The Degradtion of Humic Substance using Continuous Photocatalysis Systems

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Abstract: Photocatalytic oxidation is an emerging technology in water and wastewater treatment. Photocatalysis often leads to complete degradation of organic pollutants without the need for chemicals. This study investigated the degradation of humic substances in water using photocatalysis systems coupled with physio-chemical processes such as adsorption and/or flocculation. Dissolved Organic Carbon (DOC) removal of PAC-TiO_2 was improved by a factor of two to three times compared with TiO_2 alone. Solid Phase Micro Extraction (SPME)/Gas Chromatograph (GC) flame ionisation detector (FID) was used to investigate intermediates of photocatalytic oxidation in a batch reactor with TiO_2 alone and with powder activated carbon (PAC) with TiO_2. GC peaks showed that PAC-TiO_2 adsorbed some by-products which were photo-resistant and prevented the reverse reaction that occurred when TiO_2 was used alone. The two other types of photocatalytic reactors used were the continuous photocatalytic reactor and recirculated photocatalytic reactor. The results show that the recirculated reactor had the highest efficiency in removing organic matter in a short photo-oxidation (detention) time of less than 10 min. The use of PAC-TiO_2 in recirculated continuous reactor resulted in 80% removal of organic matter even when it was operated for a short detention time and allowed the use of a smaller dose of TiO_2.

Keywords: Photocatalytic oxidation, humic substances, Gas Chromatograph, flame ionization detector, continuous reactor, recirculated continuous reactor

INTRODUCTION

Natural organic matter (NOM) originates from the contact of water with dead and living organic matter as part of the hydrologic cycle, and is a fundamental component of aquatic ecosystems. NOM is important in water treatment processes as it produces harmful by-products with oxidants, increases chemical costs and reduces water quality during distribution. NOM consists of humic substances (humic and fulvic acids) and non-humic materials including proteins, polysaccharides, and other more labile components (1). Humic substances are a major organic residue of decaying organic matter. Fulvic acid has lower molecular weight (MW), higher oxygen, and lower carbon content and contains more functional groups of an acidic nature, particularly COOH. The detailed properties of humic and fulvic acid may differ depending on the location and are related to the origin of source material and the different degradation pathways.

The pollutant characteristics of NOM include its ability to form complexes with heavy metals and organic micro pollutants, promotes biological growth in water distribution systems, promotes corrosion in water distribution systems, and causes a discoloring of water. It can interfere with water treatment processes, as NOM can affect the stability and removal of other colloids and particles and may increase the need for disinfectant dosing. Further, it is well-recognized that a high level exposure in the short term by ingestion may lead to an increased likelihood of an acute toxic syndrome, (2).

Chlorine reacts with humic substances and forms disinfection by-products (DBPs) such as trihalomethanes (THM), haloacetic acids (HAA), etc., which are potentially harmful, and even carcinogenic to humans (3). Further the presence of organic contaminants may degrade the ion-exchange capacity and serve as a nutrient source for biological growth, (2).

Various water treatment processes can either directly or indirectly and, to varying degrees, remove aquatic organic matter from raw water, depending on their operational conditions and the specific characteristics of the NOM present in water such as molecular weight distribution (MWD), carboxylic acidity, and humic substances content (4). Conventional water treatment processes such as coagulation/flocculation and carbon adsorption have been generally used as pre-treatment to remove NOM. However, it should be noted that these treatment processes will not remove NOM to a required level. NOM with the highest carboxylic acidity and hence the highest charge density compounds are generally difficult to be removed by conventional treatment (4). Furthermore, a study of the effect of natural organic matter on powdered activated carbon adsorption revealed that the adsorptive capacity of PAC was reduced in the presence of NOM (5).

Advanced oxidation processes are treatment processes that can degrade low molecular weight herbicides pesticides and disinfection by-products (5–9). Another study on the removal of humic substances using H_2O_2/UV show that the process was not efficient and led to only 9% removal in terms of organic

carbon, (10). This was explained as the structural changes in the composition of the humic substance such as the transformation of aromatic fractions into aliphatic fractions and conversion of humic fractions to non-humic fractions, without significant conversion of organic matter to carbon dioxide (10).

The photocatalytic degradation of 4-chlorophenol with a suspended mixture of titania and of activated carbon (AC) was conducted, (11). Their result showed that the degradation of 4 chlorophenol demonstrated an increase of the first order rate constant by a factor of 2.4 with a titania mix with activated carbon and, the main intermediate products (hydroquinone and benzoquinone) were found in smaller quantities and during a much smaller lifetime (11).

In this study, the combined heterogeneous photocatalysis with the adsorption process was investigated to improve the removal of by-products of photocatalysis oxidation. The efficiency of photocatalysis systems in removing the humic substance from water was investigated. The study included the use of TiO_2 coupled with PAC in a batch reactor, a continuous reactor, and a recirculated continuous flow reactor. The organic removal rate, measured in terms of dissolved organic carbon (DOC), was used to quantify the efficiency of the photocatalysis system.

EXPERIMENTAL UNITS, MATERIALS AND ANALYSIS

Photocatalysis Batch Reactor

The batch reactor (Fig. 1) was used to find the optimum levels of TiO_2, pH, and the PAC concentrations to be used with TiO_2. The photocatalysis was conducted with powdered P25 Degussa TiO_2. The product name of the humic substance used in experimentation is Biohumic from the Bioiberica Company (Spain). For convenience, it is referred to as a humic substance in subsequent sections. The UV lamps used in the batch reactor experiments are G8T5 germicidal lamps from Sankyo Denki which can transmit UV rays at 253.7 nm. The reactor was cooled by circulating water around the reactor as temperatures above 80°C lead to a reduction in reaction rates (12). The batch reactor was covered with aluminium foil at all times during operation.

Photocatalysis Continuous Reactors

The photocatalysis continuous reactor (Fig. 2) was used to find the optimum detention time for the photo oxidation of humic substance. The three reactors L1, L2, and L3 shown in Fig. 2 are a single lamp reactor. The UV lamps are the same as those used in the batch reactor experiments. The volume of each reactor is 70 mL giving a total volume for the continuous reactor system of 210 mL. The humic solution (humic substance) and TiO_2 were injected directly
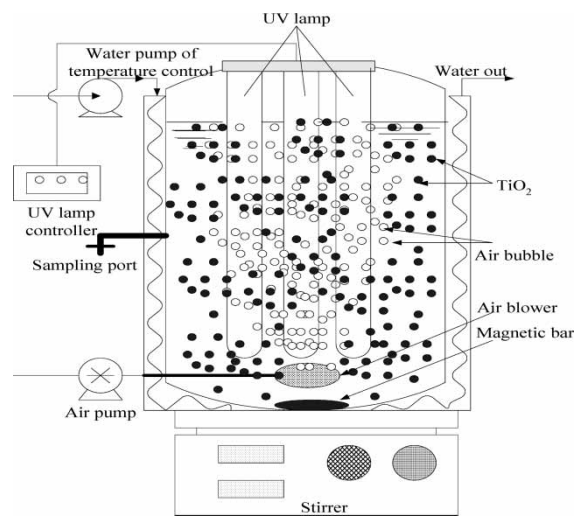
Figure 1.   Schematic of the photo-catalytic batch reactor.

into a holding tank (T1 in Fig. 2) filled with 5 L of tap water. After mixing, the tank T1 contained 10 mg/L DOC and 2 g/L of TiO_2. This solution was then fed through the continuous reactor using a pump which could operate at a variable rate thereby allowing the flow rate (Q1) to be controlled to different rates.

Recirculated Photocatalysis Continuous Reactors

The continuous reactor system consisted of three stainless steel reactors (L1, L2, and L3 in Fig. 3) each with a volume of 70 mL. TiO_2 was dosed directly
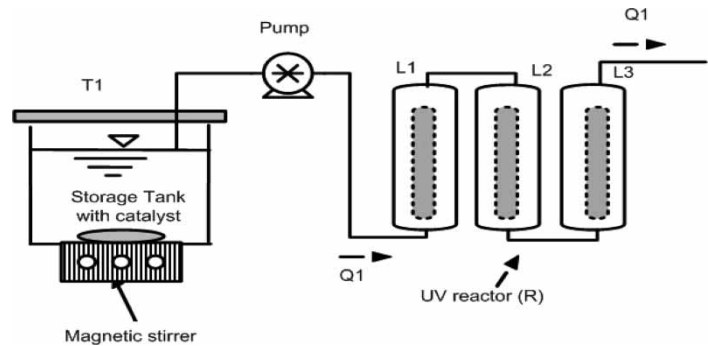

Figure 2.   Schematic of continuous reactor (T1: Mixing tank with no light source; Q1: influent and withdrawal rate; R: photo-catalytic reactor unit; L1, L2, L3 are UV lamps of 8 watts each).
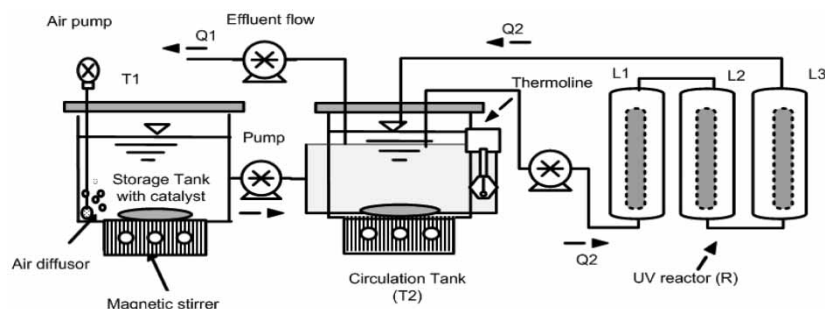
Figure 3. Schematic of the recirculating continuous flow photo-catalytic reactor with the catalyst. (T1: Mixing tank with no light source; Q1: influent and withdrawal rate; Q2: re-circulation flow; T2: re-circulation tank; R: photo-catalytic reactor unit; L1, L2, L3 are UV lamps of 8 watts each).

into a holding tank (T1) containing 5 L of stock solution. The solution was mixed with a magnetic stirrer and the concentration of humic substance in the stock solution was adjusted to 10 mg/L. In some experiments, a PAC dose of 0.05 g/L was added. Air sparging was also provided at a rate of 3.3 VVM (air volume/solution volume/minute). The same rate was used for batch and recirculated continuous reactor. The solution was fed by a pump to a circulation tank (T2). The temperature in the circulation tank was controlled by a thermoline. The solution containing TiO_2 and PAC (if present) was pumped to the continuous photo-catalytic reactor at flow rates of 20 and 40 mL/min. It was circulated in the photo-catalytic reactor at a flow rate (Q2) of 150 mL/min to prevent the settling of TiO_2 and PAC (if present) within the reactor. The effluent flow rate (Q1) was adjusted to the desired detention time. The detention time is equal to the volume of the photo-catalytic reactor divided by Q1.

Analysis

The DOC was measured using the Multi N/C 2000 analyzer (Analytik Jena AG). The sample was oxidized into end products in a combustion tube at high temperatures.

A Varian Gas Chromatograph 3400E (GC) equipped with a flame ionisation detector (FID) and a DB-5 column of 0.32 mm diameter (J&W, Folsom, CA) was utilized for studying the intermediaries of photo-oxidation. The stationary phase in the column consisted of a cross-linked surface bonded 5% phenyl methyl-polysiloxane with a non-bonded film thickness of 100 μm. The system was operated using helium as the carrier gas with a linear velocity of 1 ml/min. The injector and detector temperatures were set at 280°C. The only modification to the GC was the installation of a 0.75-mm diameter splitless glass inlet liner to

increase the linear velocity of the analyte and to leave less space for the
analyte to reabsorb onto the Solid Phase Micro Extraction (SPME) fiber.
Both these effects enhance the desorption from the fiber. The humic
substance with a higher concentration of 100 mg/L was used in these exper-
iments. The temperature in the column was increased in the following
manner. The column temperature was first kept at 40°C for 5 minutes, then
increased to 150°C where the temperature was held constant for 10
minutes, then increased at 5°C/minutes to 200°C (where it was held for
10 min), then increased at 1°C/minute to 210°C (where it was held for 10
minutes), then increased at 10°C/minutes to 270°C (where it was held for
10 minutes), and finally to 280°C at a rate of increase of 10°C per minute
(where it was held for 10 minutes). The total run time was 55 min. The
detector gases were hydrogen and air at flows of 4 and 120 mL/min,
respectively.

Initial experiments focused on determining the time at which the equili-
brium was established between the analytes in the stationary and aqueous
phases. Triplicate solutions were extracted for periods of time ranging from
10–60 min. The equilibrium times were determined by inspection of the con-
centration of the humic substance and it was observed that there was almost no
change of the peak height after 30 min. The 30 min period in 40 ml vial was
the optimum time. The optimization of the desorption temperature and time
was investigated by considering the amount desorbed from fibers after extrac-
tion of analytes from a solution of known concentration and the subsequent
carryover at a range of temperatures and time periods.

Experiments

A humic substance concentration of 10 ppm was used for all experiments.
1.5 L of tap water was added to the batch reactor and stirred with a
magnetic stirrer. The humic substance was added as required to bring its con-
centration in the batch reactor to about 10 ppm. For the continuous reactor, 5 L
of tap water was added to the storage tank. The humic substance was injected
directly into the storage tank and stirred with a magnetic stirrer to bring the
humic substance concentration to about 10 ppm. An initial TOC measurement
was taken for all experiments before treatment commences.

Experiments on flocculation were carried out with ferric chloride ($FeCl_3$).
Each container held 2 L of tap water and 10 mg/L of humic substance. Initial
TOC measurements were taken first before $FeCl_3$ was added. Different
amounts of $FeCl_3$ were added into each container to achieve concentrations
between 30–150 mg/L. The samples were then stirred rapidly for 1 minute at
100 rpm, followed by 20 minutes of slow mixing at 30 rpm, and were allowed
to settle for 30 minutes. Samples from each container was then taken and
analysed for TOC. The samples were then left for flocs to settle after which
1.5 L of the supernatant was extracted for photocatalysis in the batch reactor.

Only solution with a concentration of 50 and 60 mg/L of $FeCl_3$ were used with photo catalytic batch reactor since 50 mg/L was found to be the optimum dose. TiO_2 was added to the supernatant at a concentration of 2 g/L.

Another set of experiments was conducted to study the adsorption kinetics of PAC. Clean and dry PAC was added into 2 L beakers containing humic substance to achieve concentrations of 0.1, 0.5, 1, and 2 g/L of PAC. The solution was mixed well using a mechanical stirrer at 130 rpm for 3 hours. During the experiments, samples were taken periodically to measure the TOC concentration. After stirring, the sample was left for 2 hours for PAC to settle after which 1.5 L of the supernatant was extracted.

RESULTS AND DISCUSSIONS

Flocculation and Flocculation-Photocatalytic Reaction

Figure 4 shows the percentage of DOC removed by $FeCl_3$ acting as coagulant. The optimum dose was 50 mg/L which yielded a removal of 84% of humic substance. Large doses of the coagulant (100 and 150 mg/L of $FeCl_3$) lead to very low acidic pH. Iron species become more positively charged at lower pH. After the humic substance reacts with the iron species, a fraction of the complex undergo charge reversal (from negative to positive charge), which prevent the complexes of Fe^{3+} and colloids of humic substance from being removed (13, 14).

Figure 5 shows the results of flocculation with 50 mg/L and 60 mg/L following a period of photocatalysis. A sample of the supernatant was extracted for the TOC measurement immediately after the slow mixing of
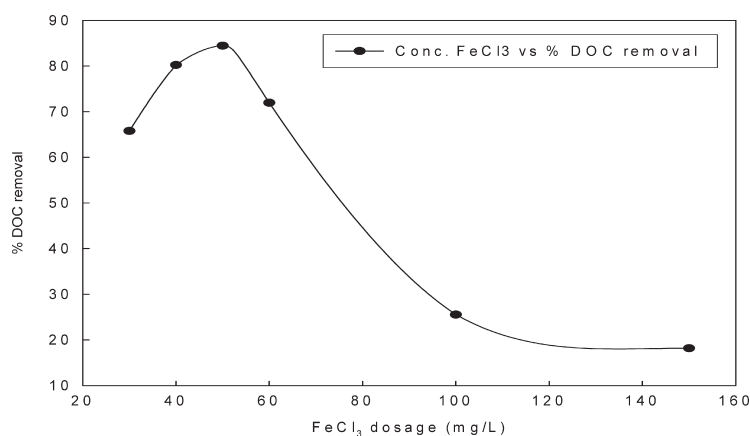

Figure 4. % DOC removal of humic substances by $FeCl_3$ flocculation (influent TOC = 10 mg/L).
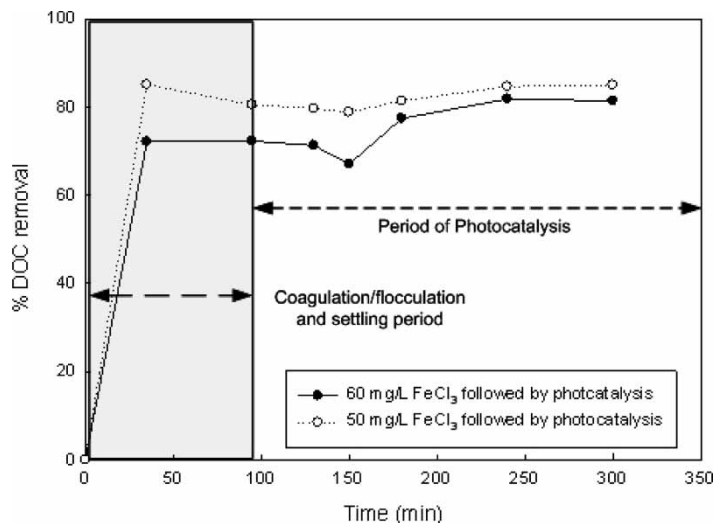
Figure 5. FeCl$_3$ flocculation as a pre treatment followed by photocatalytic reaction (influent TOC = 10 mg/L, 2 g/L TiO$_2$).

the flocculation process and another after 1 hour when settling had occurred. Further samples were extracted for the TOC measurement during the period of photocatalysis. There was little change in DOC in the period after flocculation and settling. The removal of the humic substance decreased where an amount of FeCl$_3$ (60 mg/L) in excess of the optimum dose was used. The fluctuation of DOC during the photocatalysis period may be attributed to the TOC measurement. The fluctuation may also be attributed to the reverse reaction where the reaction of hydroxyl radicals increases the portion of humic acids with less hydrophobic, less adsorbing, and less aromatic characters, in general. In the presence of iron binding compound such as humic substance, it can alter the rate constant and change the formation rate of hydroxyl radical (15).

Effect of TiO$_2$ Concentration on Photocatalytic Reaction

Two sets of experiments were conducted with a batch reactor to identify the effect of various dosages of TiO$_2$ on the photocatalytic reaction. One set of experiments were carried out without UV treatment while the second set of experiments were conducted with UV treatment.

The first set studied the affinity of humic substance to TiO$_2$ in batch equilibrium experiments without the application of UV (Fig. 6). The experiments was carried out by mixing 1.5 L solution of humic substance in a batch reactor at a neutral pH of 7.2 with varying amounts of TiO$_2$ doses between 0.5 to
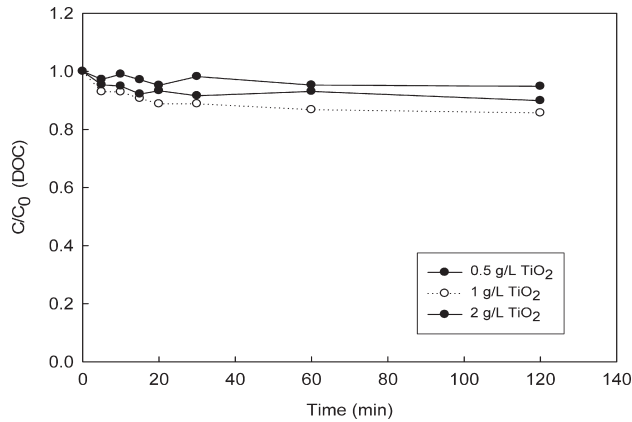
Figure 6. Removal of humic substances (DOC) with different concentration of TiO_2 without UV in a batch reactor. (Influent TOC = 10 mg/L).

2.0 g/L. The result (Fig. 6) shows that the humic substance was adsorbed quickly onto the TiO_2 particles. DOC removal was around 10 to 15% after 15 min and nearly constant up to 2 hours.

The second set of experiments used 10 mg/L of humic substance with different concentrations of TiO_2 (0 g/L (UV treatment without TiO_2), 0.5 g/L, 2.0 g/L, 3.0 g/L, and 4.0 g/L) and UV. The TiO_2 powder was added directly into the batch reactor and stirred with a magnetic stirrer. Samples were taken after 10 min, 30 min, 1 hr, 2 hr, 3 hr, 4 hr, 5 hr, 6 hr,
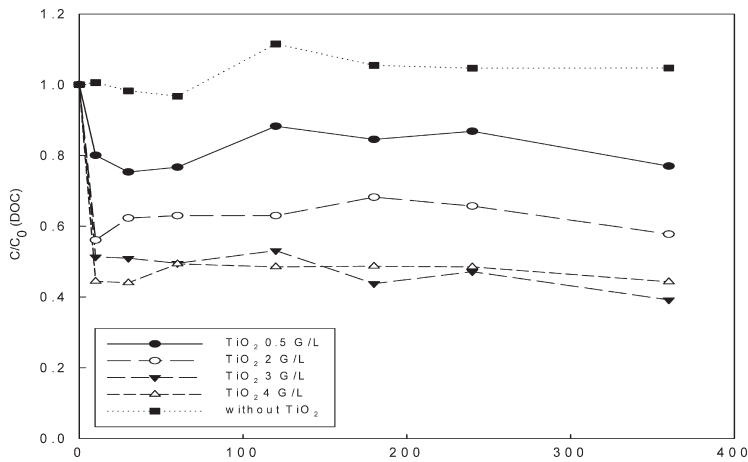

Figure 7. Removal of humic substances (DOC) with different concentration of TiO_2 with UV treatment (including UV treatment without TiO_2) in a batch reactor. (Influent TOC = 10 mg/L).

and 6.5 hr of treatment,. The results (Fig. 7) show that direct photolysis (UV treatment without TiO_2) of humic substance provides no significant removal of DOC. In fact the results shows a slight increase in TOC (DOC) which could have been induced by the slow evaporation of water during the experimental period (16). With a different dose of TiO_2, humic substance degrades quickly during the first 10 minutes of operation following which a reverse reaction was observed after 20 minutes. The degradation with TiO_2 during the initial period (10 minutes) is related to the amount of TiO_2 in suspension where a smaller concentration of TiO_2 resulted in a lower degradation rate. Following this initial period there was no significant degradation of humic substance during the 6 hours. After 6 hours of retention time, humic substance removal in terms of DOC was 25% (for 0.5 g/L of TiO_2), 43% (for 2 g/L of TiO_2), 60% (for 3 g/L of TiO_2), and 56% (for 4 g/L of TiO_2).

These results revealed that a concentration of $TiO_2 > 3$ g/L retards the reaction because the penetration of UV light was impeded by the TiO_2 in suspension and the consequent reduced formation of electron/hole pairs and active sites (17). Previous researchers also have not obtained the complete mineralisation of humic acid with UV/TiO_2 (18, 19). A reverse reaction was mainly observed during the period between 20 minutes to 4 hours. A reverse reaction is due to large MW being broken down into small MW during the photocatalytic process. Therefore, to alleviate the reverse reaction, treatment should incorporate measures to remove the large MW before the photocatalytic reaction.

For the TiO_2 dose of 2 g/L a SPME/GC FID analysis was carried out on samples at various times between 5–240 minutes to determine the intermediaries of photo-oxidation. A concentration of 100 mg/L of humic substance was used instead of 10 mg/L due to detection limit of Flame ionisation detector (FID).

The study of GC/SPME demonstrated that the humic substance is converted to several photo-products during photo-oxidation (Fig. 8). The cleavage of large MW of humic substances was confirmed by the SPME/GC FID. Unfortunately, due to the complex nature of the by-products, GC FID did not allow the identification of individual oxidation intermediates of humic substance. However, it provided some idea of the appearance of these complex compounds (intermediaries) during the photo-catalytic process.

These results indicate that the photo-degradation of humic substance led to the production of smaller MW organic intermediaries. Some are easily degraded by TiO_2/UV (retention time (rt.) of 18.3). Other compounds (such as rt. of 20.21 and 17.40) are possibly photo-resistant compounds and hardly degrade (Fig. 8a). The photo-resistant compounds that occur during photo-oxidation may lead to an increase of DOC level. However after 4 hours of operation time the concentration of photo-products seemed to have reduced. A comparison of Figs. 8a, 8b, and 8c shows peaks of photo products are lower in Fig. 8c compared to the corresponding peaks observed in Figs. 8a and b. A lower peak, or more correctly the area under
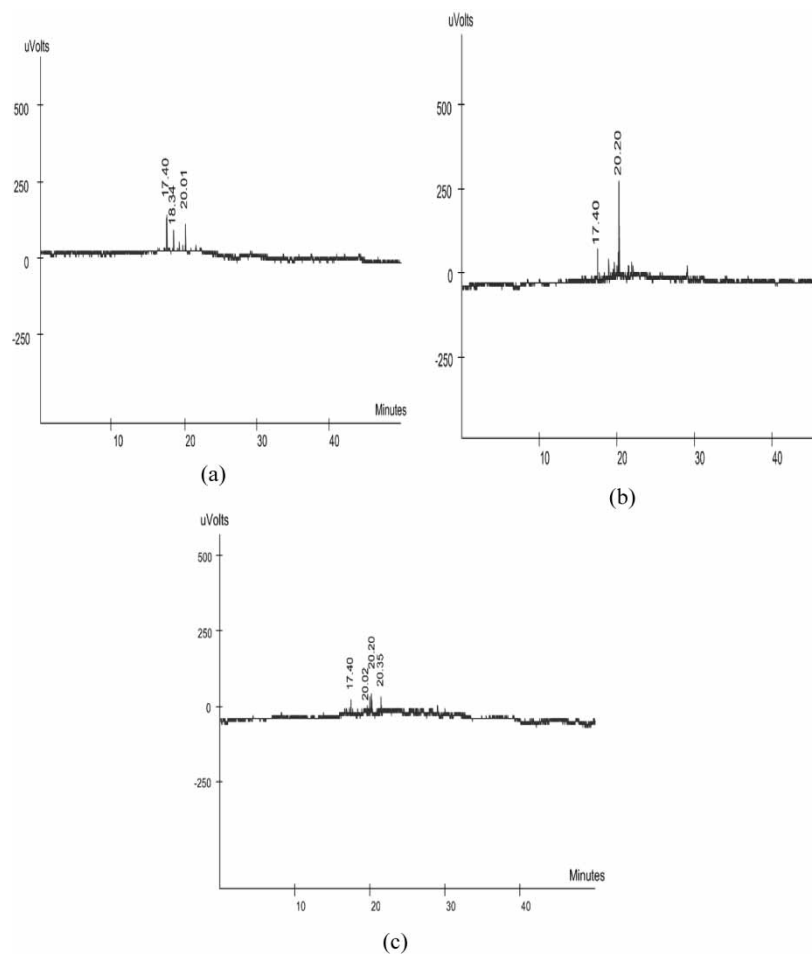
Figure 8. SPME/GC (a) at 15 min (b) at 90 min (c) at 240 min. Humic substances 100 mg/l and TiO_2 2 g/l.

the peak, corresponds to a lower concentration. It is estimated there are the incomplete degradation is equivalent to about 35% of the initial humic substance as shown by DOC levels in Fig. 7.

Effect of pH on Photocatalytic Reaction

A set of experiments was carried out in a batch reactor in order to identify the effects of pH on photocatalysis. Each experiment was conducted at different pH values of 3.6, 4.6, 7.2, 9, and 10. The pH was altered after the humic
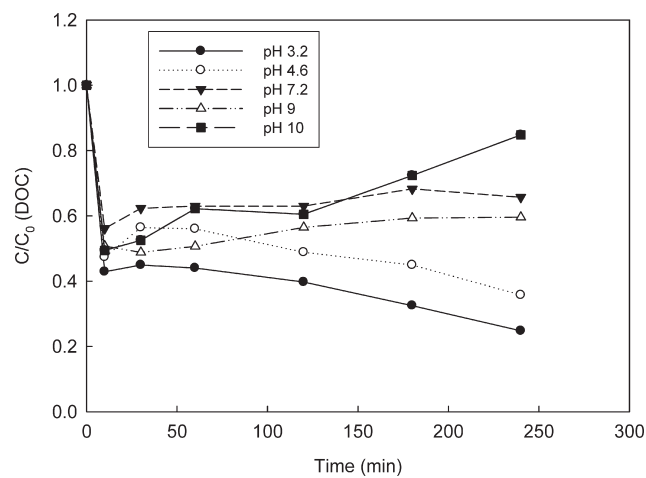
Figure 9. Removal of humic substances (DOC) with 2 g/L of TiO$_2$ at different initial levels of pH in batch reactor. (Influent TOC = 10 mg/L).

substance was injected into the batch reactor by the addition of either NaOH or HCl and monitored with a pH meter. After the required level of pH was reached, 2.0 g/L of TiO$_2$ (which is the optimum level of TiO$_2$) was added directly to the batch reactor and stirred with a magnetic stirrer. Initial samples were taken after the pH was adjusted. Further samples were taken after 10 min, 30 min, 1 hr, 2 hr, 3 hr, and 4 hr of treatment.

Figure 9 presents the effect of pH on the photocatalytic reaction of humic substance. It was observed that the highest level of humic substance removal occurred at pH 3.2 and 6 followed by pH 9.0. At pH 10.0 there is a significant amount of reverse reaction. The results showed that degradation rates were strongly dependent on pH due to the pH–dependent adsorption of humic substance on TiO$_2$. In this study, in acidic media (pH 3.2), DOC removal was up to 78% compared with 20% DOC removal in basic media and 40% DOC removal without pH adjustment. These results can be explained by the surface charge of the TiO$_2$ surface at different pH values. In acidic media (pH $<$ 7), the TiO$_2$ surface is positively charged. This improves the adsorption of TiO$_2$ particles. Whereas if the pH is too high, there will be no

Table 1. pH and photocatalysis

pH $<$ 7	pH $>$ 7
Photocatalytic reaction in different pH	
High adsorption on TiO$_2$ surface	Low adsorption on TiO$_2$ surface
Low quantum yield	High quantum yield

adsorption by the TiO_2 particles, (18). However, a high pH can increase the photocatalytic reaction rate and the TiO_2 quantum yield, thus improving the degradation of humic substance (Table 1). This explains why humic substance removal was higher at pH 9 than at neutral conditions. (18, 19). However, the need to adjust the pH prior to and after the treatment is a major impediment. Furthermore, the humic substance removal rate is only slightly higher between alkaline pH (9) and neutral pH.

Photocatalytic Reaction of TIO_2 Coupled with PAC

The PAC batch adsorption experiments (Fig. 10) show that the DOC removal increases by up to 80% with higher concentrations of PAC. However, the DOC removal efficiency was not significantly improved beyond a concentration of 1 g/L of PAC dose.

After PAC adsorption, a 2 liters of water sample was left for 3 hours until the PAC had completely settled. 1.5 liters of the supernatant was used together with TiO_2 (concentration of 2 g/L) in a photo-catalytic batch reactor. The results shown in Fig. 11 demonstrate the importance of post-photocatalysis in the degradation of humic substances. Following photocatalysis removal of humic substance further increased to between 74–83% (Fig. 11). A set of experiments was conducted at different concentrations of TiO_2 (1.0 g/L, 2.0 g/L, and 3.0 g/L), each combined with a small additional dose of PAC (0.05 g/L). These were used to investigate whether the PAC could reduce the concentration of TiO_2 required for treatment (20). TiO_2 and PAC were added directly into the batch reactor and stirred with a magnetic stirrer. Samples were taken after 10 min, 30 min, 1 hr, 2 hr, 3 hr and 4 hr of treatment. Figure 12 shows, further improvement in DOC removal when PAC was added together with
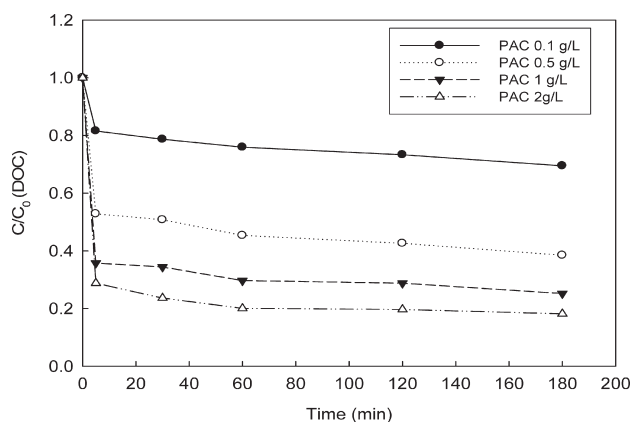

Figure 10. Removal of humic substances (DOC) at different concentrations of PAC. (Influent TOC = 10 mg/L).
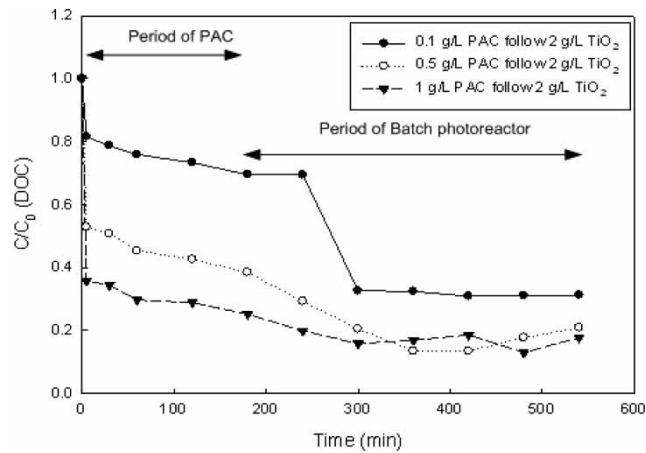
Figure 11. Removal of humic substances (DOC) using PAC as pre-treatment follow by batch photocatalytic reactor. (Influent TOC = 10 mg/L).

TiO$_2$ in the photo reactor. The results showed that 75% DOC removal of 2 g/L and 3 g/L in 10 min detention time of TiO$_2$ and PAC compared with 40% and 50% DOC removal with 2 g/L and 3 g/L of TiO$_2$ alone.

SPME/GC FID equipped with DB-5 column was used to investigate the photo products during the photo-catalytic reaction. Using a small amount of PAC coupled with TiO$_2$ revealed a superior removal of humic substance (DOC). The manner in which intermediate photo-products evolve and
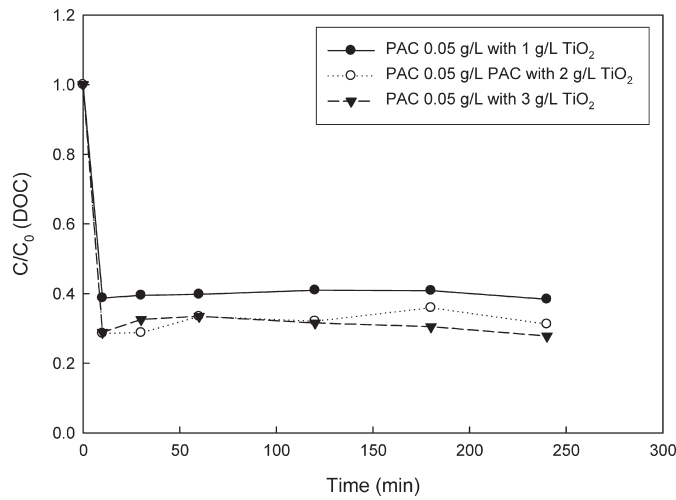

Figure 12. Removal of humic substances (DOC) with 0.05 g/L PAC and different concentration of TiO$_2$. (Influent TOC = 10 mg/L).

transform was demonstrated by the GC FID peak. These results can be summarized in the following way. The photo resistant by products was adsorbed on PAC-TiO$_2$ surface as shown in GC peak results (Figs. 13a, b, c). The GC peak after 210 min of PAC-TiO$_2$ revealed only a rt. of 19.5 min compared with several peaks (rt. of 17.4, 19.2, 20.2) of byproducts after 240 min operation time when using TiO$_2$ alone (Fig. 8c). From DOC measurements, it is estimated that less than 25% of the initial material remained (Fig. 12). Humic substances are widely known as the major organic precursors for trihalomethane formation THMFs during the chlorination processes, (3). From these results, the use of TiO$_2$-PAC demonstrated superior removal of the humic substance with shorter contact time and higher removal efficiencies compared with using TiO$_2$ alone. It is suggested that during the PAC-TiO$_2$ batch process humic substance was removed immediately without forming a large amount of intermediate macro-molecules of humic substance.
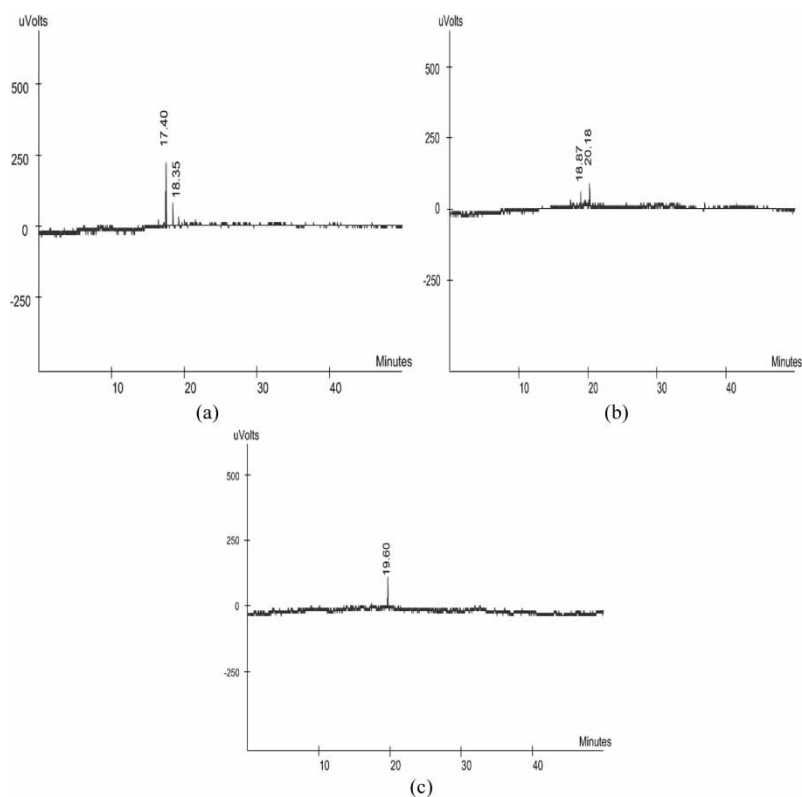

Figure 13. SPME/GC peaks PAC-TiO$_2$ (a) at 15 min (b) at 90 min (c) at 210 min. Humic substances 100 mg/L, TiO$_2$ 2 g/L, PAC 0.05 g/L.

Photocatalytic Continuous Reactor

This set of experiments was conducted with a continuous photocatalytic reactor, Fig. 2. These experiments were run at different flowrates (10 mL/min, 20 mL/min, 30 mL/min, and 40 mL/min) to investigate the effect of detention time on photocatalytic reaction. 2.0 g/L of TiO_2 was added directly in the container holding the humic substance. Samples were taken to measure TOC after 5 min, 20 min, 40 min, and 1 hr of treatment.

Figure 14 showed the humic substance removal efficiency of a photocatalytic continuous reactor at different detention times of 21 min (equivalent to a flow rate of 10 mL/min), 10.5 min (20 mL/min), 7 min (30 mL/min) and 5.2 min (40 mL/min). Better results were achieved at longer detention times as there was more contact time. At a detention time of 10.5 min, the humic substance removal with a TiO_2 dose of 2 g/L was about 60%. However, the TOC removal was 10% lower at a detention time of 21 min. It was attributed to the settling of TiO_2 particles and accumulation in the first reactor during the longer detention time.

The continuous photo-catalytic reactor was also used with a combination of 0.05 g/L of PAC and 2 g/L of TiO_2 (Fig. 15). The flow rate varied from 10 to 40 mL/min corresponding to a detention time of 20.1 min to 5.2 min. The results also indicate that the photo-catalytic adsorption hybrid system removed a significant amount of humic substance (80% TOC removal) within a short contact time.
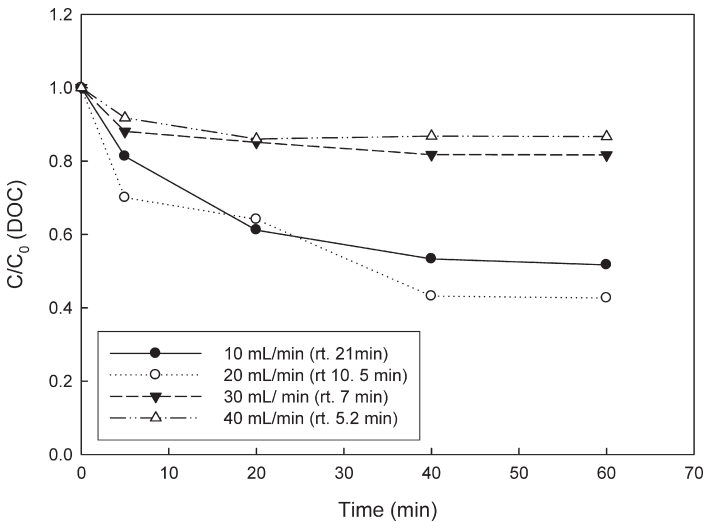

Figure 14. Removal of humic substances (DOC) with 2 g/L of TiO_2 by continuous reactor in various flow rates. (Influent TOC = 10 mg/L).
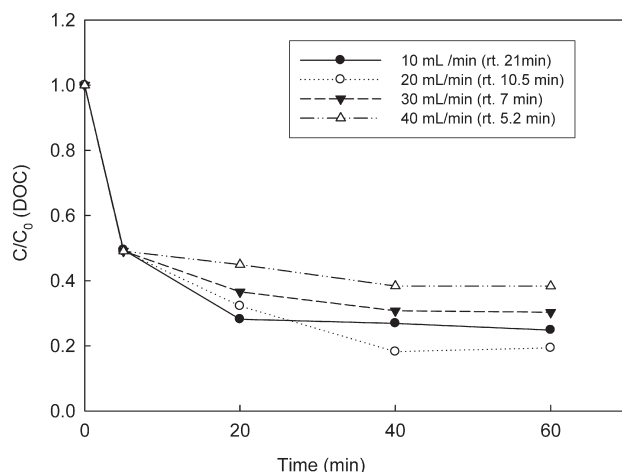
Figure 15. Removal of humic substances (DOC) with 2 g/L of TiO$_2$ and 0.05 g/L of PAC by continuous reactor in various flow rates. (Influent TOC = 10 mg/L).

Recirculated Photocatalytic Continuous Reactor

In a plug flow reactors the factors for controlling removal rates in heterogeneous catalysis are mass transfer and surface reaction controls. These factors are improved in a high recirculation flow rate of 250 mL/min where flow is turbulent. The reaction rates are increased as result. This behaviour of turbulent (Re $\geq$ 2000) plug flow reactor was observed by (21). Thus, experiments with the recirculating continuous flow reactor (Fig. 3) were carried out. 0.5 g/L of TiO$_2$ was also used in these experiments. The solution was recirculated (Q2 in Fig. 3) at a high speed of 150 mL/min by the Masterflex pump to avoid the settling of TiO$_2$ and the uniform dispersion of TiO$_2$ in the solution. The solution was initially left in the dark for a period of 15 min before feeding to the recirculating container. The solution was fed through the circulation tank at the same rate. Effluent was continuously withdrawn by another pump (Q1 shown in Fig. 3) from the circulation tank. Samples were taken to measure TOC after 5 min, 10 min, 30 min, 40 min, 60 min, 90 min, and 120 min of operation time.

Recirculated continuous flow reactor experiments were conducted at pH 7.2 with 0.5 g/L of TiO$_2$ alone and with 0.5 g/L coupled with PAC 0.05 g/L. During the initial stage, adsorption occurred in the dark for a period of 15 minutes. During this period, 15% of humic substance was removed using TiO$_2$ alone and 35% was removed using PAC-TiO$_2$ (Fig. 16). After the initial dark period, the solution was pumped through a recirculating tank following by a high speed feed through the UV reactor at 250 mL/min. Samples were taken by direct pumping from a recirculated tank at various times. A slight decrease of humic substance equivalent to approximately
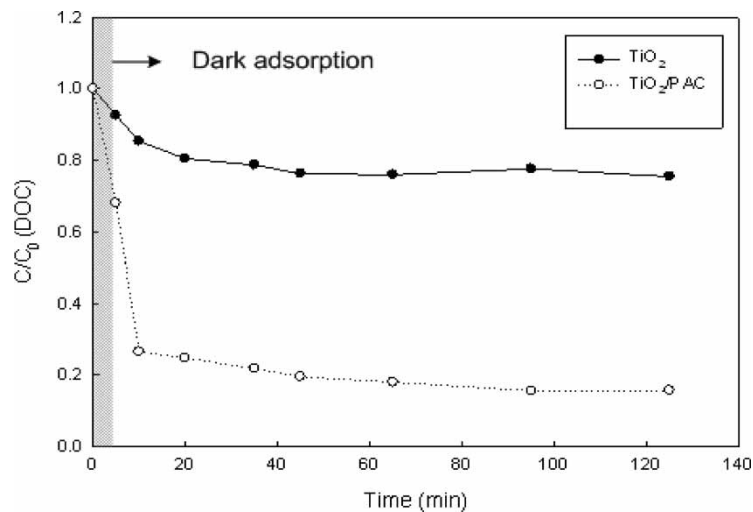
Figure 16. Removal of humic substances (DOC) in recirculated continuous flow reactor at withdrawal rate of 20 mL/min. (Influent TOC = 10 mg/L, 0.5 g/L of TiO_2 and 0.05 g/L of PAC).

20% DOC removal was observed after 20 minutes of operation time after which there was no further removal.

When a small amount of PAC was added, DOC removal improved upto 80% in a shorter operation time of less than 10 minutes. This was the point
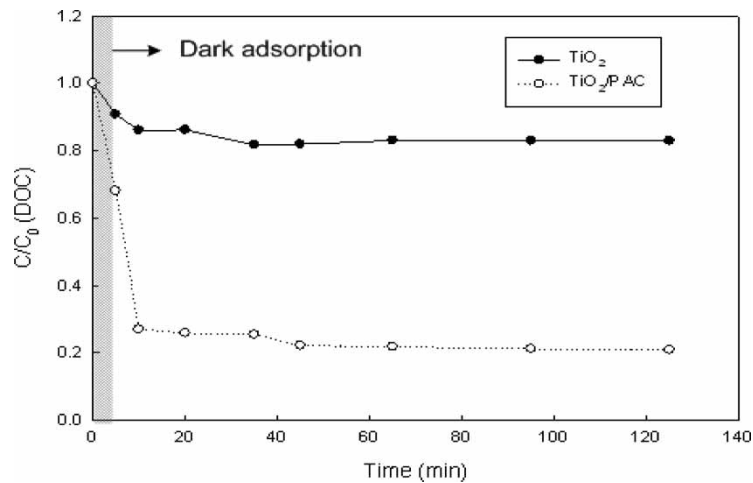

Figure 17. Removal of humic substances (DOC) in recirculated continuous flow reactor at withdrawal rate of 40 mL/min. (Influent TOC = 10 mg/L, 0.5 g/L of TiO_2 and 0.05 g/L of PAC).

to which activated carbon adsorbed photo-products that were photo-resistant as demonstrated by SPME/GC FID analysis of batch experiments.

At the higher withdrawal rate of 40 mL/min, a similar trend was demonstrated (Fig. 17). With 0.5 g/L of TiO_2 alone, DOC removal was less than 20% compared with the withdrawal rate of 20 mL/minute. However, there was no significant difference of humic substance removal with PAC-TiO_2.

CONCLUSION

The type of photocatalysts, pH, and the physio-chemical properties of humic substance such as their photo-products, play major roles in the removal of humic substance. This study showed that in low pH (pH 3.2) or acidic media the photocatalytic degradation of humic substances was higher than in basic media (pH 10). Furthermore, photo intermediate products play major roles in the photocatalytic degradation of humic substances as shown in SPME/GC FID analysis (GC peaks). A small addition of PAC could alleviate this problem and achieve an increase in the removal efficiency of humic substance in a shorter contact time. Experiments with the continuous photocatalysis reactor using TiO_2 alone as photocatalyst compared with the use of TiO_2–PAC as photocatalyst showed that the removal rate for the later was superior with a shorter detention time and higher removal efficiency.

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