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Application of Slurry Type Photocatalytic Oxidation-Submerged Hollow Fiber Microfiltration Hybrid System for the Degradation of Bisphenol A (BPA)

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Abstract: A pilot scale, slurry type photocatalytic reactor, followed by submerged hollow fiber microfiltration (MF) membrane hybrid system was evaluated for simultaneous and complete destruction of toxic organic chemical bisphenol A (BPA) and separation of photocatalyst TiO_2; in order to obtain a reusable quality water. With simple modification to the treatment operation, the effect of photocatalytic reaction at modest variations in temperature was examined. Adsorption pretreatment was carried out prior to photocatalysis (UV/TiO_2). BPA adsorption ability on TiO_2 was very less (about 15%) at 25°C. However, adsorption pretreatment followed by photocatalytic oxidation (UV/TiO_2) at an elevated nearly constant temperature (about 70°C) helped in increasing the BPA degradation efficiency. The effect of ozone introduction into the treatment stream was also analyzed. Applying ozone along with UV/TiO_2, brought about a synergistic effect on BPA degradation. Within 3 h, entire 10 ppm of BPA and the by-product organic compounds were completely removed. TiO_2 particle separation performance using hollow fiber membrane was enhanced by adopting a two-stage coagulation/sedimentation pretreatment. With initial turbidity of 4000 NTU, the turbidity of the final permeate water was well below 0.1 NTU. Almost complete removal of 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, TiO_2 easily separated after treatment and capable for reuse as it is free from chemical coagulant contaminants, reusable

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quality water is obtained, and the system has the potential for continuous operation with simple process modifications.

Keywords: Hybrid process, bisphenol A (BPA), photocatalytic oxidation, TiO_2, submerged hollow fiber microfiltration

INTRODUCTION

An important monomer chemical for the production of polycarbonate and polysulophone plastics and epoxy resins is 4,4′-isopropylidenediphenol (bisphenol A, BPA) and hence it can be commonly found in compact disks, food can linings, thermal paper and paper coatings, adhesives, plastic drink bottles and containers, composite dental fillings and sealants, and in sheating of electrical parts. It has also been used as a reaction inhibitor, antioxidant, and flame retardant. Many countries throughout the world have large production capacities for BPA, especially Germany, the Netherlands, the United States, and Japan. It is estimated that about 1 million tonnes of BPA is produced in the United States each year and in the European Union (EU) alone; in 1997/98, annual consumption of BPA was estimated at approximately 640,000 tonnes (640×10^6 kg) per year (1). The global production is reported to be increasing at about 7% per year.

A recent report by the European Commission (2) and others (1, 3, 4) have revealed the endocrine disrupting effects of BPA. BPA has exhibited estrogenic activity and alters metabolic kinetics, induces DNA damages, and results in chromosomal aberrations (3). On the other hand, the release of BPA into the natural environment as well as in surface waters occurs not only from the discharges from BPA manufacturing plants but also has been reported from aquatic streams containing plastic debris and landfill leachate (5, 6). According to the American standards the maximum allowable limit of BPA concentration in the natural water is 0.1 mg/L (7). Hence, considering the widespread application of BPA with its high risk of exposure and health hazard, there is a strong need for a suitable and effective remediation treatment technology for the destruction of BPA from water.

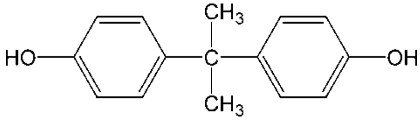
Recently, advanced oxidation processes (AOPs) with UV radiation, ozone, and hydrogen peroxide are gaining growing acceptance for the treatment of organic materials (8). These processes are based on the production of and utilization of hydroxyl radical, which serve as powerful oxidants to convert organic pollutants into carbon dioxide, water, and less toxic by-products of a low molecular weight. The photocatalytic oxidation using UV radiation along with titanium dioxide (TiO_2) photocatalyst has attracted much attention as a promising method due to its easy handling, high stability, and effectiveness (9). Although its effectiveness for treating several organic chemicals has been well documented (10–12), its performance for endocrine disrupting toxic chemicals like BPA has received comparatively less attention (13–15). 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 L.

An important factor while using the UV/TiO_2 system is the mode of TiO_2 application. TiO_2 photocatalyst in the form of powder can either be suspended as slurry in the water or fixed on a carrier material such as glass, concrete, or ceramics (16, 12, 17). Due to limiting mass transfer and a loss of photocatalytic activity by the fixation (16), using TiO_2 as slurry is far more superior compared to fixed ones with respect to photocatalytic degradation efficiency (18). However, when using TiO_2 in suspension, separation of TiO_2 from water after photocatalytic reaction, in order to prevent secondary pollution, presents a major challenge. 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. Very few attempts have been made before, in studying the separation of TiO_2 particles from water (19–21). Kagaya et al. (19) studied the TiO_2 removal by coagulation using aluminium chloride. While using the coagulation and settling process, it must be taken into account that the TiO_2 particles must be recovered from the sediment, which would require several treatment procedures before it could be reused. The other aspect is the amount of sludge generated for disposal, that must be minimized. Lee et al. (20) and Xi and Geissen et al. (21) used flat sheet ultrafiltration and microfiltration membranes, respectively, for TiO_2 separation.

The present study deals with the application aspect of photocatalytic oxidation and includes both 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. With simple modifications in the method of operation and by combining adsorption and ozone to photocatalysis, BPA degradation efficiency was briefly evaluated. Further, the separation of TiO_2 by two-stage coagulation (with ferric chloride as coagulant) followed by submerged hollow fiber MF membrane hybrid system was also studied.

MATERIALS AND METHOD

The BPA used in this study was purchased from Junsei Chemical Co., Ltd. (Japan). The chemical structure of BPA is shown below.



BPA aqueous solutions were prepared with ultra pure water from reverse osmosis (RO) treatment. A 2.5-inch (Model AG 2540FF, Osmonics) spiral wound RO membrane was used. Four membrane elements were used, with active surface area of 2.5 m^2/element. The capacity of the unit is 2.7 m^3/d, typical operating pressure is 1379 kPa, and NaCl rejection is 99.5%/99.0% (average/minimum). P-25 TiO_2 particles (Degussa, Germany) were used as photocatalyst and adsorbent for the experiments. Average diameter, (Brunauer Emmett Teller) BET (22) surface area, and density of TiO_2 particles were 20 ± 5 nm, 50 ± 15 m^2/g, and 3.89 g/cm^3 at 20°C, respectively

A 150 L capacity, cylindrical shape, batch-type semi-pilot-scale photocatalytic reactor was used. Detailed information of the reactor dimensions and the placement of the irradiation light source can be seen in Fig. 1. The TiO_2 suspension containing BPA was irradiated in the photocatalytic reactor 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 μW/cm^2 and the wavelength was 253.7 nm. The effective volume of the liquid within the reactor was about 130 L. The amount of TiO_2 used was fixed at 1 g/L and the initial solution pH at 6, throughout this experimental study. The initial concentration of BPA was varied between 10–100 mg/L. TiO_2 in aqueous solution was kept in suspension in the reaction vessel with circulation pump (centrifugal pump, 1 HP, capacity 1 m^3/h). The temperature of the solution inside the reactor was monitored periodically.

Due to constant recirculation of the suspension, using the circulation pump, and the heat from the UV lamps, the temperature of the solution in the reactor gradually increases. Initially, the increase was quicker, and after a while the variation in temperature was very slow, almost steady. So the performance of the photocatalytic system operated during the increase in temperature and after attaining a steady state was evaluated. In the case where the temperature was allowed to reach the steady state, before photocatalysis, only the recirculation pump was used to increase the solution temperature and the UV lamp remained switched off.

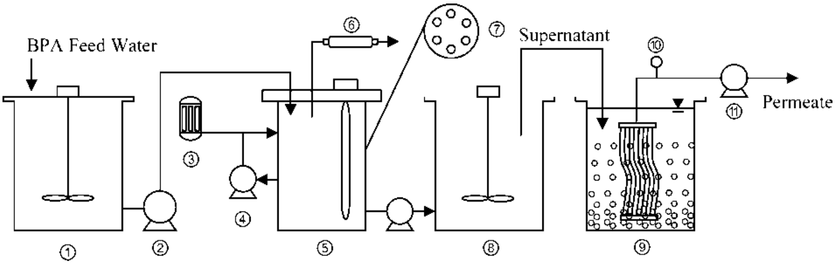


Figure 1. Schematic of entire hybrid treatment process for organic destruction and particle separation. (①: Adsorption tank, ②: Feed Pump, ③: Ozone Generator, ④: Recirculation Pump, ⑤: AOP Reactor, ⑥: Ozone Scrubber, ⑦: Inset showing the UV lamp placement in the AOP reactor, ⑧: Coagulation/Sedimentation Tank, ⑨: Submerged MF Membrane Separation Tank, ⑩: Vacuum Gauge, ⑪: Suction Pump).

BPA adsorption by TiO_2 was carried out for a period of 5 h, at different temperatures (25, 45, and 65°C), separately in a dark and constant temperature bath prior to photocatalysis. For continuous mixing, air compressor (1/3 HP, 105 L/min, 1760 rpm) was used to blow air and the tube was fitted with 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 h. Constant amount of ozone (ozone generator capacity 2.4 g/h) was introduced prior or along with photocotalysis and the performance was evaluated based on the temperature conditions explained previously. Dissolved oxygen (DO) concentration was monitored constantly, using DO meter (NEOMET 29D, Istek, Korea).

The amount of BPA in the aqueous solution was measured by total organic carbon (Shimadzu 500A, Japan) and a 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.

Separation of TiO_2 from water was performed using a coagulation membrane hybrid process. Coagulation method was carried out in two stages, in order to enhance its efficiency of TiO_2 separation. In the first step, having determined the isoelectric point (or zero point charge, ZPC) of TiO_2 as at pH 6.3 (Fig. 2), using zeta analyzer (Electrophoretic Light Scattering, ELS-8000, Photal, Otsuka, Japan), the solution was fixed at that pH and the particles were aggregated and settled by adopting the standard method for coagulation and sedimentation (23). 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 varied from 0–100 mg/L. After settling, the supernatant from the second stage was further treated using submerged hollow fiber microfiltration (MF) membrane (SuperMAK, ENE, Korea). The membrane material was PVDV, pore size 0.4 μm, surface area 0.02 m^2, and the internal and external surface areas were 1.8 mm and 2.0 mm respectively. Membrane operation was carried out with and without coagulation pretreatment. Also, the effect of operating pressure on the membrane performance was carried out.

The efficiency of TiO_2 separation was evaluated by examining turbidity (Turbidity meter, HACH 2001A), particle size (Laser Refraction Particle

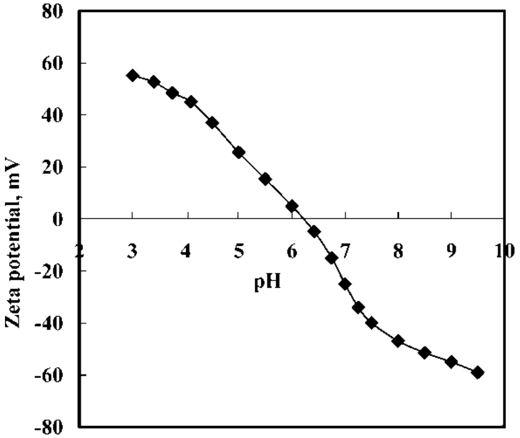


Figure 2. Zeta potential at different pH values of aqueous suspension of TiO_2.

Size Analyzer SALD-2001, Shimadzu, Japan and Electrophoretic Light Scattering, ELS-8000, Photal, Otsuka, Japan). The performances of the membrane were evaluated by examining the turbidity removal and permeate flux development. The surface of the clean and membrane with particle deposit were analyzed using Scanning Electron Microscopy (SEM) (HITACHI, Japan, Model S-4700), in order to understand the underlying effect of fouling in the membrane. The schematic diagram of the overall treatment process consisting of adsorption chamber, photocatalytic reactor followed by coagulation and submerged hollow MF membrane hybrid system is shown in Fig. 1.

RESULTS AND DISCUSSION

Degradation of BPA

Figure 3 shows the degradation efficiency of organic material in photocatalytic oxidation process. In particular, Fig. 3a shows the BPA removals at different initial concentrations (10, 50, and 100 ppm). The solution temperature sharply increases from 33°C to 69°C due to continuous recirculation (by recirculation pump) and the heat from UV lamps inside the reactor. The rate of increase in solution temperature from 33°C to 69°C was same throughout the study. The operating conditions such as the solution temperature, UV lamp intensity, and liquid circulation were maintained the same in order to have a steady and gradual increase without any sudden fluctuation in solution temperature. Under the study conditions, it can be seen that a long period of operation was required for degradation. After 10 h, removal efficiencies of 78%, 55%,

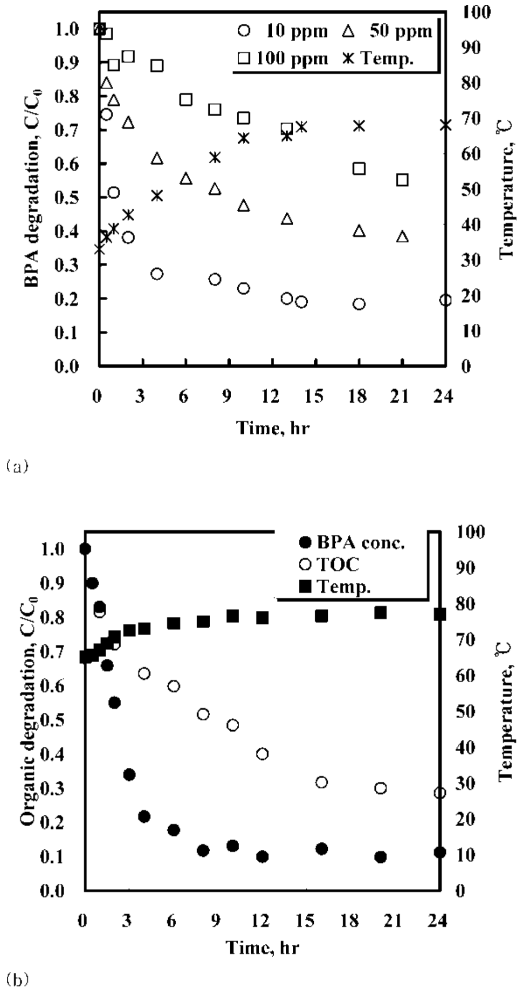


Figure 3. Organic destruction efficiency by photocatalytic oxidation process. (TiO_2 conc. 1 g/L, Initial solution pH 6) (a) BPA destruction efficiencies for different initial BPA concentrations at increasing solution temperature condition, (b) BPA and intermediate organic destruction efficiencies at an elevated and nearly constant solution temperature (Initial BPA conc. 10 ppm, Initial TOC 10.145 ppm).

and 30% were achieved for initial BPA concentration of 10, 50, and 100 ppm, respectively.

It was found that by starting the photocatalytic reaction process after the solution temperature has been raised to elevated temperature (69°C), simply by recirculating the solution within the reactor using circulation pump, the efficiency of BPA degradation increased slightly (about 10%) (Fig. 3b). No direct heat source was provided, for raising the solution temperature in the present study; however it would be possible, depending on the quantity of solution to be treated. During the course of the reaction BPA was transformed into other organic intermediates, as evident from the TOC concentration in the solution (Fig. 3b). Most of the photocatalytic studies have employed aqueous solutions at ambient temperatures and very little information is available to compare the temperature effect on photocatalytic degradation, especially in the range of 25–80°C. It is evident that increasing the temperature above 80°C, tending toward the boiling point of water, the activation energy becomes negative, thereby leading to the decrease in photocatalytic efficiency (24). However, a reasonable increase in organic degradation efficiency has been reported for phenol and trichloroethylene (TCE) with modest increase in temperature (25, 26). Although precise role of reaction temperature on photocatalytic degradation requires further understanding, a recent study by Habibi et. al. (27) reported that solution temperature could affect both TiO_2 photocatalyst and the bulk properties including organic molecules. It was also indicated that certain organic materials could have an affinity to interact with TiO_2 surface, at elevated temperature. A substantial increase in the efficiency of photocatalytic degradation of bisphenol A, due to the increase in solution temperature was also observed by Kaneco et al. (14). All these factors indicate that a moderate increase in solution temperature (30–70°C) during TiO_2 photocatalytic oxidation of organic material help in increasing the performance of the system.

Adsorption effect combined to photocatalysis had a positive effect on the overall efficiency of BPA degradation. Before discussing the combined effect, BPA adsorption by TiO_2 alone at different temperature was evaluated. Adsorption efficiency of 10 ppm concentration of BPA on 1 g/L of TiO_2 was about 16% after 5 h of operation at 25°C. However, increase in temperature (45, 65°C) had a negative effect with about 5–10% BPA degradation. Hence in the combined process (Fig. 4), adsorption (at 25°C) was carried out as pretreatment to photocatalysis. Overall efficiency of BPA degradation increased by having a combined adsorption photocatalytic combined process. Further increase in efficiency was observed when the photo catalytic reaction was carried out at a near constant elevated temperature (70–75°C), as shown in Fig. 3. All the 10 ppm of BPA including the intermediate organic materials were completely mineralized within 10 h of photocatalytic operation.

Addition of ozone to the process stream was found to be beneficial in enhancing the overall efficiency of BPA degradation (Fig. 5). Here the point of ozone application and the reaction temperature were found to have an important role. Supplying ozone prior to photocatalysis (after adsorption) was found to be less efficient compared to supplying ozone during photocatalysis as shown in Fig. 5a. The difference was more pronounced for the TOC destruction pattern than BPA. Within about 3 h 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

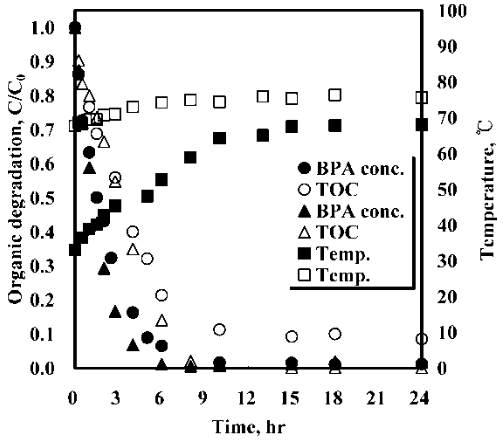


Figure 4. Overall BPA and TOC removal efficiencies at different solution temperature conditions by photocatalytic oxidation with adsorption pretreatment. (Symbols: Circles correspond to operation at increasing solution temperature and Triangles at constant solution temperature) (TiO_2 conc. 1 g/L, Initial BPA Conc. 10 ppm, Adsorption temperature 25°C, duration 5 h).

with ozonation (28). The dissolved oxygen in the aqueous solution varied with solution temperature as shown in Fig. 5b.

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 (16, 29) as well as in the alkaline (30, 14) regions. In the present study, initial pH of the solution was chosen at 6, where the surface charge on TiO_2 is minimal (Fig. 2). The point of zero charge for photocatalyst TiO_2 at around pH 6 was also reported earlier by Chou and Liao (31), Yang et al. (32) and Kosmulski (32). Operating at this pH would also avoid 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 was further oxidized to aliphatic compounds and finally mineralized to carbon dioxide. Most prominently, four kinds of derivatives such as phenol, acetophenone, 2-methyl-2,3-dihydro-1-benzofuran, 4′-Hydroxyacetophenone with molecular weights of 94, 120, 134, 136. Most of these intermediate by-products identified were

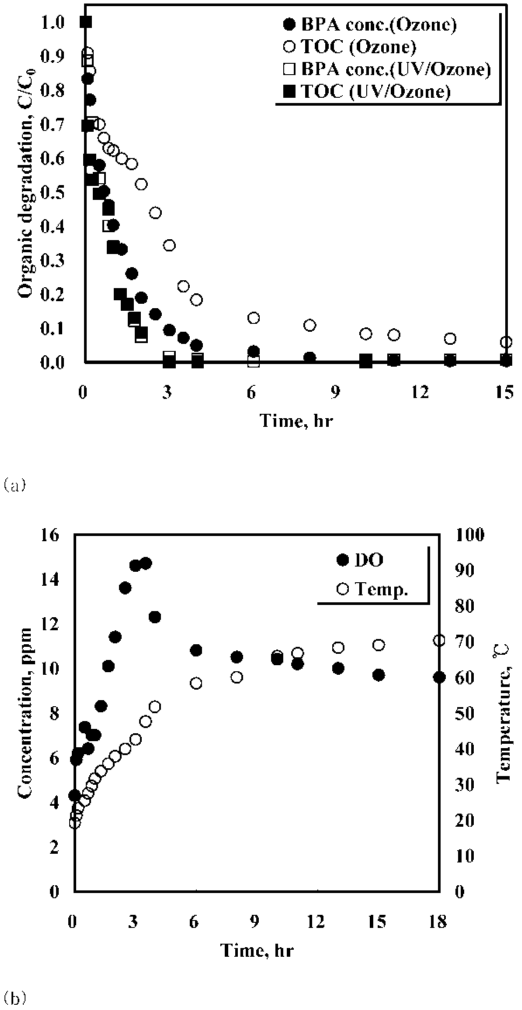


Figure 5. Performance with ozone inclusion into the process stream. (a) BPA and TOC removal efficiencies when ozone applied prior to UV oxidation (Initial BPA conc. 10 ppm, TiO_2 conc. 1 g/L), (b) dissolved oxygen conc. in solution at different temperatures).

in agreement with earlier studies in BPA degradation (16, 14). However, it is to be noted that initial pH of the solution would have a large influence on the photocatlytic pathway of BPA degradation (15).

Based on the stable intermediate materials obtained from the GC-MS data, four possible breakdown pathways, by the free radicals, can be envisaged, as shown in the Fig. 6. Some of the free radicals that could be formed during photocatalytic oxidation of BPA are hydroxyl radical, hydrogen radical, phenol free radical, propenyl free radical, and 4-isopropyl

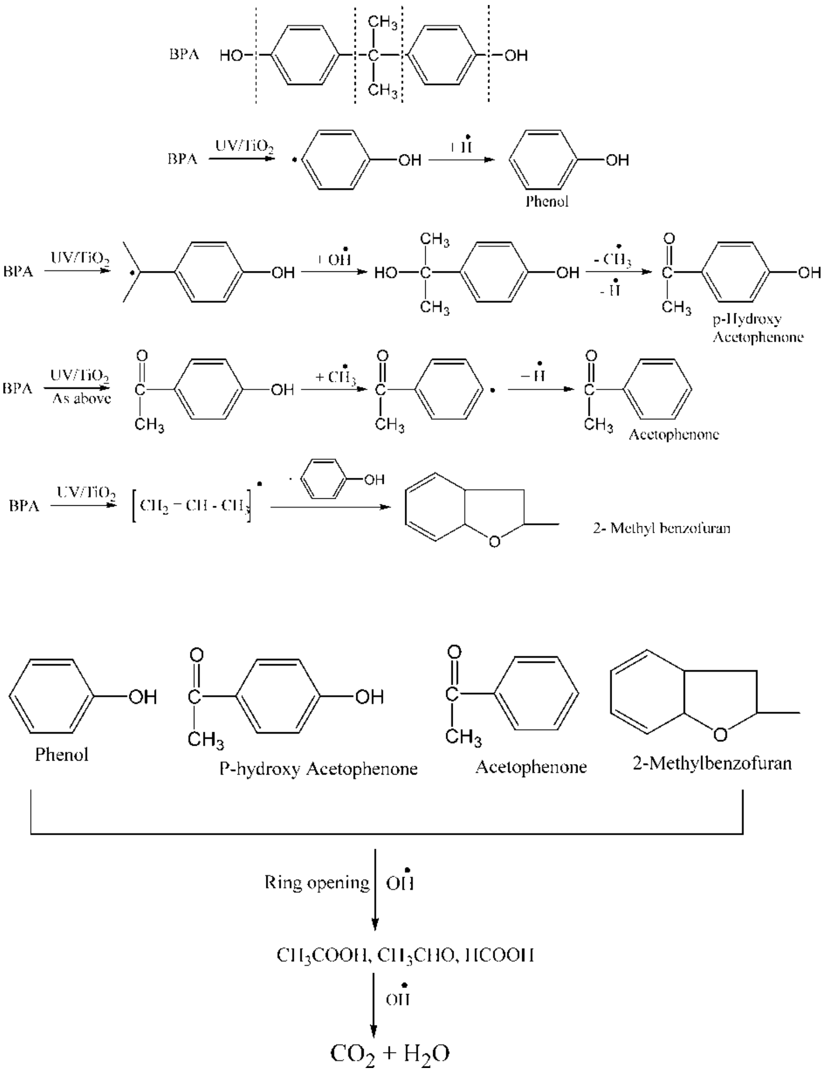


Figure 6. Possible mechanism of BPA degradation with breakdown sequence of the intermediates.

phenol radical. For understanding, the dotted lines (Fig. 6) represented in the BPA chemical structure are the possible areas for cleavage of the BPA molecule to form the above-mentioned radical species. The aliphatic compounds produced by the ring opening reactions of the above-mentioned aromatic intermediates are easily broken and mineralized to carbon dioxide and water and hence no peak was observed in the GC-MS data, for these aliphatic compounds.

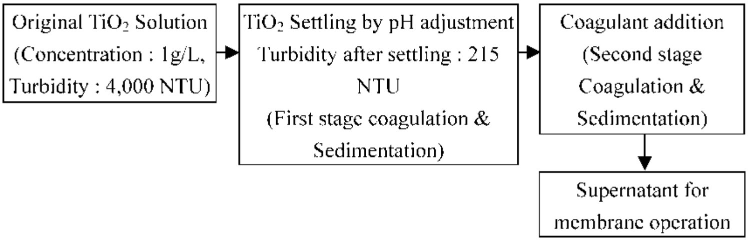


Figure 7. Flow diagram of various stages adopted for TiO_2 particle separation by coagulation-membrane hybrid process.

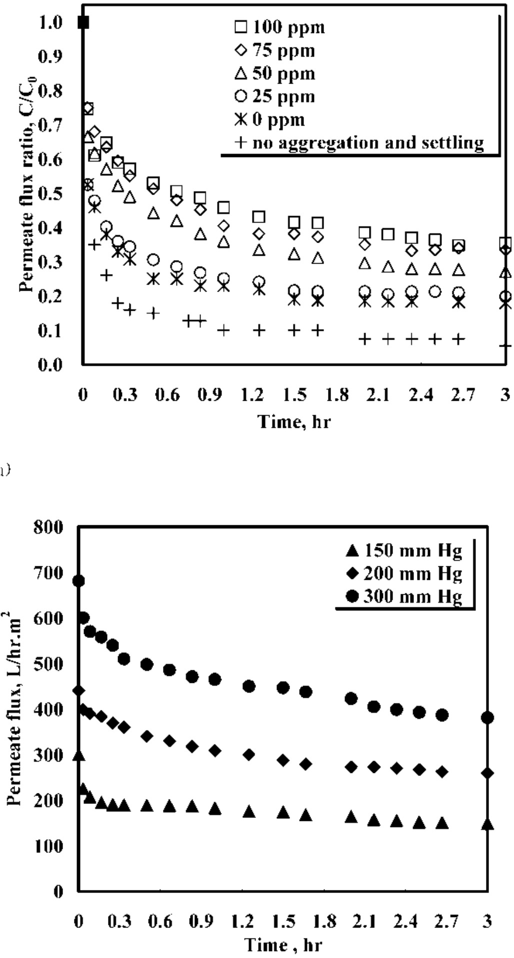
Separation of TiO_2

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, is shown as a flowchart in Fig. 7. Initial turbidity of more than 4000 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 is 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 as shown in Table 1.

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 Fig. 8. It is difficult to compare this performance as there are no similar studies (two-stage coagulation and settling followed by submerged hollow fiber MF membrane) available so far. However, based on the present study, it is evident that adopting coagulation pretreatment would significantly reduce membrane

Table 1. Coagulation efficiency (second stage coagulation) in terms of turbidity at different $FeCl_3$ coagulant dose

Coagulant dose, ppm	Supernatant turbidity, NTU
25	160
50	65
75	42
100	30



(a)

(b)

Figure 8. Performance of the membrane process based on permeate flux development (a) Flux development patterns with and without coagulation pretreatment (operating pressure 200 mmHg). (b) Permeate flux pattern at different membrane operating pressures ($FeCl_3$ conc. 50 ppm).

fouling (hence prolong the life of the membrane in long-term operation) and 50 ppm of ferric chloride concentration was found to be optimum amount based on the flux development (Fig. 8a). Increase in coagulant dose more than 50 ppm resulted in only marginal improvement in flux. Although adopting a single-stage coagulation and settling, i.e., just pH adjustment and without addition of coagulant (0 ppm, Fig. 8a), experienced considerable membrane fouling, it was far superior compared to membrane operation without coagulation pretreatment (no aggregation and settling, Fig. 8a). On the contrary, Lee et al. (20), 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 adopting TiO_2 particle separation. TiO_2 particles show greatest degree of polydispersity and are extremely sensitive to solution pH. In the study by Xi and Geissen (21), 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. It is also important to mention, in the present study, 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 significantly differ in such a case (20).

With a specific amount of coagulant (50 ppm), increase in membrane operating pressure resulted in the increase in permeate flux (Fig. 8b). However, the rate of flux decline was also slightly higher. Time taken to attain steady-state flux was also longer with the increase in operating pressure. However, the permeate turbidity constantly remained well below 0.1 NTU. The efficiency at each stage of the hybrid system, in terms of turbidity and particle removal, is given in Table 2. The particle sizes of TiO_2 and the flocs are highly sensitive to pH as the extent of aggregation is governed by the pH. Hence the pH and the standard deviation values are also reported in Table 2. The TiO_2 aggregates or the flocs are larger than the membrane pore size (0.4 μm) and hence retained by the membrane and a particle-free fluid is transported through the membrane; thereby achieving a complete separation. Figure 9 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. 9g) compared to the operation after a single stage (Fig. 9e,f) or without coagulation stage (Fig. 9c,d), would help in explaining the flux development patterns obtained. Hence the advantages of applying a two-stage coagulation membrane hybrid process includes the following; the amount of chemical coagulant requirement is decreased, TiO_2 settled after the first stage is free from coagulant

Table 2. TiO_2 separation performance at various stages of coagulation-membrane hybrid process (initial TiO_2 conc. 1 g/L, $FeCl_3$ coagulant amount 50 ppm)

Parameters	Initial	After coagulation	Permeate
Turbidity, NTU	4,000	65	0.05
Particle size, μm	0.55	3.5	<0.003
pH	2.5	6.8	6.6
Stand. dev.	0.22	0.387	—

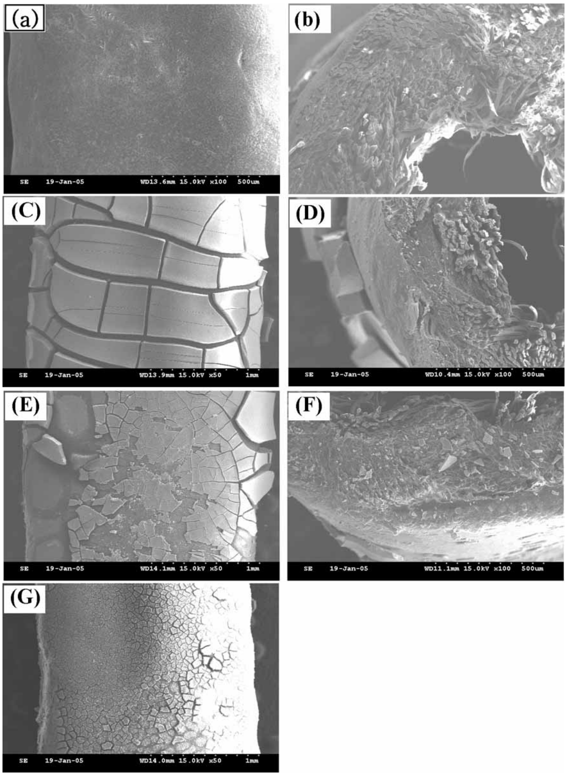


Figure 9. SEM images of membrane surface (a), (b) Side and cross-section views of clean membrane surface. (c), (d) Side and cross-section views of membrane operated without coagulation pretreatment, showing thick TiO_2 cake deposit. (e), (f) Side and cross-section views of membrane operated with single-stage coagulation/settling pretreatment. (g) Side view of the membrane after two-stage coagulation/settling pretreatments ($FeCl_3$ conc. 50 ppm).

contamination and could be reused with minimum pretreatment, low-pressure porous membrane is sufficient (decrease in energy and membrane costs) in obtaining a high-quality treated water, significantly reduces sludge production and improves the life of the membrane by minimizing fouling.

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. In a practical viewpoint, this potential for continuous treatment system is worth mentioning. However, detailed experimentation and investigation of optimum operating conditions are essential.

CONCLUSIONS

Degradation of a toxic endocrine disruptor chemical, bisphenol A (BPA), by semi-pilot-scale advanced photochemical oxidation process and subsequent removal of the photocatalyst (TiO_2) using membrane hybrid system were evaluated. Effect of temperature had a positive effect in the overall improvement in the organic degradation efficiency. Moreover, operating the system with solution at a moderately elevated constant temperature (about 70°C) obtained an appreciable increase (about 10%) in photocatalytic efficiency, compared to the condition at continuous increase in temperature (30–70°C). Under these conditions, presence of adsorption pretreatment significantly improved the overall BPA degradation efficiencies. Inclusion of ozone, achieved complete degradation of 10 ppm BPA and its photochemical organic by-products within 3 h 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 pretreatment to membrane operation was found to be imperative and significantly reduced membrane fouling. Ferric chloride 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. With the coagulation membrane hybrid system, the particle size of fine TiO_2 particles were aggregates and the flocs formed were much larger than the membrane pore size (0.4 μm) and hence able to be retained by the membrane and a particle-free fluid was transported through the membrane; thereby achieving a complete separation.

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