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Adsorption characteristics of aniline and 4-methylaniline onto bifunctional polymeric adsorbent modified by sulfonic groups

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Abstract

In this paper a new bifunctional polymeric resin (LS-2) was synthesized by introducing sulfonic groups onto the surface of the resin during the post-crossing of chloromethyl low crosslinking macroporous poly-styrene resin, and the comparison of the adsorption properties of LS-2 with Amberlite XAD-4 toward aniline and 4-methylaniline in aqueous solutions was made. The study focuses on the static equilibrium adsorption behaviors, the adsorption thermodynamics, and the column dynamic adsorption and desorption profiles. Freundlich model gives a perfect fitting to the isotherm data. Although the specific surface area of LS-2 is lower than that of Amberlite XAD-4, the adsorbing capacities for these two adsorbates on LS-2 are higher than those on Amberlite XAD-4 within the temperature range 288–318 K, which is contributed to microporous structure and the polar groups on the network of LS-2 resins. The adsorption for aniline or 4-methylaniline on LS-2 was proved to be an endothermic process and increasing temperature was favorable. From the studies on the adsorption thermodynamics, static equilibrium adsorption, and the desorption conditions, an important conclusion can be drawn that the adsorption for aniline or 4-methylaniline on the LS-2 is a coexistence process of physical adsorption and chemical transition.

Keywords: Adsorption; Bifunctional polymeric adsorbent; Aniline; 4-Methylaniline; Hypercrosslinked adsorbent; Sulfonic groups

1. Introduction

Aniline and its derivatives, as one of the most important organic intermediates, are widely used for the manufacture of pesticides, rubber, drugs, varnishes and dyestuffs; as a result, more and more aniline-containing wastewater has been introduced into water bodies. For their high toxicity, the efficient removal of these organic compounds from water has drawn significant concern.

Presently, various methods of wastewater treatment have been developed such as catalytic oxidation, liquid membrane separation, biological degradation and adsorption [1–5]. Due to the high concentrating ability of typical adsorbents [6,7], adsorption is proved to be one of the most attractive and effective techniques for purification and separation in wastewater treatment. Activated carbon, as a porous material with large specific surface area and predominant proportion of micropores, has been widely used in industrial adsorptive processes efficiently [8,9].

In recent years, polymeric adsorbents have increasingly been viewed as an alternative to activated carbon for efficient removal of specific organics from contaminated water due to their good properties and mechanical strength. Among them the commercially available Amberlite XAD-4 resin was reported to be an ideal adsorbent for a wide variety of organic compounds, especially for phenols. However, the extreme hydrophobic surface of XAD-4 lowers its adsorbing capacity for polar organic compounds [10,11]. To overcome the limitation, chemically modified polymeric adsorbents with functional groups such as phenolic hydroxyl, acetyl, benzoyl and

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hypercrosslinked polymers have been synthesized recently [12–14]. There are also reports that some hypercrosslinked resins were used in sorption of aniline compounds from aqueous solution [15].

The purpose of present work was to prepare a new chemically modified bifunctional adsorbent (LS-2) for the removal of the two aniline compounds (aniline, 4-methylaniline) from their aqueous solutions, and to compare the adsorption properties of the adsorbent with those of the commercial Amberlite XAD-4 resin.

2. Materials and synthetic methods

2.1. Chemicals

Acetone, ethanol, nitrobenzene, zinc chloride, sulfuric acid, hydrochloric acid, dibenzoyl peroxide, aniline and 4-methylaniline were used in this study. All these chemicals are of analytical grade and were purchased from Shanghai Chemical Reagent Plant (Shanghai, China). Photographic-grade gelatin was obtained from Yancheng Dafeng Gelatin Plant (Yancheng, China). Styrene and divinylbenzene (purity: 50.4%) were purchased from Dongda Chemical Co. Ltd. (Shandong province, China). Chloromethyl methylether was obtained from Langfang Chemical Co. Ltd. (Hebei province, China). The spherical Amberlite XAD-4 resin was purchased from Rohm & Haas Company (Philadelphia, USA). Physicochemical properties of the adsorbates and adsorbents used in this study are presented in Tables 1 and 2. Aniline and 4-methylaniline were dissolved in deionized water without pH adjustment.

Table 1
Typical properties of the studied adsorbents

Polymeric resins	Amberlite XAD-4	LS-2
Polarity	Nonpolar	Moderate polar
BET specific surface area (m^2/g)	880	506
Average pore diameter (nm)	5.8	4.5
Particle size (mm)	0.4–0.6	0.4–0.6
Pore volume (mL/g)	1.05	0.57
Micropore area (m^2/g)	3.1	280.4
Residual chloride content (%)	0	7.78
Strong acidic exchange content	0	1.2
Color	White	Deep gray

2.2. Synthesis of LS-2 adsorbent

The synthesis of low-crosslinked macroporous styrene–divinylbenzene copolymer and its chloromethylation were carried out as the literature [17].

The bifunctional polymeric adsorbent LS-2 was prepared through the following post-crosslinking step. In a 500 mL round-bottomed flask, 50 g chloromethylated styrene–divinylbenzene copolymers (the chlorine content 19.5%) were swollen in 300 g nitrobenzene. Under mechanical stirring, 7.5 g zinc chloride was slowly added into the flask at room temperature. Then, 10 mL sulfuric acid (mass percentage: 98%) was added. The mixture was further stirred for 12 h at 383 K. Finally, the mixture was poured into an acetone bath containing 1% (mass percentage) hydrochloric acid. The filtered polymers were extracted by ethanol for 8 h in Soxhlet apparatuses and dried under vacuum at 333 K for 8 h.

2.3. Characterization of adsorbents

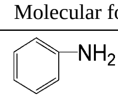
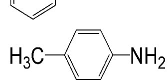
The specific surface area and the pore distribution of the adsorbents were calculated, respectively by BET and BJH methods via the nitrogen adsorption and desorption curves at 77 K using a Micromeritics ASAP-2010 automatic surface area analysis instrument (Micromeritics Instrument, Norcros, USA). Infrared spectra of the polymeric adsorbent before and after the post-crossing reaction were obtained from a Nicolet 170 SX IR spectrometer (USA) with a pellet of powdered potassium bromide and resin. The chlorine content was measured according to the method of Volhard [18]. And the strong acidic exchange content was measured by chemical titration.

3. Experimentation

3.1. Static adsorption experiment

Equilibrium adsorption of two aniline compounds was performed at four different temperatures: 288 K (risen from 275 K), 303, 318 and another 288 K (fallen from 318 K). Dry LS-2 resin (0.1 g) was weighed accurately and introduced into a 250 mL conical flask directly, while the XAD-4 resin should be wetted in 0.5 mL methanol and rinsed with deionized water for more than three times before use. Then, 100 mL aqueous solution of the adsorbates of certain concentration (C_0, mg/L) ranging from 200 to 1000 was added to each flask.

Table 2
Properties of the adsorbates

Adsorbates	Molecular formula	Molecular weight	pK_a[a]	Solubility (g/100 g H_2O)[a]
Aniline		93	4.58	3.7
4-Methylaniline		107	5.08	0.7

[a] Data from [16].