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Selective adsorption and separation of BPA from aqueous solution using novel molecularly imprinted polymers based on kaolinite/Fe_3O_4 composites

Wenlu Guo[a,*], Wei Hu[a], Jianming Pan[b], Hongchun Zhou[a], Wei Guan[b], Xue Wang[b], Jiangdong Dai[a], Longcheng Xu[a]

[a] School of Material Science and Engineering, Jiangsu University of Science and Technology, Mengxi Road 2#, Zhenjiang 212013, China
[b] School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China

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ABSTRACT

Magnetic molecularly polymers (MMIPs) based on kaolinite/Fe_3O_4 composites were successfully synthesized for the selective adsorption and separation of bisphenol A (BPA) from aqueous solutions. During polymerization, the modified kaolinite/Fe_3O_4 (KLT/Fe_3O_4) not only was used as supporter but also functional monomer. The properties of MMIPs were characterized by scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) analysis, and thermogravimetric analysis (TGA) and so on. The SEM graphs showed that much of KLT/Fe_3O_4 was successfully coated by the imprinted layer, TGA analysis suggested the grafting yield of imprinted layer to KLT/Fe_3O_4 was 72.51 wt%. The effects of pH, initial BPA concentration, contact time and temperature of the medium on the adsorption were studied by the batch mode experiment. The equilibrium data was well described by the Langmuir isotherm model. The kinetics of adsorption followed the pseudo-second-order model and the rate constant decreased with the increase of temperature, indicating exothermal nature of adsorption process. For desorption studies, the highest desorption efficiency (95.75%) was obtained using methanol and acetic acid as eluting solution (v:v = 8:2). Moreover, the selectivity of MMIPs was further demonstrated through HPLC analysis of the stimulant water samples, the result showed that MMIPs could effectively recognize BPA in mixed solution.

1. Introduction

Endocrine disrupting chemicals (EDCs), exogenous compounds that have estrogenic, antiestrogenic or antiandrogenic properties, may change the function of the endocrine system and consequently causes adverse health effects in an intact organism or its progeny [1,2]. Amongst EDCs, BPA is famous for its impact of hormonal signals and irreversible effects on the development of the reproductive organs [3], such as formation of additional female organs, enlargement of accessory sex glands and a stimulation of egg and egg mass production resulting in increasing female mortality [4]. In addition, BPA is non biodegradable and highly resistant to chemical degradation [5]. In order to eliminate the hazard, an environmental technology for rapid removal of BPA from environment is required.

Methods currently exist to remove BPA from environment contain adsorption [6–10], solvent extraction [11], membrane separation technology [12] and photodegradation [13]. In regular monitoring, the adsorption technique is accepted as an efficient and economically feasible method for BPA from aqueous samples and the adsorbents frequently used are activated carbon and mineral clay, because they have vast surface affinity for many organic chemicals. But they have no selectivity and identity, and these demerits limited the further applications. Therefore, searching for alternative adsorbents that have high capacity and recognition is highly desired. Molecular imprinting technique is an efficient method of producing a 3D cross-linked polymer network in the material that preferentially binds with a specific template [14]. In recent years, it is attracting widespread attention due to its prominent selectivity and identity of molecularly imprinted polymer (MIP) to target [15]. The MIPs prepared by conventional methods had some disadvantages, such as time-consuming, complicated preparation process and less recognition sites inside matrices particles and so on, which led to poor binding capacity and lower binding kinetic of MIPs towards the template molecules [16]. In recent years, with the purpose of overcoming these demerits, researchers have developed the surface imprinting method. BPA–MIPs prepared by surface imprinting technique have been reported, and most researchers utilized silica gel particles as matrix materials when they prepared MIPs [17,18].

When it comes to the application of MIPs in separation of pollutants from environment, the efficiency and cost should be taken into account. Magnetic assisted separation is an efficient,

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* Corresponding author. Tel.: +86 13775531862.
E-mail address: stena.1986@163.com (W. Guo).

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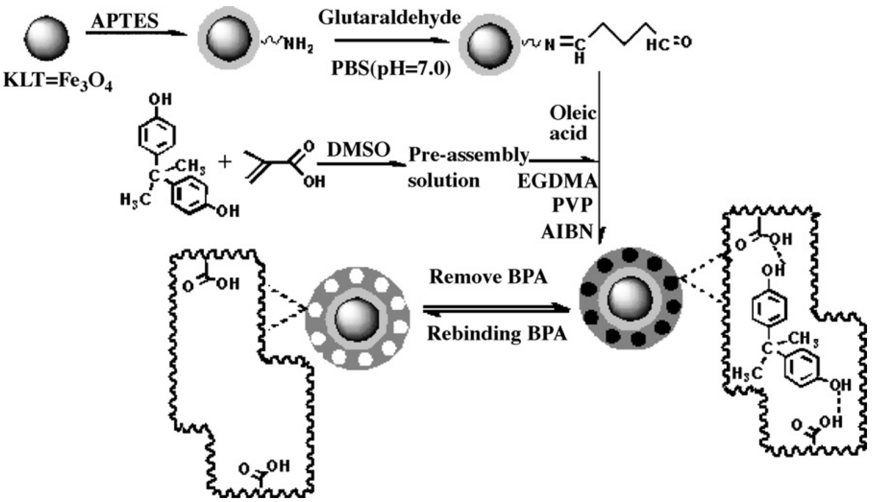

Fig. 1. Schematic illustration of synthesis procedure of MMIPs.

fast and economical technology employed in removing pollutants from environment [19–21] and Fe_3O_4 is the most common magnetic material. In previous studies, great efforts have been made to research magnetic composite adsorbents based on Fe_3O_4 [22,23]. Recently, there has been much research on magnetic molecularly imprinted polymers (MMIPs) based on Fe_3O_4 [24,25]. The separation and recycling of molecularly imprinted polymers became much easier due to incorporating Fe_3O_4. However, during absorption process, some of Fe_3O_4 was likely to leach from the imprinted magnetic beads [26]. In order to prevent leakages of magnetic particles, more and more attentions have directed to the combination of magnetic materials and nano-sized materials such as carbon nanotubes (CNTs) [27–29]. But the cost of CNTs was high and CNTs are difficult to be obtained. Thus, the substitute of CNTs should arouse people's attention. In our study, the supporter of MMIPs was prepared by using kaolinite/Fe_3O_4 (KLT/Fe_3O_4). Kaolinite is a kind of clay, which has many advantages such as wide sources, low cost, simple process and easy use. So MMIPs supported by KLT/Fe_3O_4 have a scientific and economic significance. In addition, through amination treatment and then aldehyde functionalization of KLT/Fe_3O_4, the resulting compound may be used as not only supporter but also functional monomer. Polymerization was carried out in the presence of methacrylic acid (MAA) as assistant functional monomer, polyvinyl-pyrrolidone (PVP) as dispersant, ethylene glycol dimethacrylate (EGDMA) as crosslinker, which resulted in a novel molecular imprinted polymer.

In this study, our first purpose was to assess the physicochemical properties of MMIPs. Second one, to investigate the behaviour of the MMIPs for the separation and recognition of BPA from aqueous solution. The selective adsorption capacity of MMIPs, an effective indicator of selective adsorption, was represented by the difference of adsorption capacity between MMIPs and magnetic non-template imprinted polymers (MNIPs).

2. Experimental

2.1. Materials and apparatus

Kaolinite was supplied by Aotebang International Co., China. $FeCl_2{\cdot}4H_2O$ and $FeCl_3{\cdot}6H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Bisphenol A (BPA), 4,4′-biphenol (4,4′-BIP), 2,4-dichlorophenol (2,4-DCP), methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA), polyvinyl-pyrrolidone (PVP), 3-aminopropyltriethoxysilane (APTES), were obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). Oleic acid, azobisisobutyronitrile (AIBN), and dimethylsulfoxide (DMSO) were purchased from Chemical Reagent Corporation (Shanghai, China). Methanol, ethanol, acetic acid and phosphoric acid were supplied by Nanjing Shuguang Chemical Group Co., China. Except for methanol, which was of HPLC grade, all chemicals were of analytical reagent grade. The chemical structures of BPA, 4,4′-BIP and 2,4-DCP were shown in Fig. 1, Supplementary information.

The apparatuses applied in this study are listed as follows: Nicolet NEXUS-470 FTIR apparatus (USA), Unic-2602 UV spectrophotometer (Unic Company, Shanghai), PHS-2 acidimeter (The Second Analytical Instrument Factory of Shanghai, China), Rigaku D/max-γ B X-ray diffractometer (XRD), TG16-WS high-speed centrifuge (Chang sha Xiang yi Centrifuge Factory, Province Jiangsu, China), scanning electron microscopy (SEM, S-4800), VSM (7300, Lakeshore), Diamond TG/DTA instruments (PerkinElmer, USA), Vario EL elemental analyzer (Elementar, Hanau, Germany), Agilent 1200 HPLC equipped with a UV–vis detector (Palo Alto, USA).

2.2. Preparation of KLT/Fe_3O_4

KLT/Fe_3O_4 composites were obtained via co-precipitation technique [23]. Firstly, the KLT (2.0 g) was dispersed into the solution (200 ml) in a three-necked round-bottomed flask (500 ml), in which dissolved $FeCl_3{\cdot}6H_2O$ (4.410 g). With the purpose to obtain a stable suspension, the mixture was stirred for 12 h. Then, directly add $FeCl_2{\cdot}4H_2O$ (1.614 g) to the flask in N_2 atmosphere with the solution heated to 90 °C and then $NH_3{\cdot}H_2O$ (6.0 ml, 25%, w/w) was added rapidly under stirring, and black precipitate appeared immediately. The solution continued to be kept under stirring for another 1.0 h. Finally, after the reaction mixture was cooled to room temperature, then precipitated, and washed with distilled water for three times. The obtained products were dried at 60 °C and used for further experiments.

2.3. Modification of KLT/Fe_3O_4

In this study, KLT/Fe_3O_4 was modified with reference to previous literature [30,31], including two steps. First step was to introduce amido groups on the surface of KLT–Fe_3O_4:KLT–Fe_3O_4 (3.0 g), toluene (90 ml) and distilled water (10 ml) were added to a three-necked round-bottomed flask (250 ml) equipped with a reflux condenser and an automatic stirrer. Then 3.0 ml of APTES was added into the flask. The mixture was stirred in N_2 atmosphere at 70 °C and 12 h latter, the obtained KLT–Fe_3O_4 were filtered out, washed successively with methanol and distilled water, and