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Removal of soluble organics from water by a hybrid process of clay adsorption and membrane filtration

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Abstract

The removal of phenol and *o*-cresol from water by a hybrid process of clay adsorption and ultrafiltration (clay-UF) was studied. Batch adsorption equilibrium experiments showed that the amount of adsorption for phenol and *o*-cresol decreased in the order kaolin > montmorillonite at an equilibrium pH (pH_e) of 9.1. The clay-UF experiments were performed as a function of clay dose, solution pH, and transmembrane pressure. The role of pH in clay-UF process mainly depended on the acid–base nature of phenols and clays, and the charge of UF membrane. The rejection of phenol increased with increasing pH, and had a maximum at $pH_e = 8.2$ with kaolin but at $pH_e = 9.1$ with montmorillonite. The rejection of *o*-cresol also increased with increasing pH, and had a maximum at $pH_e = 9.2$ with kaolin but at $pH_e = 10.2$ with montmorillonite. Such differences between solute rejections depended on the pK_a of the solutes, zeta potential of the clays, and surface charge of the membrane. The amount of soluble organics adsorbed onto the surface of membrane was negligible and the flux slightly decreased with increasing transmembrane pressure.

Keywords: Phenol; Cresol; Clay; Adsorption; Nanofiltration; Ultrafiltration

1. Introduction

Various physicochemical and biological methods could be used to remove soluble organics from wastewater. Among these, pressure-driven membrane processes such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) have been increasingly paid attention because they need less energy and solvent spending [1]. UF and MF processes are the alternatives to conventional clarification and filtration methods. For the removal of trace levels of dissolved organics such as methanol, ethanol, carbon tetrachloride, and phenols from water, the membrane processes are efficient only when the membranes have a smaller MWCO such as RO and NF. However, the removal can be alternatively achieved using the membranes with a large MWCO such as UF and MF when they are combined with an adsorption process [2–7]. The basic idea is that the organics can be retained by membranes after the organics are fully adsorbed on the common powder adsorbents. The advantages of such hybrid method are the fast and effective adsorption of organic matter by the adsorbents. The application of adsorption-membrane filtration system in water and wastewater treatment processes is relatively new.

Previous studies have demonstrated that the addition of PAC (powder activated carbon) to membrane filtration process is a simple and cost-effective way to remove dissolved organics [3]. The treatment efficiency of the hybrid system depends on the reactor configuration, operational modes, adsorbent dose, adsorption capacity, and influent characteristics. Depending on the operation mode, continuous-flow stirred tank reactor and plug-flow reactor are two main models used in the design of membrane hybrid systems. Until now, there are many studies examining the removal efficiencies of those combined processes. Tomaszewska and Mozia [3] have investigated the removal of phenol and humic acid by PAC-UF. They showed that backwashing process applied to combined PAC-UF was especially effective when PAC dose was less than 20 mg/L and 90% of humic acid could be removed, but complete removal of phenol was achieved for PAC dose being 100 mg/L. Suzuki et al. [6] have studied the removal of soluble organics and manganese by

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a hybrid hollow fiber MF system. They found that the decreasing rate of membrane permeability in the PAC-MF system was much less than that of a conventional MF process. This may result from the reduced organic loading to the adsorption of humic substances on PAC. Juang et al. [4] have removed sodium dodecyl benzene sulfonate and phenol from water by a combined PAC adsorption and cross-flow MF process. More than 90% of the organics was removed when the PAC dose was beyond 0.8 g/L. On the other hand, some researchers have focused on the theory and modeling of adsorption-MF or -UF operation [8,9].

Activated carbon has been widely used as adsorbent but its cost and energy consumption in regeneration are large. Recently, the natural clay has been received much attention due to its low cost. To our best knowledge, little work has been done using UF process with clay adsorbents. Our goal is to test the efficiency of hybrid process (clay-UF) of removal of organic substance. In this study, one clay (kaolin) and one clay mineral (montmorillonite) were chosen and conducted as a function of transmembrane pressure, solution pH. Besides, the isotherm and adsorption rate of clays were also investigated to realize the characteristics and behavior of the hybrid process.

2. Materials and methods

2.1. Reagents, membranes, and apparatus

Phenol, *o*-cresol, methanol, ethanol, carbon tetrachloride, and other inorganic chemicals were supplied by Merck Co., as analytical grade reagents. Montmorillonite KSF was offered from Fluka Co., which had an idealized formula of $Al_2O_3{\cdot}4SiO_2{\cdot}nH_2O$. Kaolin (KGa-1b) was offered from the University of Missouri-Columbia, Source, Clay Minerals Repository. The BET surface area was measured to be 9.8 m^2/g for montmorillonite and 20 m^2/g for kaolin from N_2 adsorption isotherms with a sorptiometer (Quantachrome NOVA 2000, USA). This area was lower than those reported previously [10], maybe due to the lack of pretreatment. For example, Goldberg et al. [11] have also measured a specific surface area of 18.6 m^2/g for a montmorillonite without pretreatment. It is likely that N_2 molecules cannot easily penetrate the interlayer regions between the layer sheets, leading to an underestimation of specific surface area. The solution pH was adjusted by adding a small amount of HCl or NaOH. The aqueous solutions were prepared by adding different amounts of dye and NaCl in deionized water (Milli-Q, Millipore).

Two types of NF membranes were screened here prior to the clay-UF experiments. They were DK and DL (thin-film composite), all supplied by Osmonics Desal Co., USA, as a flat sheet, thin membrane. In addition, an Amicon UF membrane, YM30 (regenerated cellulose acetate), was used. The characteristics of these membranes are listed in Table 1. The NF and UF experiments were performed in a stirred glass cell of 7.6 cm I.D. and 8 cm height (Amicon Model 8400). It had an effective membrane area of 41.8 cm^2 and a cell volume of about 400 cm^3.

Table 1
Physical characteristics of the membranes

Parameter	DL	DK	YM30
MWCO	300	150	30000
Diameter (cm)	7.6	7.6	7.6
Surface area (cm^2)	41.8	41.8	41.8
Permeate flux (mL/(m^2 min))	70	50	1500
Membrane material	Thin-film composite	Thin-film composite	Cellulose acetate

2.2. Batch adsorption experiments

In batch adsorption experiments, an amount of clay (0.2 g) and 0.1 L of the aqueous solution containing different concentrations of organics (20–1000 mg/L) were put into a glass-stoppered flask. The solution was agitated for 12 h using magnetic stirrers in a water bath controlled at 25 °C. At preset contact times, the concentrations of organics in the solution were analyzed with a GC (Varian CP-3800) equipped with a C18 column having a temperature gradient of 5 °C/min from 140 to 180 °C as well as a flame ionization detector. Each experiment was at least duplicated under identical conditions. The reproducibility of the concentration measurements was within 2%. The amount of adsorption at equilibrium, q_e (mg/g), was calculated by

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where C_0 and C_e are the initial and equilibrium liquid-phase concentrations (mg/L), respectively, V the volume of solution (L), and W the weight of dry clay used (g).

2.3. Membrane filtration experiments

In NF/UF stirred cell experiments, the cell pressure was monitored with N_2 gas by means of a transducer. The temperature was controlled at about 25 °C by air conditioner. The feed volume was 250 cm^3 and the cell was stirred at 500 rpm using a magnetic motor. This speed was selected because it can lead to effective agitation but prevent from formation of a serious vortex in the cell. The first 2 cm^3 of the permeate was discarded, and the rejections of organics were obtained by analyzing the next permeate set of 10 cm^3 increment. Because the permeate composition slightly varied with filtration time, the rejections were integrally averaged in nature.

The solution pH was measured using a pH meter (Horiba F-23, Japan). The concentrations of organics in the feed and permeate were similarly analyzed with a GC. The reproducibility of the concentration measurements was within 3% (mostly, 1.5%). The rejection of the organics was calculated by

$$R = 1 - \frac{C_{\text{permeate}}}{C_{\text{retentate}}} \tag{2}$$

In the clay-UF experiments, feed solution (250 cm^3) with the desired concentration was firstly put into the stirred cell, to which