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Adsorption of phenol, bisphenol A and nonylphenol ethoxylates onto hypercrosslinked and aminated adsorbents

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ABSTRACT

The presence of phenolic compounds in aquatic environments poses potential human health and ecological risks. In this study, we evaluated porous resins as adsorbents for removal of three compounds, phenol, bisphenol A and nonylphenol ethoxylates from aqueous solutions. The adsorption isotherms were well fitted by the Langmuir equation, and the strength of the adsorption was affected by the properties of polymeric adsorbent (surface area, pore size, functional group and matrix) and phenolics (distribution coefficient K_{OW}, adsorption coefficient K_d, water solubility S_w and dissociation constant pK_a). Four possible interactions, i.e., hydrophobic effect, π–π bonds, hydrogen bonding and electrostatic interaction, were discussed to explore the underlying mechanism in the adsorption affinity of phenol and BPA. Hydroxyl on the aromatic rings strengthened the interactions between phenol and aminated polymeric adsorbent and thus the adsorption affinity. Adsorption of $NPEO_{10}$ to polymeric adsorbents was dominated by pore size and molecular morphology, even on the aminated polymeric adsorbents (MN-100, MN-150). The results from thermodynamic analysis show that the adsorption of BPA and $NPEO_{10}$ by polymeric adsorbents was thermodynamically favorable and generally endothermic whereas the adsorption process of phenol was exothermic. These results help us better understand the adsorption behavior and mechanism of phenolic compound onto carbon-based adsorbent.

1. Introduction

In recent years, environmental concerns about the fate, transport, reactivity, and bioavailability of phenolic compounds have drawn much attention of many researchers. Among these chemicals, bisphenol A (BPA) and nonylphenol ethoxylates (NPEOs) are particularly important because of their wide use in industry as materials for component of polymers and nonionic surfactants. Also, the two chemicals have the potential to disrupt endocrines [1,2]. BPA comes under this category because of its weak oestrogen-like effect [1]; NPEOs are related to endocrine disrupting chemicals as their biodegradation intermediates; nonylphenol mono- and di-ethoxylates and nonylphenol, are more toxic and persistent than their parent substances in the environment [2,3]. Moreover, as a surfactant, NPEOs can remarkably enhance the solubility of hydrophobic organic contaminants, and thus worsen water quality and increase the difficulty and cost of water treatment. Exposure to BPA and NPEOs can affect the reproductive behavior of higher life forms, such as fish, wildlife, humans, and even endanger the balance of ecosystems [4]. So, removal of these compounds from waste water is important for environmental protection.

Many works have been done on adsorption of the two chemicals from their aqueous solutions by natural and engineered adsorbents, such as bentonite [5], sand [6], river sediment [7,8], mineral materials [9], and carbonaceous adsorbents [10]. The adsorption of BPA was reported to be a process of physical interaction and weakly electrostatic interaction between the adsorbates and their hosts [8,9]; several studies confirmed the presence of hydrophobic effect and hydrogen bonding for the BPA adsorption process [11,12]. The studies of NPEOs adsorption indicated that both the hydrophobic and hydrophilic moieties of surfactant molecules play an important role in the adsorption process, regardless of whether the surface is hydrophobic or hydrophilic [5–7]. Interactions between the surfactant and the adsorbent surfaces are also essential. Interactions between the oxygen atom of the oxyethylene group and the surface of the adsorbent lead to strong adsorption of ethoxylated non-ionic surfactants [13]. These pioneering studies greatly improved the understanding of alkylphenols interactions with the adsorbents. Such interactions are supportive of their adsorption affinity.

Although many aspects of the interactions on phenolic compounds adsorption in aqueous systems have been studied, the roles

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of the surface area, surface chemistry, and matrix of adsorbents as well as the molecular size (steric hindrance) of adsorbate are yet to be fully understood [14–16]. Most research in this field has ignored the influence of octane-water distribution coefficient (K_{OW}), adsorption coefficient (K_d) and water solubility of adsorbate on the adsorption process. Currently, advances in polymer science have provided opportunities to select well-structured polymeric adsorbent with high surface area, pore size, and suitable surface chemistry, such as hypercrosslinked polymeric adsorbents MN-200 and aminated polymeric adsorbents (MN-100, MN-150) [17–19]. Moreover, one of the main advantages of these polymeric adsorbents is that it can be regenerated more easily than other materials by using organic solvents such as ethanol, methanol, or acetone [20].

The main objective of this study is to investigate the mechanism and predominant factors controlling the adsorption of the phenolics to porous polymeric adsorbent. Phenol, one of the top priority contaminants was employed for comparison. Due to the fact that nonylphenol ethoxylates (NPEOs) are produced and used as mixtures, we selected the abbreviation $NPEO_{10}$ as a representative of commercial nonylphenol ethoxylates, which are complex mixtures of a series of homologues, with 10 ethoxy units being present in the highest concentration. Hypercrosslinked polymeric adsorbent MN-200 and NDA-150, aminated polystyrene polymeric adsorbent MN-150 and MN-100 were selected as adsorbent. Impacts of solution chemistry conditions on adsorption were evaluated.

2. Materials and methods

2.1. Materials

Phenol, bisphenol A, and $NPEO_{10}$ were obtained from Sigma-Aldrich Chemical Co. and used as received. Commercial available polymeric adsorbents MN-200, MN-100 and MN-150 were supplied by Shanghai Office, Purolite International Co., Ltd. The commercial adsorbent NDA-150 was donated by Jiangsu N&G Environmental Technology Co. Ltd. (Jiangsu, China). Water used in the study was purified by distillation.

2.2. Polymeric adsorbents

The polymeric adsorbents were conditioned in methanol–hydrochloric acid mixtures and finally in water before the adsorption experiments. Nitrogen adsorption and desorption experiments were carried out at 77 K to determine the surface properties of the polymeric adsorbents. Infrared spectra of the four polymeric adsorbents were obtained with a Nicolet 170 SX IR Spectrometer (Madison, WI, USA). Their zeta potentials were determined using a Malvern Instruments Zetamaster. (Zetamaster, Malvern Ltd, U.K.). The elemental analysis of the polymeric adsorbents was performed using a Perkin-Elmer 240 C Elemental Analytical Instrument (Wellesley, MA, USA). The BET surface area was calculated from desorption isotherms using the standard Brunauer-Emmert-Teller equation. The mesoporous pore size distribution was determined from desorption isotherms using the Barrett, Joyner and Halenda (BJH) method. All calculations were performed automatically by an Accelerated Surface Area and Porosimeter system (ASAP 2010, Micromeritics, USA).

2.3. Adsorption assay

Equilibrium adsorption experiments were carried out at 288, 303 and 318 K. Polymeric adsorbent (0.0500 g) was introduced into a series of 150 mL conical flasks and 100 mL of the phenolics from their stock aqueous solution was then added to each flask, respectively. The initial phenol and $NPEO_{10}$ concentrations (C_0) of the solutions were 200, 400, 600, 800 and 1000 mg L^{-1}; due to the poor water solubility of Biphenol A, its initial concentrations (C_0) of the solutions were 20, 40, 60, 80 and 100 mg L^{-1}. The flasks were then completely sealed and placed in an incubator shaker (New Brunswick, model G25) at a pre-set temperature at a shaking speed of 130 rpm. Adsorption experiments were run continuously for 72 h to ensure equilibrium. The pH of the samples before and after the sorption experiments was measured, which was within 6.5–7.5 for different systems and kept unchanged. A separate set of experiments was carried out for the adsorption of the phenolics to MN-200 and MN-150 over a pH range of 1.0–12.0 (pH adjusted with NaOH and HCl).

The concentration of the phenolics was determined after equilibrium by UV-VIS spectrophotometry at 274 nm for Phenol, 276 nm for Bisphenol A and 230 nm for $NPEO_{10}$ (UV3100-PC, Mapada, China). Quartz glass cells (Hellma) of 10 mm path length were used. Linear calibration curves (absorbance versus concentration) were used to determine the concentration of the phenolics. The adsorption capacity, q_e (mmol g^{-1}), was calculated using the following:

$$q_e = V(C_0 - C_e)/M \cdot m \tag{1}$$

where C_0 is the initial adsorbate concentration (mg L^{-1}), C_e is the residual concentration at equilibrium (mg L^{-1}), V is the volume of solution (L), M is the molecular weight of adsorbates, and m is the mass of dry polymeric adsorbent (g).

3. Results and discussion

3.1. Polymeric adsorbent characterization

Four polymeric adsorbents with different physicochemical properties were selected as adsorbents. Their properties are presented in Table 1. The BET surface area of MN-200 is the largest; while, the corresponding ones of NDA-150, MN-150 and MN-100 are between 815 and 850 $m^2\,g^{-1}$. The latter three have similar BET surface areas and micropore structures and they show a similar average pore diameter.

Fourier transform infrared (FTIR) spectroscopy was used to identify functional groups on the polymeric adsorbent surfaces (Fig. S1). FTIR spectra indicate the presence of tertiary amino groups on MN-100 and MN-150 (absorbance bands at 2772 and 2816 cm^{-1}) [21]. Tertiary amino groups are not detected in the IR spectra of MN-200 and NDA-150 polymeric adsorbents. The zeta potential of the polymeric adsorbents at different pH values is a function of the surface charge. Zero crossover points are observed at pH 4.5, 5.0, 6.8 and 7.2 for NDA-150, MN-200, MN-100 and MN-150 respectively (Fig. S2). The surface charge of the polymeric adsorbent at the pH of the adsorption experiments (pH 7 ± 0.5) would be negative for the MN-200 and NDA-150. The tertiary amine functionality of the MN-100 and MN-150 rendered their surface positive, neutral or negative dependent on small shifts in pH.

3.2. Role of polymeric adsorbent properties in adsorption

The amounts of the phenolic compounds adsorbed on a unit millimole basis per gram of the polymeric adsorbents (q_e) against the equilibrium concentration (C_e) have been plotted in Fig. 1.

For phenol and BPA adsorption by hypercrosslinked polymeric adsorbents MN-200 and NDA-150, the adsorption capacities are consistent with their specific surface area and micropore area (Table 1, MN-200 > NDA-150), indicating that the interactions between the phenolic compounds and the surface of hypercrosslinked polymeric