Chemical Engineering Journal 171 (2011) 152–158

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Adsorption of Cu(II), Pb(II), Co(II), Ni(II), and Cd(II) from aqueous solution by poly(aryl ether ketone) containing pendant carboxyl groups (PEK-L): Equilibrium, kinetics, and thermodynamics

Xiaowei Zhao[a], Gang Zhang[b], Qiong Jia[a,*], Chengji Zhao[b], Weihong Zhou[a], Weijie Li[a]

[a] College of Chemistry, Jilin University, Changchun 130022, PR China
[b] Alan G MacDiarmid Institute, College of Chemistry, Jilin University, Changchun 130012, PR China

ARTICLE INFO

Article history:
Received 6 December 2010
Received in revised form 22 March 2011
Accepted 23 March 2011

Keywords:
Adsorption
PEK-L
Heavy metal ions
Flame atomic absorption spectrometry (FAAS)

ABSTRACT

In the present work, poly(aryl ether ketone) containing pendant carboxyl groups (PEK-L) is prepared to develop efficient adsorbent for heavy metal ions, Cu(II), Pb(II), Co(II), Ni(II), and Cd(II), from aqueous solution. The property of PEK-L is investigated by using FT-IR and XRD analysis. Effects of pH and contact time, kinetics, adsorption isotherms, and thermodynamics are examined in batch experiments. Kinetic experiments indicate that the processes can be simulated by a pseudo-second-order model. Langmuir, Freundlich, and Tempkin models are applied to analyze the experimental data, and the best interpretation for the experimental data is given by the Freundlich isotherm equation. Thermodynamic parameters, the Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°), are calculated and show that adsorption of heavy metals on PEK-L is spontaneous and endothermic in nature. The regeneration study indicates that PEK-L can be used repeatedly without significantly changed their adsorption capacities and desorption percentage.

1. Introduction

Environmental pollution caused by heavy metal ions is deteriorating the inhabited environment and endangers the human health, which has become a serious problem due to their toxic properties and the tendency for bio-accumulation in the food chain. The determination of ultra trace of heavy metals in environmental samples plays an important role in the environmental pollution monitoring. Despite the selectivity and sensitivity of modern analytical techniques, there is a crucial need for the preconcentration of trace elements before their analysis. Consequently, several different types of methods, such as chemical precipitation [1,2], solvent extraction [3], nanofiltration [4], and adsorption [5–22], have been used for the removal of heavy metal ions.

Among all of the methods, adsorption has increasingly received much attention because of its high efficiency, simple operation, and environmental friendliness. Up to now, a variety of adsorbents have been reported as materials for the adsorption of heavy metals including activated carbon [5,6], modified silica gel [7,8], multiwalled carbon nanotubes (MWCNTs) [9,10], biomaterials [11], ion-imprinted materials [12,13], polymers [14–18], inorganic materials [19], and sorption resins [20–22]. For example, thiourea-modified magnetic chitosan microspheres (TMCS) have been prepared by Zhou et al. [11]. The adsorption equilibrium and the kinetics of Hg(II), Cu(II), and Ni(II) in aqueous solutions with TMCS have been investigated, and the maximum adsorption capacities are 625.2, 66.7, and 15.3 mg g^{-1} for Hg(II), Cu(II), and Ni(II), respectively. Li et al. [15] have described the sorption behaviors of toxic metal ions on sulfonic acid-modified microporous hypercrosslinked polymers (SAM-HCPs), and the polymers have been found to attain very good adsorption capacity for metal ions (e.g., Cu^{2+} 51.45 mg g^{-1} at 303 K, 54.82 mg g^{-1} at 313 K, and 57.68 mg g^{-1} at 323 K), which is due to the synergic effect of microporous structure and active sites. In order to remove heavy metals from the environment, some special requirements for the adsorbents should be met, such as high mechanical and thermal stability, strong chemical union with the metals, and high adsorption capacity. For these reasons, choice of suitable materials for adsorption is of particular importance.

Aromatic poly(ether ketone)s (PEKs) are a class of high performance engineering thermoplastics known for their excellent combination of chemical, physical, and mechanical properties. This class of advanced materials is currently receiving considerable attention for potential applications in aerospace, automobile, electronics, and other high technology fields [23–27]. Much effort has been devoted to modify PEKs with different functional groups, e.g., phenyl [28], amide [29], carboxyl [30], butyl [31], methyl [32], and bromomethyl moieties [33], in order to obtain

---

[*] Corresponding author. Tel.: +86 431 85095621; fax: +86 431 85095621.
E-mail address: jiaqiong@jlu.edu.cn (Q. Jia).

1385-8947/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2011.03.080

the desired solubility, processability, and other properties. For instance, Liu et al. [28] have synthesized aromatic PEKs with high thermal stabilities based on a novel bisphenol monomer (3,5-ditrifluoromethyl)phenylhydroquinone. In Lin et al.'s work [30], poly(aryl ether ketone)s containing pendent carboxyl groups (PEK-L) have been prepared and attached with benzimidazole and sulfonic groups simultaneously. The balance of proton conductivity, methanol permeability, thermal and mechanical stabilities is designed and can be expected to be applicable in direct methanol fuel cells. However, to the best of our knowledge, apart from a large number of studies concerning the synthesis of novel PEKs or their derivatives, the assessment of PEKs for the adsorption of metal ions has not been reported. As can be expected, carboxylic groups contained in the adsorbent may lead to the ion-exchange interactions between the metal ions and the adsorbent. Therefore, it will be of interest to develop PEKs containing carboxylic groups and investigate their potential applications to the adsorption of metal ions.

The aim of this work is to employ PEK-L as a novel adsorbent and to study the adsorption behavior of transitional metal ions from aqueous solutions. The influence of experimental conditions, pH value, and contact time on the sorption behavior is investigated. The adsorption isotherm, kinetics, and thermodynamics have also been studied.

2. Experimental

2.1. Materials

All chemicals used in this study were of analytical grade. Stock solutions (1000 μg mL^{-1}) of Cu(II), Pb(II), Co(II), Ni(II), and Cd(II) were prepared by dissolving the appropriate amounts of $CuCl_2{\cdot}2H_2O$, $PbCl_2$, $CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, and $CdCl_2{\cdot}2.5H_2O$ in deionized water, respectively. The working standard solutions were prepared daily by stepwise dilution of stock solutions. Adjustment of pH was undertaken using 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} $NH_3{\cdot}H_2O$.

2.2. Preparation of the poly(aryl ether ketone)s containing pendent carboxyl groups (PEK-L)

The PEK-L was prepared according to our previous work [30] (Scheme 1). Phenolphthalein, sodium hydroxide, and zinc were added to 1500 mL water, and the mixture was heated at 60 °C under continuously stirring until a grayish-white reaction mixture was resulted. Then the product was poured into aqueous hydrochloride acid and filtered to separate the white solid. Then it was dried in a vacuum oven at 120 °C for 48 h. In the following, phenolphthalin, 4,4′-difluorobenzophenone, and anhydrous potassium carbonate were placed in a three-neck round-bottomed flask equipped with a mechanical stirrer. The reaction mixture was then heated until the toluene began to reflux. The product was isolated by coagulation in HCl solution. The precipitated copolymer was then washed several times with ethanol, and dried in a vacuum oven for 24 h.

2.3. Instruments

The analysis was carried out using a flame atomic absorption spectrometry (FAAS) (Beijing Purkinje General Instruments Co. Ltd., China) equipped with a flame burner. Operational parameters for the metals under study, including lamp currents and wavelength, were those recommended by the manufacturer. All metals were measured under optimized operating conditions by FAAS with an air-acetylene flame.

X-ray diffraction (XRD) patterns were determined by means of a Siemens D-500 diffractometer employing a nickel-filtered Cu Kα radiation in the 2θ diffraction angle range extending from 5 to 60°, intensity values were read at $\Delta(2\theta)$ intervals of 0.02° employing a step time of 1.2 s.

For the main functional groups that might be involved in metal adsorption, an Fourier Transform Infrared analysis (Affinity-1, Shimadzu, Japan) was done on natural PEK-L and metals loaded PEK-L to determine the surface functional groups, and the spectra were recorded from 4000 to 400 cm^{-1}.

2.4. Adsorption experiments

Studies on the adsorption of metal ions were carried out by batch experiments. For this purpose, a portion of 0.02 g adsorbents mixed with a 10 mL solution of metal ions in special glass-stoppered tubes were shaken under a controlled temperature of (293 ± 1) K. The initial metal concentrations were fixed at 10 mg L^{-1} unless otherwise stated. Batch adsorption experiments were conducted to investigate metal ions adsorption at certain aqueous pH values (2.0–7.0) and contact time (10–150 min). After reaching the sorption equilibrium, the suspension was filtered through 0.45 μm filters and the metal concentration in the liquid phase was determined using FAAS. All the experimental work was carried out in triplicate and the average result was presented. The adsorption percentage of metal ions was calculated using Eq. (1) and the adsorption capacity was calculated using Eq. (2).

$$\text{Adsorption}\,(\%) = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (2)$$

where C_0 and C_e represent the initial and equilibrium metal ion concentrations (mg L^{-1}), respectively; V is the volume of the metal ion solution (mL) and m is the amount of adsorbent (mg).

3. Results and discussion

3.1. Characterization of PEK-L

PEK-L has been characterized by XRD and FT-IR. In the spectrum of the X-ray diffraction analysis, a wide diffraction pattern is obtained, indicating that PEK-L is amorphous [18,34,35].

Fig. 1 shows the FTIR spectra of PEK-L before and after loaded with metal ions. For the PEK-L in natural form (Fig. 1a), the broad band at over 3000 cm^{-1} was dominated by the stretching vibrations of hydroxyl in carboxylic acid. The sharp peaks at 1773 cm^{-1} and 1734 cm^{-1} are attributed to free carboxyl group and hydrogen-bonded carboxyl group, respectively. The above IR analysis shows the presence of carboxyl group in PEK-L. The stretching vibration of =C–H in benzene ring is at about 3057 cm^{-1}, while the skeletal C=C vibration in benzene rings causes another two bands at 1591 cm^{-1} and 1497 cm^{-1}. The band at 1654 cm^{-1} can be attributed to Ar–C=O stretching vibration, and symmetric and asymmetric stretching vibration of Ar–O–Ar are at 1235 cm^{-1} and 1082 cm^{-1}, respectively. The spectra for PEK-L loaded with metal ions have also been shown in Fig. 1, where Ni(II) and Cd(II) are selected as representatives. As can be seen from Fig. 1b and c, after loaded with metal ions, the peak intensities of carboxyl group at 1773 cm^{-1} and 1734 cm^{-1} decrease, whereas intensity changes of the bands at about 1388 cm^{-1} are observed, which may be related to adsorption of metal ions [36].

3.2. Effect of pH

The initial pH of metal solutions has been regarded by many authors as the major parameter controlling metal adsorption processes [5,22]. In this study, the adsorption experiments have been