in Equations (6) and (7).

$$\text{Langmuir model: } q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (6)$$

$$\text{Freundlich model: } q_e = K_F \cdot C_e^{1/n} \quad (7)$$

In Equations (6) and (7), C_e is the concentration of crotamiton in the liquid phase at equilibrium (mol/L), q_{\max} is the maximum adsorption capacity (mol/g), K_L is the Langmuir constant (L/mol), K_F is the Freundlich affinity coefficient [(mol/g)/(mol/L)^(1/n)], and n is a dimensionless number related to surface heterogeneity. The fitting results for the adsorption of crotamiton by the HSZ-385 and TiO₂-zeolite composites are shown in Table 3. The Langmuir isotherm is a theoretical single-layer adsorption model, and the Freundlich isotherm is an empirical model. The coefficients of determination (R^2) were higher for the Langmuir isotherm model than for the Freundlich model, implying that the adsorption of crotamiton by the HSZ-385 and TiO₂-zeolite composites predominantly involved single-layer adsorption.

Table 3 | Langmuir and Freundlich model fitting parameters for the adsorption of crotamiton

	Langmuir model			Freundlich model		
	q_{\max} (mol/g)	K_L (L/mol)	R^2 (-)	K_F [(mol/g)/(mol/L) ^(1/n)]	$1/n$ (-)	R^2 (-)
HSZ-385	9.80×10^{-4}	7.29×10^5	0.995	0.017	0.259	0.903
TiO ₂ -zeolite composites	7.82×10^{-4}	6.39×10^6	1.00	0.004	0.134	0.835

Photocatalytic decomposition of crotamiton by TiO₂

The changes in the crotamiton concentration over time through TiO₂-catalyzed photodegradation under different conditions are shown in Figure 2. No direct photodegradation of crotamiton (i.e., without a catalyst present) or no crotamiton adsorption by TiO₂ without UV irradiation was observed (Figures S1 and S2 in the Supplementary Material, available with the online version of this paper). Linear relationships were found between $\ln(C_t/C_0)$ and the UV irradiation time t , as shown in the inset of Figure 2. Therefore the first-order kinetic model shown in Equation (8) was used to evaluate the photocatalysis of crotamiton. In that equation, k_1 is the pseudo-first-order rate constant.

$$\ln\left(\frac{C_t}{C_0}\right) = -k_1 t \quad (8)$$

Comparing the degradation performances at different initial concentrations, much lower rate constants were obtained at higher initial crotamiton concentration. When the initial crotamiton concentration was 100 µg/L, the k_1 values for crotamiton degradation in ultrapure water and secondary effluent were 2.99 and 0.45 1/hr, respectively, while much lower rate constants were obtained at initial concentration of 10 mg/L: 0.21 and 0.20 1/hr in ultrapure water and secondary effluent, respectively. Yang *et al.* proposed that two factors could hinder the degradation of paracetamol at a higher initial concentration (2–10 mM): firstly, increased amount of

substances could occupy more TiO₂ active sites, which subsequently suppresses generation of the oxidants; secondly, a higher paracetamol concentration absorbs more photons, consequently decreasing available photons to activate TiO₂ (Yang *et al.* 2008). Similar results have been observed for the TiO₂ photocatalysis of sulfa pharmaceuticals (Yang *et al.* 2010), as well as the removal of sulfamethazine from secondary effluent by TiO₂-zeolite composites (Ito *et al.* 2014).

More than 90% of the crotamiton in ultrapure water was degraded after 1 hr treatment at crotamiton initial concentration of 100 µg/L, while it took 6 hr for 90% of the crotamiton in secondary effluent to be degraded. As is shown in Table 1, the secondary effluent contained various inorganic ions and organic matter. Obviously, the lower degradation rates for crotamiton in secondary effluent reflect the effect of the other components. Similar rate constants when the initial crotamiton concentration was 10 mg/L suggested that the other components in secondary effluent had much weaker effect on the photocatalysis of crotamiton.

The TiO₂ photocatalysis could be inhibited via the scavenger effect by coexisting ions (Kanakaraju *et al.* 2015; Kudlek *et al.* 2016). Photocatalysis has been found to be inhibited by Cl⁻ and HCO₃⁻ ions through hydroxyl radical and valence band hole scavenging, and NO₃⁻ has been reported to screen UV from the photocatalyst (Burns *et al.* 1999; Chong *et al.* 2010). Rioja *et al.* reported a marked deactivation effect caused by added salts for two tested acidic drugs (Rioja *et al.* 2014). Furthermore, Tokumura *et al.* mentioned that the coexisting matters could mitigate the generation of hydroxyl radicals through direct reactions with holes in the valence band and electrons in the conduction band of the photocatalyst (Tokumura *et al.* 2016). Song *et al.* reported that Cl⁻ can cause agglomeration of TiO₂ particles in a slurry by suppressing the stabilizing effect of electrostatic repulsion, reducing the effective contact surface between the photocatalyst and the pollutants (Song *et al.* 2016). Organic matter in secondary effluent could also compete with target pharmaceutical during photodegradation (Ito *et al.* 2014). The TOC concentration of the secondary effluent was 4.98 mg C/L (Table 1), and the TOC concentration of the 10 mg/L crotamiton ultrapure water solution was 7.67 mg C/L. Crotamiton was the main organic carbon source in the treated solution, so the radicals may attack crotamiton in preference to the coexisting organic matter during photocatalysis.

Mineralization during photocatalytic degradation was evaluated by plotting the TOC concentration against time

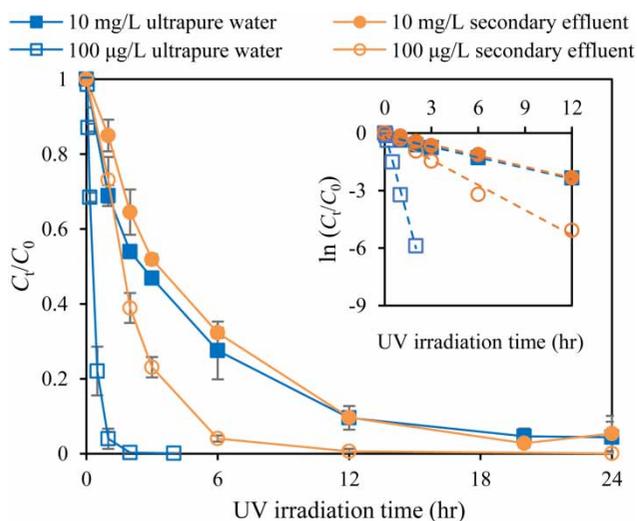


Figure 2 | Photocatalytic degradation of crotamiton catalyzed by TiO₂ under UV irradiation. The first-order kinetic model fitting results are shown in the inset. Results are means ± standard deviations ($n = 2$).

at an initial crotamiton concentration of 10 mg/L (Figure 3). The TOC concentration derived from the residual amount of crotamiton was also determined by performing stoichiometric calculations. Similar TOC degradation trends were found for crotamiton in ultrapure water and in secondary effluent. The TOC derived from crotamiton clearly decreased in the initial stage of photocatalytic degradation because the crotamiton was quickly degraded, but the TOC concentration in the treated solutions remained high for 3 hr and 6 hr for the solutions of ultrapure water and secondary effluent, respectively. This implied that crotamiton in secondary effluent was degraded slightly more slowly than that in ultrapure water in the initial photocatalytic degradation stage. After the initial stage, with the further photocatalytic degradation, the TOC concentrations in the treated solutions gradually decreased.

More than 95% of the crotamiton in both ultrapure water and secondary effluent was removed after 24 hr of UV irradiation, but less than 50% of the TOC was removed. The lower removal rate for TOC implied that crotamiton was degraded step by step and that the intermediate compounds accumulated at the same time. Kuo *et al.* investigated the photocatalytic mineralization of methamphetamine and codeine in a UVA/TiO₂ system and found that TOC disappeared more slowly than the target pollutants because it took some time for the intermediates to be mineralized (Kuo *et al.* 2015; Kuo *et al.* 2016). A more detailed discussion on the degradation intermediates is given in a later section.

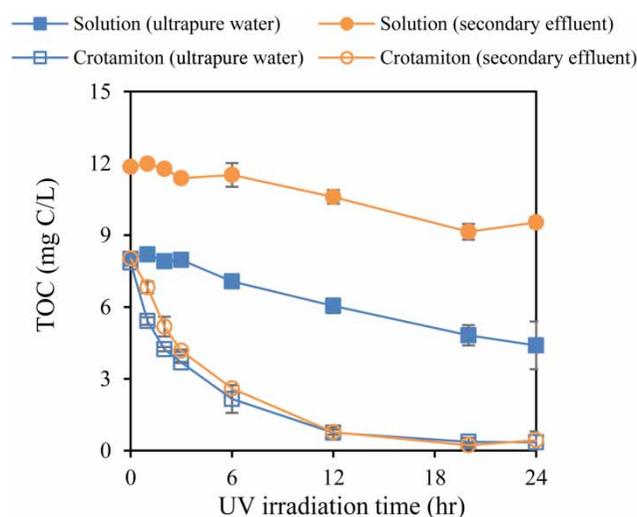


Figure 3 | TOC concentrations in the solutions treated by TiO₂-catalyzed photodegradation plotted against time and the TOC derived from the residual crotamiton plotted against time ($C_0 = 10$ mg/L). Results are means \pm standard deviations ($n = 2$).

Adsorptive removal and photocatalytic degradation of crotamiton using the TiO₂-zeolite composites

The amounts of crotamiton removed from the test solutions by the TiO₂-zeolite composites under UV irradiation are plotted against time in Figure 4. Similar trends were observed for the treatments in ultrapure water and secondary effluent at different crotamiton initial concentrations. The amount of crotamiton in the treated solution, $M_{in\ water}$, decreased dramatically at the very beginning of the treatment and remained low afterward under each of the experimental conditions used. These results matched the increase in the amount of crotamiton adsorbed onto the composites, $M_{in\ composite}$, which reached a maximum value rapidly and then gradually decreased. As shown in Figure 1, we have found that crotamiton was rapidly adsorbed by the HSZ-385, but the adsorbed crotamiton would be retained on the composites if the system was not exposed to UV irradiation. Crotamiton was rapidly adsorbed and most of the crotamiton was gradually decomposed through photocatalysis under UV irradiation. These results demonstrate that crotamiton was effectively removed by the TiO₂-zeolite composites through adsorption and photocatalysis.

Using an initial crotamiton concentration of 10 mg/L, half the crotamiton initially present was decomposed by the TiO₂-zeolite composites from ultrapure water within 2 hr, as is shown in Figure 4(a), but slightly less (32.4%) crotamiton was decomposed from secondary effluent after 2 hr (Figure 4(b)). This result was consistent with the abovementioned results, and was caused by the effect of the other components in the secondary effluent.

As is shown in Figure 4(c), at an initial crotamiton concentration of 100 μ g/L, the TiO₂-zeolite composites degraded ca. 97% of the crotamiton in secondary effluent after about 3 hr treatment. On the other hand, much lower removal efficiency (ca. 77%) was observed in the secondary effluent when only TiO₂ was used, and marked inhibition of the TiO₂ photodegradation of crotamiton was confirmed at an initial crotamiton concentration of 100 μ g/L (Figure 2). The higher degradation efficiency of crotamiton indicated in Figure 4(c) suggests that the inhibitory effect in secondary effluent was mitigated when the TiO₂-zeolite composites were used to treat crotamiton at lower initial concentration. These results suggest that the TiO₂-zeolite composites are potential material to treat crotamiton at a practical concentration level in secondary effluent. Yoneyama & Torimoto (2000) found that target substrates were adsorbed by the adsorbent support of TiO₂/adsorbent composites, resulting in a high substrate concentration around the loaded TiO₂

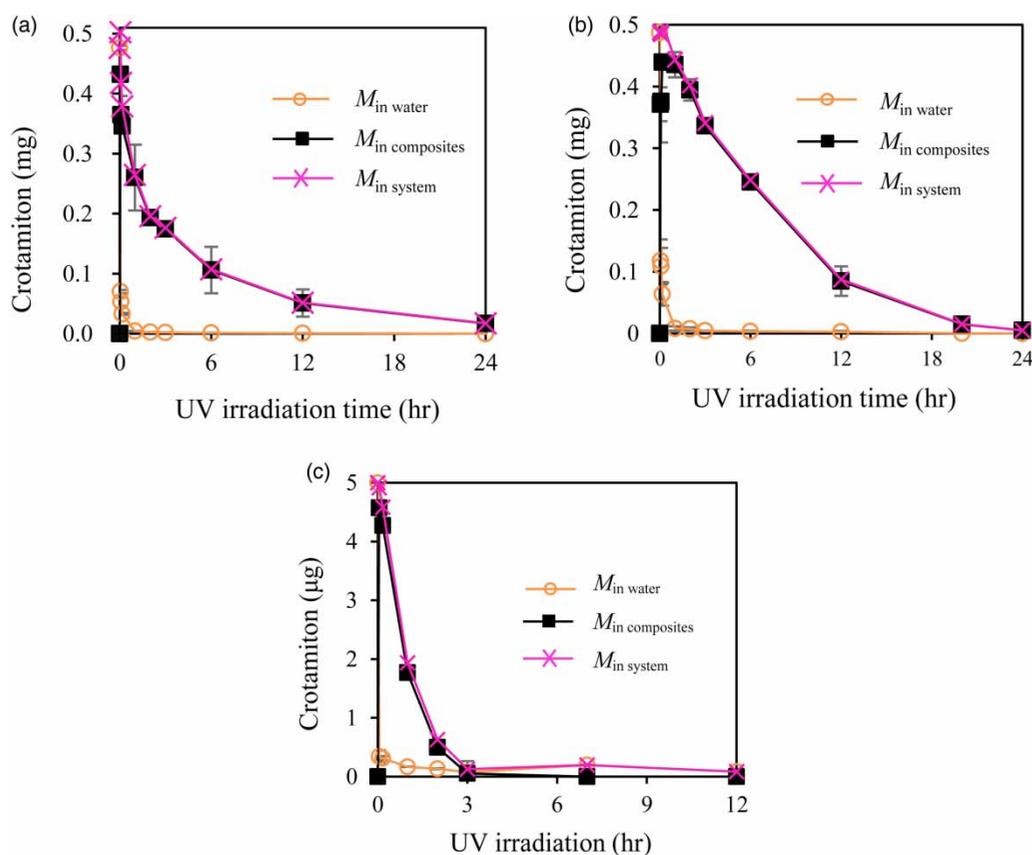


Figure 4 | Removal of crotamiton by the TiO₂-zeolite composites under UV irradiation. (a) 10 mg/L crotamiton in ultrapure water, (b) 10 mg/L crotamiton in secondary effluent, (c) 100 µg/L crotamiton in secondary effluent. Results are means ± standard deviations ($n = 2$).

and increasing the photodegradation rate. In our previous work, the TiO₂-HSZ-385 composite was applied for the removal of sulfonamide antibiotic (sulfamethazine) and the kinetic parameters of adsorption and photocatalytic decomposition were evaluated (Fukahori & Fujiwara 2014). We concluded from the kinetic and modeling approach that a synergistic effect existed between TiO₂ and zeolite. In this study, the same composite was used for the removal of crotamiton and it was clarified the adsorption behavior of crotamiton could be expressed with the Langmuir model, similar to sulfamethazine. From these results, we conclude crotamiton was synergistically removed by the TiO₂-zeolite composite.

The TOC concentrations found in the TiO₂-zeolite composite experiment samples are plotted against time in Figure 5. The TOC concentrations in the solutions changed quite differently comparing to that when only TiO₂ was used. The TOC concentration in each treated solution decreased rapidly in the initial stage of each treatment and then increased. The crotamiton could be quickly removed through the adsorption by HSZ-385 in the composites,

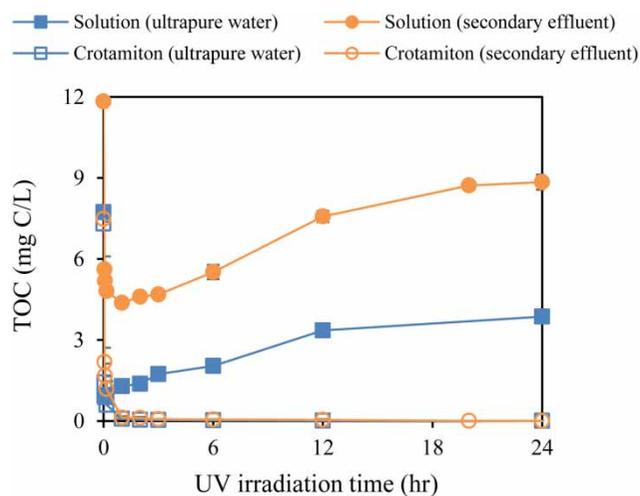


Figure 5 | TOC concentrations in the treated solutions plotted against time and the TOC derived from residual crotamiton plotted against time for the TiO₂-zeolite composite experiments ($C_0 = 10$ mg/L). Results are means ± standard deviations ($n = 2$).

resulting in the TOC concentration derived from crotamiton decreasing largely. The occurrence of crotamiton degradation intermediates is another source of TOC in the

solution in the later stage of the treatment; i.e., accumulation of the intermediates desorbed from the composites increased the TOC concentration.

As is shown in Figures 2 and 4(a), ca. 73% and 79% of the crotamiton in the ultrapure water was degraded in the TiO₂ and TiO₂-zeolite composite systems after 6 hr treatment, respectively, when the initial crotamiton concentration was 10 mg/L. This is to say, a similar amount of degradation intermediates should have been produced in the treated solutions. However, only ca. 12% of the TOC in the ultrapure water was removed after 6 hr of TiO₂-photocatalysis (Figure 3). In contrast, when the TiO₂-zeolite composites were used, ca. 74% of the TOC in the ultrapure water was removed after 6 hr of UV irradiation (Figure 5). In addition, the removal efficiency of TOC derived from crotamiton was ca. 99% after 1 hr treatment in the TiO₂-zeolite composite system, when the initial crotamiton concentration was 10 mg/L (Figure 5), which indicated that the degradation intermediates were the dominating sources of TOC after 1 hr treatment in the TiO₂-zeolite composite test system. The much lower residual TOC concentration in the TiO₂-zeolite composite system compared to the TiO₂ system indicated that not only crotamiton in the solution but also the intermediates produced through the degradation of crotamiton were captured by the TiO₂-zeolite composites.

We proposed in a previous study that the aromatic ring, the propenyl group double bond, and the ethyl group were initially hydroxylated for the TiO₂-photocatalytic degradation of crotamiton (Fukahori *et al.* 2012). The crotamiton intermediates produced in the early stages of photocatalytic degradation may therefore easily become adsorbed onto HSZ-385 owing to the similar chemical structures. With the gradual degradation of crotamiton, the intermediates may become adsorbed to HSZ-385 at different extents because of the different hydrophobicity/hydrophilicity (which is dominant factor for the adsorption performance of HSZ-385). As is shown in Figure 5, the TOC concentrations in the solutions gradually increased after 6 hr in the composite systems. About 50% of the TOC in the ultrapure water was removed after 24 hr when the TiO₂-zeolite composites were used, and this value was close to the value found when TiO₂ was used (ca. 45%). Similar TOC removal efficiencies in the two systems indicated that the capture of intermediates by HSZ-385 may be limited to the hydrophobic intermediates, and hydrophilic intermediates produced in the later stage of the treatment may be desorbed from the composites, which need to be further studied.

Behaviors of the major intermediates

The degradation intermediates were characterized following the methods described in our previous study (Fukahori *et al.* 2012). The appearance of new peaks was revealed by LC/MS/MS full scan and selective ion recording mode as the crotamiton gradually disappeared. The spectra showed that the molecular weight of the most noticeable product ion was 219, which was 16 Da higher than the molecular weight of crotamiton (203.28 g/mol). This indicates that the signals may have been caused by hydroxylated analogs of crotamiton (labeled P219). One of the most abundant fragments of P219 was *m/z* 69, indicating the presence of a propenyl carbonyl moiety and that hydroxylation of the aromatic ring or ethyl moiety had occurred. The P219 fragmentation pattern contained fragment ion *m/z* 107 rather than the benzyl cation (*m/z* 91), suggesting that the aromatic ring in crotamiton had been hydroxylated.

The changes in the peak areas of the major intermediate P219 during the photocatalysis of crotamiton using TiO₂ are shown in Figure 6(a). The peak areas quickly increased and reached maxima at 3 hr and 6 hr for the treatment in ultrapure water and secondary effluent, respectively, and then the peak areas gradually decreased. The accumulation of degradation intermediates corresponded well to the high TOC concentrations in the treated solutions (Figure 3). The relatively lower and later occurrence of top values of P219 peak areas for the treatment in secondary effluent indicated that the intermediates were formed more slowly than in ultrapure water, reflecting the effect of the other components of secondary effluent on the photocatalytic degradation of crotamiton.

Treatment with the TiO₂-zeolite composites (Figure 6(b)) was compared with that using the TiO₂. The P219 peak areas were clearly two orders of magnitude lower throughout the treatments using the TiO₂-zeolite composites than using TiO₂. Although the trends shown in Figure 6(a) and 6(b) are different, the difference was not significant taking into account the magnitudes of the peak areas. After 24 hr of treatment with the TiO₂-zeolite composites, the majority of the P219 disappeared, while the peak areas of P219 after 24 hr treatment by TiO₂ were still at quite high level. The much lower peak areas of degradation intermediates confirmed that the degradation intermediates could be captured by the TiO₂-zeolite composites. Degradation intermediates were also found to be captured when using paper-like composites containing TiO₂ and zeolites to treat bisphenol A with UV irradiation; most of the intermediates were temporarily captured by the zeolite adsorbent and eventually decomposed through TiO₂ photocatalysis (Fukahori *et al.* 2003). In

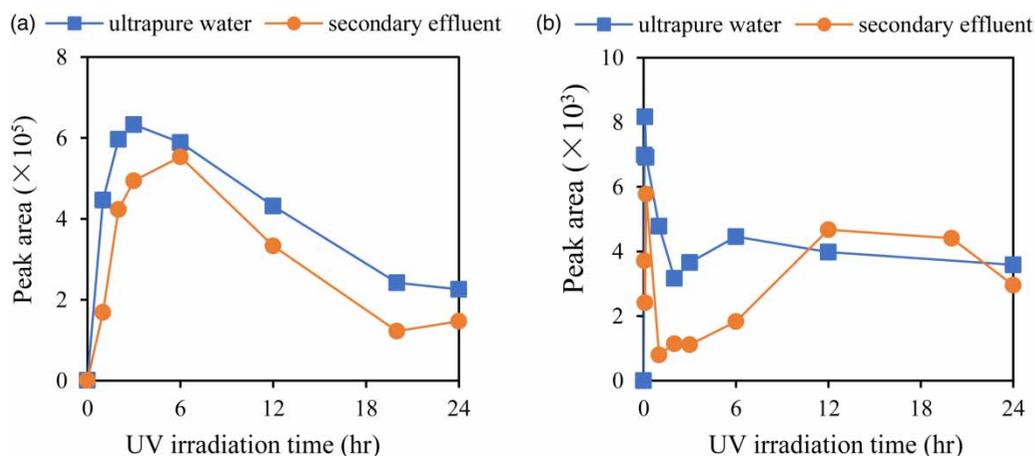


Figure 6 | Changes in the peak areas of the major intermediate P219 (retention time 4.8 min) over time when crotamiton was photocatalytically degraded by (a) TiO₂ and (b) TiO₂-zeolite composites ($C_0 = 10$ mg/L).

conclusion, the TiO₂-zeolite composites were effective not only for removing crotamiton from the secondary effluent but also for capturing the degradation intermediates of crotamiton. This provides a new method to mitigate the negative impact of harmful degradation intermediates produced by advanced oxidation processes.

CONCLUSIONS

TiO₂-zeolite composites were synthesized and used to treat crotamiton in secondary effluent. Crotamiton was rapidly adsorbed by the HSZ-385, and the adsorption performance of crotamiton in the secondary effluent was quite close to that in the test using the ultrapure water. When the TiO₂-zeolite composites were used to photocatalytically degrade crotamiton in secondary effluent, the crotamiton was rapidly adsorbed onto the composites and gradually decomposed through photocatalysis. Inhibition caused by coexisting material of the removal of crotamiton was mitigated when using the TiO₂-zeolite composites at a low initial crotamiton concentration of 100 µg/L. Changes in the TOC concentrations and the behaviors of intermediates indicated that the degradation intermediates were captured by the TiO₂-zeolite composites.

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