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.
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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 m²/g for montmorillonite and 20 m²/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 m²/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 cm² and a cell volume of about 400 cm³.

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 (cm²)	41.8	41.8	41.8
Permeate flux (mL/(m² 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 cm³ 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 cm³ of the permeate was discarded, and the rejections of organics were obtained by analyzing the next permeate set of 10 cm³ 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

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

In the clay-UF experiments, feed solution (250 cm³) with the desired concentration was firstly put into the stirred cell, to which
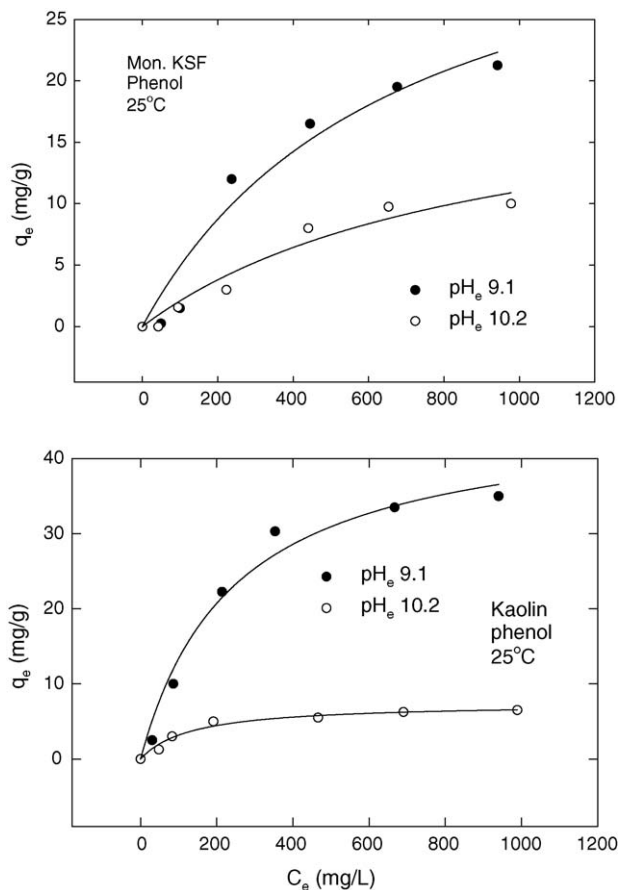
Fig. 1. Adsorption isotherms of phenol onto montmorillonite and kaolin at different pH_e values (25 °C).
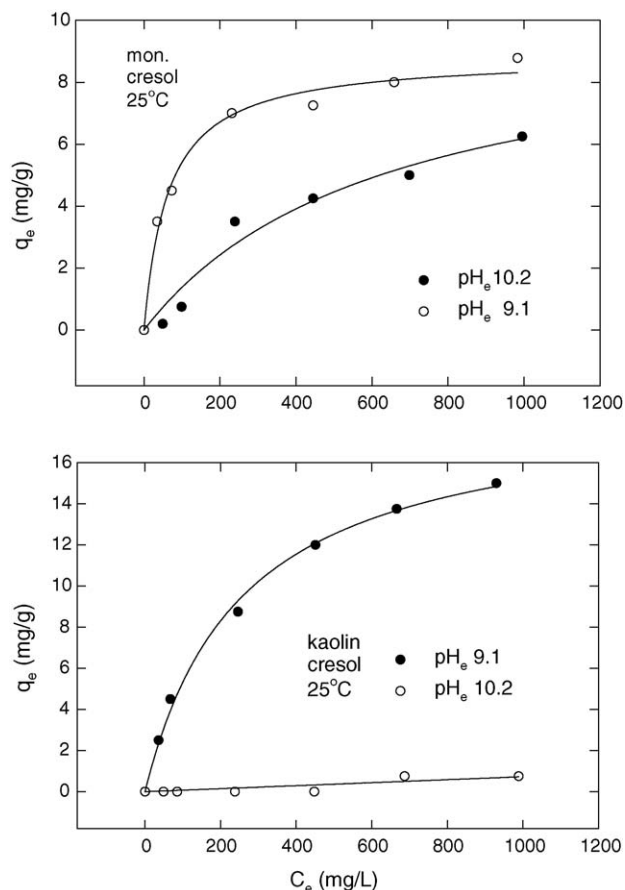

Fig. 2. Adsorption isotherms of *o*-cresol onto montmorillonite and kaolin at different pH_e values (25 °C).

an appropriate amount of clay was simultaneously added. The filtration was then started and the permeate was collected. The concentrations of organics in the permeate was analyzed and the permeate flux was determined.

In some cases, zeta potentials of the clay suspensions at different pH values were measured at 25 °C with laser Doppler electrophoresis using a Malvern Zatasizer instrument (Model 3000HS). These data could identify the ionic characteristics of the adsorbents.

3. Results and discussion

3.1. Equilibrium adsorption of organics

The adsorption isotherm is critical in optimizing the use of the adsorbents. Figs. 1 and 2 show the adsorption isotherms of phenol and *o*-cresol adsorbed onto clay adsorbents at pH_e values of 9.1 and 10.2, respectively. Here, the following two-parameter Langmuir equation is tested:

$$q_e = \frac{Q_{max} K C_e}{1 + K C_e} \tag{3}$$

where K is the Langmuir constant (L/mg) and Q_{max} the saturated amount of adsorption (mg/g) corresponding to a complete monolayer (the so-called adsorption capacity).

A linear plot of $1/q_e$ versus $1/C_e$ yields K and Q_{max} from the intercept and slope. Figs. 1 and 2 show that the fitting is good under the conditions studied (correlation coefficient, $R^2 = 0.98$). The values of K and Q_{max} for phenol and *o*-cresol are listed in Table 2.

It is evident that the amount of adsorption strongly depends on solution pH. The adsorption capacity of phenol with kaolin is similar to that with montmorillonite at $pH_e = 9.1$. However, the adsorption capacity of phenol with montmorillonite at $pH_e = 10.2$ is smaller than that at $pH_e = 9.1$. This is because phenol may dissociate to $C_6H_5O^-$ at $pH > pK_a$ and such negatively charged species is hard to be adsorbed onto montmorillonite (zeta potential: -30 mV as shown in Fig. 8). The pK_a values of phenol and *o*-cresol are 9.92 and 10.21, respectively. Besides, kaolin is more negatively charged than montmorillonite under the conditions studied (the zeta potentials of clays are shown later). The amount of phenol adsorbed onto montmorillonite is larger than that of *o*-cresol at both pH values, indicating that phenol has a stronger affinity with the clay than *o*-cresol.

3.2. Kinetics of organics adsorption

Fig. 3 shows the time profile of the amount of *o*-cresol and phenol adsorbed onto the clays. The kinetic model used in this

Table 2
Parameters of organics adsorption on the clays at 25 °C

Parameters	Montmorillonite		Kaolin	
	Phenol	*o*-Cresol	Phenol	*o*-Cresol
Equilibrium				
K (mg/L): pH_e 9.1	1.47×10^{-3}	1.50×10^{-2}	4.09×10^{-3}	3.90×10^{-3}
K (mg/L): pH_e 10.2	1.14×10^{-3}	1.58×10^{-3}	7.48×10^{-3}	–
Q_{max} (mg/g): pH_e 9.1	40.4	8.8	41.0	–
Q_{max} (mg/g): pH_e 10.2	20.8	10.1	7.4	–
Kinetics				
a (mg/(g min))	0.75	3.6	1.49	2.5
b (g/mg)	0.74	1.4	0.64	0.77

work is based on the Elovich equation [13–15]

$$\frac{dq_t}{dt} = a \exp(-bq_t) \tag{4}$$

Integration of the Elovich equation with boundary conditions $q_t = q_t$ at $t = t$ and $q_t = 0$ at $t = 0$, Eq. (4) becomes

$$q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln(t + t_0) \tag{5}$$

Fig. 3. Time profiles for the adsorption of phenol and *o*-cresol onto the clays (25 °C).

where a and b are the parameters of the equation and $t_0 = 1/ab$. When $t \gg t_0$, Eq. (5) can be expressed as

$$q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln t \tag{6}$$

This equation is commonly used in the kinetics of chemisorption of gasses on the solids [13]. It has also been applied to liquid-phase adsorption systems. For example, Taylor et al. [14] have successfully used this model in the sorption of zinc ions onto soils. Juang and Chen [15] also used this equation in the sorption of ion, cobalt, nickel, copper, and zinc ions on solvent-impregnated resins. Basically, the parameters a and b in Eq. (4) can be determined by a linear plot of q_t versus $\ln t$ with experimental data according to Eq. (6). The results are also listed in Table 2. It reveals that the adsorption of phenol onto kaolin is faster than that onto montmorillonite. However, the adsorption of *o*-cresol onto montmorillonite is faster than that onto kaolin.

3.3. Rejection of organics by single NF

Figs. 4 and 5 show the permeate flux (J_v) and the rejections of methanol, ethanol, CCl$_4$, and phenol by DK and DL membranes. The flux ratios of methanol and ethanol, J_v/J_w, maintain nearly constant in the pressure range 1–5 bar, where J_w refers to the corresponding flux of pure water. However, the J_v/J_w value for phenol system slightly decreases with increasing the transmembrane pressure (ΔP). The decreased permeate volume is likely due to slight fouling, resulting from the adsorption of organics on the membrane.

It is found that the rejections of methanol and carbon tetrachloride are 10–20% only with DK and DL membranes, although the rejections of CCl$_4$ and phenol are 20–30% and increases with increasing the pressure. In a word, single NF process is not able to satisfactorily remove or reject the dissolved organics from water. The trend is similar to that observed by Garba et al. [12], who indicated that the rejections of CdSO$_4$, Cd(NO$_3$)$_2$, and CdCl$_2$ through NF membranes (Nanomax 50) increase from 0.28, 0.41, and 0.97 to 0.45, 0.31, and 0.99, respectively, when the pressure increases from 0.03 to 1 MPa.
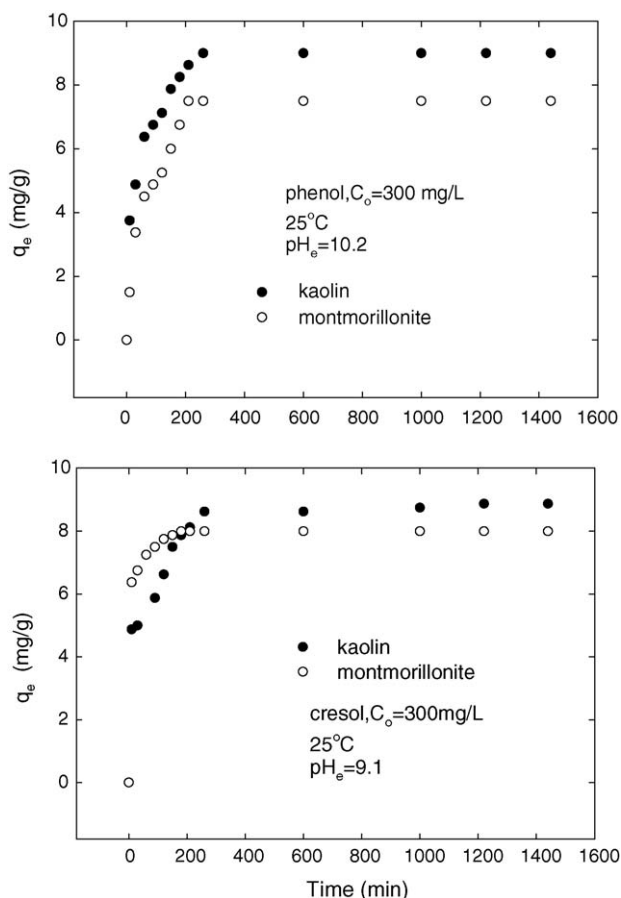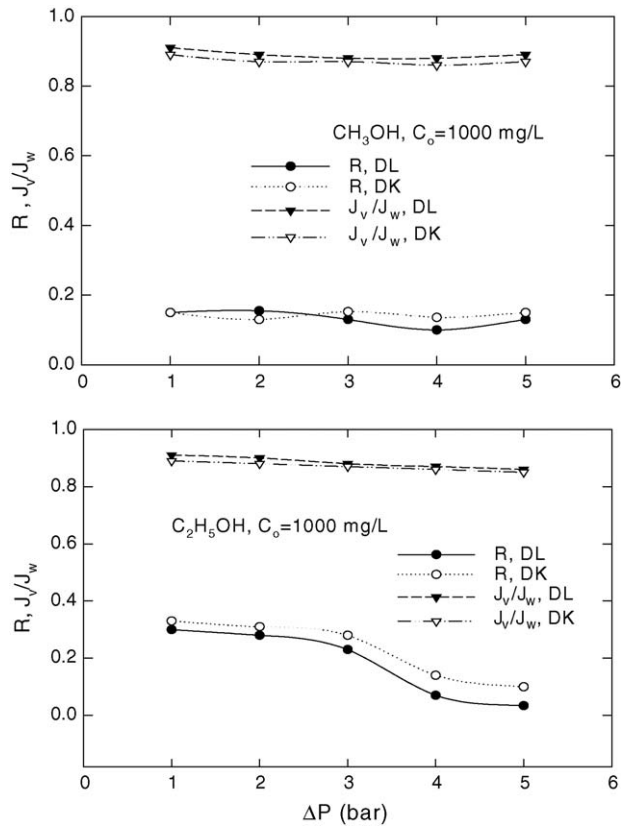
Fig. 4. Permeate fluxes and rejections of methanol and ethanol by DK and DL membranes at different transmembrane pressures.
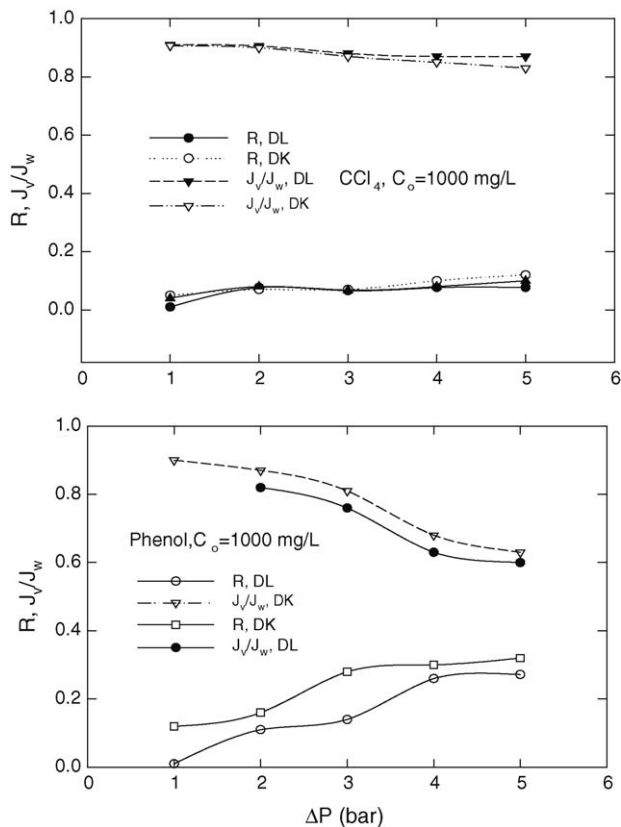

Fig. 5. Permeate fluxes and rejections of tetrachloride carbon and phenol by DK and DL membranes at different transmembrane pressures.
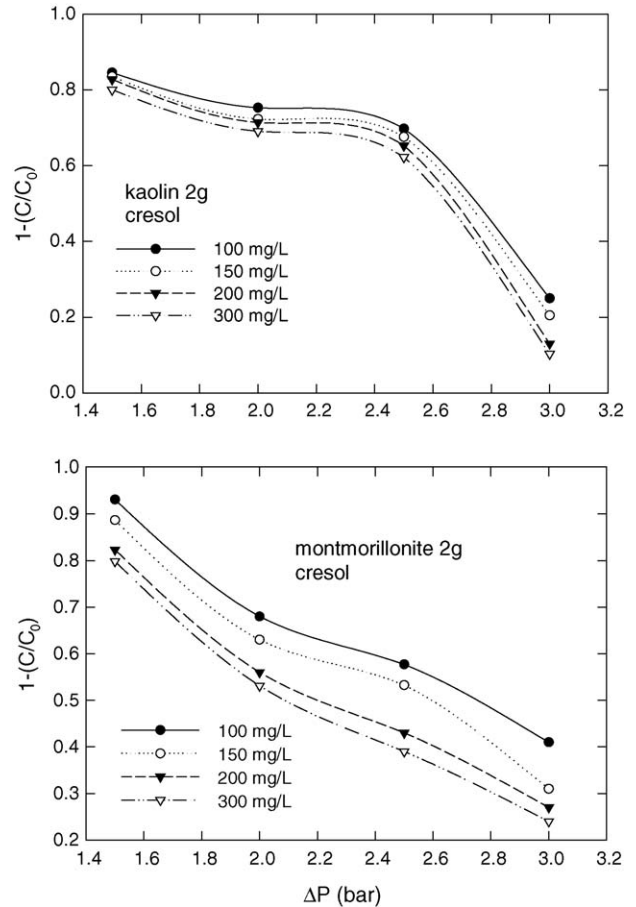

Fig. 6. Rejections of *o*-cresol by clay-UF with the addition of 2 g (a) kaolin and (b) montmorillonite at different *o*-cresol concentrations and transmembrane pressures.

3.4. Rejection of organics by clay-UF

As indicated above, the rejection of organics by single NF is too low to apply for this purpose, so the feasibility of combining UF membrane (YM30) with clay adsorption was tested. Figs. 6 and 7 show the rejections of *o*-cresol and phenol using clay-UF process at different transmembrane pressures. It is expected that the removal efficiency depends on many factors including reactor size, configuration, and filtration mode (dead-end versus cross-flow), as well as operating conditions such as transmembrane pressure, clay dose, and solution pH.

The rejection of *o*-cresol by clay-UF decreases with increasing the pressure when 2 g kaolin is added (Fig. 6). It appears that the time required for attaining adsorption equilibrium depends on the transmembrane pressure. The retention time is longer in stirred cell when the pressure is lower. A decrease of rejection is found when *o*-cresol concentration increases from 100 to 300 mg/L. However, the amount of organics adsorbed at a higher organics concentration is still larger than that at a lower concentration. The rejection of *o*-cresol with montmorillonite is larger than that with kaolin at $pH_e = 9.1$.

Fig. 7 shows the rejection of phenol by clay-UF at different transmembrane pressures with the addition of 1 g montmorillonite. A higher rejection of phenol is obtained at a lower
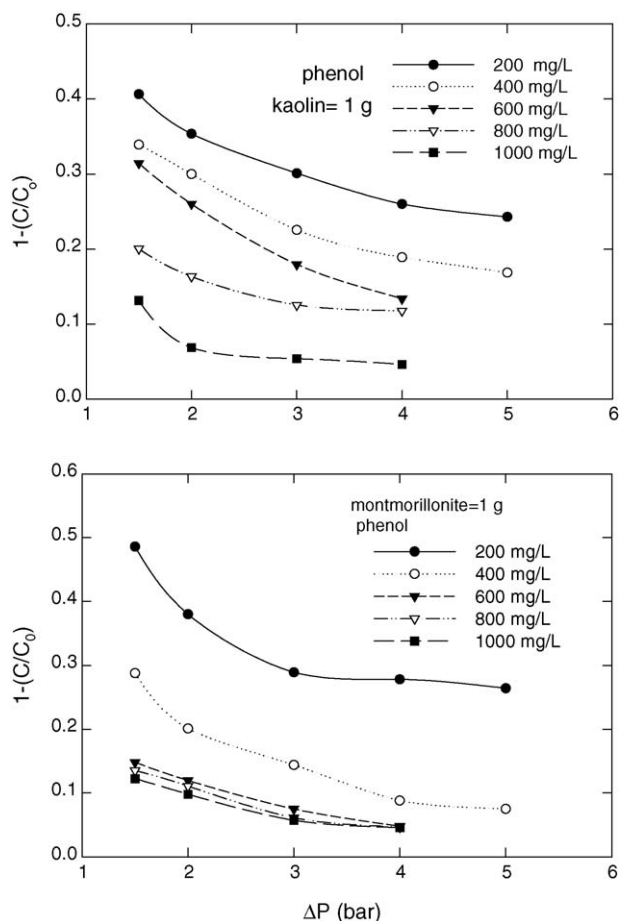
Fig. 7. Rejections of phenol by clay-UF with the addition of 1 g (a) kaolin and (b) montmorillonite at different phenol concentrations and transmembrane pressures.

pressure and at a lower initial phenol concentration. This is because a long time is needed for attaining adsorption equilibrium at a lower pressure. The difference between the curves of Fig. 7 with different clays is due to the difference of the adsorption rates. That is, the adsorption of phenols onto kaolin is faster than that onto montmorillonite (Table 2).

3.5. Effect of pH on the clay-UF rejection

The zeta potentials of clay suspensions are shown in Fig. 8. Kaolin is negatively charged at the whole pH range (2–12), but montmorillonite is positively charged at pH < 6.4 and negatively charged at pH > 6.4. Fig. 9 shows the permeate flux and the rejections of organics at pH 5–11 by clay-UF with the addition of 2 g clay (feed concentration, 100 mg/L). It is seen that the rejection of phenol gradually increases with increasing pH_e and then reaches a maximum at $pH_e = 8.2$ with kaolin, but at $pH_e = 9.1$ with montmorillonite. The different zeta potentials of the clays can explain such a difference. When the rejection reaches maximum, the flux declines. Here, the rejection of organics is contributed by two factors: its amount of adsorption onto the clay and the electrostatic force between the organics and membrane surface.
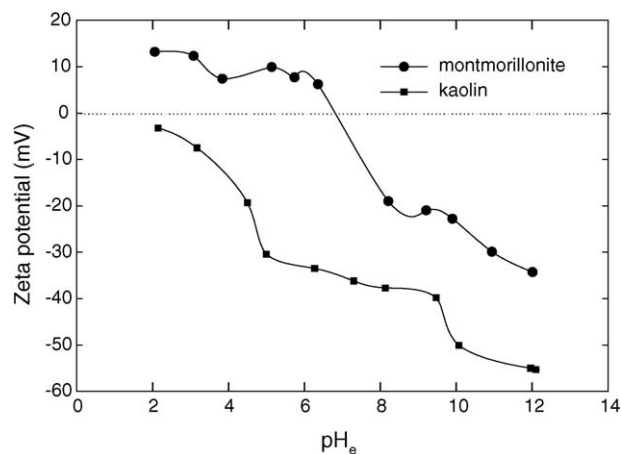

Fig. 8. Zeta potentials of kaolin and montmorillonite at different pH values.

According to batch adsorption results, the amount of phenol adsorbed onto clay at $pH_e = 9.1$ is larger than that at $pH_e = 10.2$. However, the amount of o-cresol adsorbed with montmorillonite at $pH_e = 10.2$ is larger than that at $pH_e = 9.2$. This is because the pK_a of o-cresol is larger than that of phenol. Meanwhile, the membrane surface becomes more negatively charged with increasing solution pH. Therefore, an increased repulsive force between the dissolved organic ions (pH > pK_a) and negatively
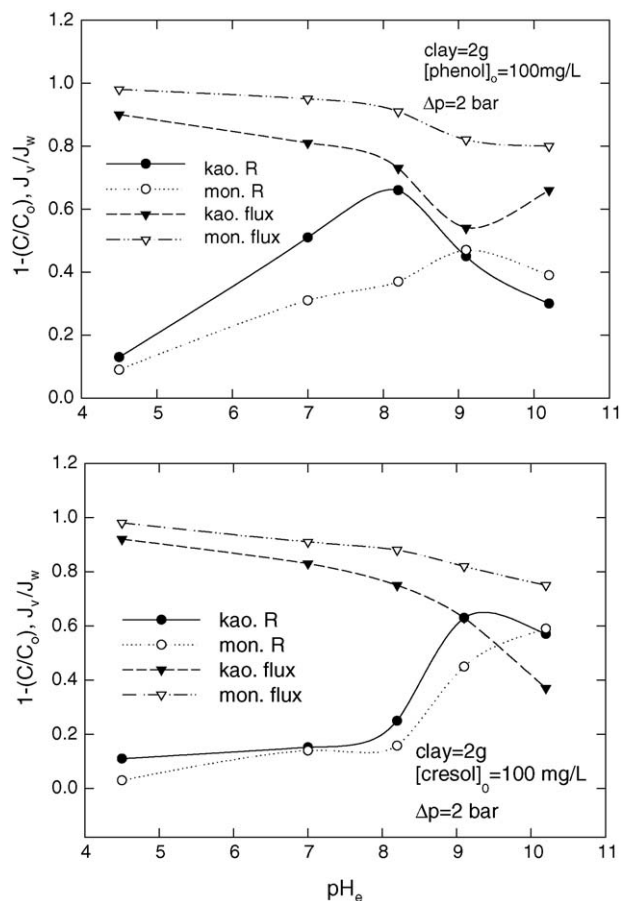

Fig. 9. Permeate fluxes and rejections of phenol and o-cresol by clay-UF at different pH values.

charged membrane exists at higher pH. This also reduces the permeate flux, due to the increased fouling at higher pH.

4. Conclusions

The removal of phenol and *o*-cresol from water by a combined process of clay adsorption and UF was investigated. The clay-UF experiments were performed as a function of clay dose, solution pH, and the transmembrane pressure. The removal efficiency of soluble organics at low pressures (20%) was too low to apply by single NF. However, the removal efficiency of phenols (80%) was enhanced by the clay-UF process. The rejection of the organics of interest strongly depended on solution pH and clay dose. The rejection of phenol increased with increasing solution 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 increased with increasing solution pH and had a maximum at pH_e 9.2 with kaolin, but at pH_e 10.2 with montmorillonite. The difference between the pK_a of phenols and the zeta potential of clays could explain such different rejection phenomena.

Acknowledgement

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