Competition and enhancement effect in coremoval of atenolol and copper by an easily regenerative magnetic cation exchange resin

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HIGHLIGHTS

- Atenolol (ATL) and Cu^{2+} were co-removed by self-prepared MECR.
- The ATL adsorption was suppressed for the direct competition of adsorptive sites.
- The Cu^{2+} adsorption was enhanced by additional bridging interaction.
- The salinity could obviously amplify the competition and enhancement effect.
- The MCER was easily regenerated by 0.01 M HCl solution with no Fe leaching.

GRAPHICAL ABSTRACT
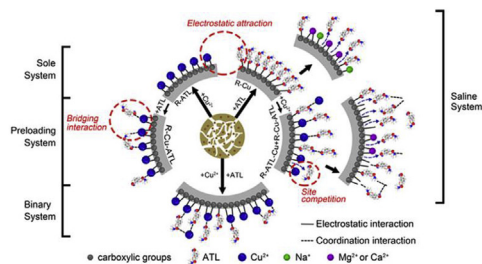
ABSTRACT

This paper aimed to investigate the removal of combined Cu^{2+} and atenolol (ATL) in aqueous solution by using a newly synthesized magnetic cation exchange resin (MCER) as the adsorbent. The MCER exhibited efficient removal performance in sole, binary, pre-loading and saline systems. The adsorption kinetics of Cu^{2+} and ATL fitted both pseudo-first-order and pseudo-second order model, while better described by pseudo-second order model in binary system. In mixed Cu^{2+} and ATL solution, the adsorption of ATL was suppressed due to direct competition of carboxylic groups, while Cu^{2+} adsorption was enhanced because of the formation of surface complexes. This increasing in heterogeneity was demonstrated by adsorption isotherms, which were more suitable for Freundlich model in binary system, while better described by Langmuir model in sole system. As proved by FTIR and XPS spectra, both amino and hydroxyl groups of ATL could form complexes with Cu^{2+}. Decomplexing-bridging interaction was elucidated as the leading mechanism in coremoval of Cu^{2+} and ATL, which involved [Cu-ATL] decomplexing and newly created Cu- or ATL sites for additional bridging. For saline system, the resulting competition and enhancement effects in mixed solution were amplified with the addition of co-existing cations. Moreover, the MCER could be effectively regenerated by 0.01 M HCl solution and maintain high stability over 5 adsorption-desorption cycles, which render it great potential for practical applications.

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1. Introduction

In recent years, combined pollution of heavy metal ions (HMIs) and pharmaceuticals have caused much concern for their hazards

to ecological environment and human health (Sayari et al., 2005; Hospido et al., 2010; Vystavna et al., 2013; Lu et al., 2016). HMIs, which are toxic to organisms even at trace level, have been widely applied in electroplating, tannery manufacturing and agricultural production (Dábrowski et al., 2004; Cheng et al., 2014; Guo et al., 2016). Since HMIs are characterized as persistent and non-degradable, they are circulated in soil and aquatic environment and eventually accumulated in food chains (Dábrowski et al., 2004; Cavaco et al., 2007; Wang et al., 2015). Meanwhile, various kinds of pharmaceuticals and their intermediates are widely existed in sewage effluents, surface and groundwater because of their incomplete degradability by conventional biological treatments (Elder, 2005; Suarez et al., 2010; Martucci et al., 2012; Al-Khateeb et al., 2014). And the combined pollution of HMIs and pharmaceuticals always lead to the elevated toxicity and carcinogenicity of contaminated water (Garcia-Armisen et al., 2011; Yang et al., 2015; Andreu et al., 2016). Many of these pharmaceuticals can represent mono- or poly-dentate ligands, which render them high complexation affinities towards HMIs like copper, zinc and iron, suggesting more complicated environmental behaviors of adsorption, degradation and bioavailability (Gölcü et al., 2004; Garcia-Armisen et al., 2011; Delgado et al., 2015). Therefore, it is of vital importance to deal with these combined pollutants of HMIs and pharmaceuticals.

Traditional technologies to deal with multiple contaminants involve chemical precipitation, advanced oxidation, biological treatment, membrane filtration and adsorption (Ma and Zhang, 2008; Gharabaghi et al., 2012; Li et al., 2012; Pantke et al., 2012; Zhang et al., 2016; Lee et al., 2017). Among these methods, adsorption, as an effective and economic technique, has been widely utilized to remove numerous pollutants in current water treatment processes (Ma et al., 2014; Delgado et al., 2015; Zhang et al., 2015). Adsorption by ion-exchange resin has received much attention for its better adsorption and regeneration performance than activated carbon (Shuang et al., 2012b; Chen et al., 2013; Zagklis et al., 2015). Magnetic ion exchange resin, due to its fast adsorption kinetics, easy agglomeration and large treatment flux, has been extensively utilized to effectively remove various organic and inorganic pollutants in wastewater (Shuang et al., 2012a; Fu et al., 2014; Arias-Paic et al., 2016). Fu et al., 2015 investigated the synergistic removal of Cu^{2+}, Ni^{2+} and tannic acid by using magnetic anion and cation exchange resin. The simultaneous or sequential adsorption processes showed superior synergistic removal performance. Different researches have also mentioned that HMIs could form stable complex species with N- and O-donor groups of pharmaceuticals (Mechmeche et al., 2008; Guo et al., 2012; Ahmad Panahi et al., 2015; Kyzas et al., 2015). As reported, Han et al., 2015 simultaneously removed Cu^{2+} and phenol by using carboxylic functionalized porous beads as the adsorbents. It was demonstrated that Cu^{2+} was first absorbed at the interface of beads and then the ions-enrichment interface layer was benefit for phenol adsorption. Ma et al., 2014 synthesized a bifunctional adsorbent HAR-1 with high surface area and cation exchange capacity. This novel resin could effectively remove Cu^{2+} and tetracycline in their aqueous solution. In this regard, the complexities in pharmaceuticals structure could either positively or negatively affect the adsorption capacity. However, limited studies focus on the mutual interactions between combined pollutants and adsorbents.

The objective of this work was to remove the combined pollutants of HMIs and pharmaceuticals in aqueous solution using a new type of magnetic cation exchange resin (MCER). The MCER was a macroporous polyacrylic weak acid resin with large amounts of carboxylic groups. Cu^{2+} and a commonly used β-blocker atenolol

(ATL, Fig. S1) were chosen as the model compounds for their representativeness of HMIs and pharmaceuticals (Fu et al., 2014; Kyzas et al., 2015). The adsorption behaviors were systematically investigated in sole, binary, pre-loading and saline systems, and the adsorption mechanisms were further discussed. Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) were also used to reveal the mutual interactions.

2. Materials and methods

2.1. Materials

Methyl acrylate (MA, AR), divinylbenzene (DVB, 80 wt%) were purchased from J&K Chemical Co., Ltd., China. Titanate coupling agent (TCA) and benzoyl peroxide (BPO, CR) were obtained from Nanjing Capture Chemical Co., Ltd and triallyl isocyanurate (TAIC) was supplied by Shanghai Farida Chemical Co., Ltd. The model beta-blocker used (ATL, ≥98%) was supplied by Sigma-Aldrich. All other reagents were of analytical grade.

2.2. Synthesis of magnetic cation exchange resin (MCER)

The magnetic cation exchange resin, called MCER, was synthesized through copolymerization and hydrolysis reaction. In the preparation of MCER, TCA was used in copolymerization process to enhance the acid resistance and lipophilicity of inorganic γ-Fe_2O_3 particles. The detailed synthetic steps were shown in Text S1, supplementary material.

2.3. Characterization

FT-IR (NEXUS 870, USA) and XPS (PHI 5000, Japan) analysis were applied to identify the differences of resin before and after the adsorption of Cu^{2+} and/or ATL. All XPS spectra were calibrated against C1s bands at 284.6 eV. The surface morphology of obtained resin was observed by scanning electron microscopy (SEM, Hitachi S-3400, Japan). The magnetization analysis was conducted with a vibrating sample magnetometer and the thermo-gravimetric curves were obtained by the thermal analyzer (Pyris 1 DSC, Perki-nElmer, USA).

2.4. Batch adsorption

Batch adsorption experiments were performed to investigate the adsorption processes of Cu^{2+} and ATL onto MECR. For kinetic study, 0.250 g of MCER was added and stirred in 1000 mL of single or mixed solution with pre-settled concentrations of Cu^{2+} and/or ATL at pH 5 and 293 K. Samples were withdrawn at pre-determined time intervals (5 min, 10 min, 20 min, 30 min, 45 min, 60 min···) and measured. For each time interval, at least three parallel runs were performed to confirm the repeatability and only the average value was given. The presented average values were used with an error <5%. The pseudo-first-order and pseudo-second-order kinetic equation (Text S2, supplementary material) were applied to further elucidate the adsorption behaviors.

Adsorption isotherms were obtained by varying the initial concentration of adsorbates in sole or binary systems. 0.025 g of MECR and 100 mL solution (initial pH 5) were transferred into the flasks. All flasks were shaken at 293 K and 150 rpm for 24 h to attain equilibrium. The Langmuir and Freundlich isotherm model (Text S3, supplementary material) were employed to describe the adsorption behaviors.

The adsorption capacity Q_t (mmol/g) was also withdrawn at pre-determined time and measured, then calculated according to Equation (1):