Journal of Cleaner Production 203 (2018) 655–663

Contents lists available at ScienceDirect

Journal of Cleaner Production

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

Environmental-friendly one-step fabrication of tertiary amine-functionalized adsorption resins for removal of benzophenone-4 from water

Xia Zhou [a], Ye Yang [a], Chao Li [a], Zhen Yang [a, b, c, *], Weiben Yang [a, **], Ziqi Tian [d], Limin Zhang [a], Tao Tao [b]

[a] School of Chemistry and Materials Science, School of Environment, Jiangsu Provincial Key Laboratory of Materials Cycling and Pollution Control, Nanjing Normal University, Nanjing 210023, China
[b] Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control (AEMPC), Nanjing University of Information Science & Technology, Nanjing 210044, China
[c] Changzhou Institute of Innovation & Development, Nanjing Normal University, 7 Taihu West Rd., Xinbei District, Changzhou 213001, China
[d] Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences 1219 Zhongguan West Road, Zhenhai District, Ningbo 315201, China

ARTICLE INFO

Article history:
Received 2 May 2018
Received in revised form
24 August 2018
Accepted 27 August 2018
Available online 28 August 2018

Keywords:
Sunscreen reagent
Tertiary amine-functionalized adsorption resins
Adsorption
One-step fabrication
Electrostatic attraction

ABSTRACT

2-hydroxy-4-methoxybenzophenone-5-sulfonic acid with a trade name of benzophenone-4, a typical anti-UV product, is increasingly detected in real aqueous environment. Few literature using cost-effective adsorption means with enough high adsorption capacity for the removal of benzophenone-4 is available. In this work, a series of novel tertiary amine-functionalized crosslinking polymeric resins, synthesized using different proportions of raw materials including 2-dimethylamino ethyl methacrylate as the monomer, divinylbenzene as the crosslinking reagent and toluene as the pore-forming reagent, were employed for the adsorption of benzophenone-4. During the synthesis process, an environmental-friendly one-step fabrication method, following the concept of cleaner production, was established for the reduction of unnecessary derivatization steps, extra pollution risk, costs and time. Among these resins, the optimal one with relatively larger pore diameter, larger specific surface area, and fewer inner defects, exhibited the highest adsorption capacity of 154 mg/g. Such a value was notably larger than several frequently reported commercial adsorbents, including activated carbon, ion exchange resins and macroporous resins. The performance of the resin not only owned strong resistance against influences of coexisting natural organic matter and inorganic ions, but also bore reuse without much capacity loss after six adsorption-desorption cycles. Adsorption interfacial interactions were studied, *via* both experimental analyses and chemical calculations. Electrostatic attraction between tertiary amine of the resin and $-SO_3^-$ of benzophenone-4 played a leading role during adsorption.

1. Introduction

During the past half century, much environmental concern has been placed to Pharmaceutical and Personal Care Products (PPCPs), which bring potential dangers to both humans and ecosystem owing to their strong persistence, biological activity and bioaccumulation (Ortiz de Garcia et al., 2017). Sunscreen reagents, applied for the adsorption or reflection of sun's UV radiation, are a sort of widely used PPCPs and being increasingly detected in real water (Vidal-Linan et al., 2018). For example, 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid (benzophenone-4, BP-4), a typical anti-UV agent, is extensively used in sunscreen products (DiNardo and Downs, 2018; Molins-Delgado et al., 2016). The common concentration levels of BP-4 are normally not to lead to acute toxicity. However, the chronic effects can hardly be ignored (Kunz et al., 2006; Valle-Sistac et al., 2016). Consequently, elimination of BP-4 from water environment is required.

* Corresponding author. School of Chemistry and Materials Science, School of Environment, Jiangsu Provincial Key Laboratory of Materials Cycling and Pollution Control, Nanjing Normal University, Nanjing 210023, China.
** Corresponding author.
E-mail addresses: yangzhen@njnu.edu.cn (Z. Yang), yangwb007@njnu.edu.cn (W. Yang).

https://doi.org/10.1016/j.jclepro.2018.08.290

Among methods to remove organic pollutants, adsorption is one economical and less time-consuming technology used in environmental engineering (Elwakeel et al., 2017; Rezgui et al., 2017). More importantly, adsorption method provides a possibility for recovery of organic contaminants as resources for reuse, *via* further desorption of these contaminants from adsorbents (Li et al., 2017; Park et al., 2018). However, although a number of literature have reported the successful removal of BP-4 using other methods (Liu et al., 2016; Peng et al., 2017; Semones et al., 2017; Yang et al., 2017), few report about efficient adsorption (with enough high adsorption capacity) of this contaminant is available.

If adsorption method is employed, the selection of appropriate adsorbents matters much to the performance. Various types of adsorbents, including synthetic polymeric resins (Cechinel et al., 2018; Li et al., 2018a), biopolymer-based materials (Demey et al., 2014; Elwakeel et al., 2016), activated carbon (De Franco et al., 2018), and nano-materials (Kim and Choi, 2017), have been demonstrated to be efficient candidates for different contaminants. Among them, synthetic polymeric resins have the advantages of relatively low cost, high capacity and strong regeneration ability. On the other hand, according to the structural characteristics of certain contaminant, the corresponding characteristics of resins (functional groups and pore structure) can be designed and easily controlled by adjusting both types and proportions of monomers, pore-forming agents, crosslinking agents, modification agents and others in synthetic processes. For example, in authors' previous work (Zhang et al., 2016c), aiming at the recovery of an organic product 1-amino-8-naphthol-3,6-disulfonic, with anionic sulfonic and phenolic groups in its chemical structure, a series of amine-functionalized polymeric resins with different structure characteristics were synthesized; Among them, the resin with a certain content of tertiary amine groups and suitable pore structure was selected to be the optimal one through careful evaluation. Given that BP-4 also has sulfonic and phenolic groups, it is deduced that resins with similar tertiary amine groups and structure are also quite possible to be suitable for adsorption of BP-4.

Although control of characteristics of resins can be achieved as aforementioned, one problem that has to be noted is that the fabrication process of resins usually contains multi-steps (Elwakeel and Guibal, 2015; Wang et al., 2016c). Generally, resin beads without functional groups (usually called "white beads") are firstly formed through a suspension polymerization process; then the white beads are post-cross-linked to generate desired pore structure; lastly, functional groups are chemically introduced on resins. During the multi-step process, extra pollution may be caused, as well as the increased capital cost and time. If the multi-steps can be integrated into one-step, the synthesis process will considerably reduce unnecessary derivatization steps, decrease extra pollution risk, and save costs and time, which is consistent with the concept of cleaner production (Fresner and Yaacoub, 2006). However, to the best of our knowledge, one-step fabrication method of tertiary amine resins has been rarely reported.

In this work, a series of tertiary amine-functionalized polymeric resins were synthesized by one-step fabrication method with different ratios of monomer (2-dimethylamino ethyl methacrylate, DMA), crosslinking reagent (divinylbenzene, DVB) and pore-forming reagent (toluene), and applied for BP-4 elimination. The optimal synthetic condition was obtained according to the adsorption capacity (Q_e) of various resins, and analyzed from the viewpoint of pore structure. Effects of pH, coexisting nature organic matter (NOM) and inorganic ions on the adsorption performance, as well as desorption performance and reusability, of the optimized resin, were systematically evaluated. In-depth adsorption mechanism was explored by thermodynamic and kinetic analyses, instrumental and theoretical investigations.

2. Materials and methods

2.1. Materials

BP-4 was provided by Aladdin Industrial Co. Its structure is given in Fig. 1a. The monomer (DMA), crosslinking reagent (DVB), pore-forming reagent (toluene), and other chemicals (Sinopharm Chemical Reagent Co. Ltd.) were of reagent grade. All the experiments used deionized water.

2.2. Preparation of the tertiary amine-functionalized resins

Fig. 1b showed the synthesis route: 3 g of gelatin, 1.05 g of Na_3PO_4, 4.2 g of Na_2HPO_4, 32 g of NaCl and 250 mL of water were fully mixed in a flask as dispersion phase. Then, different proportions (listed in Table 1) of DMA, DVB and toluene were added. After the addition of 0.5 g of BPO and 0.5 g of AIBN as initiators, stirring at 363 K is kept for 12 h with a stirring speed of 200 rpm. Resin beads were gradually formed during this process. After 12 h, these beads were collected, rinsed with water, 1 wt% HCl aqueous solution, methanol, and water in turn, until the effluent was clarified with neutral pH. Finally, the products (named as Resin DMA-T), with dimeters of 0.3–0.5 mm were dried in vacuum at 60 °C for 12 h. According to the proportions, a series of resins were numbered differently (Table 1).

2.3. Characterizations

The obtained resins were systematically characterized by Fourier transform infrared (FTIR) recording, pore structure analyses, elemental analyses, scanning electron microscope (SEM) observation, zeta potential (ZP) determination, and X-ray photoelectron spectroscopy (XPS). Details were provided in Supporting Information (SI) Text S1.

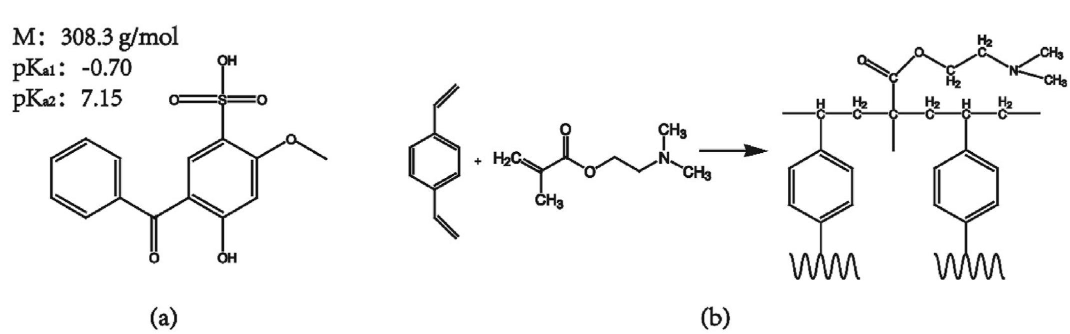

Fig. 1. (a) Chemical structure and physico-chemical properties of BP-4; (b) Synthetic route of DMA-T resins.