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TiO_2/UV and Ultrafiltration Membrane Process for the Degradation of Bisphenol A Dissolved in Water

Key-Hwan Noh[a], Tea-Ouk Kwon[a], Jae-Wook Lee[b], Il-Shik Moon[a*]

[a]Department of Chemical Engineering, Sunchon National University, Suncheon 540-742, Korea
Tel. +82 (61) 750-3581; Fax +82 (61) 750-3580; email:reaction@sunchon.ac.kr
[b]Department of Chemical Engineering, Seonam University, Namwon 590-170, Korea

Introduction

Many types for environmental pollutant of endocrine disruptors have been reported on abnormal sexual development and abnormal feminizing responses of animals in a number of literatures [1]. Conventional biological methods for the removal of pollutants in wastewater require long times, and chemical oxiation methods in general cannot completely eliminate. Among various removal technologies, photocatalysis on TiO_2 particles is one of the most promising techniques [2]. However, the pollutants in water are usually much diluted, and those such as endocrine disputors are thought to be harmful even if they are present in an extremely low concentration in the environment. The photocatalytic degradation rate is low in very diluted solutions. Therefore, enrichment of reactants by adsorption is required for highly efficient photocatalytic performance. The separation of TiO_2 particles from treated water, however, is a main problem for practical application process [3]. Thus, we investigated the performance of ultrafiltration membrane for the separation of TiO_2 photocatalysts adsorbing pollutants from water. Especially, the influence of key operating conditions on membrane flux and BPA removal was examined in lab-scale photocatalytic membrane reactor. BPA (bisphenol A) chosen in this study is widely used as a raw material for epoxy and polycarbonate resins and is suspected to act as an endocrine disruptor.

Theory

Flux decline can be caused by several factors, such as concentration polarization, adsorption, gel layer formation and plugging of the pores [4]. The extent of these phenomena is strongly dependent on the types of membrane process and feed solution employed. Eq. (1) is the new working equation of the combined film theory and the solution-diffusion model.

$$R_0/(1-R_0) = [J_V/(D_{AM}K/\delta)][\exp(-J_v/K)] \qquad (1)$$

By supplying R_0 vs. J_V data, taken at different pressures but at a constant feed rate and constant feed concentration for each set, the parameter $(D_{AM}K/\delta)$ and the mass transfer coefficient, k, can be estimated numerically. On the other hand, the working equations of the nonlinear Spiegler-Kedem model is:

$$R_0/(1-R_0) = a_1[1-\exp(-J_V a_2)][\exp(-J_V/k)] \quad (2)$$

where, $a_1 = \delta/(1-\delta)$ (3)

$$a_2 = (1-\delta)/P_M \quad (4)$$

$$R_0 \equiv (C_b - C_p)/C_b \quad (5)$$

Here, δ is the reflection coefficient which represents the rejection capability of a membrane, i.e., $\delta = 0$ means no rejection and $\delta = 1$ means 100% rejection, P_M is the overall permeability coefficient. By using a nonlinear parameter estimation method, we can estimate the membrane parameters o and P_M and the mass transfer coefficient, k, simultaneously, namely, by supplying the data of R_0 vs. J_V taken at different pressures but at constant feed rate and constant feed concentration for each set.

Experimental

The BPA used in this study was purchased from Junsei Chemical Co., Ltd. (Extra pure grade, Japan). Synthetic wastewater samples were prepared by mixing BPA with distilled and deionized water. The concentration of BPA in all of the samples was 100 mg/L. Prior to the photodegradation experiments, the suspension was stirred for more than 12 h in the dark to achieve adsorption equilibrium of BPA on the TiO_2 photocatalysts. The adsorption equilibrium experiments were carried out by contacting a given amount of adsorbent with BPA solution of 100 mg/L in a constant temperature (298.15 K) shaking incubator. Solution pH was adjusted using HCl and NaOH. Three days are enough to reach equilibrium. After equilibrium was reached, the excess BPA left in the solution was analyzed by using UV spectrophotometer (UV 160A, Shimadzu, Japan) at 254 nm. The adsorption capacity of the TiO_2 was determined from material balance. Fig. 1 shows a schematic diagram of the experimental apparatus, which consists of a cross-flow ultrafiltration module and a photocatalytic reactor.

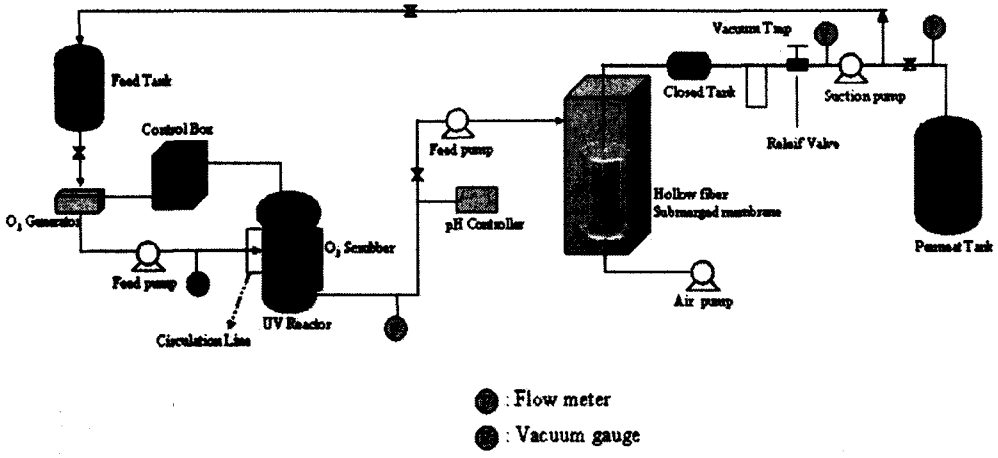

Fig. 1. Schematic diagram of a lab-scale photocatalysis/ultrafiltration system.

Results and Discussion

Adsorption isotherms are the most fundamental and informative data on an adsorption system. Adsorption onto TiO_2 mainly occurs by the dispersed force between the BPA and TiO_2. Therefore, the adsorption capacity depends on the property of adsorbate, temperature, solution pH, and the amount of impurities contained in the solution. Fig. 2 shows adsorption isotherm of BPA on TiO_2 photocatalyst at 298.15 K. The adsorption capacity at 100 mg/L was considerably high (approximately 60 mg/g). There is no effect of light on the adsorption capacity.

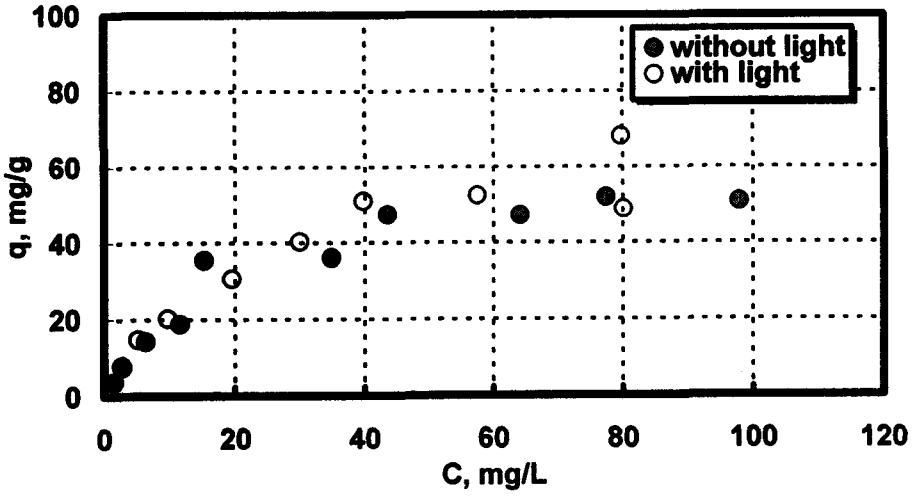

Fig. 2. Adsorption isotherm of BPA on TiO_2 photocalyst at 298.15 K.

As shown in Fig. 3, the effect of pH on the concentration decay curves of BPA in batch adsorber was very low. Also, the experimental results show that 5 h is enough to

reach the adsorption equilibrium and the adsorption capacity is independent on the solution pH. Contrary to our expectation, the flux decline of ultrafiltration membrane was relatively substantial because of the formation of denser cake layers by TiO_2 particles. The flux decline was evaluated by membrane parameters and the mass transfer coefficient determined by indirect measurements using the combined film theory/solution-diffusion (CFSD) model and the combined film theory/Spiegler-Kedem (CFSK) model by a nonlinear parameter estimation method.

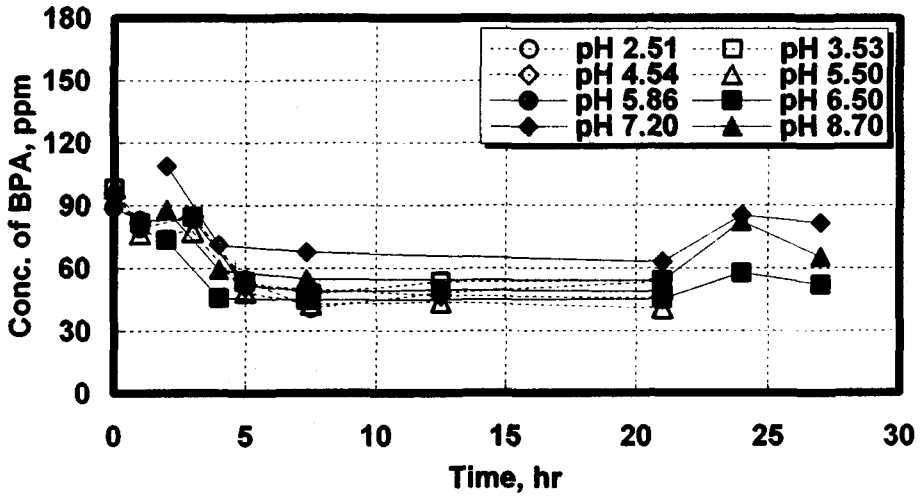

Fig. 3. Effect of pH on the concentration decay curves of BPA in batch adsorber.

Acknowledgement

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