

## Coagulation-flocculation of TiO<sub>2</sub> in Suspension Used in Heterogeneous Photocatalysis

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**Abstract:** The coagulation-flocculation of TiO<sub>2</sub> in aqueous suspensions of low and intermediate ionic strength was investigated as a function of pH, of addition of aluminum sulfate and of stirring the suspension. This process was maximized after the addition of aluminum sulfate when the mixture was subjected to rapid and slow shaking and by using tap water at pH 7.0. Under these conditions, the turbidity of a suspension with 0.5 g L<sup>-1</sup> of TiO<sub>2</sub>, which is higher than 4000 NTU, can be lowered to less than 10 NTU in 120 minutes. The filtration of the remaining suspension after coagulation-flocculation was 70 times faster than that of the initial suspension.

**Keywords:** coagulation-flocculation; aluminum sulfate; titania

### 1. INTRODUCTION

Heterogeneous photocatalysis has received a great deal of attention as an advanced oxidation process (AOP) for degrading persistent organic compounds, reducing chemical oxygen demand (COD) and eliminating microorganisms in contaminated waters [1-4]. The advantage of this process is that it leads to the complete mineralization of organic contaminants, whether they are simple or complex molecules. To date, the most efficient procedure for the treatment of contaminated waters by heterogeneous photocatalysis consists of UV light irradiation on suspensions of TiO<sub>2</sub> catalyst in solutions containing the organic substrate to be degraded. Although this process allows for good photodegradation, the recovery or separation of this oxide makes the large-scale use of this technique unfeasible owing to the high stability and turbidity of TiO<sub>2</sub> suspensions [5-10]. TiO<sub>2</sub> is chemically and biologically inert (nontoxic). However, its highly stable aqueous suspensions (opaque with a milky aspect) may cause problems when discharged into the environment, due to their notable ability to scatter

light, and should therefore be removed from the suspension. It is very difficult to separate TiO<sub>2</sub> particles from the suspension by conventional methods and removal efficiency rates are considered low. Microfiltration is an efficient technique, but the cost of separating the fine particles from TiO<sub>2</sub> agglomerates is high [7]. To overcome these limitations, many researchers have studied the immobilization of TiO<sub>2</sub> on supports in the form of films, but, face the problem of reduced photo-oxidative efficiency due to the diminution of mass transport to the catalyst surface [11, 12].

The coagulation-flocculation of natural and waste waters is effective in removing a broad range of impurities from water, including colloidal particles (organic and metal oxides) and dissolved organic substances [13]. The difficulty of separating TiO<sub>2</sub>, especially in crystalline anatase form, from aqueous suspensions by sedimentation is due to the strong repulsive forces between the surface loads that stabilize the colloidal solution. Thus, despite the high density of TiO<sub>2</sub> (~3.8 g mL<sup>-1</sup>), it does not sediment easily because the forces of gravity are

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counterbalanced by the electrostatic forces of repulsion among the oxide particles. Kagaya *et al.* [14] reported briefly that they achieved the separation of TiO<sub>2</sub> from 100 mL of suspension by adding 2 mL of 1% basic aluminum chloride solution. Their experiments were performed in a 100 mL cylinder and the pH of the suspensions prepared with distilled water was adjusted using 0.1 mol L<sup>-1</sup> of sodium hydroxide solution. A pH of 8-9 was suitable for the sedimentation of at least 100 mg of titanium in 100 mL of the suspensions. In a major study, Fernández-Ibáñez *et al.* [7] examined two procedures to induce aggregation and fast sedimentation, namely, the change in the pH of suspensions to the isoelectric point (IEP), and the addition of an electrolyte (NaCl). These researchers removed about 97% of TiO<sub>2</sub> from the suspension in approximately 5 hours. This result was considered excellent when compared to the sedimentation obtained in a suspension with adjustment of the pH or the addition of NaCl, which took more than 24 hours to reduce about 30% of the particles. However, the authors do not recommend the use of NaCl when the catalyst is to be reused, because the chloride ions adsorbed in the oxide interfere in the speed of the photocatalytic degradation. They also reported that the addition of sedimentation aids such as aluminum sulfate is another possibility that should be investigated for the separation of TiO<sub>2</sub>. Baran *et al.* [8] devised a method to separate TiO<sub>2</sub> from the suspension, whereby the photocatalytic reaction for the degradation of Acid Orange 7 is conducted in the presence of TiO<sub>2</sub>/FeCl<sub>3</sub>/UV. After photodegradation of the dye, the pH of the suspension was corrected with a solution of NaOH (1.0 mol L<sup>-1</sup>) while simultaneously stirring with strongly compressed air. After 3 minutes of stirring, the solutions were allowed to rest for 60 minutes in order to settle.

This work investigated the coagulation-flocculation mechanism and the sedimentation speed of TiO<sub>2</sub> in aqueous suspensions of low ionic strength (distilled water) and intermediate ionic strength (tap water) as a function of pH and of the addition of aluminum sulfate. The influence of stirring the suspension immediately after the addition of the coagulant was also evaluated.

## 2. MATERIAL AND METHODS

The coagulation-flocculation study was performed using TiO<sub>2</sub> suspensions of low ionic strength (electric conductivity 18 μS cm<sup>-1</sup>) and intermediate ionic strength (electric conductivity 55

μS cm<sup>-1</sup>). The mechanism of coagulation-flocculation was evaluated as a function of the solution's pH and the added Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.

### Characteristics of the TiO<sub>2</sub>

The TiO<sub>2</sub> used here was P25 from Degussa. The main characteristics of this oxide are: it is nonporous; has cubic particles with rounded edges; more than 99.5% purity; its crystal structure consists of about 70% anatase and 30% rutile; density of approximately 3.8 g mL<sup>-1</sup>; specific surface area of about 50 ± 15 m<sup>2</sup> g<sup>-1</sup> and average primary particle size of about 21 nm (with 90% of its primary particles having a size of 9-38 nm). However, it should be noted that this semiconductor does not exist as isolated particles but as aggregates that cannot be modified [10-16].

### Concentration of the TiO<sub>2</sub>

The initial speed of a photocatalytic reaction is up to a limit directly proportional to the mass of the catalyst used. This speed limit corresponds to the concentration at which all the particles of the catalyst are exposed to light. Higher concentrations of TiO<sub>2</sub> cause light scattering and reduction of the amount of light penetrating into the suspension, with the effect of concealing part of the particles of the catalyst that are not illuminated by the light. The speed limit of the photocatalytic reaction also depends on the type of organic substrate, and the diameter and geometry of the reactor [15, 16]. Mills & Wang [17] recommend a concentration of 0.5 g L<sup>-1</sup> as the standard for the heterogeneous photocatalysis of aqueous samples. In general, this value is below the aforementioned limit, so it was used in our experiments a concentration of 0.5 g L<sup>-1</sup> for the suspensions of titania.

### pH

The pH was studied in the range of 3.0 to 9.0, with variations of one unit. It was adjusted by adding dropwise a strong acid (H<sub>2</sub>SO<sub>4</sub> 0.1 mol L<sup>-1</sup>) or strong base (NaOH 0.1 mol L<sup>-1</sup>). Above or below this range, there is a great resistance to change the pH values, requiring for this a relatively high amount of acid or base.

### Jar Test and Turbidity Measures

The coagulation-flocculation was performed in

a Milan JT 101 jar test apparatus. Immediately after the addition of the coagulant to the suspension, the mixture was subjected to rapid shaking and slow shaking, after which it was allowed to rest and settle for a given period of time. Preliminary tests indicated that the suitable conditions for this procedure were: rapid shaking for 1 min at 120 rpm, followed by slow shaking for 9 min at 60 rpm, 4 min at 25 rpm, and 2 min at 10 rpm. The turbidity of the supernatant suspension was then measured with a Hach 2100P turbidimeter. These readings were carried out in a matter of seconds to minimize error of the dynamic sedimentation.

### Filtration

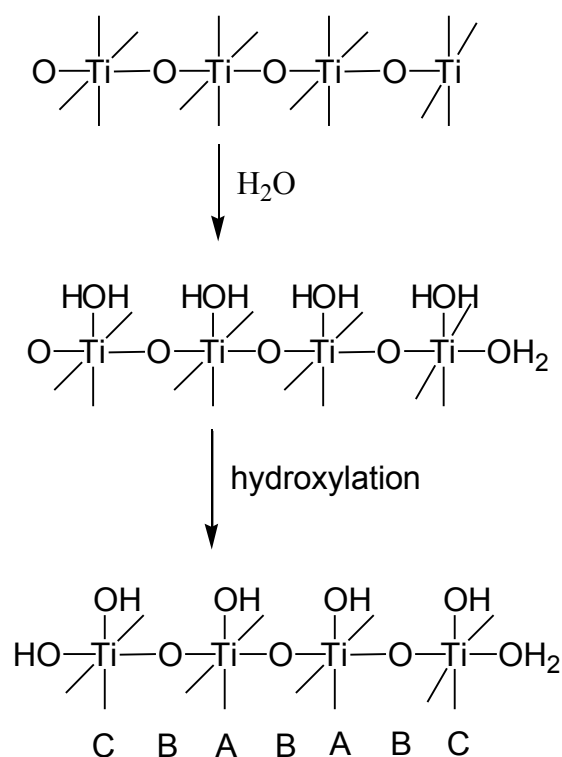
The  $\text{TiO}_2$  in the suspension ( $0.5 \text{ g L}^{-1}$ ) and the particles remaining in the water after coagulation-flocculation were separated by filtration, using a vacuum system (Marconi) under 80 kPa of pressure and a filtering membrane with  $0.22 \mu\text{m}$  and 47 mm diameter size pores (Millipore).

### 3. RESULTS AND DISCUSSION

The addition of  $\text{TiO}_2$  in distilled water (0.5 g in

a liter) caused a gradual reduction of the pH of the suspension, which stabilized naturally at 4.4. The measured electrical conductivity was  $18 \mu\text{S cm}^{-1}$ . In tap water, the pH stabilized at pH 5.5 and the electrical conductivity was  $55 \mu\text{S cm}^{-1}$ . This behavior can be explained by hydroxylation of the  $\text{TiO}_2$  surface due to the chemical adsorption of water on the  $\text{TiO}_2$ . More specifically, when dissociative adsorption of water occurs on the surface of the  $\text{TiO}_2$  001 crystallographic phase, two groups of hydroxyl sites are generated, which Candal *et al.* [18] called sites (A) and (B), Fig.1.

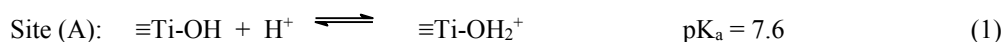
The  $\text{Ti}^{4+}$  ion is hexacoordinated inside the  $\text{TiO}_2$  crystal, while the  $\text{O}^{2-}$  is tricoordinated. When the crystal is cleaved, the  $\text{Ti}^{4+}$  and  $\text{O}^{2-}$  coordination numbers on the surface shift, respectively, to penta- and dicoordinated. These and other defects confer a greater reactivity to the titania surface, since the reactions occur to complete the coordination in the empty orbitals. Moreover,  $\text{Ti}^{4+}$  is better stabilized by  $\text{OH}^-$  ions than by divalent  $\text{O}^{2-}$  ions because its structure allows for a better approximation of the  $\text{Ti}^{4+}$  charge center. This greater charge stabilization causes a decrease of the electrostatic potential, resulting in better neutralization of charges, so that stabilization occurs at the observed pHs [19].



**Figure 1.** Schematic representation of the OH groups on the surface of the  $\text{TiO}_2$ : site (A), –OH groups bound to a single titanium atom; site (B), –OH group bound to two titanium atoms; site (C), –OH group bound to the crystal's edges. Adapted from Candal *et al.* [18].

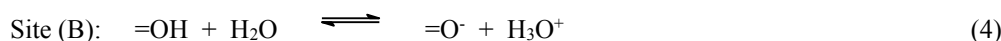
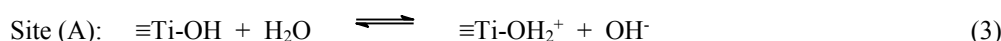
Since the bonds in TiO<sub>2</sub>, as in most oxides, are not purely ionic, the OH<sup>-</sup> ionic groups can be represented by OH groups. Hence, in this article, the

hydroxylated sites will be represented by ≡Ti-OH, site (A), and =OH, site (B).



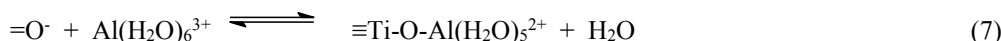
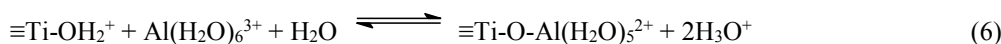
In TiO<sub>2</sub> anatase, approximately 40% of the surface is hydroxylated, and these hydroxyl groups have an amphoteric nature, with one half displaying an acid characteristic and the other half basic, which can be exchanged for other anions [19]. The (A) sites

act as Brönsted bases while the (B) sites act as Brönsted acids. Thus, the lowering of the suspension's pH to 4.4 in distilled water is explained by the predominance of reaction (4):



The addition of quantities of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> to the TiO<sub>2</sub> suspension to give 0.1 g L<sup>-1</sup> or higher concentration causes the pH of the solution to drop naturally to 3.8. At this pH, the Al<sup>3+</sup> ions predominate in the form of Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>. Surface complexation

models describe adsorption phenomena as chemical equilibria [18], and the variation of the suspension's pH can be explained by reactions (5), and especially by (6).



It should be pointed out that this type of chemical adsorption is only possible with hydrolysable cations, since the reaction can be considered a surface hydrolysis.

The adsorption-hydrolysis of aluminum ions caused coagulation-flocculation of the TiO<sub>2</sub>, which was evaluated based on the decrease of turbidity. Fig. 2 shows that the concentration of aluminum sulfate for this process should be higher than 0.05 g L<sup>-1</sup>. At concentrations between 0.1 g L<sup>-1</sup> and 0.8 g L<sup>-1</sup> there was practically no variation in the coagulation-flocculation rate, so that the optimal dosage of coagulant was 0.1 g L<sup>-1</sup>.

The coagulation-flocculation studies using TiO<sub>2</sub> suspensions in low strength and intermediate strength ionic solutions, with and without the addition of aluminum sulfate, were carried out in different values of pH. The results are showed in Table 1.

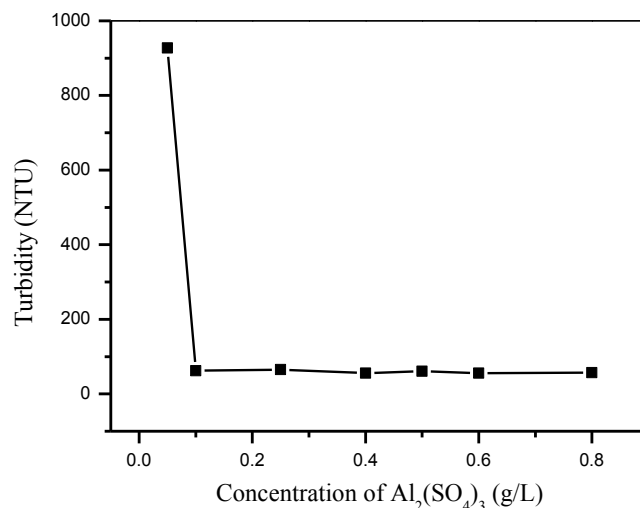
TiO<sub>2</sub> suspensions in distilled water (low ionic strength) were significantly coagulated-flocculated at pHs 3.0, 6.0 and 7.0 without adding aluminum sulfate, indicating that this process depends basically on the oxide surface. Although pH 3.0 aids the sedimentation, the high acid consumption for the pH adjustment and the need for neutralizing the treated water at the final process, turns this condition economically unfeasible.

The addition of aluminum sulfate increased sedimentation significantly at pH 4.0, 5.0, 8.0 and 9.0. However, it has little influence in the coagulation-flocculation process in tap water (intermediate ionic strength).

Flocculation was higher with increasing ionic strength. High concentrations of positive and negative ions (high ionic strength) lead to an increase in the number of ions in the diffusion layer that, to keep

itself electrically null, has its volume decreased (decreased thickness) causing the Van der Waals

forces to predominate and eliminating the electrostatic stabilization [20].



**Figure 2.** Sedimentation of suspensions of  $0.5 \text{ g L}^{-1}$  of  $\text{TiO}_2$  P25 in pH 4.4 as a function of the concentration of aluminum sulfate after 60 min at  $23 \text{ }^\circ\text{C}$ .

**Table 1.** Sedimentation of  $\text{TiO}_2$  suspensions,  $0.5 \text{ g L}^{-1}$ , in distilled water and in tap water, with and without added aluminum sulfate ( $0.1 \text{ g L}^{-1}$ ), as a function of pH, after 60 min of sedimentation at  $23 \text{ }^\circ\text{C}$ . Initial turbidity:  $>4000 \text{ NTU}$  in titania suspensions of distilled water and tap water.

pH of the suspension	Turbidity of the distilled water (NTU)		Turbidity of the tap water (NTU)	
	Without aluminum	With aluminum	Without aluminum	With aluminum
3.0*	47	69	88	71
4.0	$>4000$	63	92	60
5.0	$>4000$	121	103	65
6.0	63	106	73	67
7.0	35	71	13	9.3
8.0	$>4000$	101	54	56
9.0	$>4000$	162	56	51

\*A relatively large amount of  $\text{H}_2\text{SO}_4$  was added to adjust the pH.

As described earlier, the stability of the aqueous suspension of  $\text{TiO}_2$  is due to the adsorption of water molecules on the surface of the oxide, causing hydroxylation and the formation of surface charges as the hydroxyl groups become ionized (acid and base sites). This leads to the formation of a double electrical layer that mutually repels the colloidal particles, preventing agglomeration and sedimentation. Variations in pH modify the surface charges, and there is a pH at which the surface hydroxyl groups are not ionized, i.e., there are no surface charges. This pH, called point zero charge (PZC), causes the oxide to precipitate. In practice, it is

more common to use the pH of the isoelectric point (IEP), which is the pH at which the zeta potential is zero [21-24]. The zeta potential, an indicator of surface charges, is measured on the shear plane (potential difference between shear plane and bulk liquid). In the absence of potential determining ions ( $\text{H}^+$  and  $\text{OH}^-$ ), the pH of the PZC and the IEP are similar; in fact, they are usually considered the same in practice [21-24]. In the presence of other potential determining ions such as hydrolysable ions, the difference between the pH of the PZC and the IEP may be significant, depending on the concentration of these ions. For  $\text{TiO}_2$  P25 used, the IEP occurs near pH

7.0 [7, 25, 26]. Neutralization of the charges on the surface of the oxide takes place close to this pH, allowing for its coagulation and flocculation.

So, the addition of aluminum sulfate causes coagulation-flocculation in the entire range of pH examined here, occurring by the adsorption-hydrolysis of  $\text{Al}^{3+}$  ions, according to the chemical equations (5) to (8). So, the titania surface becomes more positively charged and attracts with more intensity the anions in suspension, leading to the neutrality of  $\text{TiO}_2$  favoring the coagulation-flocculation process. However, this process is maximized by the addition of  $\text{Al}^{3+}$  ions at pH close to the IEP (7.0), as indicated in Table 1. Then, comparisons were made between this pH and normal pH, nonadjusted, under the following conditions: distilled water and tap water, with and without the addition of aluminum sulfate and with and without shaking. The suitable shaking conditions were described in item jar test and turbidity measures (Material and Methods). The results, depicted in figures 3 to 6, indicate that shaking the mixture improves efficiency of  $\text{TiO}_2$  removal regarding spontaneous decantation, and corroborate that the process of decantation occurs through coagulation-flocculation.

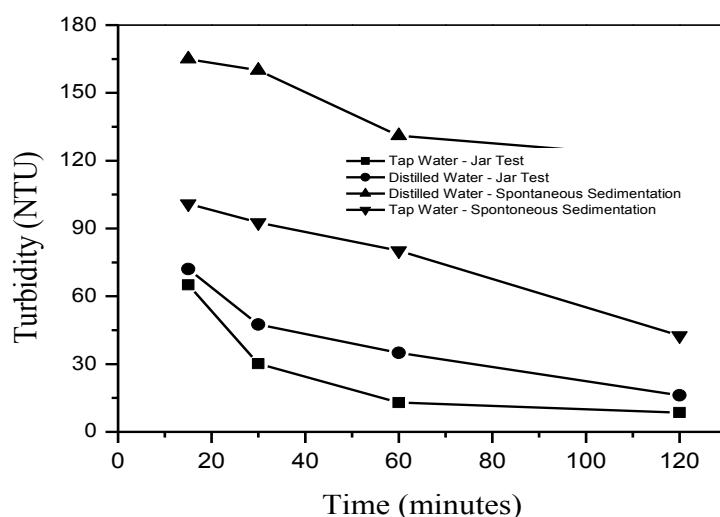
Furthermore, the addition of aluminum sulfate to the suspensions with distilled water and tap water caused the electrical conductivity to increase to  $71 \mu\text{S cm}^{-1}$  and  $87 \mu\text{S cm}^{-1}$  and the pH to drop to 3.7 and 4.1,

respectively. Upon adjusting the pH of the suspensions containing aluminum sulfate to 7.0, the electrical conductivity increased to  $66 \mu\text{S cm}^{-1}$  and  $84 \mu\text{S cm}^{-1}$  in distilled water and tap water, respectively. In the  $\text{TiO}_2$  suspensions adjusted to pH 7.0, without added aluminum sulfate, the electrical conductivity did not vary significantly compared to that of the suspensions whose pH was not adjusted.

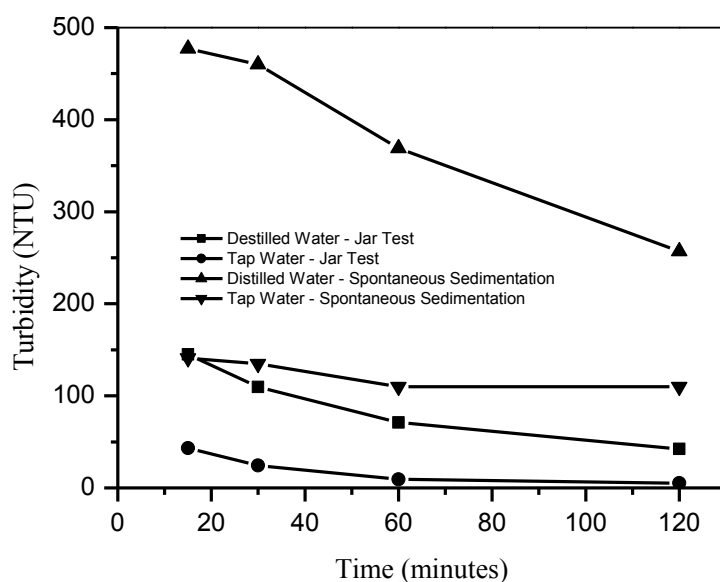
Figures 2 to 6 do not plot the turbidity values at time zero. The turbidity of the initial suspension ( $0.5 \text{ g L}^{-1}$  de  $\text{TiO}_2$ ) is very high, above 4000 NTU, which is the uppermost limit of quantification of the turbidimeter. Fig. 5 does not show two turbidity decay curves of the suspensions with distilled water because their values continued to exceed 4000 NTU after the 120 minutes of the test.

The results showed that the coagulation-flocculation process was maximized when the mixture was subjected to rapid and slow shaking, after the addition of aluminum sulfate in suspension at pH 7.0 (Figs. 3 and 4). In this condition, the turbidity of a suspension with  $0.5 \text{ g L}^{-1}$  of  $\text{TiO}_2$ , which is higher than 4000 NTU, can be removed to less than 10 NTU in 120 minutes (a removal rate of more than 99.8%).

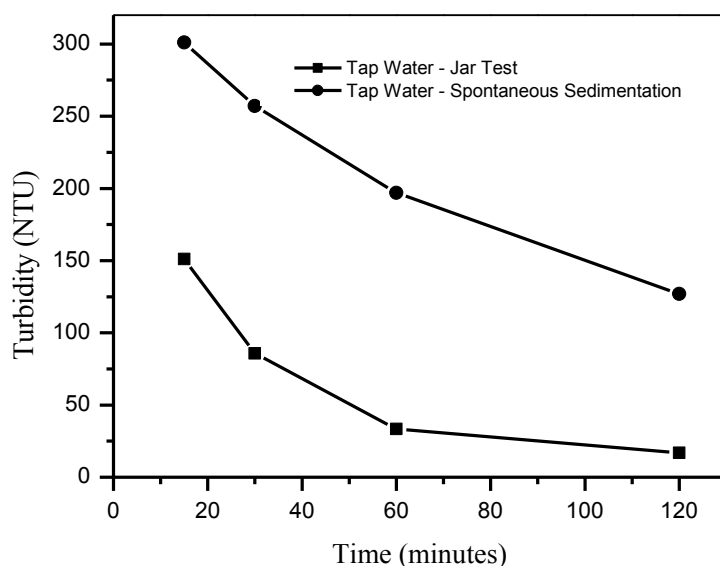
Filtration is a necessary procedure when treated water is to be reused. Therefore, it was compared the filtration time of 500 mL of the remaining suspension, after separation by siphoning, to that of the initial suspension.



**Figure 3.**  $\text{TiO}_2$  sedimentation, spontaneous and in the Jar Test, at pH adjusted to 7.0 and without the addition of aluminum sulfate. The initial turbidity of each suspension was higher than 4000 NTU at  $27^\circ\text{C}$ .



**Figure 4.** TiO<sub>2</sub> sedimentation, spontaneous and in the Jar Test, at pH adjusted to 7.0 and with the addition of aluminum sulfate. The initial turbidity of each suspension was higher than 4000 NTU at 27 °C.

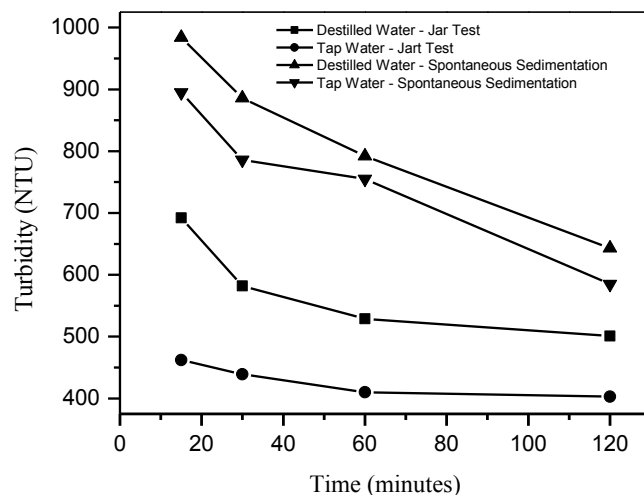


**Figure 5.** TiO<sub>2</sub> sedimentation, spontaneous and in the Jar Test, without adjustment of pH and without the addition of aluminum sulfate. The turbidity of the suspensions with distilled water did not fall below 4000 NTU in 24 hours.

The filtration of the remaining suspension was about 70 times faster than that of the initial suspension when vacuum filtered (80 kPa) using a 47 mm diameter filtering membrane with 0.22 μm

diameter pores. This comparison indicated that filtering the remaining suspension prolongs the time required for the filter to become saturated and thus increases the filtration speed, reducing the costs of the

procedure.



**Figure 6.** TiO<sub>2</sub> sedimentation, spontaneous and in the Jar Test, without adjustment of pH and with the addition of aluminum sulfate. The initial turbidity of each suspension was higher than 4000 NTU at 27 °C.

The TiO<sub>2</sub> removed could be used for two purposes: a) considering that this oxide is used in small quantities and is relatively cheap (US\$1.5/Kg), it could be discarded in a landfill; b) the TiO<sub>2</sub> could be recovered for reuse. Currently, however, the cost of its treatment for reuse with the same efficiency as the initial oxide is higher than the purchase price of the new catalyst

#### 4. CONCLUSION

The coagulation-flocculation of TiO<sub>2</sub> in aqueous suspensions can be carried out by adjusting the suspension's pH to close to the IEP of TiO<sub>2</sub> P25, by increasing the ionic strength using indifferent electrolytes, or by adsorption-hydrolysis of aluminum ions. TiO<sub>2</sub> coagulation-flocculation is maximized at pH 7.0, by adding aluminum sulfate and shaking the mixtures rapidly and slowly before allowing the suspension to rest and settle. Tap water has sufficient ionic strength to favor faster sedimentation. The results presented here, in principle, indicate the feasibility of using the coagulation-flocculation process for the separation of TiO<sub>2</sub> in aqueous suspensions used in heterogeneous photocatalysis.

#### 5. ACKNOWLEDGMENTS

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