

## Effect of experimental conditions on photocatalytic efficiency in TiO<sub>2</sub> powder slurry systems

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The photocatalytic efficiencies of three commercially-available TiO<sub>2</sub> samples were evaluated and compared for TiO<sub>2</sub> powder dispersed systems with respect to several experimental variables such as pH, types and concentrations of cation and anion ions, dissolved oxygen, UV, and target organics to be photo-catalytically decomposed. All the TiO<sub>2</sub> samples of P-25, NT-C, NT-20 showed a significant dependence of the photocatalytic efficiency on pH and exhibited higher photocatalytic efficiency in the pH range between 5 and 7. The water used for the preparation of the TiO<sub>2</sub> slurry also affected the photocatalytic efficiency of the TiO<sub>2</sub> samples presumably due to a few cation ions existing in the water. The degree of oxygen content dissolved in the slurry enhanced the photocatalytic efficiency by its role as an electron scavenger. The effect of several anions except Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> on the photocatalytic efficiency varied depending on their concentrations and source of TiO<sub>2</sub> powder. The photocatalytic properties of TiO<sub>2</sub> samples varied significantly depending on the key experimental conditions applied to the TiO<sub>2</sub> slurry. In the photocatalytic decomposition of organics, any particular TiO<sub>2</sub> sample did not always show a better efficiency than other sources of TiO<sub>2</sub> powder.

**Key words:** Photocatalyst, TiO<sub>2</sub>, Organic decomposition, Dissolved oxygen, pH, Cation, Anion, UV.

### Introduction

A photocatalyst generates electrons and holes when absorbing light with an energy higher than the band gap and it produces hydroxyl radicals (OH<sup>•</sup>) on its surface through a combination of the holes and the hydroxyl ions adsorbed on the photocatalyst surface. The active OH radicals with a highly oxidative potential can decompose organics at room temperature. Such a photocatalyst also can remove and separate heavy metal ions in the solution by its reduction ability due to the electrons generated. TiO<sub>2</sub> photocatalysts have attracted a great deal of attention in environmental waste water treatment in the past decade, because they generate hydroxyl radicals which can degrade refractory organics under UV irradiation, and because they have chemical stability, non-toxicity, and low cost [1-16].

A lot of studies on photocatalysts have been conducted in order to improve their industrial applications. First, by changing the processing conditions during manufacturing, the physicochemical properties of a photocatalyst can be improved and it may result in an enhancement of photocatalytic efficiency. Secondly, by changing the environmental conditions, enhanced photocatalytic efficiency could also be obtained. The environmental factors affecting the TiO<sub>2</sub> photocatalytic reaction in a solution are

the amount of TiO<sub>2</sub> to be used in a slurry, pH, DO (dissolved oxygen), UV, coexisting elements, presence of oxidizable substances, target organic materials, etc.

Many photocatalytic TiO<sub>2</sub> powders have been commercialized in the industrial field. However, a standard method for estimating their efficiencies has not been suggested yet, and the products have been usually evaluated after testing them in view of a few aspects, not taking into consideration the more general environmental factors influencing their photocatalytic activities. In this study, we attempted to evaluate how the environmental conditions affected commercially available TiO<sub>2</sub> photocatalyst powders. The effects of pH, anions, cations, DO, UV light and target organic materials were examined and compared.

### Experimental

Three types of TiO<sub>2</sub> photocatalysts, P-25 of Degussa, NT-20 and NT-C of NANO, Korea were used for these experiments. Table 1 shows the physical properties of these TiO<sub>2</sub> photocatalysts. The detailed properties of the TiO<sub>2</sub> samples have been described in our previous papers [17, 18]. A schematic of the experimental set-up is shown in Fig. 1. A 450W mercury vapor UV lamp (Hanovia Co.) was used for the photocatalytic reaction, and a Vycor adsorption sleeve to cut the wavelengths lower than 250 nm was placed between the lamp and a quartz immersion well (Ace glass Co.) inside which the lamp was put. The quartz immersion well was kept at 25 ± 0.5 °C by circulating

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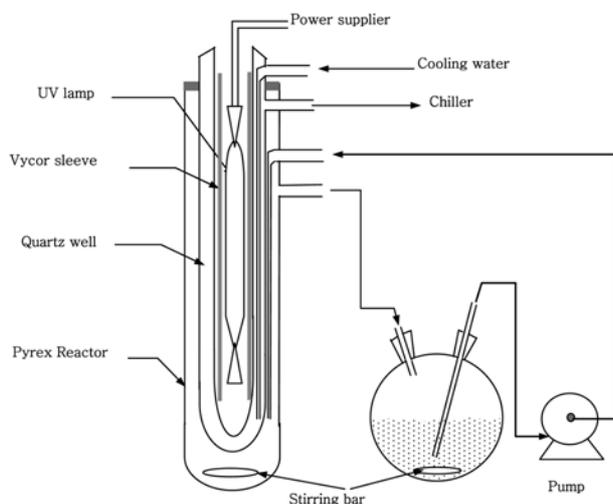
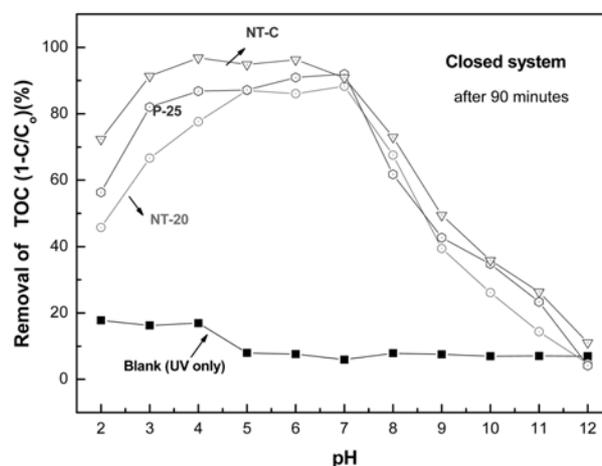
**Table 1.** Physical properties of TiO<sub>2</sub> samples

Sample	P - 25	NT - 20	NT - C
Crystalline structure	Anatase + Rutile	Anatase	Anatase
Purity(%)	> 99	> 99	> 98.5
Specific surface area (m <sup>2</sup> /g)	55	110	100
non-stoichiometric ratio (TiO <sub>x</sub> /TiO <sub>2</sub> )	0.338	0.469	0.681
Crystalline size (nm)	25	< 10	< 30

coolant from a chiller inserted into a Pyrex tube reactor (Ace reaction vessel 7863) of 500 ml. TiO<sub>2</sub> slurry of 1.5 g/l was prepared by mixing TiO<sub>2</sub> powder thoroughly in water with magnetic stirring and sonification, and then 1,000 ml of the slurry was put into the photo-reactor, and was circulated inside the reactor by a pump and an external reservoir. A magnetic bar was placed at the bottom of the reactor in order to disperse homogeneously the TiO<sub>2</sub> particles within the reactor without sedimentation during the photocatalytic reaction. To control the pH, either 0.1 M HNO<sub>3</sub> or 0.1 M NaOH was added in the photocatalytic reaction system using a pH/ORP controller. In order to see the effect of dissolved oxygen, the reaction system was operated either in a closed or an open system, depending on the contact of the solution with air during the photocatalytic reaction, and was also purged by Ar or O<sub>2</sub> gas before the reaction. For the evaluation of photocatalytic efficiency, the decomposition yield from 50 ppm of 4CP (4-chlorophenol) in the photocatalytic slurry for 90 minutes was measured with a TOC analyzer (Shimadzu TOC-5000A).

## Results and Discussion

The pH dependence of the tested TiO<sub>2</sub> samples were performed in the range of pH 2 to 11 by measuring the TOC removal yields of 4CP in the closed photocatalytic

**Fig. 1.** Experimental set-up for a photocatalytic reactor.**Fig. 2.** Changes of TOC removal yields in the closed TiO<sub>2</sub> slurry systems prepared with distilled water as a function of pH.

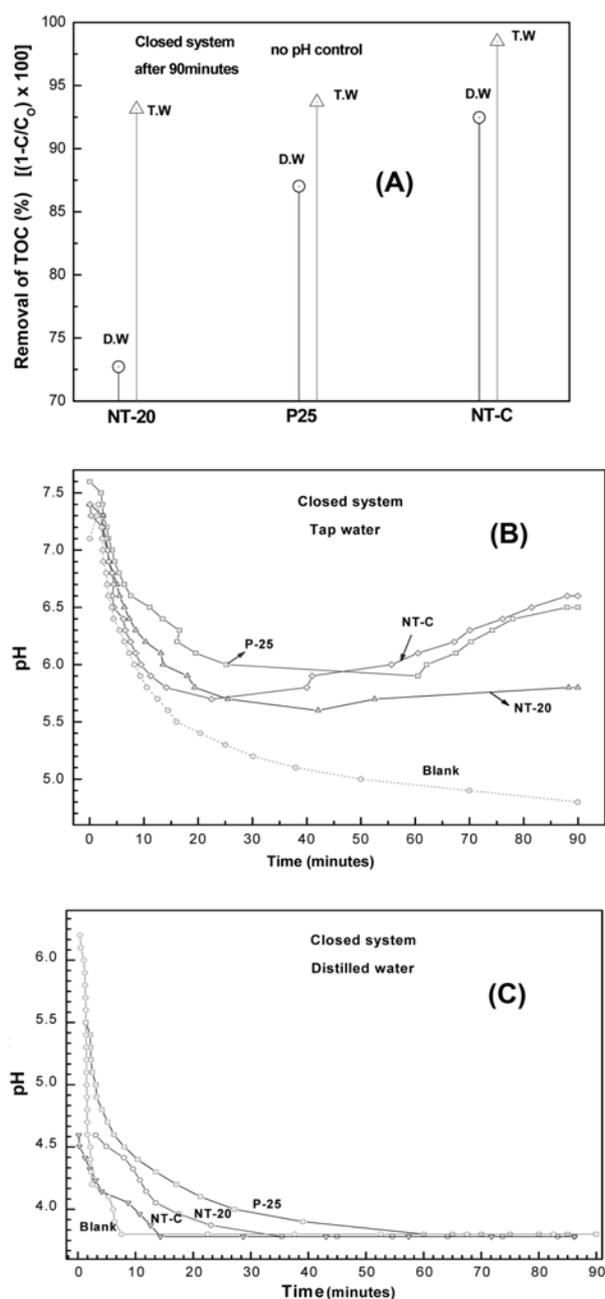
slurry system for 90 minutes and the results are shown in Fig.2. Figure 2 shows that the degree of 4CP decomposition by all the samples was high in the range of pH 5 to 7 whereas the degree became low in the basic solution above pH 7 and in the acid solution below pH 3. The metal oxides such as TiO<sub>2</sub> have a tendency of changing their surface charge by a pH variation and their photocatalytic reactivities change at the same time [5-9]. Below pH 6, the surface of TiO<sub>2</sub> is positively charged with TiOH<sub>2</sub><sup>+</sup>, while, above pH 6, it is negatively charged because of increasing TiO<sup>-</sup>. Accordingly, in the acid condition, the adsorption of anions or polar materials on the surface increases, while in the basic condition, the adsorption of cations increases. It is known that the oxidation potential of the holes occurring on the TiO<sub>2</sub> surface generated by the photocatalytic reaction decreases with pH at a 59 mV/pH, so the redox potential of photocatalyst can be controlled by pH [15]. As shown in Fig. 2, the degree of 4CP decomposition rapidly decreases at pH higher than 7. This could be the negatively charged TiO<sub>2</sub> surface. Therefore, the OH<sup>-</sup> to be changed to an OH radical on the TiO<sub>2</sub> surface is hard to be adsorbed on the TiO<sub>2</sub> surface at a pH higher than 7, even though there are plenty of OH<sup>-</sup> ions in the solution. This is because the oxidation potential of holes generated at the surface becomes less in the basic condition. This causes a decrease of generation of effective OH radicals on the surface, which results in the decrease of 4CP decomposition above pH 7. On the other hand, below pH 4, the TiO<sub>2</sub> surface in the solution is positively charged so that the negatively-charged species of OH<sup>-</sup> is prone to be easily adsorbed on the TiO<sub>2</sub> surface and the holes generated on the surface become strongly oxidative. Nevertheless, the amount of OH<sup>-</sup> ions in the solution is basically scant so that the OH radicals attacking organics in the solution are few. This results in the decrease of 4CP decomposition below pH 4 as well. Therefore, the OH radical is thought to be the most effectively generated in an optimal pH range between 4 and 7 with a suitable combination of an adequate amount of OH<sup>-</sup> ions in the

solution, the moderately charged surface of TiO<sub>2</sub>, and the good pH condition to make the holes generated on the TiO<sub>2</sub> surface oxidative. As shown in Fig. 2, three TiO<sub>2</sub> samples tested in this study show a very similar pH effect. Compared with previous studies, some discrepancies between their experimental results are found on the pH effect. Oliveira et al. [24] observed that when a photocatalytic degradation of 3-chlorophenol was tested, the reaction rate was slow below a pH 3.5 while there was no change of reaction rate in the range between pH 3.5 and pH 9 and it increased above pH 9. Matthews [25] found that there was no change of reaction rate and photon efficiency in the range between pH 2.6 and pH 6.0. He reported that the reaction rate at pH 12 was higher than that at pH 7. The difference between the photocatalytic experiments means that the photocatalytic activities of TiO<sub>2</sub> samples strongly depends on the target organic materials and the experimental conditions.

When a photocatalyst is applied in an industrial field, distilled water can not always be used for preparing a TiO<sub>2</sub> dispersed solution. Thus, the effect of types of water on the photocatalytic activity was investigated using distilled and tap water. The distilled water used in this study was produced by the double distillations of tap water and one ion exchange process to have a resistance of about 18 MΩ. Table 2 shows the analyses of the two types of water used for the preparation of TiO<sub>2</sub> slurries in this study. In the tap water, Si, Mg, and Ca ions are higher in concentration than in the distilled water. In both types of water, several impurities of transient metal ions were detected coexisting in extremely small amounts at ppb concentrations. Even a very small amount of minerals, absent in distilled water, existing in tap water could affect the photocatalytic reaction. With NT-C, P-25 and NT-20 TiO<sub>2</sub> slurries, which were prepared with both types of water, the TOC removal yields of 4CP for 90 minutes were observed, and the results are shown in Fig. 3(A). The TOC removal yields of 4CP by NT-C, P-25 and NT-20 TiO<sub>2</sub> samples in the tap water are higher than those in the distilled water. Also the NT-C TiO<sub>2</sub> sample showed the highest value among these three TiO<sub>2</sub> samples in both tap and distilled water. Fig. 3(B) and 3(C) show the pH variations during the photocatalytic reaction. In the case of distilled water, the pH for all of the three TiO<sub>2</sub> samples rapidly decreased to about pH 3.5 like the blank case where only UV was irradiated into the solution without a TiO<sub>2</sub> addition. On the other hand, in the case of tap water, the pH for all of the three TiO<sub>2</sub> samples decreased to around 6.0 and then

**Table 2.** Ions existing in distilled water and tap water.

Water	Major ion (ppm)					
	Si	Mg	Ca	Ba	Sr	
Tap water	0.3	3.1	15	0.02	0.1	
Distilled water	< 0.1	0.03	0.11	0.01	< 0.1	
Commonly detected impurities in ppb unit	Mo, Cr, B, Zn, Pb, Cd, Co, Ni, Ba, Mn, Th, Cu, Ti, Zr, Sr, Fe, etc					



**Fig. 3.** Changes of TOC removal yields in the closed TiO<sub>2</sub> slurry systems and their pH changes with time.

began to increase gradually again, being different from the case of distilled water. The pH did not decrease below 5 where the TOC removal yields of 4CP decreased because of an insufficient amount of OH<sup>-</sup> in the solution, as shown in Fig. 2. The pH changes during the last period of the photocatalytic reaction by NT-C and P-25 TiO<sub>2</sub> samples went up to around 6.5 higher than that by NT-20 TiO<sub>2</sub> sample. This result can be explain the reason that the TOC removal yields of 4CP by NT-C and P-25 TiO<sub>2</sub> samples is higher than that by NT-20 TiO<sub>2</sub> samples, as shown in Fig. 3(A). The water used for the preparation of the TiO<sub>2</sub> slurry can significantly affect the photocatalytic efficiency of TiO<sub>2</sub> with changing the pH during the photocatalytic

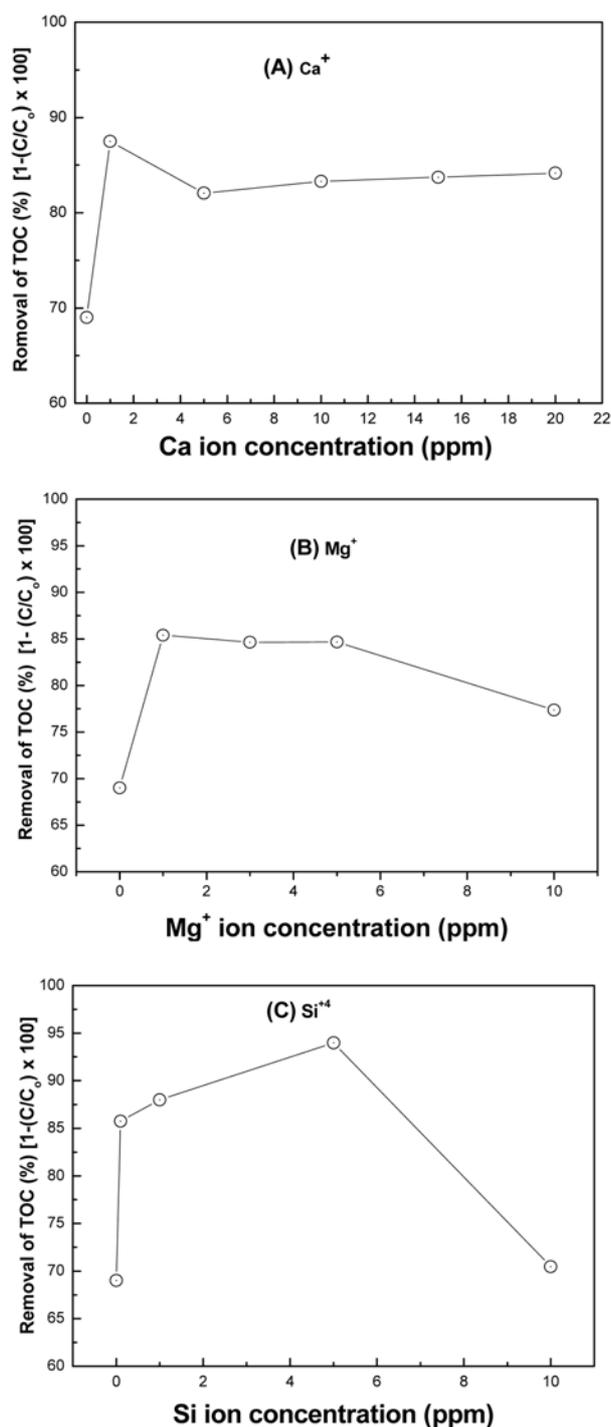


Fig. 4. Effects of cations on photocatalytic reaction in the closed NT-20 TiO<sub>2</sub> slurry systems prepared with distilled water.

reaction. The difference in photocatalytic efficiency caused by the type of water used for the TiO<sub>2</sub> slurry could originate from the metal ions existing in the water.

In order to confirm the effect of metal ions in tap water on the photocatalytic reaction, the photocatalytic decomposition of 4CP in the NT-20 TiO<sub>2</sub> slurry prepared with distilled water in which the metal ions of Ca<sup>+</sup>, Mg<sup>+</sup>, and Si<sup>4+</sup> existing in the tap water were added was investigated. The results are shown in Fig. 4. The existence

of the metal ions increased the photocatalytic decomposition yields of 4CP. In the case of the Ca ion, the positive effect was observed upto about 1-2 ppm after which there was no more change with an increase of the ion concentration. However, in the cases of Mg and Si ions, the positive effects were observed upto concentrations of the ions of 3-4 ppm in the TiO<sub>2</sub> slurry. Above these concentrations, the metal ions acted negatively on the photocatalytic reaction. From these results, the enhancement of the photocatalytic decomposition yield of 4CP in the TiO<sub>2</sub> slurries using tap water, as shown in Fig. 3, would be attributed to the Ca, Mg, and Si ions existing in the tap water. In Fig. 4(C), as the concentration of the Si ions in the slurry was more than about 5 ppm, the decomposition yield of 4CP rapidly decreased. The increase of Si ions produced a number of carbonate or bicarbonate ions during the photocatalytic reaction, which are created from the carbon dioxide generated by the photocatalytic decomposition of 4CP, depending on the pH in the solution. These ions are known to act as the scavengers of OH radicals in the solution according to equations (1) and (2):



To confirm this, the IC (inorganic carbon) concentration due to CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, and H<sub>2</sub>CO<sub>3</sub> generated in the solution during the photocatalytic reaction was observed with an addition of Si ions into the initial NT-20 slurry, and the results are presented in Fig. 5. The IC increased markedly at above 5 ppm of Si ions. In the cases of the same amount of additions of Ca and Mg ions, such significant increases of IC were not detected. These results could explain that small amounts of cations existing in water could affect either positively or negatively the photocatalytic reaction depending on their amounts in solution.

In order to evaluate the effect of oxygen dissolved in the slurry for the three TiO<sub>2</sub> samples, the photocatalytic

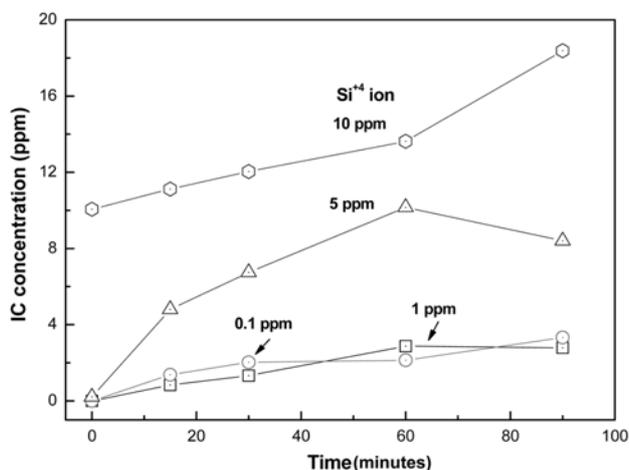


Fig. 5. Change of concentrations of carbonate species in the closed TiO<sub>2</sub> slurry systems prepared with distilled water with time.

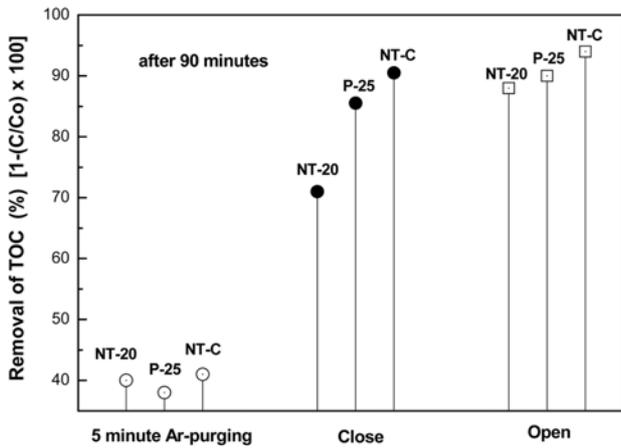


Fig. 6. Effect of air on photocatalytic reaction in the TiO<sub>2</sub> slurry systems prepared with distilled water.

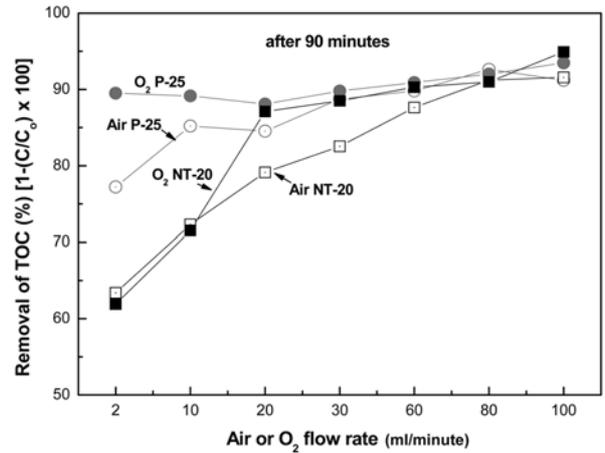


Fig. 7. Effect of air or oxygen gas-bubbling on photocatalytic reaction in the closed TiO<sub>2</sub> slurry systems prepared with distilled water.

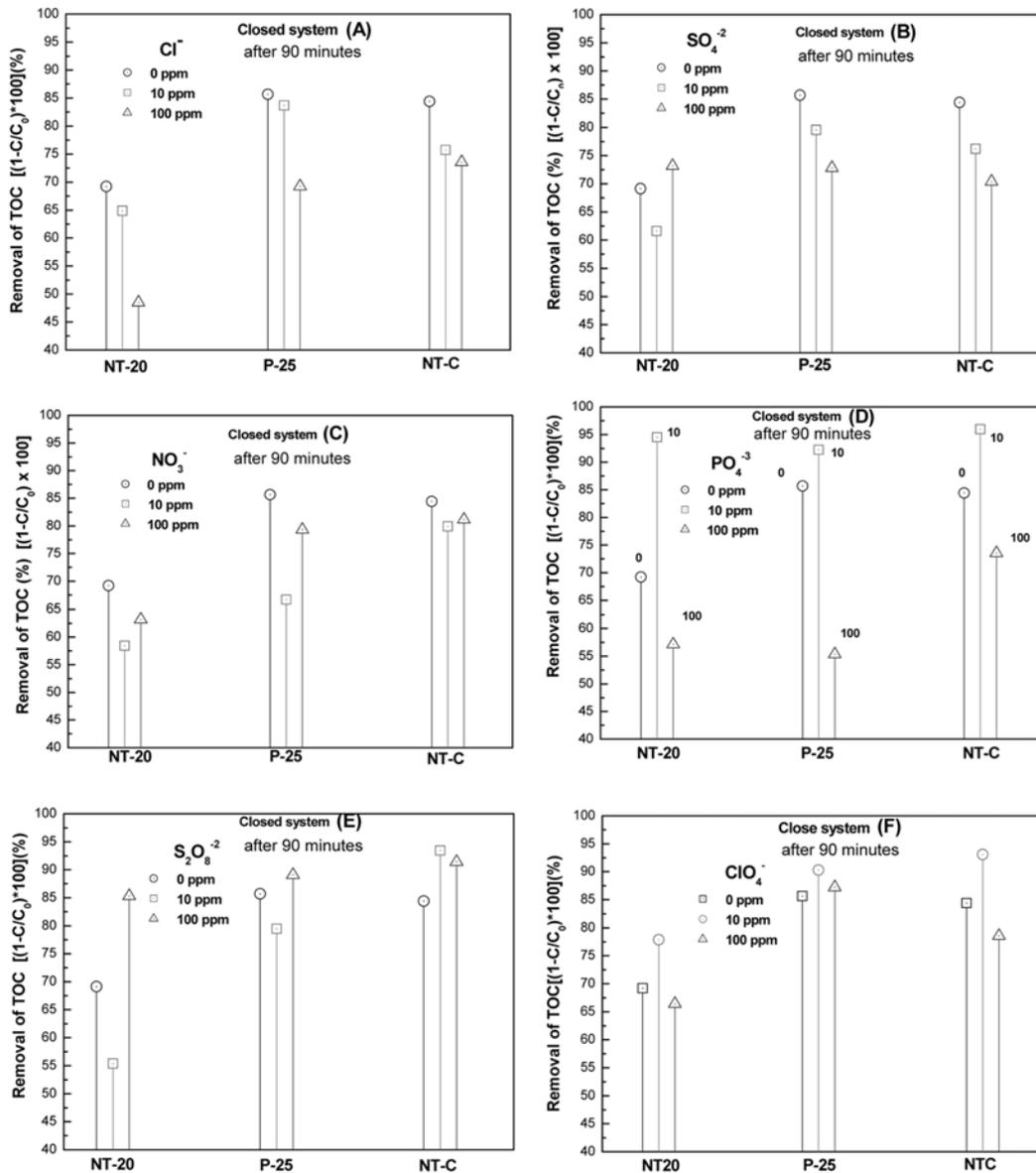


Fig. 8. Effect of anions on photocatalytic reactions in the closed TiO<sub>2</sub> slurry systems prepared with distilled water.

decomposition of 4CP decomposition was carried out in a closed as well as an open system. The slurry was purged by Ar gas for 5 minutes before the reaction, and the results are shown in Fig. 6. NT-C TiO<sub>2</sub> showed the highest decomposition yield of 4CP amongst all of the slurries. In this system with very little dissolved air due to Ar purging, the TOC removal yields of 4CP by the three TiO<sub>2</sub> samples were very low with only small differences. However, in the open system where oxygen from the air was continuously supplied and dissolved into the slurry during the reaction, the yield increased significantly. The dependence of the efficiency of the photocatalytic reaction on air contact could be attributed to the oxygen in the air. The oxygen dissolved in the solution could act as electron scavenger during the photocatalytic reaction as suggested by equation (3). The oxygen improves the photocatalytic reaction activity, not only by prohibiting the recombination of electrons and holes generated on the TiO<sub>2</sub> surface by UV irradiation, but also by being transformed into superoxide ions (O<sub>2</sub><sup>-</sup>). Oxygen reacts very fast with electrons with a reaction rate constant of  $1.9 \times 10^{10}$  l/mol\*s. The superoxide generated can be transformed into OH radicals through the reactions with water or protons in the solution accompanying complicated reaction paths [24]:



From this result, the higher the concentration of oxygen in the slurry, the more the oxygen combines with electrons. Accordingly, the effect of air or pure oxygen gas flowing into the TiO<sub>2</sub> slurries during the photocatalytic reaction are examined in Fig. 7. The degree of photocatalytic decomposition of 4CP increased with the flow rate. Flowing oxygen showed a higher decomposition yield than air.

Many types of anions usually exist in waste water. The effects of such anions existing in the waste solution on the TiO<sub>2</sub> photocatalytic reaction should be understood prior to applying the photocatalytic TiO<sub>2</sub> for the treatment of waste water. The anions are generally considered to have a negative effect to the photocatalytic reaction. Therefore, the effects of several types of anions such as Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, ClO<sub>4</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup> on the photocatalytic reactions of P-25, NT-C, and NT-20 TiO<sub>2</sub> samples were investigated with changes of their concentrations as shown in Fig. 8. The photocatalytic behavior of the TiO<sub>2</sub> samples with different types of anions are very complicated. SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> ions showed a distinct reduction of photocatalytic decomposition of 4CP. In the cases of NO<sub>3</sub><sup>-</sup> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> ions, the decomposition yields decreased at low concentrations and then increased again at high concentrations. By contraries, in the cases of PO<sub>4</sub><sup>3-</sup> and ClO<sub>4</sub><sup>-</sup> ions, they showed higher values at lower concentrations. These results differ in part from the previous studies [26]. The TiO<sub>2</sub> samples did not always shows consistent photocatalytic efficiency, which varies depending on the type of ions.

Figure 9 shows the effect of UV wavelength on the photocatalytic reaction in the closed TiO<sub>2</sub> slurry systems.

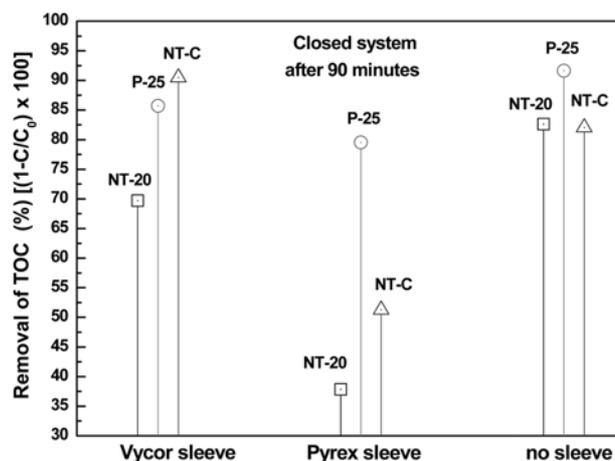


Fig. 9. Effect of UV wavelength on photocatalytic reaction in the closed TiO<sub>2</sub> slurry systems prepared with distilled water.

The UV light spectrum used in this work consisted of 16% of far UV below 250 nm, 16.5% of middle UV between 280 and 320 nm, 16% of near UV between 320 and 400 nm, 43% of visible UV between 400 and 1,000 nm, and 9% of IR between 1,000 and 1,400 nm. When the Vycor sleeve together with the Pyrex sleeve were placed around the UV light source, they cut the wavelengths less than 340 nm. The short wavelength UV is known to facilitate the recombination of holes and electrons. In the case of filtering the short wavelength UV by the Vycor sleeve, the NT-C TiO<sub>2</sub> sample showed the highest photocatalytic efficiency. However, in the case of filtering most of the UV by the Pyrex sleeve, the P-25 TiO<sub>2</sub> sample showed the highest efficiency. This means that the P-25 sample exhibited a better photocatalytic response to visible light. Without any filtering of the UV source, the difference of photocatalytic efficiencies between the TiO<sub>2</sub> samples was significantly reduced. This means that the properties of photocatalytic TiO<sub>2</sub> samples can be greatly affected by the UV light source itself.

Figure 10 shows the photocatalytic decomposition yields of ethanol, EDTA, dyes of methylene blue, methylene orange, and surfactants of, LAS (linear alkyl sulfonate) and SDS (sodium dodecyl sulfate) by the three TiO<sub>2</sub> samples in open and closed photocatalytic reaction systems. The photocatalytic efficiency of a TiO<sub>2</sub> sample varied significantly depending on the target organics and the condition of the oxygen dissolved in the solution. The results did not show a consistency of superiority of any particular TiO<sub>2</sub> sample in comparison with the other TiO<sub>2</sub> samples. In general, dyes, EDTA, SDS were more effectively decomposed by the photocatalytic reaction than ethanol and LAS.

## Conclusions

Three commercially available TiO<sub>2</sub> photocatalytic powders with trade names of P-25, NT-C, NT-20 showed a significant dependency of the efficiency on pH and exhibited higher photocatalytic efficiency in the pH range

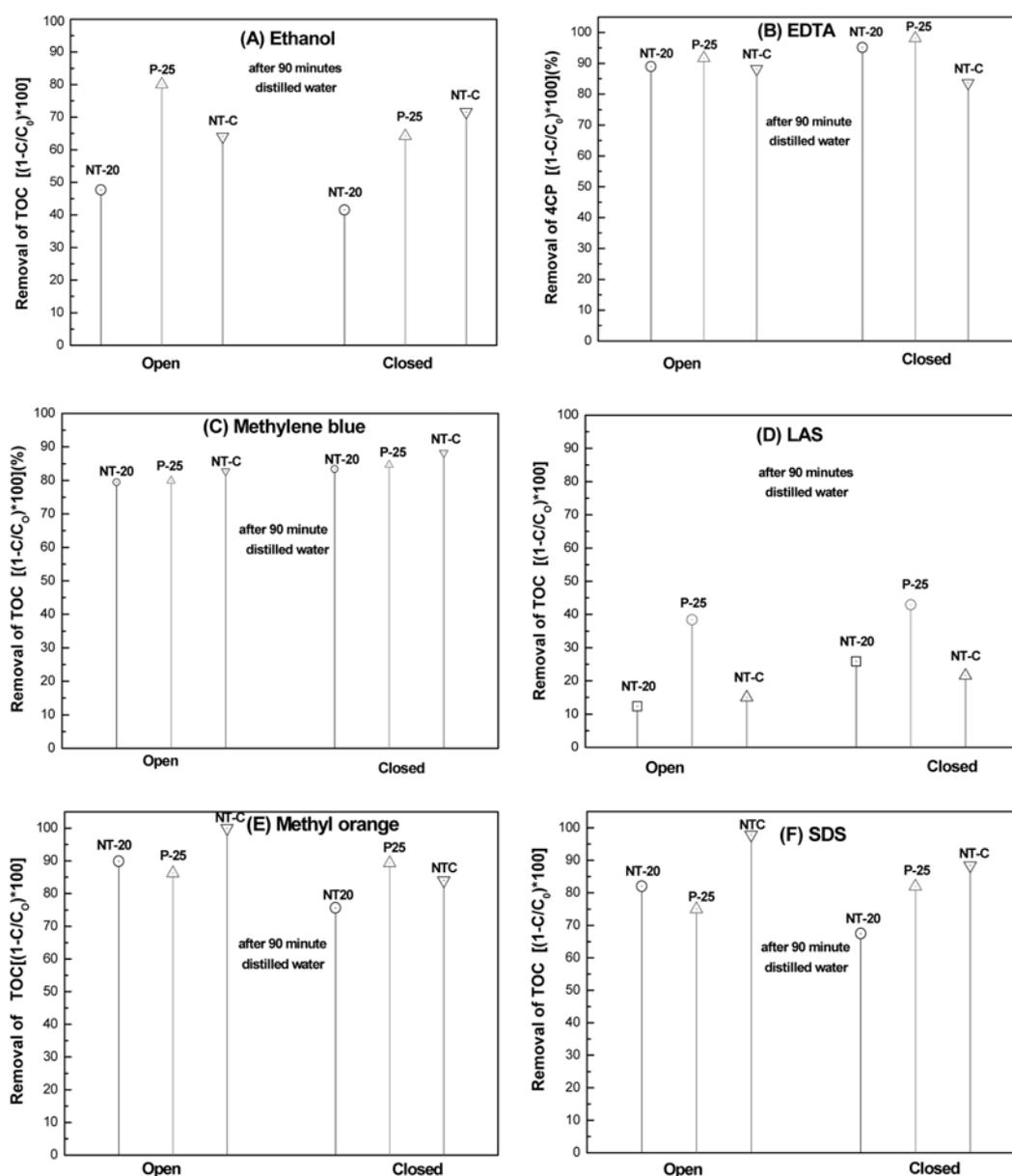


Fig. 10. TOC removal yield of several organics in the closed  $\text{TiO}_2$  slurry systems prepared with distilled water.

of 5 to 7. The type of water used for the preparation of the  $\text{TiO}_2$  slurry also affected the photocatalytic efficiency due to the cations existing in the water. The oxygen dissolved in the slurry enhanced the efficiency by acting as an electron scavenger. The effect of anions except  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  on the photocatalytic efficiency varied depending on their concentrations and the type of  $\text{TiO}_2$  powder. The properties of photocatalytic  $\text{TiO}_2$  samples were also significantly affected by the UV light source. Any particular  $\text{TiO}_2$  powder did not always show a better efficiency in comparison with other  $\text{TiO}_2$  powders in the photocatalytic decompositions of organics. The photocatalytic properties of  $\text{TiO}_2$  samples were sensitively affected by even a small change of experimental conditions. Thus the superiority of photocatalytic properties should be cautiously mentioned with the details of experimental conditions.

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