

A study on removal efficiency of phenol and humic acid using spherical activated carbon doped by TiO₂

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Abstract—This study aimed to find a way to remove organic pollutants, phenol and humic acid in aqueous solutions using TiO₂ spherical activated carbon (Ti-SPAC). The Ti-SPAC was manufactured by resin ion-exchange and a heating process. This method was very effective not only in creating TiO₂ on the surface of the supports evenly, but also in making activated carbon that has highly-developed micro pores. To estimate whether Ti-SPAC has the proper features as a photocatalyst and adsorbent, it was examined in detail by X-ray patterns, SEM image, EDXS, BET, EPMA. The results proved that Ti-SPAC is a very useful material for treating wastewater by photocatalysis and absorption.

Key words: Ti-SPAC, Photocatalyst, Activated Carbon, Humic Acid, Phenol

INTRODUCTION

Photocatalyst oxidation is one of the most promising ways to remove environmental pollutants. It has recently been extensively studied by many scientists and technologists because it is able to completely oxidize organic molecules by low cost treatment. Titanium dioxide (TiO₂) is able to form electrons (e⁻) in the conduction band and positive holes (h⁺) in the valence band with higher UV irradiation on TiO₂ than its own band gap energy (=3.2 eV). In this condition, it can make hydroxyl radicals and superoxide species that are very strong oxidizing agents and these agents degrade organic matter to CO₂ or H₂O [1]. The photocatalytic activity of TiO₂ for the degradation of organic and inorganic pollutants is well-known and established because of this phenomenon [2]. TiO₂ is generally used in the form of powder (Degussa P-25) in the polluted aqueous solution, but it is almost impossible to use practically because powder has many problems in recovering raw materials after the reactions are finished and the pollutants on the TiO₂ surface are washed. The powder form also shows low light-utilization because the suspension of the powder blocks the illumination and absorbs the light in aqueous solutions [3]. For these reasons, many attempts to fix the catalyst on supports, such as glass beads, silica balls, stainless steel and activated carbon have been made using various methods, such as CVD, impregnation, plasma coating, dip-coating, sol-gel, and mechanical coating [4-7]. However, these methods are very hard to photocatalyze effectively because fixing the catalyst evenly is very difficult and the processes of these methods are complicated. Moreover, in aqueous solutions, mobilizing supports for effective photocatalysis cannot be performed due to their heavy weight. When binders are used to fix TiO₂ on supports, the photocatalytic activity decreases because photocatalysts are covered with a binder. Even if this binder is organic material, the binder might also be oxidized by photocatalysts. This means that it is possible to make more pollut-

ants in the polluted solution [8], and the removal rate of harmful organic materials could be slow [9].

In this study, TiO₂ was formed on porous adsorbents such as spherical-activated carbon to increase the photocatalyst efficiency by high adsorption and reaction giving more chances to react on the wide surface area of an adsorbent. We manufactured this TiO₂ spherical-activated carbon (Ti-SPAC) using resin ion-exchange and a heating process. This method makes it easy to fix TiO₂ on the supports; in addition, binders do not need to be used. Furthermore, we estimated the Ti-SPAC's physical features using various experiments, X-ray patterns, SEM image, EDXS, BET, and EPMA, and then observed its efficiency in removing phenol [10] and humic acid [11] under various water conditions. Our results prove that Ti-SPAC is a very usable material for treating wastewater, phenol and humic acid. We conclude that Ti-SPAC has promising potential for use in commercial water treatment systems because of its capacity for photocatalysis and absorption of water pollutants.

EXPERIMENTAL SECTION

1. Material and Manufacturing Method of Ti-SPAC

A strong acid ion-exchange resin (SK1BH, DIAION) was used as a starting material of Ti-SPAC to fix the TiO₂. It consisted of polystyrene and divinylbenzene (DVB) and had a sulfonate group as the exchangeable functional group. A TiCl₃ 20 wt% solution (KANTO CHEMICAL) was used as a precursor of the photocatalyst TiO₂. A resin ion-exchange process between strong acid ion-exchange resins and titanium ions in the TiCl₃ solution was performed with a weight ratio of [TiCl₃ 20 wt% : H₂O=1 : 30] by being stirred sufficiently for one hour at room temperature and then washed many times and dried at 110 °C in the oven. The next day the samples were carbonized under nitrogen gas to 700 °C with 1 °C/min speed and activated under nitrogen/H₂O-vapor at 900 °C for 0.5 hours.

2. Characterization of the Samples

The specific surface area and pore distribution of the Ti-SPAC were measured by adsorption-desorption of N₂ at 77 K using Miro-

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meritics ASAP 2010, and the capacity of the specific surface area and the size of the micropores were calculated with Langmuir and Horvath-Kawazoe (HK) methods [12,13].

The composition of the Ti-SPAC and amounts of TiO_2 immobilized on Ti-SPAC were examined by EDXS (Energy dispersive X-ray spectroscopy, Phoenix No. of Instrument) and the crystal structure of TiO_2 was recorded using X-ray diffraction analyzer (Rigaku model D/MAX-3B) equipped with a graphite monochromator, operating in the reflection mode with $\text{CuK}\alpha$ radiation between 20° and 80° (2θ). The distribution and amounts of TiO_2 on the surface of the Ti-SPAC were observed using electron probe micro analyzer (JXA-8100) and the morphologies of the Ti-SPAC following the heating process were examined by scanning electron microscopy (PHILIPS model XL30SFEG). The degree of the crush strength of the Ti-SPAC in each unit was measured using FS-1010 to predict the possibility of applying it to the fluidized bed reactor directly.

3. Preparation and Measurements

A 99.0% JUNSEI Corp. phenol solution was diluted with distilled water; additionally, ALDRICH Corp. humic acid was filtered by a $0.45\ \mu\text{m}$ membrane filter to remove ash after being dissolved for a day.

First, the adsorption efficiency of the Ti-SPAC toward target substances, phenol and humic acid, was examined by a batch type adsorption method. This method involves reacting a 100 ml substance sample by pouring a fixed Ti-SPAC weight into each flask and placing them into the dark stirrer reactor, with each at a constant temperature and a 200 rpm speed to block photocatalytic activity.

Second, the photocatalytic efficiency was examined by measuring the concentration change under irradiating UV in the Ti-SPAC floating reactor and then comparing it with the P25 floating reactor. The reactor was a batch type with a 1.7 L capacity equipped with a UV source, low pressure mercury lamp UV-C (254 nm) [LIGHTTECH Crop.]. On the bottom of this reactor, a sampling port was equipped with mesh to prevent losing the Ti-SPAC, and air blowing equipment was installed to react in an aeration condition and to fluidize the Ti-SPAC for effective photocatalytic activity. Aluminum foil covered the reactor to block the influence of other lights. In addition, the degradation of phenol and humic acid by Ti-SPAC photocatalytic reaction was examined by checking their concentrations according to the COD_C (chemical oxygen demand) chromium method using a UV/vis spectrophotometer at 270 nm.

RESULTS AND DISCUSSION

1. Characterization of Ti-SPAC

Ti-SPAC and SPAC measured the specific surface area and pore distribution according to adsorption-desorption isotherms of N_2 at 77 K. The Ti-SPAC was manufactured by the ion-exchange method and a heating process, but the SPAC was made only by the heating process without ion-exchange. As shown in Fig. 1, these two materials had very excellent adsorption isotherms such as activated carbon. This is because they had well-developed pores especially in the micro region of under $10\ \text{\AA}$ as shown in Fig. 2.

However, the specific surface area of the Ti-SPAC ($654\ \text{m}^2/\text{g}$) in Table 1 was higher than the SPAC. This result is because the Ti-SPAC had more pores from being oxidized by a strong acidic TiCl_3 solution with an ion-exchange and heating process. The pore vol-

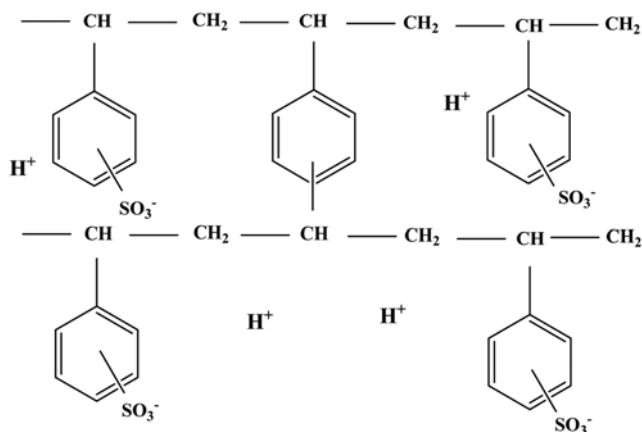


Fig. 1. The chemical structural formula of the strong acid cation resin SK1BH.

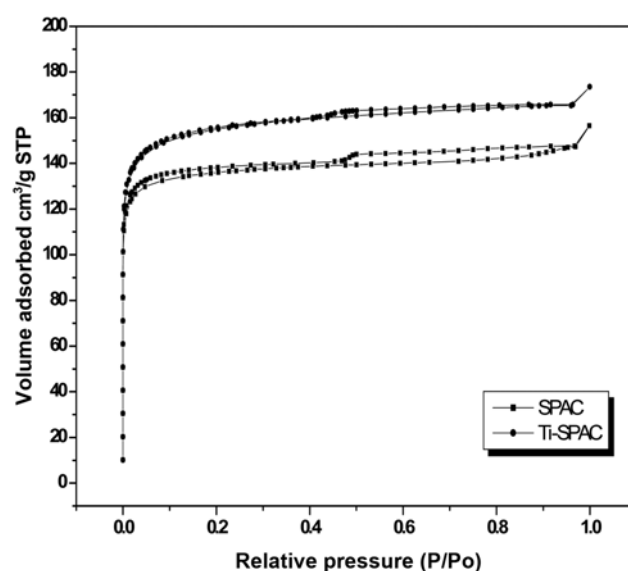


Fig. 2. Nitrogen adsorption-desorption isotherms of the SPAC and Ti-SPAC.

Table 1. Adsorption properties of the SPAC, Ti-SPAC and AC

Sample name	S_{BET} (m^2/g)	S_{Langmuir} (m^2/g)	Pore volume (cm^3/g)	Median pore diameter (\AA)
SPAC	515	581	0.242	9.61
Ti-SPAC	594	654	0.268	9.90
AC	1,190-1,200	1,353	0.573	10.53

ume of the Ti-SPAC calculated by the HK method was $0.268\ \text{cm}^3/\text{g}$ and the pore size was on average $9.9\ \text{\AA}$. Since a high specific surface area and well-developed micro pore distribution can quickly remove aromatic compounds by absorption [14], we estimated that there are advantages to quickly removing phenol and humic acid with Ti-SPAC.

The results of the Ti-SPAC morphologies by scanning electron microscopy, showed that the Ti-SPAC was spherical and had a smooth surface as in Fig. 3(a). On the other hand, when fixing TiO_2 on activated carbon supports, a rough surface was easily made, and the

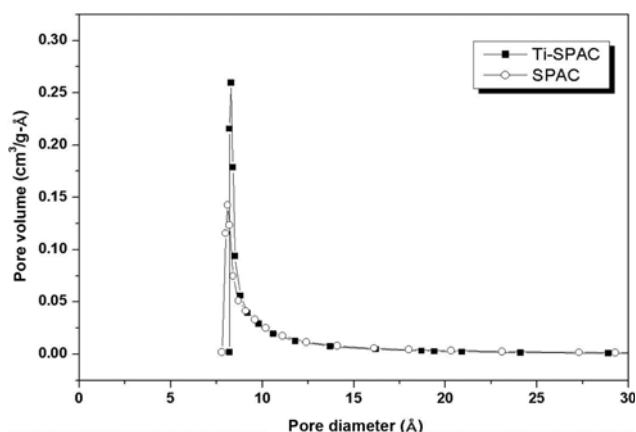


Fig. 3. Pore size distribution of the SPAC and Ti-SPAC.

photocatalytic activity was reduced by elution of the photocatalyst or deterioration of the fixing force [15]. In contrast, the Ti-SPAC manufactured by a titanium ion exchange and heating process fixed the ions on the activated carbon surface without using a binder and it had a smooth surface. In addition, it prevented exfoliation of the photocatalyst and deterioration of durability, so it has many advantages in water treatment systems. The size of the Ti-SPAC was about 0.35-0.4 mm and could be re-collected simply by some mesh in the bottom of the sampling port without an expensive or special separation process. The average strength of Ti-SPAC was 9 kg/unit; it is quite a large number, so the ability to prevent photocatalyst is weakened by floating in the reactor.

Ti-SPAC has not only an adsorbent feature, but also a photocatalyst because of its TiO_2 forms. The crystal structure of TiO_2 on Ti-SPAC is shown mixing both anatase and rutile in its formation in Fig. 4. These two types of TiO_2 have been used in various fields [16]. The rutile type is very stable at all temperatures; however, anatase is unstable because it forms at 450-550 °C, but it easily changes to the rutile type when the heat treatment is over 600 °C [17]. In photocatalytic efficiency, anatase has a higher activity than rutile, because it has higher band gap energy (3.23 eV) than rutile (3.02 eV). Therefore, it needs a higher energy source [18]. However, an-

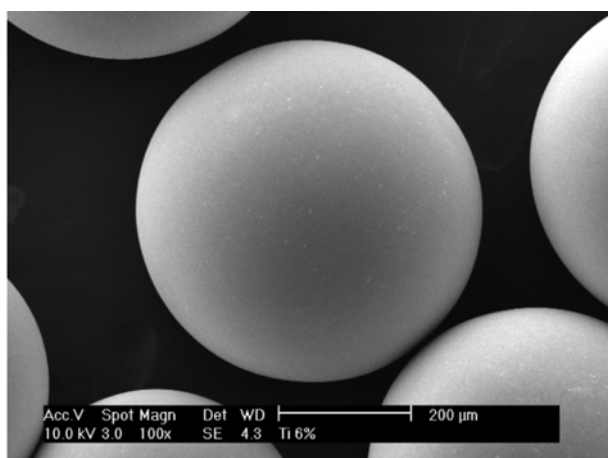


Fig. 4. SEM image of Ti-SPAC.

Table 2. Element contents of samples by EDXS analysis

(unit: wt%)

Element	SK1BH	Ion exchanged SK1BH	Ti-SPAC
C	53.44	59.04	77.12
O	26.45	25.74	13.52
S	20.11	12.20	3.33
Ti	0	3.02	6.03
Total	100	100	100

atase is not always better in photocatalyst efficiency. P25, for example, consists of 70-80% anatase and 20-30% rutile; it was shown to have a better removal efficiency of organic substances than only raw anatase or raw rutile. Therefore, in this study, the photocatalyst efficiency of Ti-SPAC in phenol solution and humic acid was examined to compare it with P25.

The composition elements of Ti-SPAC examined by EDXS were C, O, S, and Ti. The element makeup was different before the ion-exchange, as indicated in Table 2. We observed that titanium ions were generated after the ion-exchange in the Ti-SPAC, and the number of titanium ions increased to 6.03 wt% of the Ti-SPAC through the heating process. This phenomenon was inferred because the burn-off percentage of the heating process was 50%, so even if we exchanged titanium ions to only 3.02 wt%, it could still be increased to 6.03 wt%. This amount was also calculated as 10.5 the wt% TiO_2 of Ti-SPAC. This was also the same for the remaining inorganic substances after continuing to burn all the Ti-SPAC with 1,000 °C air. The distribution and amounts of TiO_2 on the surface of the Ti-SPAC were observed by using EPMA. It showed 6 wt% of the titanium was uniformly distributed on the surface of the spherical activated carbon as shown in Fig. 3(b). This is because the titanium ions were uniformly distributed on the surface, and this can solve many problems such as decreasing the specific surface area, blocking micro-meso pore, and immobilizing TiO_2 disproportion-

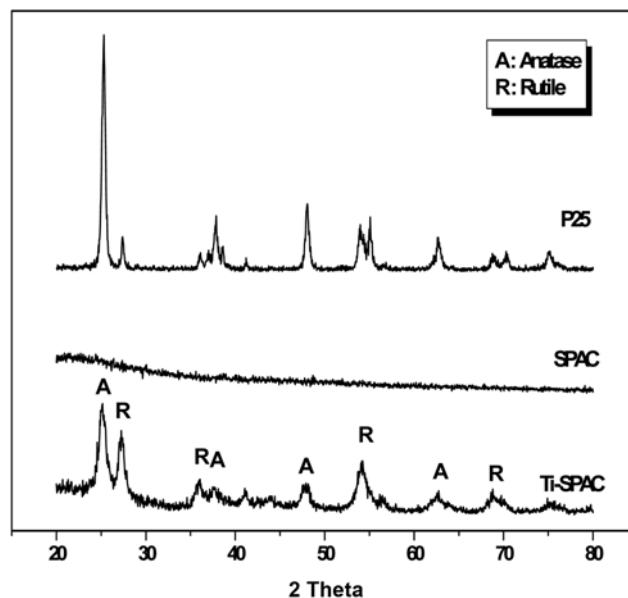


Fig. 5. X-ray patterns of SPAC and Ti-SPAC.

ately on the surface of supports from generating TiO_2 [15].

2. Photocatalysis and Adsorption Activity of Phenol by Using Ti-SPAC

The phenol adsorption efficiency of Ti-SPAC according to the time change was examined by a batch type method: 100 ml of phenol 5,000 ppm was poured into each flask, with a fixed Ti-SPAC weight and shaken in the dark stirring reactor with a constant temperature and a speed of 200 rpm. The change of phenol concentration by absorption showed both Ti-SPAC and SPAC, and those adsorptions removed up to 70% of phenol 5,000 ppm per 10 minutes as shown in Fig. 5. In contrast to commercial activated carbon (AC), the adsorption speeds of Ti-SPAC and SPAC were much faster, so it is expected that they can be usable adsorbents to remove pollutants in the water.

The photocatalytic efficiency of Ti-SPAC with phenol 5,000 ppm was examined following the adsorption of phenol. First, phenol 5,000 ppm was poured into the reactor equipped with a UV-C lamp (254 nm) and then was reacted with Ti-SPAC for 120 minutes under dark conditions to progress without photocatalytic activity. Both adsorption and photocatalyst oxidation of Ti-SPAC were performed simultaneously under UV-C light. The Ti-SPAC in UV-C light removed more phenol than in dark conditions as shown in Fig. 6. This is because in dark conditions, only adsorption was performed. On the other hand, photocatalytic activity worked with adsorption simultaneously in UV-C light, so it increased its removal efficiency. However, photocatalytic activity did not clearly appear in comparison with a high adsorption of phenol in this examination, so a more proper examination about photocatalytic activity of Ti-SPAC was performed next with humic acid. P25, shown as the best photocatalyst, was also studied with phenol 5,000 ppm in the same conditions to compare it with Ti-SPAC as shown in Fig. 6. However, its removal efficiency was not remarkable. Based on a detailed and critical analysis of the existing literature on photocatalytic oxidation of contaminants, the important operating parameters, which affect the overall destruction efficiency of the photocatalytic oxidation process, can be given as follows: amount and type of catalyst, reactor design,

wavelength of irradiation, initial concentration of the reactant, temperature, radiant flux, medium pH, aeration, and effect of ionic species. An especially low concentration of the reactant showed better photocatalytic efficiency [19]. Beltran-Heredia et al. [23] showed that a photocatalyst with 100 ppm reactant has up to 70% removal efficiency, but 10 ppm has up to 45% in the same conditions. This means that a higher initial concentration is decreased more by the photocatalyst [21]. Therefore, that is the reason the removal efficiency of P25 was not as remarkable in this experiment as in other studies, where P25 could remove phenol properly at a 100 ppm concentration [22-24]. However, they didn't indicate clearly a result at high concentrations, such as the 5,000 ppm concentration in this study.

The mechanism of phenol degradation had not been presented definitely until now, but Sobczynski et al. [25] studied the mechanism of phenol degradation by TiO_2 . This degradation generates intermediate materials like hydroquinone, P-benzoquinone, catechol under aeration, and also aliphatic-disintegrated compounds containing oxygen following the destruction of benzene rings. Phenol, which gives a fatal toxic effect to microorganisms, changes to a biological degradable substance and then disintegrates totally to CO_2 and H_2O . Ti-SPAC is also predicted to have the ability to remove not only toxic phenol, but also intermediate materials by photocatalytic activity and adsorption. It is therefore expected to be able to remove toxic organic materials in water excellently.

In photocatalytic oxidation, pH is one factor that can affect the organic removal activity. In addition, various pollutants and ZPC (zeropoint charge) affect the pH. Metal oxide (including TiO_2) and activated carbon have an amphoteric character in which the surface electric charge can be changed according to the pH, so the surface electric charge of Ti-SPAC can also be changed by ZPC of Ti-SPAC ($\text{pH} \approx 5.6-6.6$) [26]. Adsorption of phenol using Ti-SPAC was examined by adjusting pH 4, pH 7, and pH 10 using 1 N KOH and 1 N HCl because phenol's removal efficiency can be different according to its pH conditions. This demonstrates that Ti-SPAC possesses higher phenol adsorption ability in a pH 4 acidic condition than the other conditions as shown in Fig. 7. This is because phenol can easily

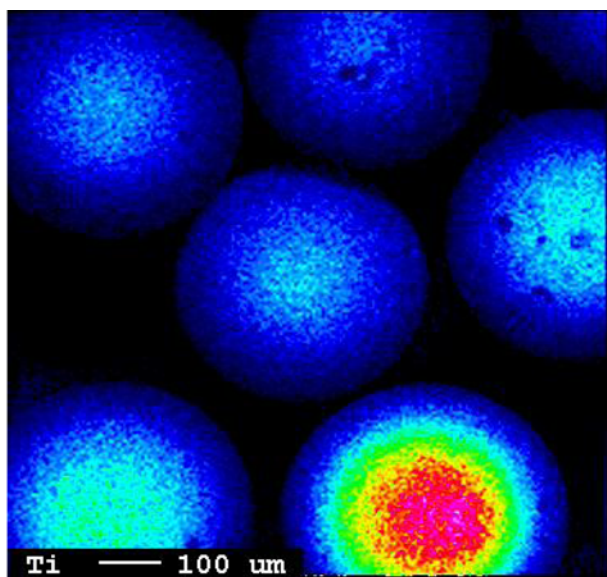


Fig. 6. EPMA image of Ti-SPAC.

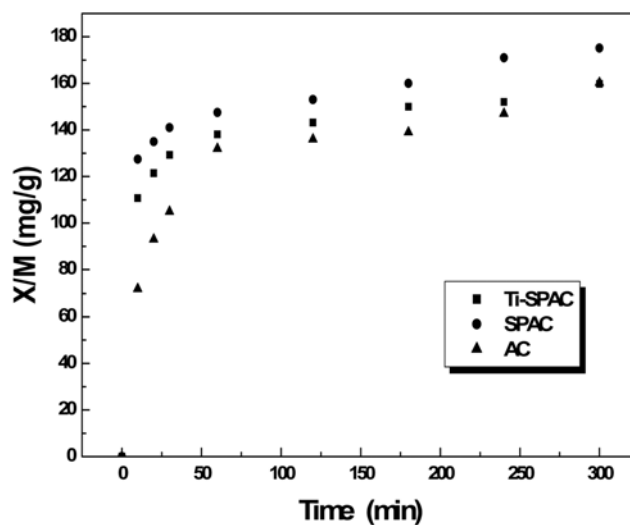


Fig. 7. The adsorption ability evaluation of phenol according to the time variation; by SPAC, Ti-SPAC and AC.

lose its H^+ ion in the hydroxyl group in water and exists as anions of $C_6H_5O^-$, so anionic phenol was adsorbed easily on the surface of Ti-SPAC covered with cations.

3. Photocatalysis and Adsorption Activity of Humic Acid Using Ti-SPAC

Humic acid is one of the major components of humic substances, which are dark brown and constituents of soil organic matters, and is not only a precursor of disinfection of by-products (DBPs) in chlorination and ozonation process, but also is hard to remove by conventional systems. Schulten et al. [27] studied the structure of humic acid which showed a 5,539.7 molecular weight and a $C_{308}H_{328}O_{90}N_5$ empirical formula.

The adsorption efficiency of humic acid according to time change was examined by the batch type method, similar to phenol examination. Here, the 100 ml of phenol 10 ppm was poured into each flask with a weight measured by Ti-SPAC and placed in the dark stirring reactor (UV OFF), each with a constant temperature and a speed of 200 rpm. Regardless of the change of concentration, humic acid was not removed after the adsorption reaction. This is because humic acid is too big to adsorb into the micro pores of the Ti-SPAC,

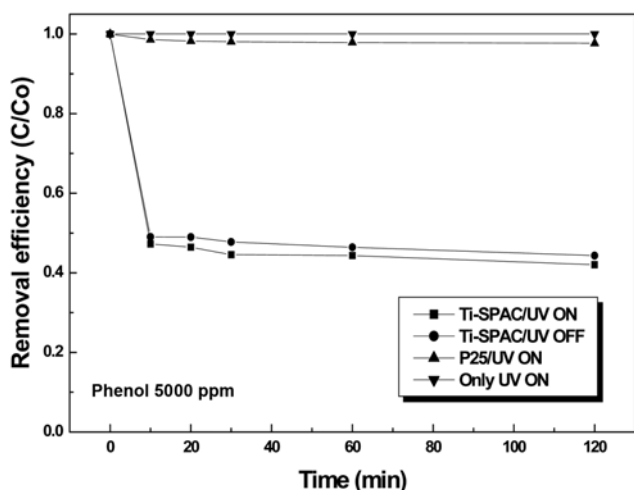


Fig. 8. Removal efficiency of phenol according to the UV on/off experimental conditions using Ti-SPAC and P25.

so to remove organic substances of high molecular weight such as humic acid, photocatalytic oxidation needs more than adsorption. Therefore, we observed the photocatalytic efficiency of Ti-SPAC on humic acid in UV-C light (UV ON) and found that Ti-SPAC (as TiO_2 2.6 g/l) removed humic acid as in Fig. 8. In this sense, Ti-SPAC can apply to all various organic matter, not only to toxic substances such as phenol but also to substances disadvantageous in adsorption.

The mechanism of humic acid degradation by photocatalytic oxidation has been studied actively; Eggins et al. [28] confirmed that the transformation ratio of aromatic carbons to aliphatic and carboxylic carbons increased with UV irradiation time, and the ratios of aromatic carbons of the treated humic acid were reduced. On the other hand, carboxylic carbon contents were in peak positions in the spectra. Therefore, we can infer that aromatic and aliphatic components, including alcohol, amine, and carbohydrates, were effectively transformed into various types of carboxylic acids ahead of their mineralization. Wiszniowski et al. [29] studied photocatalytic decomposition of humic acids on TiO_2 , and demonstrated that the photocatalysis process can break long organic molecules into smaller biodegradable compounds and can make their biological treatment eligible for commercial use. Uyguner et al. [30] observed that high molecular substances of over 100,000 daltons reduced from 20% to 10% and low molecular substances of under 1,000 daltons increased from 10% to 80% after photocatalytic oxidation of humic acid, so they concluded that the photocatalytic oxidation of humic acid has a positive effect on biodegradation.

Overall, humic acid degradation of Ti-SPAC is expected to increase biodegradable aliphatic carbons and decrease toxic aromatic carbons through the TiO_2 photocatalytic degradation reaction with humic acid, which means it will be easy to make minerals that can be removed simply by photocatalytic oxidation of humic acid.

Among the important operating parameters, the removal efficiency of humic acid according to the amount of the catalyst was examined by loading 1.3, 2.6, 3.9, 5.2, and 6.5 g/l (as TiO_2) of Ti-SPAC. The Ti-SPAC removal efficiency increased from 1.3 g/l to 3.9 g/l, but it decreased when the loaded amount was over the limit as shown in Fig. 9. The first reason for this result is that, as opposed to a general catalyst reaction, only a few photocatalysts degrade pollutants by absorbing light [1]. The second reason is that an amount

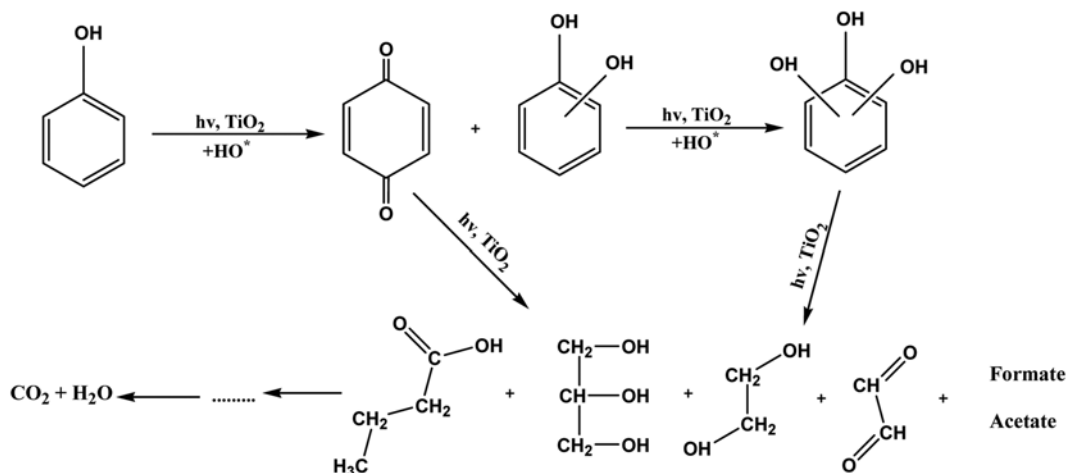


Fig. 9. A possible mechanism of phenol destruction on illuminated TiO_2 .

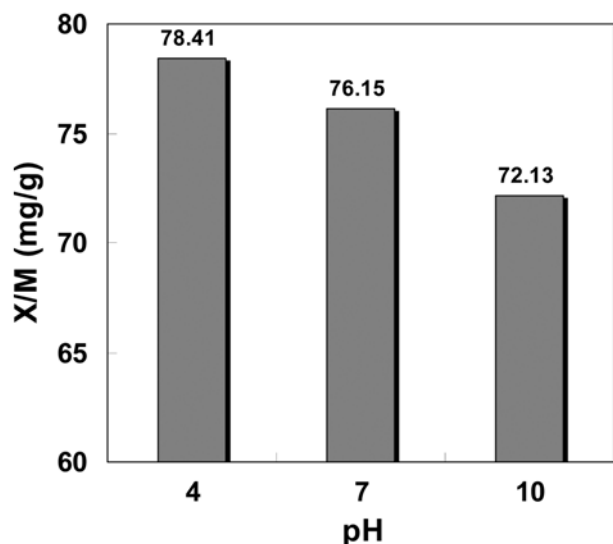


Fig. 10. The adsorption ability (X/M) of Ti-SPAC about phenol according to the initial pH [phenol 1,000 ppm, reaction time 120 min].

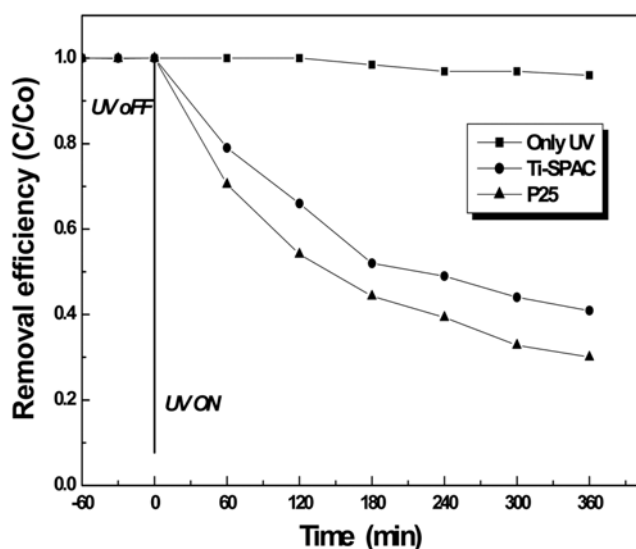


Fig. 11. Removal efficiency of humic acid according to the UV On/Off experimental conditions using Ti-SPAC and P25.

of Ti-SPAC over the limit can block the light and disturb the adsorption of light on the surface [18].

According to the removal efficiency change of phenol in various pH conditions, humic acid was also examined in various pH conditions, and the results confirmed that high photocatalytic efficiency was indicated at a pH4 acidic condition as shown in Fig. 10. This is because humic acid existed as anions in water, so it was easy to be adsorbed on the surface of Ti-SPAC covered with cations; additionally, the positive holes (h^+) in the valence have a stronger oxidation force in an acidic condition [31].

CONCLUSIONS

We formed TiO_2 on a porous adsorbent such as spherical-acti-

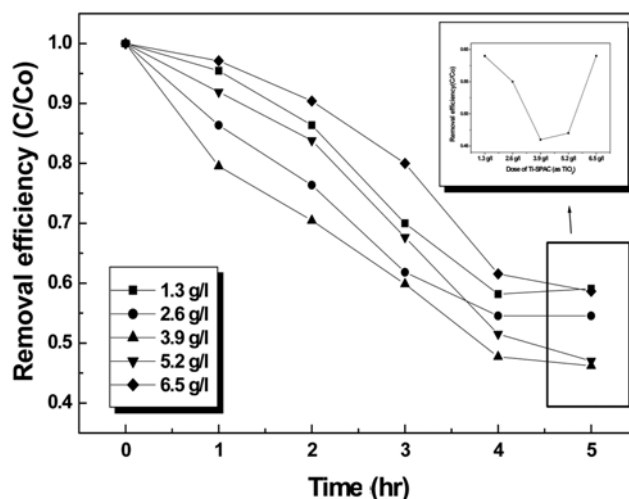


Fig. 12. Removal efficiency of humic acid according to the loading amount of Ti-SPAC.

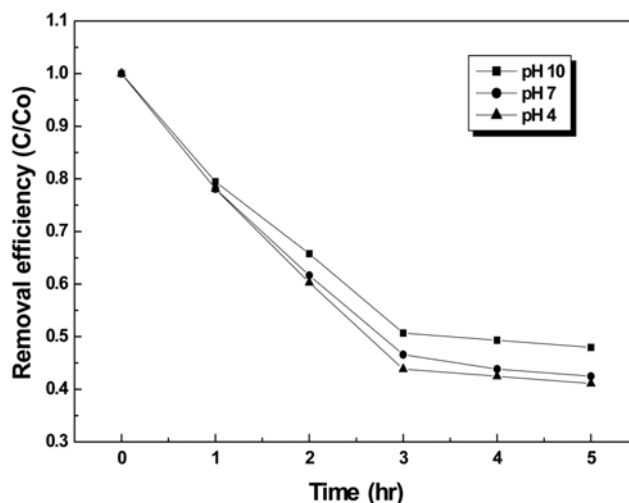


Fig. 13. Removal efficiency of humic acid according to the initial pH.

vated carbon, to increase photocatalyst efficiency by high adsorption and manufactured this TiO_2 spherical-activated carbon (Ti-SPAC) using a resin ion-exchange and heating process. With this method it is easy to fix TiO_2 on the supports, and binders are not needed. In addition, we estimated Ti-SPAC's physical features using various experiments, such as X-ray patterns, SEM image, EDXS, BET, and EPMA, and observed its efficiency in removing phenol and humic acid in various water conditions. Our results proved that Ti-SPAC is a very usable material for treating wastewater, such as phenol and humic acid. For example, a high specific surface area is very well-generated on Ti-SPAC, so it can absorb organic matter easily; additionally, a unified distribution of TiO_2 formations of Ti-SPAC can affect stable photocatalytic efficiency. Ti-SPAC is appropriate for use in a flatter reactor because the strength is high and the Ti-SPAC's size is enough to separate the solutions simply after the reaction is finished.

In addition, it was possible for Ti-SPAC to remove not only high-concentrated toxic substances, such as phenol 5,000 ppm, but also

high molecular substances like humic acid because of Ti-SPAC's photocatalytic activity and adsorption ability. This means Ti-SPAC can remove organic matter that needs oxidation or adsorption. This method is expected to be a useful system which will apply to advanced processes for the treatment of non-degradable pollutants.

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