광촉매 공정에 사용된 TiO_2의 효과적 분리를 위한 연구

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Effective Post Treatment for Photocatalytic Oxidation for the Separation of Titanium Dioxide (TiO_2) from Aqueous Solution

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Introduction

Among many semiconductor materials, titanium dioxide (TiO_2) is widely used as the photocatalyst in the Advanced Oxidation Process (AOP), as it is non toxic, chemically stable, and possesses relatively high photocatalytic activity (Chiang et al. 2004). It is evident that the use of TiO_2 powder used as suspension or slurry in the water is far more superior in terms of photocatalytic degradation efficiency compared to fixed TiO_2 on a carrier material such as glass, concrete or ceramics (Ollis 1991, Xi and Geissen 2001), due to limiting mass transfer and a loss of photocatalytic activity by the fixation. However in such a case, the major challenge is the removal of the submicron TiO_2 particles from aqueous solution after photocatalysis, in order to ovoid unnecessary secondary pollution. This study evaluates the TiO_2 separation efficiency in a two stage coagulation treatment followed by submerged microfiltration hybrid process. Although individually coagulation and flat sheet membrane process have been applied before, for the separation of TiO2 from suspension, this study is unique in the sense that it adopts two stage coagulation process coupled with submerged hollow fiber microfiltration for TiO_2 separation.

Materials and Method

P-25 TiO_2 particles (Degussa, Germany) were used as photocatalyst. The physical properties of the TiO2 used is given in Table 1. Coagulation method was carried out in two stages, in order to enhance its efficiency of TiO_2 separation. In the first step, no coagulant was added and simply by adjusting the pH of the solution at 6.3 (Zero Point Charge ZPC for TiO_2), the particles were aggregated and settled by adopting the standard method for coagulation and sedimentation (APHA 1998). The supernatant was taken to the second stage, where ferric chloride ($FeCl_3$)

coagulant was added at a predetermined optimum pH of 6.8. Ferric chloride dose was increased up to 100mg/L. After settling, the supernatant from the second stage was further treated using submerged hollow fiber microfiltration (MF) membrane (SuperMAK, ENE, Korea).

Table 1. Properties of TiO_2.

Property	Unit	Value
Surface area (BET)	m^2/g	50
Surface area (Astakov)	m^2/g	62.4
Pore volume	cm^3/g	0.19
Average pore size	Å	69
Average particle size	nm	21
Density at 20℃	g/cm^3	3.89
Purity	%	> 99.5 [a]
Supply	Degussa	P25

The membrane used was PVDF with pore size 0.4 ㎛ and the surface area was 0.02 m^2. The effect of point of coagulant addition, i.e., when the coagulant was added after the first stage of ph Treatment or before pH treatment, was also studied. Various stages involved in the coagulation- membrane hybrid system adopted in this study is given shown in Figure 1. The separation of TiO_2 was examined based on the turbidity removal. The amount of fouling in the membrane was examined from the permeate flux patterns. Scanning electron microscope (SEM) was used to analyze the surface of the membrane.

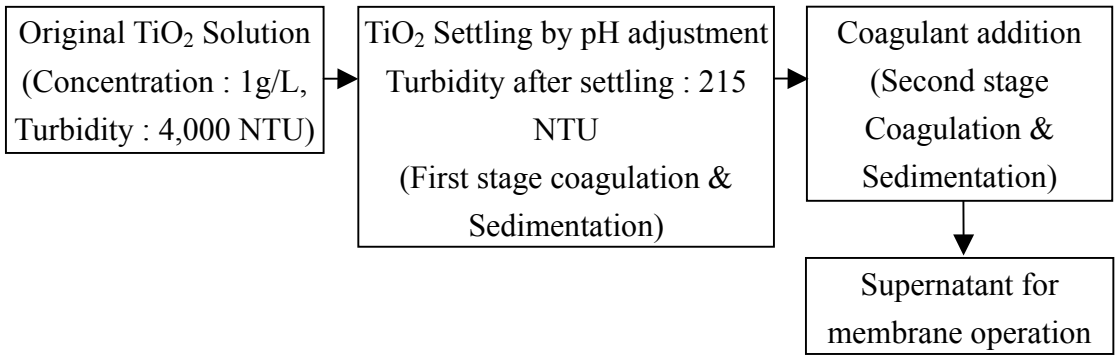

Figure 1. Process sequence of the coagulation-membrane hybrid process.

Results and Discussion

In the first stage of coagulation, with simple pH adjustment most of the TiO_2 was effectively settled as shown in Figure 2. It was identified that increasing the initial concentration of TiO_2

increased the amount of TiO_2 settling, as more number of particles was able to aggregate effectively. However there was a limit beyond which further increase in TiO2 particles was not beneficial. Although, most of the particles were able to be settled, the final turbidity was still very high. Coagulant addition directly into the TiO_2 solution, without the first stage of pH treatment was not found to be effective for two reasons. The coagulant dose requirement was found to high and the settled TiO_2 could not be reused in photocatalysis directly, as it was contaminated with coagulant chemicals. On the contrary, the TiO_2 settled (more than 90 % for initial TiO_2 conc. of 1 g/L) after the first stage of coagulation by simple pH adjustment, could be directly reused and would require very less coagulant chemical for subsequent settling. The permeate flux decline pattern at various coagulant dose and the membrane operation without coagulation is shown in Figure 4. It can be seen that the presence of two stage coagulation was found to significantly limit membrane fouling Coagulant dose of 50 ppm added after the first stage of coagulation was found to be the optimum amount in terms of permeate flux development. For the initial TiO_2 concentration of 1 g/L, with initial turbidity of about 4000 NTU, the final permeate turbidity was well below 0.1 NTU. This permeate water with almost no particles present, could be successfully reused.

Conclusions

Two stage coagulation followed by microfiltration membrane separation hybrid system was found to be effectively remove TiO_2 particles almost completely. For the initial turbidity of 4000 NTU, the final turbidity of the treated water was well below 0.1 NTU, which is of reusable quality. Almost 90 % of TiO_2 settled after first stage of coagulation, by simple pH adjustment was able to be reused directly and lowered the amount of chemical coagulant required in the subsequent treatment stage. Ferric chloride concentration of 50 ppm was found to obtimum amount in terms of floc formation and permeate flux development.

Acknowledgement

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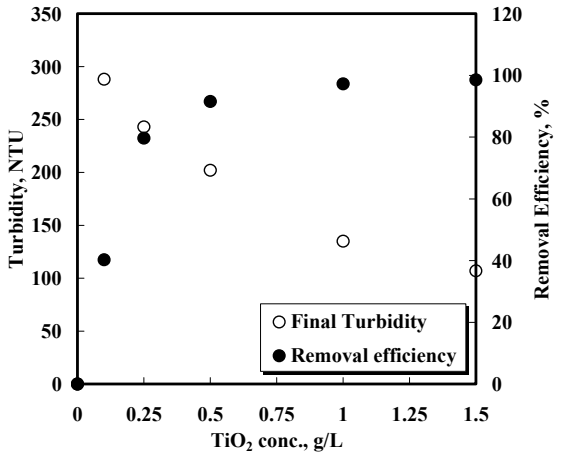

Figure 2. Performance of first stage coagulation

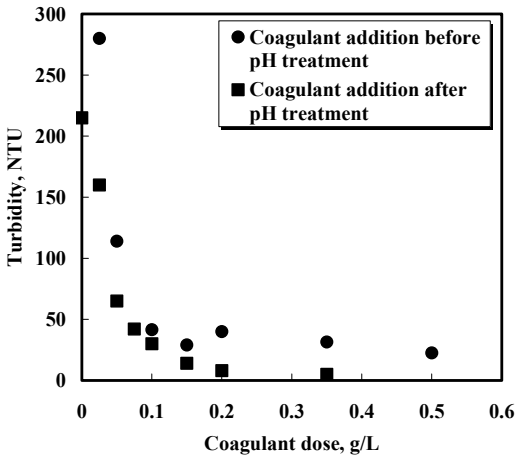

Figure 3. Comparison of single stage coagulation and dual stage coagulation

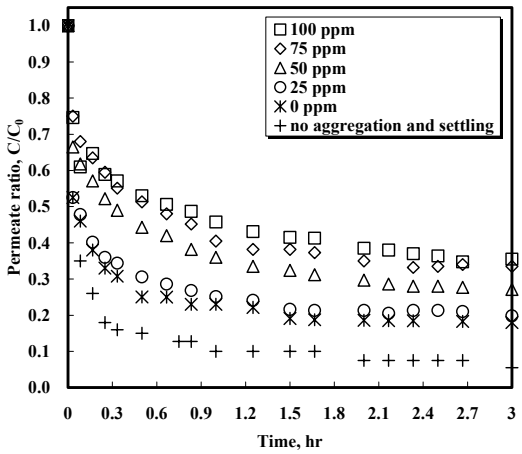

Figure 4. Permeate flux development for the coagulation – membrane hybrid system

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