Sorptive separation of phenolic compounds from wastewater

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Introduction

Phenolic compounds are common organic pollutants from industries such as oil refineries, petrochemical units, coal gasification, coking operations, phenolic resins production and some medical industries [1]. Phenols discharged to aqueous systems can produce unpleasant odour and are harmful to human health. Therefore, phenolic wastewater becomes a great concern in wastewater treatment. Numerous technologies have been employed to remove phenol and its derivatives from wastewater, including the conventional methods of distillation and extraction [2], chemical oxidation [3], biodegradation [4], and membrane separation [5]. Of these methods, sorption appears to be a suitable process based on overall separation performance. It is effective for a large variety of compounds, and has the advantages of easy operation and high efficiency to treat low-concentration pollutants. Moreover, sorption is generally reversible, and the sorbent can be regenerated for reuse.

Accordingly research has been undertaken to explore suitable sorbents for phenolic compounds. Activated carbon has been widely used as a sorbent because of its known effectiveness. However, the high regeneration cost of activated carbon has motivated research to seek other better sorbents for phenolic compounds. Polymeric sorbents have attracted a lot of attention in recent years due to its mechanical strength and feasibility to regenerate. Poly (block ether amide) (PEBA) is a copolymer containing a linear chain of polyamide and polyether blocks in an ordered pattern. PEBA membranes have been used in pervaporation separation and show excellent selectivity to phenol [6, 7]. PEBA 2533 (short D hardness 25) has a polyether content as high as 80 wt.%, which has been proved to have good affinity to phenol [5]. Examining the
good pervaporative performance of PEBA membranes for phenol separation revealed that PEBA 2533 has excellent affinity to phenol, and it is thus expected to be an effective sorbent for phenolic compounds.

This study explored the potential of using PEBA 2533 as a new sorbent for phenolic compounds. The sorption characteristics of PEBA 2533 for the removal of phenol, 4-chlorophenol (4-CP), 4-nitrophenol (4-NP), p-cresol, and catechol from aqueous solutions were investigated through a batch study. Sorption capacities were investigated by the equilibrium study, and sorption kinetics and sorption mechanisms were investigated by the kinetic study.

**Experimental**

In order to get well defined surface area and thickness, PEBA 2533 was used in membrane forms in this study. Pellets of PEBA 2533 were dissolved in N, N-dimethylacetamide to form a 15 wt. % solution. The mixture was heated for two hours and then the homogenous solution was allowed to stand for 24 hours to remove entrapped air bubbles. The membranes were prepared by pouring the solution into a Petri dish, followed by heating to evaporate the solvent. The membranes were washed and dried in the oven to ensure that all residual solvent was completely removed.

For equilibrium study, each sorption measurement lasted for 24 hours at desired temperatures (298K to 343K). The concentration of phenolic compounds was determined by spectrophotometer. The equilibrium sorption uptake $Q_e$ (mmol/g) was calculated by

$$Q_e = \frac{V \times (C_0 - C_e)}{M}$$  \hspace{1cm} (1)
where $C_0$ and $C_e$ are the concentrations of solute in the solution at the beginning and at sorption equilibrium (mmol/L), $V$ represents the volume of the solution (L), and $M$ is the weight of the PEBA (g).

The kinetic study was conducted at 298K. $Q_t$ (mmol/g), the amount of sorption at time $t$, was calculated by the following relationship:

$$Q_t = \frac{V \times (C_0 - C_t)}{M}$$

(2)

where $C_t$ represents the sorbate concentration at time $t$ (mmol/L).

**Results**

1. **Equilibrium study**

The sorption isotherms of phenol and 4-chlorophenol by PEBA 2533 were shown in Fig 1. It is shown a lower temperature is favourable for sorption, which indicates that the sorption process is exothermic in nature.

The experimental data were analyzed by the linear model, the Langmuir model and the Freundlich model. It was found that the linear model is suitable to describe the sorption equilibrium of phenol and p-cresol in PEBA; the Langmuir model is suitable to represent the sorption equilibrium sorption of 4-CP, 4-NP, catechol and p-cresol in PEBA; the Freundlich model is suitable for the sorption all phenolic compounds studied in PEBA. In addition, the sorption capacity of the phenolic compounds increases in the following order: catechol<phenol<p-cresol<4-NP<4-CP. The sorption capacity of phenolic compounds by PEBA 2533 was affected by solubility, hydrophobicity and chemical properties of phenolic compounds.
Fig 1. Equilibrium sorption isotherms of (a) phenol, (b) 4-chlorophenol in PEBA 2533 at different temperatures

2. Kinetic study

In order to identify the sorption process, kinetics of two kinds of PEBA membranes were compared: one with the same surface area but different weights, the other with the same weight but different surface areas. Fig 2(a) and (b) show the sorption kinetics of phenol by two different kinds of PEBA 2533 membranes. It was found sorption of phenol, 4-CP, 4-NP, p-Cresol and catechol by PEBA membrane took place at the surface of the membrane, followed by the diffusion in the membrane. The sorption uptake is determined by the mass of the PEBA sorbent, not the area of the sorbent.

Three kinetic models (pseudo-first order, pseudo-second order, and intraparticle diffusion) were used to analyze the kinetic data. It was found pseudo-second order model is more suitable to represent the experimental data than the pseudo-first order model, and the diffusion model can also describe the initial stage of the sorption process. Kinetics of phenol, 4-CP, 4-NP, p-Cresol and catechol by PEBA membrane could be presented by the pseudo-second order reaction model, though diffusion inside the membrane was also not negligible for thick membranes.
Fig 2. Sorption kinetics of phenol by PEBA membranes: of (a) the same surface area but different weights, (b) the same weight but different surface areas.

Reference


