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# A Total Solution for Simultaneous Organic Degradation and Particle Separation Using Photocatalytic Oxidation and Submerged Microfiltration Membrane Hybrid Process

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**Abstract**−Advanced oxidation process (AOP) with reactor capacity of 150 L, using ultraviolet (UV) radiation and titanium dioxide ($TiO_2$) photocatalyst, was evaluated for the destruction of toxic organic chemical, bisphenol A (BPA). $TiO_2$ in the form of powder, was suspended as slurry in the water, as against the commonly adopted practice of immobilizing it onto a carrier material such as glass, concrete or ceramics. Adsorption of BPA by $TiO_2$ was evaluated and was performed as a pretreatment to AOP. The combined effect of ozone with the AOP process was also studied. Applying ozone along with UV/$TiO_2$, brought about a synergistic effect on BPA degradation. Within three hours, entire 10 ppm of BPA and the intermediate organic compounds were completely removed. The highlight of this study was the simultaneous degradation of BPA and separation of $TiO_2$ particles from water after photocatalysis, in order to obtain reusable quality water. Separation of $TiO_2$ particles was carried out by a unique two stage coagulation and settling process followed by submerged hollow fiber microfiltration membrane technique. With initial turbidity of 4,000 NTU, the turbidity of the final permeate water was well below 0.1 NTU. Almost complete removal of $TiO_2$ particles was achieved. Some of the main advantages of this hybrid treatment system include, large scale treatment, complete and efficient BPA and its organic intermediates degradation; easy separation of $TiO_2$ after treatment and reuse as it is free from chemical coagulant contaminants; reusable quality water, and the potential for continuous operation with simple process modifications.

Key words: Hybrid Process, Bisphenol A (BPA), Photocatalytic Oxidation, $TiO_2$, Submerged Hollow Fiber Microfiltration

## INTRODUCTION

4,4'-Isopropylidenediphenol (bisphenol A, BPA) is widely used in the production of polycarbonate and polysulphone plastics and epoxy resins. It is also being used as a reaction inhibitor, anti-oxidant, and flame retardant. The global production is reported to be increasing at about 7% per year. However, reports indicate that BPA exhibits estrogenic activity and alters metabolism kinetics, induces DNA damage and results in chromosomal aberrations [Schafer et al., 1999; European Commission, 2000]. Hence, the wastewater containing BPA can be a source of contamination in aquatic environments [Staples et al., 1998]. Considering the widespread application of BPA with its high risk of exposure and health hazard, a simple and effective wastewater treatment method is very important.

A variety of treatment techniques such as chemical [Li, 1999], biological [Armenante et al., 1999] and photochemical [Chen and Ray, 1998] processes exist for the treatment of wastewater containing phenolic compounds. Recently, advanced oxidation processes (AOPs) with UV radiation and photocatalyst titanium dioxide ($TiO_2$) is gaining growing acceptance for the treatment of organic materials [Chun et al., 2001; You et al., 2001; Gogate and Pandit, 2004; Na et al., 2005]. Among many semiconductors, $TiO_2$ is frequently used as a photocatalyst because it is non-toxic, chemically stable, and possesses relatively high photocatalytic activity [Legrini et al., 1993]. Upon illumination, $TiO_2$ absorbs impinging photons and reaches an excited state to produce electron and hole pairs ($e^-/h^+$) [Hoffman et al., 1995]. The valance band potential ($h^+$) is positive enough to generate hydroxyl radicals, which are used as a strong oxidizing agent to convert organic pollutants into less toxic intermediate byproducts with low molecular weight and eventually mineralize to carbon dioxide and water.

Although, the effectiveness of this process for treating several organic chemicals has been well documented, its performance for endocrine disrupting toxic chemicals like BPA has received comparatively less attention [Ohko et al., 2001; Kaneco et al., 2004; Chiang et al., 2004]. Moreover, these studies on BPA degradation have been carried out in small scale reactors with solution volumes ranging from micro liters to a maximum of 1 liter. Also, most of the studies on photocatalytic oxidation have used $TiO_2$ after immobilizing it on matrix material [Fukahori et al., 2003; Lee et al., 2004]. However, studies indicate that due to limiting mass transfer and loss of photocatalytic activity by the fixation, a slurry type reactor system excels the fixed type with respect to photocatalytic degradation efficiency [Ollis, 1991; Xi and Geissen, 2001]. But, a major limitation while using $TiO_2$ in suspension is the removal of submicron $TiO_2$ particles from water after photocatalytic reaction that would otherwise cause non-acceptable secondary pollution. Due to its fine particle size when suspended in water (less than 1 micron), it is very difficult to be settled by simple gravity settling. Only very few attempts have been made before, in studying the separation of $TiO_2$ particles from water [Kagaya et al., 1999; Lee et al., 2001; Xi and Geissen, 2001]. Kagaya et al. [1999], studied the $TiO_2$ removal by coagulation alone using aluminum chloride coagulant. Lee et al.

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**Table 1. Physico-chemical 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 °C | $g/cm^3$ | 3.89 |
| Purity | % | >99.5[a] |
| Supply | Degussa | P25 |

[2001]; Xi and Geissen et al. [2001], used flat sheet membranes like ultrafiltration and microfiltration respectively, for $TiO_2$ separation.

The present study deals with the application aspect of photocatalytic oxidation and aims to achieve simultaneous degradation of BPA in a semi-pilot scale photocatalytic reactor and separation of $TiO_2$ from water using simple two stage coagulation followed by submerged hollow fiber low pressure microfiltration (MF) membrane process, in order to obtain the final treated water of reusable quality.

## MATERIALS AND METHOD

The BPA used in this study was purchased from Junsei Chemical Co., Ltd. (Japan). BPA aqueous solutions were prepared with ultra pure water from reverse osmosis treatment. The initial concentration of BPA was 10 mg/L, for this study. P-25 $TiO_2$ particles (Degussa, Germany) were used as photocatalyst and adsorbent for the experiments. The physico-chemical properties of $TiO_2$ used are shown in Table 1.

A 150 L capacity, cylindrical shape, batch type semi pilot scale photocatalytic reactor was used. The effective volume of the liquid within the reactor was about 130 L. The $TiO_2$ suspension containing BPA was irradiated in the photocatalytic reactor by using six quartz tube mercury vapor lamps (TUV 36 SP T5, Philips, USA) with a power input of 40 W. The irradiation intensity was 144 $\mu W/cm^2$ and the wavelength was 253.7 nm. The amount of $TiO_2$ used was fixed at 1 g/L and the initial solution pH at 6.0, throughout this experimental study. $TiO_2$ in aqueous solution was kept in suspension in the reaction vessel with circulation pump (centrifugal pump, 1 HP, capacity 1 $m^3/hr$). The temperature of the solution inside the reactor was monitored periodically.

BPA adsorption by $TiO_2$ was carried out for a period of 5 hours, at different temperatures (25, 45 and 65 °C), separately in a dark and constant temperature bath prior to photocatalysis. For continuous mixing, an air compressor (1/3 HP, 105 L/min, 1,760 rpm) was used to blow air and the tube was fitted with a diffuser for dispersion. The usual adsorption equilibrium and kinetic experiments were not carried out. Considering the practicality of the system, the adsorption time was not intended to be extended more than 5 hours. Constant amount of ozone (2.4 g/hr) was introduced prior or along with photocatalysis and the performance was evaluated based on the temperature conditions explained above. The schematic diagram for BPA degradation equipment using advanced oxidation hybrid system with adsorption pretreatment is shown in Fig. 1.

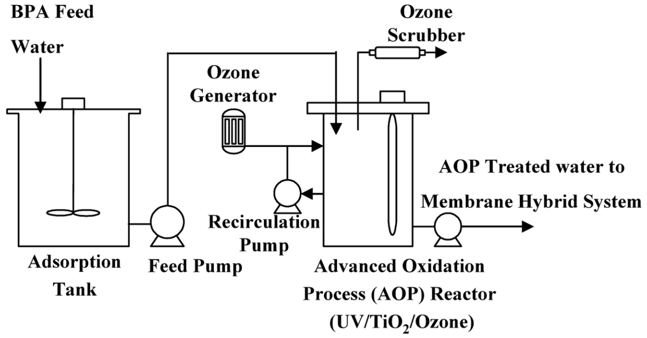


**Fig. 1. Schematic of adsorption-advanced photocatalytic oxidation hybrid process.**

The amount of BPA in the aqueous solution was measured by total organic carbon (Shimadzu 500A, Japan) and high-performance liquid chromatography HPLC (Shimadzu LC-10 VP, Japan) equipped with a UV detector (Shimadzu SPD-10A VP) and a Shim-pack CLC-ODS column. The elution was monitored at 275 nm. The elutant used was a solvent mixture of methanol and water (7 : 3 v/v). The flow rate of the mobile phase was 1 ml/min. The $TiO_2$ photocatalyst was removed from the solution by filtration, and the resulting solution was analyzed with HPLC. Total organic carbon (TOC Analyzer, TOC 5000A, Shimadzu, Japan) was also analyzed to determine the amount of by-product organic materials formed during the reaction. For detailed analysis of intermediate products, a GC/MS (Shimadzu QP2010, Japan) equipped with HP-5 capillary column (30 m ×0.25 mm i.d) was used. Each peak obtained from GC-MS chromatogram, was identified by comparing with GC-MS WILEY7 library data.

On the other hand, separation of $TiO_2$ from water was performed by coagulation membrane hybrid process. The 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 100 mg/L. After settling, the supernatant from the second stage was further treated using a submerged hollow fiber microfiltration (MF) membrane (SuperMAK, ENE, Korea). The properties of the membrane used are given in Table 2. Membrane operation was carried out with and without coagulation pretreatment. The schematic diagram for $TiO_2$ particle separation using two stage coagulation followed by submerged hollow MF membrane hybrid system is shown in Fig. 2.

**Table 2. Specifications of hollow fiber microfiltration membrane**

| | |
|---|---|
| Material | PVDF |
| Pore size, µm | 0.4 |
| Surface area, $m^2$ | 0.02 |
| Internal diameter, mm | 1.8 |
| External diameter, mm | 2.0 |

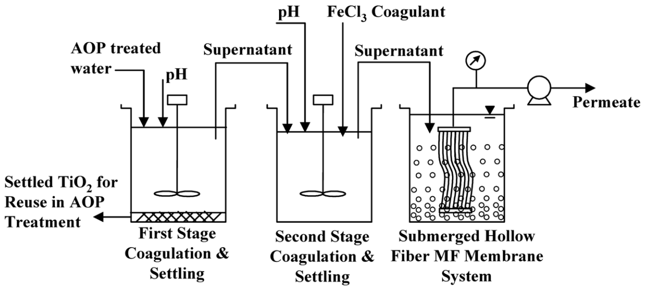


**Fig. 2. Schematic of two stage coagulation with submerged membrane hybrid process.**

The efficiency of $TiO_2$ separation was evaluated by examining the turbidity (Turbidity meter, HACH 2001A). The performance of the membrane was evaluated by examining the turbidity removal and permeate flux development. The surface of the clean and membrane with particle deposit were analyzed by Scanning Electron Microscopy (SEM) (HITACHI, Japan, Model S-4700), in order to understand the underlying effect of fouling in the membrane.

## RESULTS AND DISCUSSION

### 1. Degradation of BPA

Fig. 3 shows the degradation efficiency of organic material in the photocatalytic oxidation process. The efficiencies of BPA and its organic intermediates destruction are indicated in the figure. During the course of the reaction BPA was transformed into other organic intermediates, as is evident from the TOC concentration in the solution. The gradual increase in temperature due to constant recirculation of solution using a circulation pump (to bring about mixing and to keep $TiO_2$ in suspension) can be seen in Fig. 3. Under the study conditions, it can be seen that an extremely long period of operation was required for degradation. After 10 hours, BPA removal efficiency of 78% was achieved for initial BPA concentration of 10 ppm. The initial pH of the solution is known to have a significant effect on the photocatalytic degradation efficiency of organic materials. However, there are mixed opinions, wherein results indicate an increased efficiency in the acidic region [Lee et al., 2004; Bianco-Prevot et al., 1999] as well as in the alkaline [Kaneco et al., 2004] regions. In the present study, initial pH of the solution was chosen at 6.0 (where the surface charge on $TiO_2$ would be minimal), as this would avoid an unnecessary chemical neutralization treatment step. However, at this pH, it was expected that the operation of the recirculation pump produced high agitation so as to minimize the agglomeration of the $TiO_2$ particles, which could decrease the available surface area during photoreaction.

During photocatalytic degradation of BPA using $TiO_2$, several intermediate organic compounds were noticed. Examining the GC-MS chromatogram results, it was evident that as time progressed the initial peak representing BPA, gradually reduced and corresponding smaller peaks, representing the formation of intermediates, appeared and disappeared. It can be understood that the aromatic intermediates formed presumably were further oxidized to aliphatic compounds and finally mineralized to carbon dioxide. The intermediate products with corresponding molecular weight, formed at various retention times, are given in Table 3. Most of these intermediate by-products identified were in agreement with earlier studies in BPA degradation [Lee et al., 2004; Kaneco et al., 2004]. However, it is to be noted that initial pH of the solution would have a large influence on the photocatalytic pathway of BPA degradation [Chaing et al., 2004].

The amount of BPA removal due to adsorption on $TiO_2$ at three different temperatures is shown in Fig. 4. Adsorption efficiency of 10 ppm concentration of BPA on 1 g/L of $TiO_2$ was about 20% after 5 hours of operation at 25 °C. However, an increase in temperature (45, 65 °C) had a negative effect with about 5-10% BPA degradation. Hence, in the combined process (Fig. 5), adsorption (at 25 °C) was carried out as pretreatment to photocatalysis. The overall efficiency of BPA degradation increased by having a combined adsorption photocatalytic process (Fig. 5).

Addition of ozone to the process stream was found to be beneficial in enhancing the overall efficiency of degradation of BPA and

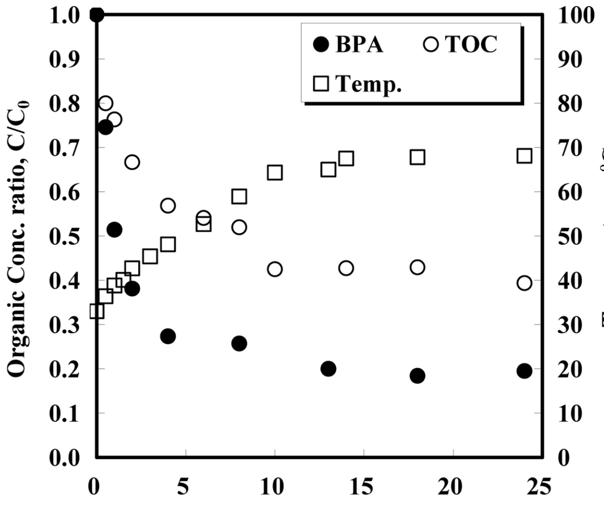
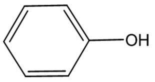
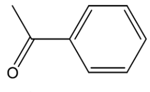
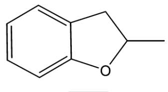
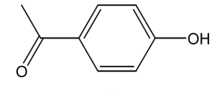
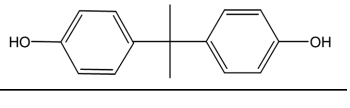


**Fig. 3. Performance of AOP process based on organic removal ($TiO_2$ conc. 1 g/L, initial BPA conc. 10 mg/L).**

**Table 3. BPA and some of the major intermediate organic materials identified during photocatalytic oxidation process**

| Retention time (min) | Molecular weight | Molecular structure |
|---|---|---|
| 12.95 | 94 |  |
| 15.35 | 120 |  |
| 23.07 | 134 |  |
| 25.95 | 136 |  |
| 41.908 | 228 |  |

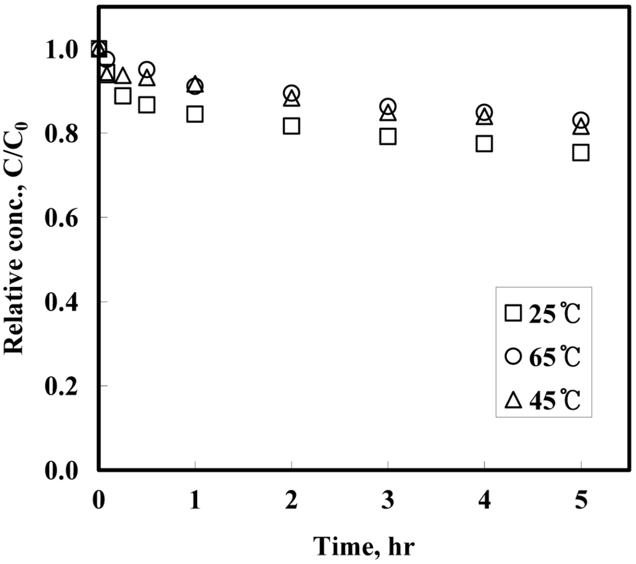


**Fig. 4. BPA adsorption efficiency of $TiO_2$ at different temperatures ($TiO_2$ conc. 1 g/L, initial BPA conc. 10 mg/L).**

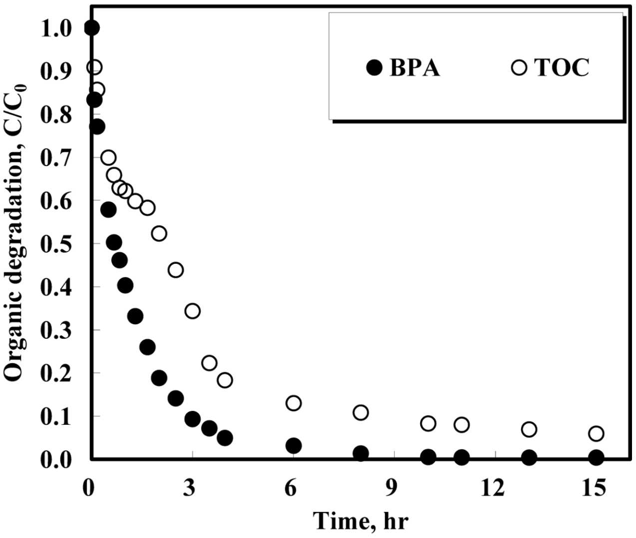


**Fig. 5. Overall organic degradation efficiency of AOP treatment with adsorption pretreatment ($TiO_2$ conc. 1 g/L, initial BPA conc. 10 mg/L).**

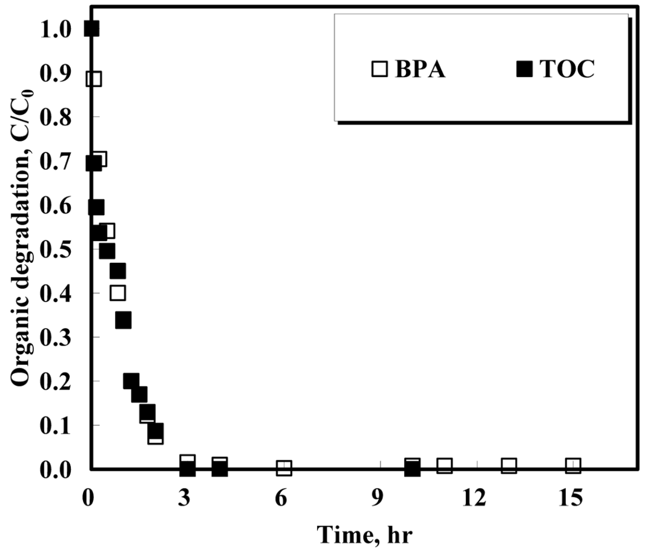


**Fig. 6. BPA and TOC removal efficiencies of hybrid photooxidation process (UV/$TiO_2$/Ozone) with adsorption pretreatment ($TiO_2$ conc. 1 g/L, initial BPA conc. 10 mg/L, adsorption time 5 hrs, temp. 25 °C).**

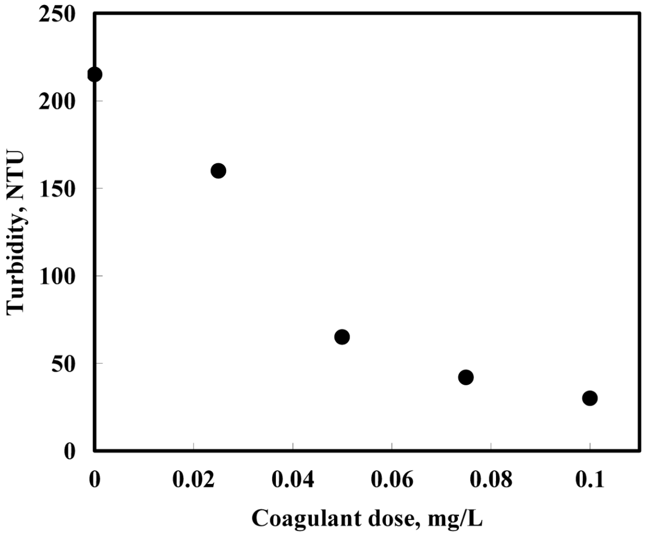


**Fig. 7. Second stage coagulation efficiencies in terms of turbidity removal for various $FeCl_3$ coagulant doses.**

its intermediate compounds (Fig. 6). Rapid destruction of TOC was observed. Within about 3 hours of photocatalytic operation, all the BPA and the organic by-products were removed completely when operated in combination with ozone. A similar synergistic organic degradation effect was reported when $TiO_2$ photocatalyst was combined with ozonation [Hur et al., 2005].

### 2. Separation of $TiO_2$

Fig. 2 shows the various treatment stages involved in the separation of $TiO_2$ particles from solution that would be necessary after photocatalysis, in order to prevent any secondary pollution and to obtain reusable quality final treated water. Initial turbidity of more than 4,000 NTU for initial $TiO_2$ concentration of 1 g/L was decreased to about 215 NTU in the first stage of coagulation and settling by simple pH adjustment (pH 6.3, isoelectric point for $TiO_2$). More than 90% of $TiO_2$ was settled in this stage. The settled $TiO_2$ could be reused as photocatalyst with minimum treatment, as it would be free from coagulant chemicals. With ferric chloride ($FeCl_3$) coagulant addition, at various concentrations, in the second stage, further decrease in turbidity (hence $TiO_2$ removal) was achieved (Fig. 7).

The performance of hollow fiber submerged MF membrane (pore size 0.4 μm), based on permeate flux, for the separation of $TiO_2$, with and without coagulation pretreatment system, is shown in Figs. 8 and 9, respectively. Fig. 8 shows the permeate flux patterns when no coagulation process was applied ($TiO_2$ suspension from AOP process was directly used for the membrane process) and after first stage coagulation and settling (using simple pH adjustment). It was found that although with single stage coagulation, membrane foul-

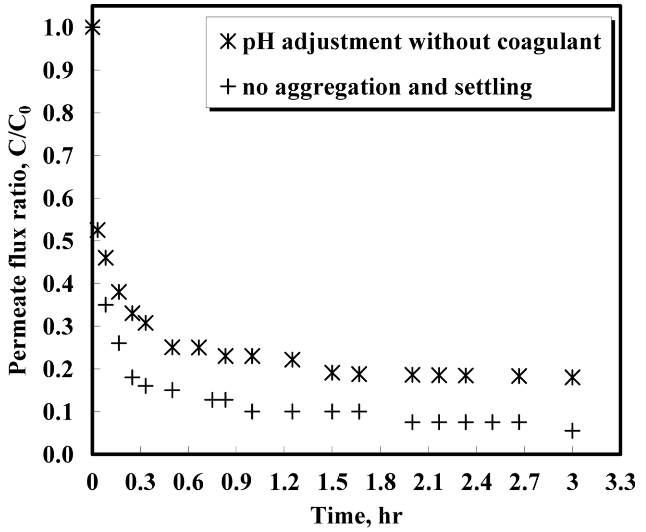


**Fig. 8. Permeate flux pattern in microfiltration membrane without coagulation pretreatment and with first stage coagulation.**

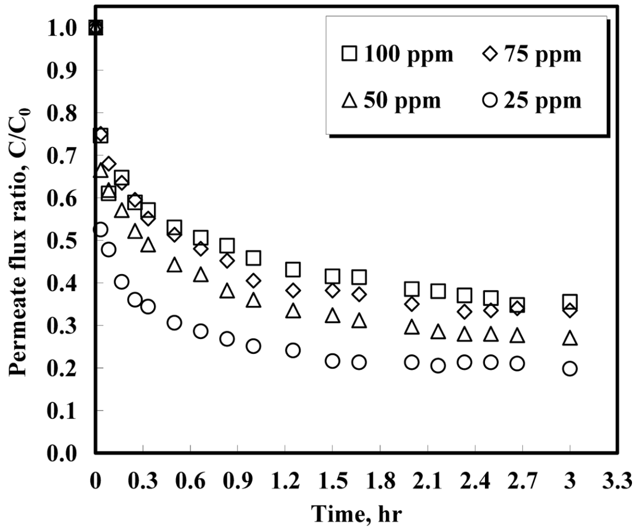


**Fig. 9. Permeate flux development for two stage coagulation-membrane hybrid system at various coagulant concentrations.**

ing was reduced compared to the process without any coagulation, fouling was still significant in both cases. On the contrary, Lee et al., 2001, reported no flux decline while using $TiO_2$ suspension with cross flow ultrafiltration (UF) membrane. Several factors such as pH of the solution, feed concentration, and hydrodynamic conditions play an important role, especially while $TiO_2$ particle separation is adopted. $TiO_2$ particles show the greatest degree of polydispersity and are extremely sensitive to solution pH. In the study by Xi and Geissen [2001], on $TiO_2$ separation using cross flow membrane, an increase in permeate flux by about 60% was noticed at pH 6.9, in comparison with only 16% at pH 5.0. It is also important to mention, in the present study, that organic materials (BPA and its by-products from oxidation) were not present in the $TiO_2$ suspension. The fouling pattern, cake resistance and hence the flux development would all be significantly different in such a case [Lee

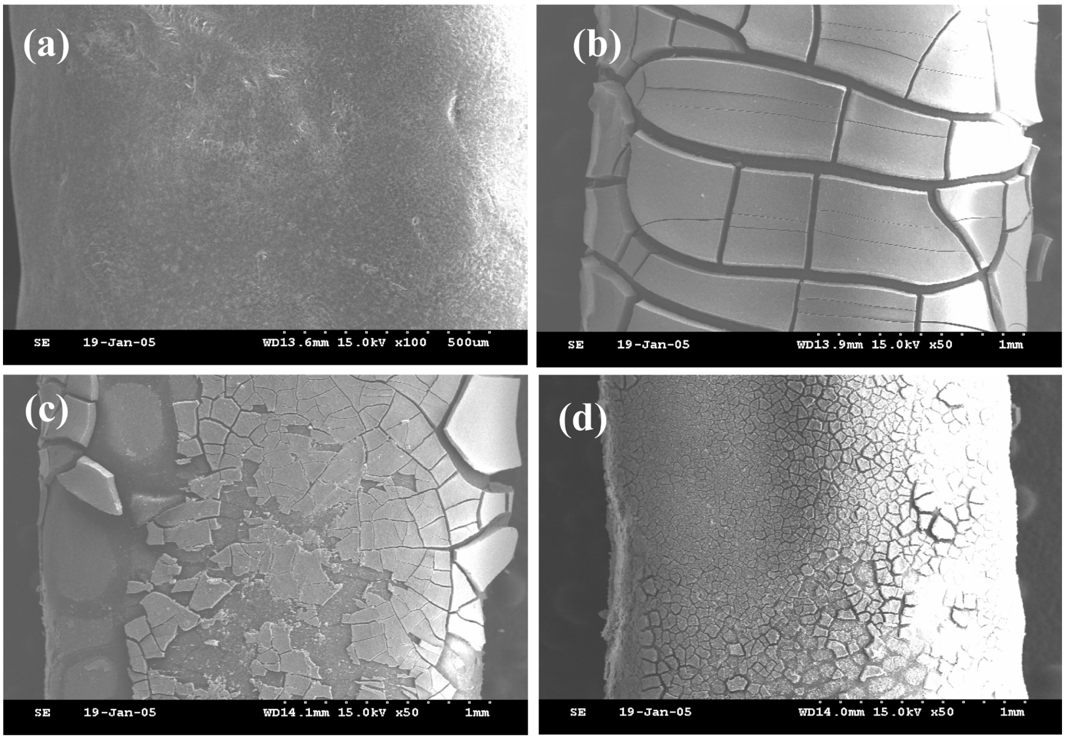


**Fig. 10. SEM images of membrane surface (a) Surface of clean membrane, (b) Surface of membrane with $TiO_2$ deposit when carried out without coagulation pre-treatment, (c) Surface of membrane with $TiO_2$ deposit when carried out with single stage coagulation pre-treatment, (d) Surface of membrane with cake deposit when carried out with two stage coagulation pre-treatment.**

et al., 2001].

However, based on the present study, it is evident that adopting two stage coagulation pre-treatment would significantly reduce membrane fouling (hence prolong the life of the membrane in long-term operation) and 50 ppm of ferric chloride concentration was found to be the optimum amount based on the flux development (Fig. 9). Increase in coagulant dose more than 50 ppm, resulted in only marginal improvement in flux. The permeate turbidity constantly remained well below 0.1 NTU. The $TiO_2$ aggregates or the flocs were made larger than the membrane pore size (0.4 μm) and hence particle-free fluid was transported through the membrane, thereby achieving a complete separation. Fig. 10 shows the amount of particles (cake thickness) on the surface of the membrane, when studied under SEM. Significant reduction in the amount of particle deposit on the membrane after two stage coagulation and sedimentation (Fig. 10d) compared to the operation after a single stage (Fig. 10c) or without coagulation stage (Fig. 10b), would help in explaining the flux development patterns obtained. Hence the advantages of applying a two stage coagulation membrane hybrid process include the following: amount of chemical coagulant requirement is decreased; $TiO_2$ settling after the first stage is free from coagulant contamination and could be reused with minimum pretreatment; and a low pressure porous membrane is sufficient (decrease in energy and membrane costs) in obtaining a high quality treated water, significantly reduce sludge production and improve the life of the membrane by minimizing fouling.

### 3. Potential for Continuous Treatment Operation

The series of individual treatment processes adopted in this study can be easily combined together, for continuous treatment operation, with simple process modifications. From a practical viewpoint, this potential for a continuous treatment system is very important. However, detailed experimentation and investigation of optimum operating conditions are needed to evaluate its performance. Although it is beyond the scope of this paper, a brief description of the process stream can be envisaged. With simple modification, adsorption pretreatment (at 25 °C), photocatalytic oxidation (UV/$TiO_2$/ozone) processes can be adopted in the same reactor (effective volume 130 L). After organic degradation, $TiO_2$ can be separated from solution in the first stage of coagulation/settling by simple pH adjustment and more than 90% of $TiO_2$ would be settled. The settled $TiO_2$ can be recovered and can be directly reused in the photocatalytic reactor, as it is free from any chemical coagulant contamination. The supernatant solution (approx. 115 L) can then be treated in the second stage coagulation (using chemical coagulant), further settling most of the remaining suspended particles. The supernatant (approx. 100 L) from the second stage of coagulation is taken to the collection tank and then transferred to the membrane chamber. A collection tank before the membrane operation would help to maintain a constant float for the membrane operation. The permeate water can also be used as make up water in an AOP reactor.

## CONCLUSIONS

Degradation of a toxic endocrine disruptor chemical, bisphenol A (BPA), by advanced photochemical oxidation process and subsequent removal of the photocatalyst ($TiO_2$) using a membrane hybrid system were evaluated. A large size (150 L) photocatalytic reactor with $TiO_2$ as suspension was used in this study. Under these conditions, the presence of adsorption pretreatment significantly improved the overall BPA degradation efficiencies. Inclusion of ozone resulted in the complete degradation of 10 ppm BPA and its photochemical organic by-products within 3 hours of operation. Application of ozone simultaneously during photoreaction produced a synergistic effect in the organic destruction. For the separation of $TiO_2$ photocatalyst (1 g/L), having coagulation pre-treatment to membrane operation significantly reduced membrane fouling. $FeCl_3$ coagulant concentration as little as 50 ppm was found to be the optimum dose to minimize fouling. The final permeate water turbidity was well below 0.1 NTU.

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