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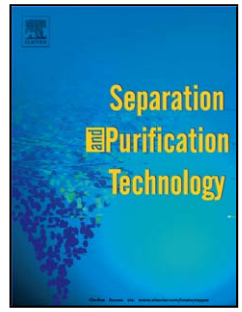

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Effect of Flocculation as a Pretreatment to Photocatalysis in the Removal of Organic Matter from Wastewater

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Abstract

Effects of different flocculants (chloride-based salts and ferric and ferrous salts) and initial organic concentration of wastewater on flocculation-photocatalysis hybrid process were investigated. Titanium Dioxide (TiO_2) adsorption alone, flocculation alone, flocculation followed by TiO_2 adsorption, photocatalysis alone, and flocculation followed by photocatalysis removed 60%, 72%, 80%, 85%, and 92% of dissolved organic matter, respectively. The effect of photo-Fenton reaction in removing organic matter was found to be marginal on the flocculation-photocatalysis hybrid system. The organic removal with the flocculation-photocatalysis hybrid system showed similar results for different flocculants such as chloride-based salts, ferric and ferrous salts and there is no comparative beneficial effect. Flocculation followed by photocatalysis removed up to 92% of organic matter. Different initial concentrations of organic matter were significantly reduced by flocculation to a low level before loading to the photocatalysis process.

Keywords: Flocculation, TiO_2, Organic matter, Photocatalysis, Wastewater

1. Introduction

Advanced treatment technology is required to remove organic matters, pathogenic microorganisms and persistent organic pollutants (POPs) in wastewater to make it suitable for reuse. Photocatalysis is an attractive process to degrade POPs from biologically treated sewage effluent. In many cases photocatalytic reactions gives a complete degradation of organic pollutants into very small and harmless species without a large chemical requirement, the subsequent large sludge production and associated disposal problems [1, 2]. Titanium dioxide (TiO_2) photocatalysis is widely used because of its ability in removing a wide range of pollutants. Its photochemical stability, low toxicity and low cost are the other advantages [3, 4].

It is known from previous studies that the following conditions favor the organic removal in the photocatalysis process; i) acidic condition, ii) photo-fenton reaction iii) Cl-based chemical flocculant and iv) use of ferric, ferrous, and aluminum salt [5,6,7]. In this study, the effect of TiO_2 adsorption and photocatalysis was studied i) at different pH, ii) in the presence of chloride-based salts, and iii) ferric and ferrous salts as flocculants. The effect of iv) initial concentrations of organic matter were also investigated. No previous studies have dealt with the beneficial effect of using flocculation as a pre-treatment to photocatalysis.

2 Experimental

Synthetic wastewater - The synthetic wastewater used in this study represents biologically treated sewage effluent and its composition is given elsewhere [8]. The MW of the synthetic wastewater ranged from 291 daltons to about 34118 with the highest fraction at 943 – 1196 daltons. The weight-averaged MW of the wastewater was 29000 daltons.

Flocculants - Ferric chloride ($FeCl_3$), alum ($Al_2(SO_4)_3 \cdot 18H_2O$), and ferrous sulfate

($FeSO_4{\bullet}7H_2O$) were used as flocculants. These flocculants were selected as they have different ferric, aluminum, and ferrous salts and different chloride and sulfate ions. The synthetic wastewater was placed in a 2L container, where known amounts of ferric chloride were added to adjust the Fe^{3+}, Al^{3+} and Fe^{2+} concentrations to 20 mg/L of ferric (20 mg-Fe^{3+}/L), aluminum (20 mg-Al^{3+}/L), and ferrous (20 mg-Fe^{2+}/L) salts. The samples were then stirred rapidly for 1 minute at 100 rpm, followed by 20 minutes of slow mixing at 30 rpm, and 30 minutes of settling. The supernatant was taken and analyzed for dissolved organic matter (DOC) to determine the effects of the flocculants in the removal of organic matter from the wastewater.

Photocatalysis experiments (as post-treatment to flocculation) were conducted with powdered P25 Degussa TiO_2 particle as catalyst [8, 9, 10]. The photoreactor consisted of a batch reactor with three 8 W UV lamps, air blower, and magnetic bar. The total surface area of all three UV lamps was 537 cm^2. The volume of the reactor was 1.5 L. Air sparging was provided to supply oxygen into the reactor (0.5 VVM-air volume/solution volume/minute). The circulation of tap water around the reactor controlled the temperature at 25 °C.

Dissolved organic carbon (DOC) was measured by using the UV-persulfate TOC analyzer. All samples were filtered through 0.45 μm membrane prior to the DOC measurement.

3 Results and Discussion

3.1 DOC removal and pH change with different flocculants

Figure 1 shows the results of DOC removal where different flocculants ($FeCl_3$, $Al_2(SO_4)_3{\bullet}18H_2O$, and $FeSO_4{\bullet}7H_2O$) were used. The concentrations of the flocculants were varied from 30 to 250 mg/L to compare the effect of equivalent concentrations of the ferric, aluminum, and ferrous salts. Ferric chloride of 68 mg/L, alum of 250 mg/L, and ferrous sulfate of 100 mg/L are equivalent to the metal salts (ferric, aluminum, and ferrous compounds) of 20 mg/L (as metal ion/L). For flocculation with $FeCl_3$, DOC removal increased until a flocculent concentration of 100 mg/L. Then, it rapidly decreased. With $Al_2(SO_4)_3{\bullet}18H_2O$ and $FeSO_4{\bullet}7H_2O$ as flocculants, DOC removal increased with higher concentration of flocculants. The similar equivalent concentration of approximately 20 mg/L with different metal salts resulted in high DOC removal. Thus, the optimal concentrations of $FeCl_3$, $Al_2(SO_4)_3{\bullet}18H_2O$, and $FeSO_4{\bullet}7H_2O$ of 60 mg/L, 250 mg/L, and 100 mg/L, respectively were selected.

Figure 1 also indicates pH variations with different flocculants. The pH of the flocculated solution decreased to pH 3 with large $FeCl_3$ doses. The flocculation by alum and ferrous sulfate slightly decreased the pH to pH 4.3 and 5.4 at 250 mg/L of flocculant, respectively. This suggests that ferric hydrolysis by $FeCl_3$ flocculation releases hydrogen ions which depleted the alkalinity of the system and significantly decreased pH.

3.2 Effect of TiO_2 adsorption

TiO_2 adsorption experiment was conducted at pH values of 2, 4, 7, 9, and 11 to investigate the relationship between pH change and DOC removal. Except at pH 2, all other pH resulted in similar removal efficiency after 5 hours of operation. The best result in removing organic by TiO_2 adsorption was between pH 4 and 7 and therefore this pH range was chosen as the optimal pH for identifying the pH effect using other flocculants.

The supernatant produced from wastewater which has undergone flocculation with different flocculants was used for TiO_2 photocatalysis experiments. $FeCl_3$ (60 mg/L),

$Al_2(SO_4)_3$•$18H_2O$ (250 mg/L), and $FeSO_4$•$7H_2O$ (100 mg/L) were used as flocculants. Alum and $FeCl_3$ had the highest DOC removal (80%) while the removal with $FeSO_4$ was significantly lower (50-70%). At a dose of $FeCl_3$ of 60 mg/L (or 20 mg-Fe^{3+}/L) and pH of 4, the DOC removal by TiO_2 adsorption alone, flocculation alone and flocculation followed by TiO_2 adsorption was 60%, 72% and 80% respectively (Figure 2). The remaining processes shown in Figure 2 will be discussed later. The removal of DOC with TiO_2 adsorption increased only by 10% after flocculation. Since both the flocculation process and TiO_2 adsorption process selectively removes the large MW [11, 12], the combined flocculation and TiO_2 adsorption process does not result in a significant increase in DOC removal.

3.3 Effect of photo-Fenton reaction

Ferric and aluminum salts were selected to study whether the photo-Fenton reaction ($hv/Fe^{3+}/O_2$) significantly affected DOC removal in the flocculation-photocatalysis hybrid system. 20 mg/L of flocculants (as ferric and aluminum salts) were used. The final pH after $FeCl_3$ and alum flocculation was 5.5 and 4.5 respectively. After 5 hours, the DOC removal was up to 92% with both salts. This suggests that the photo-Fenton reaction in the hybrid photocatalysis system is marginal (Figure 2). If photo-Fenton reaction was predominant, hybrid photocatalysis process with $FeCl_3$ would have shown superior DOC removal.

3.4 Effects of chloride-based salts and ferric and ferrous salts

Ferric chloride and ferrous sulfate were used to identify the influence of chloride-based salts on flocculation followed by photocatalysis hybrid system without any pH adjustment. Here, it was assumed that the effect of photo-Fenton reaction was the same.

Same amounts of $FeCl_3$ and $FeSO_4$ were used (20 mg/L as ferric and ferrous salts). The pH was 5.5 and 6 after the addition of ferric chloride and ferrous sulfate flocculants, respectively. The DOC removal by the hybrid system was up to 92% and was similar for both flocculants (Figure 2). This suggests that the chloride-based salt of $FeCl_3$ did not have any additional effect on photocatalysis.

3.5 Effect of pH

To study the effect of pH on photocatalysis alone, experiments were conducted at different pH values of 2, 4, 6, 7, 9, and 11. The DOC removal at pH 4, 6, and 7 reached up to 85%. At pH 2, 9, and 11 the DOC removal was lower. Further the reaction rates at the optimal pH were estimated at 20 times faster, suggesting that acidic conditions were favorable to photocatalytic reactions. This result is in agreement with previous research [7, 8, 9]. Lee et al. [7] reported that the surface hydroxyl of TiO_2 exist in the form of $TiOH_2^+$ and TiO^- in strong acidic and basic conditions, respectively. Thus, the negative charged organic matter under the acidic pH could be adsorbed on the TiO_2 particles with significantly less repulsion.

The performance of various flocculants ($FeCl_3$, $Al_2(SO_4)_3 \bullet 18H_2O$, and $FeSO_4 \bullet 7H_2O$) followed by photocatalysis in the optimal pH range (for photocatalysis) of 4-7 was studied. The pH of the solution after the addition of 60 mg/L, 100 mg/L, and 250 mg/L of $FeCl_3$ was 5.92, 3.88, and 2.80, respectively. The pH was adjusted to values of 4 and 7 by the addition of HCl and NaOH. The DOC removals with different concentrations of $FeCl_3$ and pH were approximately 90% except at a $FeCl_3$ dose of 250 mg/L and at a pH of 4 (where the DOC removal was lower at 80%). Flocculation with $Al_2(SO_4)_3 \bullet 18H_2O$ followed by photocatalysis at pH of 4 and 7 showed that DOC removal was between 80-90% although

DOC removal was generally better at pH 4. Flocculation with $FeSO_4•7H_2O$ followed by photocatalysis at pH of 4 and 7 showed a high DOC removal in the range of 80-90%. The highest DOC removal occurred at a dose of 60 mg/L of $FeSO_4•7H_2O$ (same dose as $FeCl_3$). The trend of DOC variation for the flocculation-photocatalysis hybrid process was similar for the three types of flocculants used.

Figure 2 summarises the effects of i) TiO_2 adsorption, ii) pH, iii) photo-Fenton reaction (flocculation followed by photocatalysis), iv) chloride-based flocculants and v) ferric and ferrous salts as flocculants based on the above results for optimal DOC removal. The DOC removal by TiO_2 adsorption alone, flocculation alone, flocculation followed by TiO_2 adsorption, photocatalysis alone, and flocculation followed by photocatalysis are 60%, 72%, 80%, 85%, and 92%, respectively. The removal with flocculation followed by photocatalysis showed similar results for all the three different flocculants used in this study. Thus, it can be concluded that there is a small beneficial effect in using chloride or iron based flocculants for the wastewater used.

3.6 Effect of initial DOC concentration

Figure 3 presents the effect of initial DOC concentrations of the wastewater. After flocculation, the DOC concentration was approximately 2 mg/L irrespective of the initial concentration of wastewater. The concentration could be reduced by up to 92%, which was equivalent to the removal of flocculation followed by photocatalysis. Superior dissolved organic removal with flocculation followed by photocatalysis was thus found to be due to flocculation delivering a lower organic loading to the photocatalysis process.

4 Conclusions

This study was conducted to investigate beneficial effects of the combined process of flocculation followed by photocatalysis. Effects of TiO_2 adsorptions, pH, photo-Fenton reactions, chloride-based salts, ferric and ferrous salts, and initial concentrations of organic matter were investigated in terms of removal of organic matter. For the wastewater studied

- the optimum DOC removals were 60% (by TiO_2 adsorption), 72% (by flocculation) and 80% (by flocculation followed by TiO_2 adsorption). The marginally better DOC removal by flocculation followed by photocatalysis may be due to overlapping of different MW removals by flocculation and TiO_2 adsorption.

- the effect of photo-Fenton reaction in removing organic matter was marginal because the DOC removal with ferric and non ferric (in this case aluminum) salts of 20 mg/L was similar at 92%.

- the performance of chloride-based salts was not significantly different from non-chloride based flocculants in the flocculation-photocatalysis process (without any pH adjustment).

- the effect of ferric and ferrous salts without pH adjustment was not significant as the DOC removal were similar.

- flocculation had a significant effect on reducing the different initial concentrations of organic matter to a low level before loading to the photocatalysis system. This resulted in a superior DOC removal of the flocculation-photocatalysis hybrid system.

5 Acknowledgements

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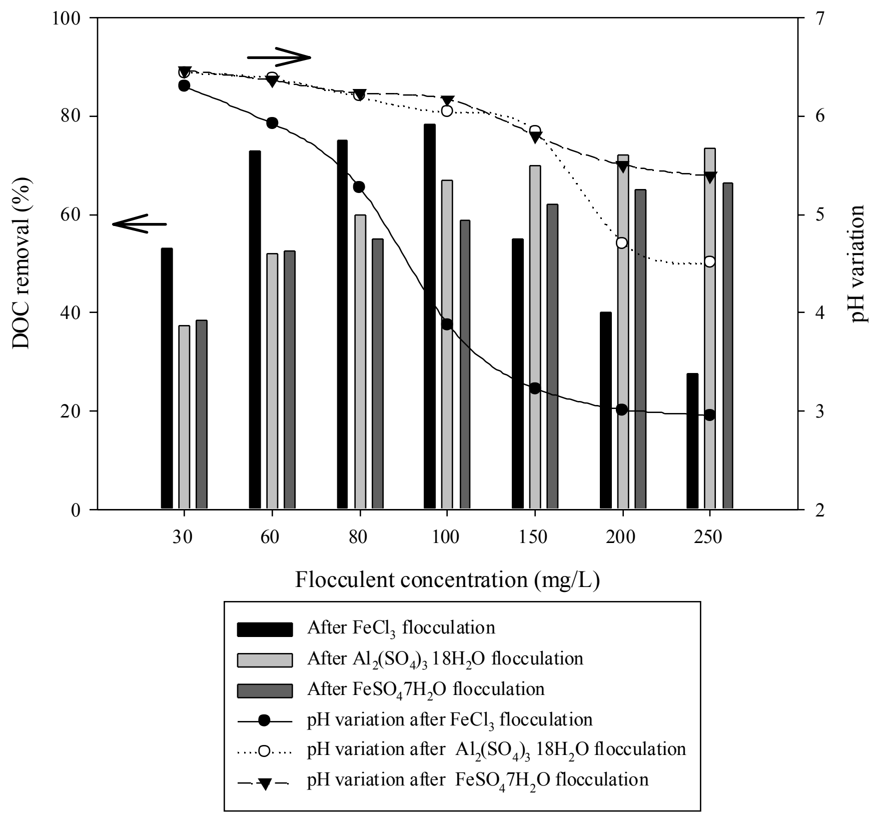

Figure 1 DOC removal and pH variation after $FeCl_3$, $Al_2(SO_4)_3$•$18H_2O$, and $FeSO_4$•$7H_2O$ flocculation (initial DOC concentration = 10.58 mg/L; initial pH = 7.3)

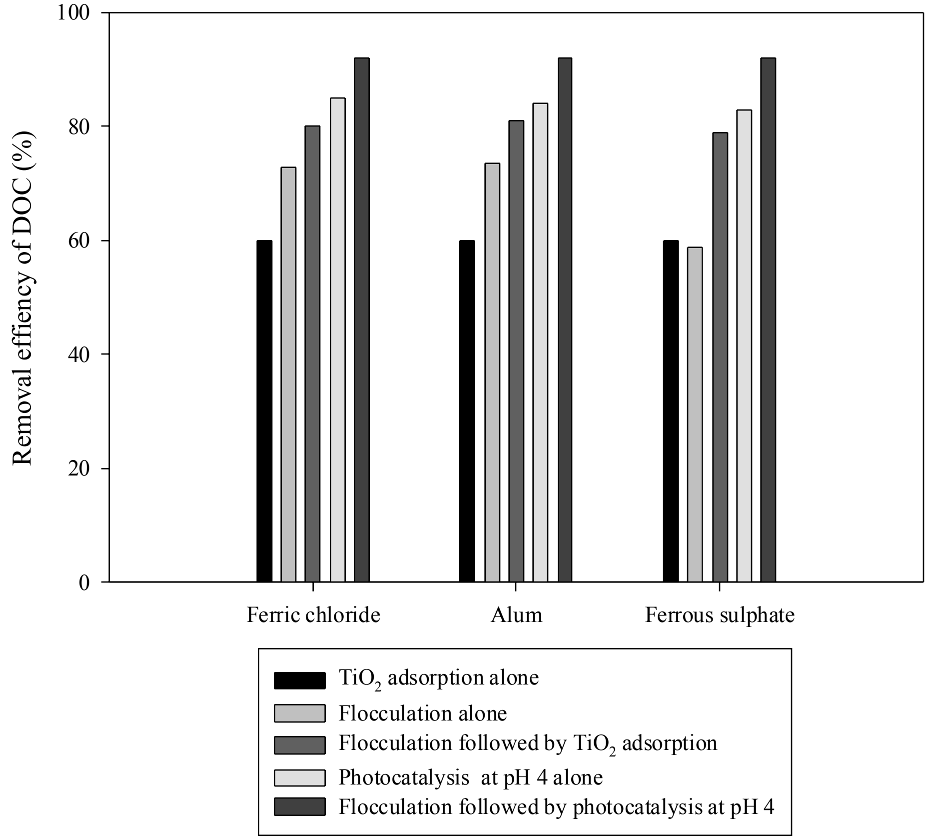

Figure 2 Summary of DOC removal with different flocculants

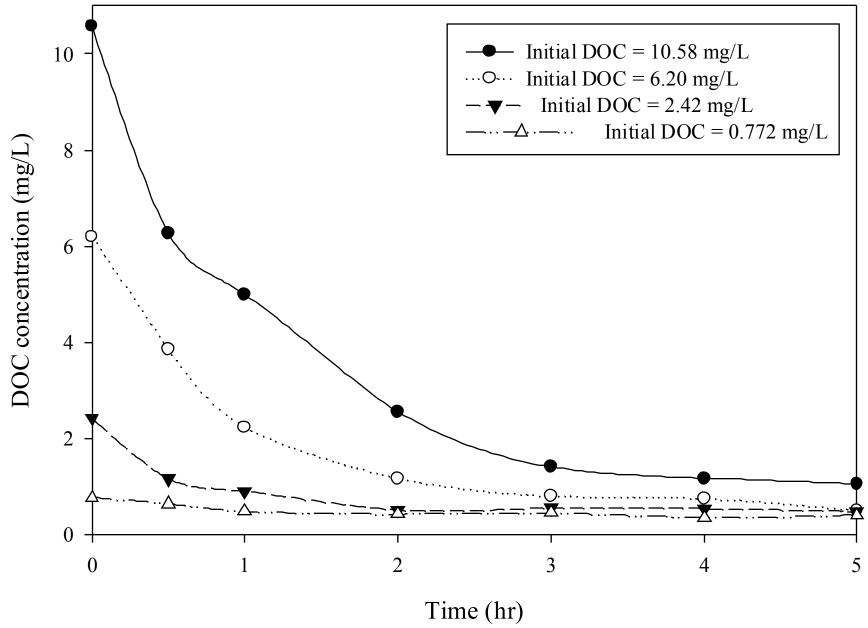

Figure 3 DOC variations of different initial concentrations in photocatalysis (T = 30 °C; Air = 0.5 VVM; intensity = 8 W with the 3 lamps)