Chemical Engineering Journal 219 (2013) 238–244

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Resorcinol modified hypercrosslinked poly(styrene-co-divinlybenzene) resin and its adsorption equilibriums, kinetics and dynamics towards *p*-hydroxylbenzaldehyde from aqueous solution

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HIGHLIGHTS

- ▶ Novel carbonyl and hydroxyl groups modified hypercrosslinked resins were synthesized.
- ▶ These resins possessed different adsorption selectivity.
- ▶ Surface energy heterogeneity of the resin could be described by Do's model.
- ▶ The dynamics matched the equilibrium and kinetics very well.
- ▶ The dynamic data could be described by Thomas model.

ARTICLE INFO

Article history:
Received 16 November 2012
Received in revised form 4 January 2013
Accepted 5 January 2013
Available online 11 January 2013

Keywords:
Hypercrosslinked poly (styrene-co-divinlybenzene) resin
Adsorption
p-Hydroxylbenzaldehyde
Equilibrium
Kinetics
Dynamics

ABSTRACT

A series of resorcinol modified hypercrosslinked poly(styrene-co-divinlybenzene) (PS) resins, named as HJ-H00, HJ-H02, HJ-H05, HJ-H10 and HJ-H15, were synthesized from macroporous cross-linked chloromethylated PS by adding 0%, 2%, 5%, 10% and 15% of resorcinol in the Friedel–Crafts reaction, and these resins were characterized and evaluated for adsorption of *p*-hydroxylbenzaldehyde from aqueous solution. The characterization indicated that these resins possessed different chemical structure and pore structure, indicative of their adsorption selectivity. HJ-H02 had the largest adsorption capacity towards *p*-hydroxylbenzaldehyde among the five resins and the mechanism was a combination of hydrogen bonding, micropore filling, capillary condensation and π–π stacking. Freundlich equation was suitable for fitting the equilibrium data and the isosteric adsorption enthalpies were applied to describe the surface energy heterogeneity of the resin. The pseudo-second-order rate equation-I was appropriate for the kinetic data and Thomas model was suitable for the dynamic data. The dynamic adsorption capacity was calculated to be 225.5 mg/g dry resin, very close to the equilibrium capacity of 241.4 mg/g and the resin column could be desorbed by 60 mL of 1% of sodium hydroxide and 75% of ethanol completely.

1. Introduction

p-Hydroxylbenzaldehyde ($C_6H_4CHO(p\text{-}OH)$) is a kind of typical aromatic aldehyde and one of the most useful compound in industry. It can be synthesized from phenol by the Reimer–Tiemann or Gattermann reaction and it can also be prepared from *p*-nitrotoluene by a continuous redox, diazotization and hydrolysis reaction. In fact, *p*-hydroxylbenzaldehyde is the primary raw materials for producing a lot of medicines such as amoxicillin, trimethoprimand (TMP), 3,4,5-trimethoxybenzaldehyde and *p*-hydoxygylcine as well as some perfumes such as vanillin, heliotropin and syringaldehyde. However, it is toxic to mankind and it has bad effects on eyes, respiratory system and skins, and hence efficient removal of *p*-hydroxylbenzaldehyde from wastewater is of great importance.

Various porous materials such as zeolites, active carbons, silica gels, metal–organic frameworks (MOFs) and macroporous polymeric adsorbents are very important in many research areas, especially in adsorption, catalysis, energy storage and electrochemistry [1–5]. Among these porous materials, macroporous polymeric adsorbents, especially the newly developed hypercrosslinked poly(styrene-co-divinylbenzene) (PS) resins in 1970s, have been extensively used in various industrial adsorption and separation processes of organic aromatic compounds such as benzene, toluene, β-naphthol and phenol from aqueous solutions [6–8],

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http://dx.doi.org/10.1016/j.cej.2013.01.020

and they are considered as powerfully potential replacement of activated carbon for organic compounds removal from wastewater. In addition, the hypercrosslinked PS resins have also been widely used for large scale adsorption of organic compounds from gaseous media and for solid-phase extraction of trace components and they are often applied as column packing materials in high-performance liquid chromatography (HPLC) and ion size-exclusion chromatography materials [9–13].

The hypercrosslinked PS resins are usually synthesized from a linear PS or a low cross-linked PS by adding bi-functional/multi-functional cross-linking reagents such as bischloromethylated benzene, trichloromethylatedmesethylene (TCMM), monochlorodimethylether (MCDE) and *p*-dibenzenylchloride and Friedel–Crafts catalysts including anhydrous zinc chloride, iron (III) chloride and stannic (IV) chloride [14]. They can also be prepared from a macroporous low cross-linked chloromethylated PS by two sequential Friedel–Crafts alkylation reaction [15]. After the corresponding reactions, the obtained hypercrosslinked PS networks consist of an intensive bridging of strongly solvated PS chains with conformationally rigid links, leading a major shift of their pore diameter distribution from predominate mesopores to mesopores–micropores bimodal distribution, and hence results in a sharp increase of the Brunauer–Emmet–Teller (BET) surface area and pore volume. Because of these significant changes, the hypercrosslinked PS resin displays very large adsorption capacities towards non-polar and weakly polar aromatic compounds from aqueous solution. In order to increase their adsorption capacities towards polar aromatic compounds, the resins were frequently modified by introducing polar units into the copolymers, using polar compounds as the cross-linking reagent and addition of polar compounds in the Friedel–Crafts reaction [16,17]. The results indicated that the chemically modified hypercrosslinked PS resins exhibited improved adsorption properties towards polar aromatic compounds by introducing certain specific functional groups on their surface.

In this study, we firstly synthesized a type of resorcinol modified hypercrosslinked PS resins, labeled as HJ-H00, HJ-H02, HJ-H05, HJ-H10 and HJ-H15, from macroporous cross-linked chloromethylated PS by adding 0%, 2%, 5%, 10% and 15% of resorcinol in the Friedel–Crafts reaction. After characterizing these resins by nitrogen adsorption–desorption isotherms, chemical analysis, elemental analysis and Fourier transform infrared (FT-IR) spectroscopy, their adsorption selectivity towards benzaldehyde and *p*-hydroxylbenzaldehyde was confirmed by the batch adsorption experiment from aqueous solution. The most promising resin HJ-H02 was thereafter selected for the equilibrium, kinetics and dynamic adsorption of *p*-hydroxylbenzaldehyde from aqueous solution in detail.

2. Experimental method

2.1. Materials and reagents

Macroporous cross-linked chloromethylated PS applied as the synthetic precursor in this study was purchased from Langfang Chemical Co. Ltd. (Hebei, China). Benzaldehyde (Molecular formula: C_6H_5CHO, Molecular weight: 106.1) and *p*-hydroxylbenzaldehyde applied as the adsorbates in the present study were analytical reagents and used without further purification.

2.2. Preparation of resorcinol modified hypercrosslinked PS resins

The preparation procedure for the resorcinol modified hypercrosslinked PS resins was performed according to the Friedel–Crafts reaction in Ref. [8] and the detailed synthetic method was shown in Scheme S1. 1,2-dichloroethane was applied as the solvent and iron (III) chloride was employed as the catalysts in the Friede–Crafts reaction. Additionally, the mass percentage of resorcinol was set to be 0%, 2%, 5%, 10% and 15% relative to the chlorine content of macroporous cross-linked chloromethylated PS (w/w), respectively, and the resorcinol modified hypercrosslinked PS resin named as HJ-H00, HJ-H02, HJ-H05, HJ-H10 and HJ-H15 were synthesized accordingly.

2.3. Equilibrium and kinetic adsorption experiment

Firstly about 0.1000 g of resins was weighed accurately in a series of flasks with a stopper and they were mixed with 50 mL of *p*-hydroxylbenzaldehyde aqueous solution at different initial concentrations. The initial concentrations of *p*-hydroxylbenzaldehyde were set to be 200.1 mg/L, 400.2 mg/L, 600.3 mg/L, 800.4 mg/L and 1000.5 mg/L, respectively. The series of flasks were then shaken in a water-bath thermostatic oscillator (the agitation speed was set to be 200 rpm) for 8 h at a desired temperature (298 K, 308 K or 318 K) so that the adsorption process reach equilibrium (From the kinetic adsorption experiments, it is observed that 8 h is enough for the adsorption reaching equilibrium). After that, the solid resins were filtered and the equilibrium concentration of *p*-hydroxylbenzaldehyde aqueous solution C_e (mg/L) was determined and the equilibrium adsorption capacity q_e (mg/g) was calculated by conducting a mass balance on *p*-hydroxylbenzaldehyde before and after the experiment. The kinetic curves of *p*-hydroxylbenzaldehyde adsorbed on the resin were performed by analyzing the adsorption uptakes on the resin until the equilibrium was reached (the initial concentration of *p*-hydroxylbenzaldehyde was set to be 300.2 mg/L, 500.4 mg/L and 800.1 mg/L, respectively).

2.4. Dynamic adsorption and desorption experiment

2.5740 g of dry resin was accurately weighed and immersed by de-ionized water with the temperature at 298 K for 24 h, then they were packed in a glass column (16 mm diameter) densely to assemble into a resin column and the wet resin column was measured to be 10 mL. 500.4 mg/L of *p*-hydroxylbenzaldehyde aqueous solution was passed through the resin column at a flow rate of 6.0 BV/h (1 BV = 10 mL) and the residual concentration of *p*-hydroxylbenzaldehyde of the effluent C (mg/L) was dynamically recorded until it reached the initial concentration. After the dynamic adsorption experiment, the resin column was roughly rinsed by 50 mL of de-ionized water and then a mixed aqueous solution containing 1% of sodium hydroxide and 75% of ethanol was applied as the desorption solvent to the dynamic desorption experiment. The solvent was passed through the resin column at a flow rate of 4.6 BV/h and the concentration of *p*-hydroxylbenzaldehyde from the effluent was determined until it was about zero.

2.5. Analysis

The specific surface area and pore volume of the resin were determined by nitrogen adsorption–desorption isotherms at 77 K using a Micromeritics Tristar 3000 surface area and porosity analyzer. The total specific surface area and pore volume were calculated according to Brunauer–Emmett–Teller (BET) model while the pore size distribution was calculated by applying Barrett–Joyner–Halenda (BJH) method to the nitrogen desorption data. The chorine content of the resin was measured according to a Volhard method in Ref. [18]. The elemental analysis of the resin was performed by a VarioEL Elemental Analysis System and the oxygen content of the resin was calculated as: O (%)=100–C (%)–H (%)–Cl (%). FT-IR spectrum of the resin was collected on a Nicolet 510P Fourier transformed infrared instrument. The weak acid exchange capacity of the resin was performed according to the method in