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Effect of pore structure on adsorption behavior of ibuprofen by magnetic anion exchange resins

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ABSTRACT

A series of magnetic anion exchange resins (ND-1, ND-2 and ND-3) with different pore structure were prepared for ibuprofen (IBU) adsorption by using different amount of cyclohexanol as porogen in this work. For adsorption kinetics, resins with larger pore structure showed faster adsorption rates and higher equilibrium adsorption capacities because the internal diffusion process was facilitated by the increase of pore diameter and pore volume. As for adsorption isotherms, the experimental data was better fitted by Freundlich model especially for the resins with broader pores, suggesting that heterogeneous interactions took place in pores. The counter ion released by resin was measured, and ratios of equilibrium adsorption capacity to the counter ion were between 1.22 and 1.56, which confirmed that adsorption process was predominantly attributed to ion exchange while other interactions also existed. Hence, the co-existent anion reduced the adsorption amount of IBU onto resin by competing adsorption in ion exchange process, and the optimal pH ranged from 6 to 8. Resins with more open structure showed better regeneration abilities, of which the adsorption amounts witnessed no significant decrease during 7 circles of use, indicating the advantages of larger pore canal in the adsorption and regeneration behavior.

1. Introduction

Nowadays pharmaceutical and personal care products (PPCPs), such as antibiotics, anti-inflammatories, hormones, and cosmetic ingredients, are widely used in human life. The overuse and the incomplete metabolization of pharmaceuticals by human body lead to the discharge of PPCPs into municipal sewage [1–4]. However, PPCPs cannot be effectively removed by conventional treatment in sewage treatment plants [5–8]. Increasing variety and amount of PPCPs in surface and ground water were detected in many countries, which have caused increasing public concern. The residual PPCPs in the environment would pose potential threats to human health and ecological safety due to their chronic toxicity to human body or aquatic organism [9–12]. Therefore, it is important to remove PPCP from wastewater.

The feasibility of treatment process for PPCPs has been assessed in the recent decade. Biological process is the most conventional method in sewage treatment plants. However, previous studies have showed that removal of PPCPs by traditional activated sludge process can only reach 20%–60% [13–16]. Furthermore, a significant portion of unbiodegraded PPCPs absorbed on activated sludge would be subsequently released into the environment after disposal [14,15]. Because many types of PPCPs are resistant to biological degradation, various physicochemical methods have been applied in the removal of PPCPs. Coagulation was reported to have a limited effect in PPCPs removal so that considerable amount of PPCPs still remained in aqueous phase [3]. The study of P. Westerhoff et al. has showed that the removal efficiency of PPCPs by coagulation was lower than 25% [12]. Coagulation also produces chemical sludge which needs to be properly handled. Although oxidation by ozone or chlorine has been reported to be effective in the removal of organic contaminants, some generated intermediates known as disinfection by-products are carcinogenic,

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including trichloromethane, haloacetic acid and bromate [11,12]. Nanofiltration (NF) and Reverse osmosis (RO) are considered to be the most effective technologies for advanced water treatment, but the high cost and the problem of membrane fouling limit its wide application in developing countries [1,17,18].

Among physicochemical technologies, adsorption has the advantages of easy operation and low cost. Activated carbon can remove a substantial part of PPCPs within a short time [19–21]. A. Ziylan and N.H. Ince has demonstrated that 16%–93% of anti-inflammatory drugs can be removed by granular activated carbon [11]. However, the regeneration of activated carbon is highly costly or unfeasible, and its adsorption capacity reduces greatly at the presence of dissolved organic matter (DOM) [20]. Ion exchange resins, a kind of polymeric absorbents which have different functional groups and pore structure, show different adsorption selectivity to specific compounds. Since the majority of organic pollutants are negatively charged in natural water, anion exchange resins are appropriate for the removal of DOM [22]. Magnetic anion exchange resins, which can easily assemble and settle for their magnetism, are increasingly used in water treatment processes. Comparing to conventional fixed bed resin adsorption process, the fully mixing process of magnetic resin has a greater processing capacity in wastewater treatment. The removal of PPCPs by magnetic ion exchange resins has been reported in some literatures [9,10]. Magnetic ion exchange resins exhibit great adsorption performance for negatively charged PPCPs due to their high specific surface area, excellent exchange and regeneration capacity [10]. While the main mechanism of PPCPs removal by resin is proved to be ion exchange, T.H. Boyer and P.C. Singer indicated that size exclusion is one of the crucial influence factors in pollutant removal, which is related to pore structure [23]. M. Zhang et al. reported that larger pore size brought better adsorption behavior to porous hypercrosslinked resins in physical adsorption process [24]. As for other absorbents, such as mesoporous material, pore structure plays an important role in drug delivery into mesoporous material. P. Horcajada et al. found that delivery rate of drugs into MCM-41 material increased with the increase of pore size although the drug molecule is much smaller than the pore size of MCM-41 [25]. J. Andersson et al. reported that pore structure is the critical parameter in drug loading into micro- and mesoporous silica matrices, comprising size, connectivity and geometry of pore [26]. However, only few studies focus on the influence of the pore structure of magnetic ion exchange resin, especially in PPCPs adsorption process, which limits the understanding of the elimination mechanism of PPCPs and the application of resin adsorption.

In this study, a series of magnetic anion exchange resins with different pore structure were prepared by using different amount of porogen in suspension polymerization. Ibuprofen (IBU) was used in laboratory adsorption experiments as a representative of PPCPs, as IBU was massively produced and frequently found in natural waters [11]. The effect of pore structure on the adsorption behavior of IBU onto the magnetic anion exchange resins was investigated. Furthermore, the effect of pH and inorganic anions as well as the regeneration performance were estimated in this work.

2. Materials and methods

2.1. Chemical

Ibuprofen (IBU), benzoyl peroxide (BPO), sodium sulfate (Na_2SO_4), sodium chloride (NaCl), sodium hydroxide (NaOH), hydrochloric acid (HCl), polyvinyl alcohol (PVA), methanol, cyclohexanol and trimethylamine (TMA) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Divinylbenzene (63.3%, DVB) was provided by Jiangsu Jinkai Resin Chemical Co., Ltd. (China). Glycidyl methacrylate (GMA) was purchased from Dow Chemical Co. (American), and titanate coupling agent was obtained from Kenrich Petrochemicals Inc. (American). γ-Fe_2O_3 was purchased from Zhongke magnetoelectricity Co., Ltd. (Henan, China).

2.2. Resin preparation

The magnetic resins were prepared by suspension polymerization and functionalization method. For suspension polymerization, 2.5 g of Na_2SO_4 and 2.5 g of PVA were added into a 1000 mL round bottomed flask which contained 500 mL of pure water. The mixture was stirred for dissolution in 80 °C water bath. Then this water phase was cooled down to room temperature. 84 g of GMA, 16 g of DVB, 1 g of titanate coupling agent and 1 g of BPO were added into a 500 mL beaker, then cyclohexanol was mixed with the monomers used as porogen. Three polymerization systems were conducted by adding cyclohexanol of 30 g, 50 g and 80 g, which were named the ND-1, ND-2 and ND-3 resin. This organic phase was stirred at 50 °C for 30 min 30 g of γ-Fe_2O_3 was added into the organic phase and stirred for another 30 min. Afterward, the organic phase was poured into the water phase with continuous mechanical stirring. The mixture was heated to 80 °C in water bath for 2 h in order to accomplish polymerization reaction.

The obtained polymers after polymerization were successively washed by distilled water and methanol for 5 times. The resins were stored in methanol. The functionalization was carried out at 80 °C stirring for 8 h by using 400 mL of trimethylamine solution mixing with 100 mL of resin. After functionalization, the products of ND-1, ND-2 and ND-3 were extracted for 10 h by methanol in a Soxhlet extractor, respectively. After washing by pure water, the resin was dried at 60 °C in a vacuum drying oven.

2.3. Adsorption and regeneration

The experiments of IBU adsorption onto resin were conducted in conical flasks at the resin dosage of 0.1 g in 100 mL of IBU solution. In all experiments, conical flasks were shaken in a shaking table (DQHZ-2001A, Huamei Biochemistry Instruments, China) at 150 rpm and 20 °C. IBU was dissolved in chromatographic grade methanol (TEDIA Co., American), and diluted by MilliQ water due to its low solubility in aqueous phase. Adsorption kinetics experiments were conducted at different IBU initial concentrations (0.05, 0.10 and 0.20 mM) for 240 min. Pre-experiment was conducted to determine the equilibrium time of IBU adsorption onto resins, and the adsorption can reach equilibrium within 24 h. Hence, isothermal adsorption experiments were studied in five different IBU initial concentrations (0.05, 0.10, 0.15, 0.20 and 0.25 mM) for 24 h Na_2SO_4 and NaCl were used to investigate the influence of inorganic anions on IBU adsorption process. The pH in all the above experiments was not adjusted. To evaluate the effect of pH on IBU adsorption, the pH values were adjusted by 1 mM HCl and NaOH solution. After adsorption, the solution was separated by virtue of a magnet and samples were taken for IBU measurement. For the regeneration of spent resins, NaCl solution (15%, w/w) was employed.

2.4. Analysis

Automatic specific surface and pore size distribution analyzer (AUTOSORB-iQ2-MP, Quantachrome Instruments, American) was employed for the characterization of the pore structure and the measurement of the surface area by nitrogen adsorption and desorption. Brunauer–Emmett–Teller (BET) method was used for the surface area measurement, and Barrett–Joyner–Halienda (BJH)