Chemical Engineering Journal 263 (2015) 83–91

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

High-efficient technique to simultaneous removal of Cu(II), Ni(II) and tannic acid with magnetic resins: Complex mechanism behind integrative application

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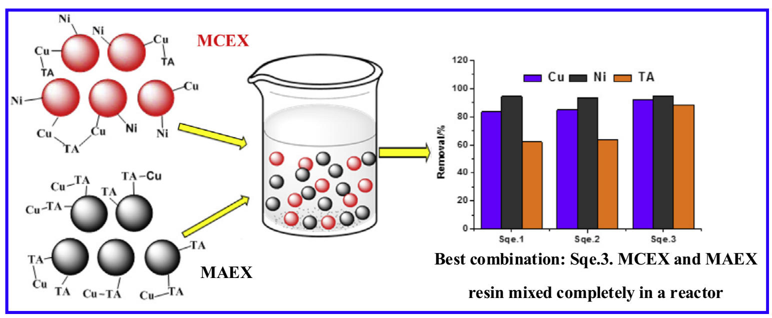
HIGHLIGHTS

- Cu(II), Ni(II) and tannic acid were simultaneously removed by combined magnetic resins.
- Complexing-bridging was ascribed as the predominant co-removal mechanism.
- Hydrogen bond and ion exchange interaction were ascribed to TA adsorption onto MAEX.
- Three adsorbates could be recovered with 0.1 M NaOH followed by 0.01 M HCl.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 August 2014
Received in revised form 4 November 2014
Accepted 5 November 2014
Available online 13 November 2014

Keywords:
Magnetic resin
Simultaneous removal
Tannic acid
Copper
Nickel

ABSTRACT

Magnetic strongly basic anion exchange resin (MAEX) and weakly acidic cation exchange resin (MCEX) and their combined processes were employed to simultaneously remove such heavy metals (HMs) as Cu(II), Ni(II) and tannic acid (TA). Both MAEX and MCEX resins exhibited co-removal capability for Cu(II) and TA in binary solutions. Complexing-bridging was ascribed as the primary mechanism for the co-removal of TA and Cu(II) based on Density-Functional-Theory (DFT) calculation, fluorescence spectra, Fourier Transform Infrared Spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) characterization. Moreover, an interesting discovery was found that hydrogen bond interaction between both nitrogen atom of the secondary amine (—NH—) and oxygen atom of carbonyl (C═O) with un-ionized TA, and quaternary ammonium (—$N^+(CH_3)_3$) ion exchange with ionized TA were ascribed to the mechanism of TA adsorption onto MAEX. The novel integrative technique based on MAEX and MCEX mixed completely in the same reactor could simultaneously remove Cu(II), Ni(II) and TA with high efficiencies of 92.1%, 94.8% and 88.4%, respectively. Three adsorbates could be successfully recovered with 0.1 M NaOH followed by 0.01 M HCl solution. Given the stable application for five cycles, combined magnetic resin treatment showed great potential in simultaneous removal of Cu(II), Ni(II) and TA.

1. Introduction

Organic and inorganic pollutants such as phytic substances (PS) and heavy metals (HMs) are common in the environment and pose a serious toxicological threat to the ecosystem and human health. Tannic acid (TA) which contains multiple adjacent phenolic hydroxyls is one of the major components of phytic substances

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http://dx.doi.org/10.1016/j.cej.2014.11.041
1385-8947/

[1]. Ingestion of large quantities of tannins may result in adverse health effects [2]. TA may injure the intestinal mucosa [3], alter intestinal secretions [4], inhibit digestive enzymes and increase the excretion of endogenous proteins [5]. In the meantime, HMs, which are mostly acute toxic to human and wildlife even at trace level, are widely used in industrial and agricultural production. The coexistence of TA and HMs as complex mixtures in contaminated water has significantly influenced humans and the ecosystem because of their mobility, combined toxicity, and carcinogenic properties, rendering their environmental behaviors more complicated [6–9]. Consequently, the effective control of the combined pollution of TA and HMs has attracted continuous concern recently. Traditional methods for removing combined pollution involve chemical precipitation, advanced oxidation, membrane treatment and biological treatment, which suffer from such disadvantages as high cost, low efficiency, and secondary pollution [10–13]. As a green and simple technology, adsorption has been widely utilized in recent years for the removal of combined pollutants [14]. Among different adsorbents, ion-exchange resin with high removal efficiency is regarded as one of the most effective separation and purification processes [15,16].

The ion exchange process typically used for water treatment occurs in fixed-bed columns filled with ion exchange resins, which range from 0.3 to 1.2 mm in diameter. However, the full-scale application of fixed-bed columns for water treatment has some inevitable shortcomings, such as high capital costs and limited flux [17–19]. MIEX resin, developed by Orica, is a magnetic ion exchange resin that has fast adsorption kinetics, because of its small size [20]. It can be used in completely mixed contactors for ion exchange, in which the resin is mixed with water for adsorption and self-agglomerated for separation [21,22]. Nonetheless, the exchange capacity of MIEX is low, and its backbone is susceptible to mechanical disruption in mixing contactors, which can result in the loss of resins and secondary pollution [23–29]. Therefore, the preparation of novel magnetic resins with high exchange capacity and good mechanical strength is necessary.

Recently, a novel magnetic strongly basic anion resin MAEX and a magnetic weakly acidic cation resin MCEX were developed in our group [23,30,31]. The exchange capacity of MAEX and MCEX was about 3.78 and 8.80 meq/g, respectively, which was much higher than that of MIEX–Cl and MIEX–Na resin. Besides, with the addition of iron oxide into the resin beads, MAEX and MCEX exhibit easy separation property and high mechanical strength [32].

Although previous researchers have investigated anion exchange for organics removal and cation exchange for HMs removal, only a few previous reports combined anion and cation exchange into a single unit process for the simultaneous removal of combined pollutants [24]. The overall goal of this work is to evaluate the removal efficiency of TA and HMs by combined anion and cation exchange treatment. Cu(II) and Ni(II) are the most common heavy metal ions in industrial wastewater, especially in the electroplating wastewater. Cu(II) and Ni(II) were chosen as the typical HMs. Previous studies showed that the presence of HMs and TA could either positively or negatively affect the sorption of each other, because of strong complexation of solutes [1,7,33]. Therefore, it is of significance to explore combined treatment for co-removal of TA and HMs. The specific objectives are: (1) to compare the removal efficiencies of combined pollutants by anion, cation, and combined ion exchange treatment; (2) to systematically investigate the complexing mechanism of Cu(II), Ni(II) and TA by fluorescence spectra, Density-Functional-Theory (DFT), FTIR and XPS characterization; (3) to demonstrate the mutual effect between TA and Cu(II) or Ni(II) during the sorption of each other onto MAEX and MCEX by adsorption isotherms and kinetics; (4) to study the regeneration performance of the combined ion exchange treatment process.

2. Materials and methods

2.1. Materials

The magnetic resin MAEX and MCEX were employed for batch adsorption assay in this work. In this study, MCEX is the NDMC resin in the previous literature [31], and MAEX is NDMP resin in the previous report [23]. The physicochemical properties including water content, BET, ion exchange capacity are listed in Table 1. Before the experiments the resins were extracted with ethanol for 12 h in a Soxhlet apparatus. Afterwards, the resins were washed with distilled water and dried at 333 K. MAEX and MCEX were converted to the chlorine form (R-Cl^-) and sodium (R-Na^+) form prior to use.

Tannic acid (TA, $C_{76}H_{52}O_{46}$, molecular weight = 1701 per mole) was of analytical grade and purchased from Aladdin Industrial Corporation (Southern California, USA). All the other chemicals were analytical reagents and purchased from Nanjing NingShi Reagent Company (Nanjing, JiangSu, PRC).

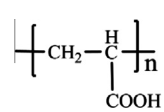
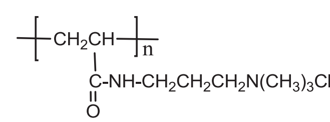
2.2. Single and multiple components adsorption assay

0.05 g of each adsorbent was introduced into conical flasks, and then 100 mL of aqueous solutions with different concentrations of adsorbate were added into those flasks. The flasks were shaken under 298 K at 150 rpm for 24 h to reach equilibrium. The initial concentration of Ni(II), Cu(II) and TA single component is 20, 20 and 100 mg/L, respectively. The initial concentrations of Ni–TA and Cu–TA double components are both 20 mg/L and 100 mg/L. The initial concentrations of Ni–Cu–TA three-components are 20 mg/L for Ni(II), 20 mg/L for Cu(II) and 100 mg/L for TA. The residual Cu(II) and Ni(II) concentration was determined using atomic adsorption spectrophotometer (AAS, TAS-990, Beijing Pgeneral Co.). The residual TA concentration was determined using total organic carbon (TOC) analyzer (OI-1030D, USA).

The adsorption efficiency of HMs and TA was calculated from the following equation:

$$\text{Adsorption efficiency} = \frac{(C_0 - C_e)}{C_0} \quad (1)$$

Table 1
Physicochemical properties of MAEX and MCEX.

Parameters	MCEX	MAEX
Matrix structure	Acrylic	Acrylic
Functional groups		
Resin type	Weakly acidic	Strongly basic
Water content (%)	45.1	56.2
BET specific surface area (m^2/g)	2.37	5.20
Selected diameter (mm)	0.1∼0.15	0.1∼0.15
Anionic exchange capacity (meq/g)	8.80	–
Cationic exchange capacity (meq/g)	–	3.78