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Research paper

Recovery of uranium ions from simulated seawater with palygorskite/amidoxime polyacrylonitrile composite

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ABSTRACT

A polyacrylonitrile/palygorskite composite chemically modified with amidoxime groups was prepared by free-radical graft polymerization of acrylonitrile onto 3-glycidyloxypropyl trimethoxy silane (KH-560)-modified palygorskite and characterized by Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD). Adsorption of uranium(VI) from simulated seawater on the material was investigated. Batch experiments were carried out to study the effects of initial pH, contact time, initial feed concentration and ionic strength on uranium removal. The solution pH values had a major impact on uranium(VI) adsorption with optimal adsorption observed around pH 5. The kinetic data followed the pseudo second-order process. The equilibrium data fitted the Freundlich model well and the maximum adsorption capacity was found to be 78.13 mg/g. The ionic strength did not significantly affect uranium removal and chemisorption was assumed to describe the uranium adsorption. Desorption was performed using 0.1 M HCl solution, and the regenerated adsorbents could be reused with little loss of adsorption capacity after five cycles.

1. Introduction

Uranium is the most important element for the nuclear industry, and has further commercial use as a fuel for electricity generation (Ilaiyaraja et al., 2013). The concentration of uranium in seawater is of the order of 1.4×10^{-8} mol/L (3.3 mg/m^3) and is found to be present principally as the anionic tricarbon atouranate(VI) $[UO_2(CO_3)_3]^{4-}$ species. The total amount of uranium stored in seawater is very large, at 4–4.5 $\times 10^9$ t (Zhang et al., 2003, 2005). It may be possible to recover uranium from seawater and thus provide an additional head-end option to the nuclear fuel cycle. Separation processes such as solvent extraction, ion exchange, precipitation and others can be considered to recover uranium from seawater. Among these, adsorption is an effective method in view of uranium ions with low concentration in seawater because of its simplicity of operation, low costs, and energy use (Cui et al., 2013). A variety of adsorbents used for the recovery of uranium ions in seawater have been reported (Choi et al., 2003; Das et al., 2008, 2009; Song et al., 2012; Akkaya, 2013). Adsorbents containing amidoxime groups, which make chelate complexes with uranyl ions, are notable for the recovery of uranium from seawater due to: (1) their selectivity towards uranium, (2) their high uranium loading capacity, and (3) their good mechanical strength (Choi et al., 2003; Zhang et al., 2003; Das et al., 2008). Although they have the advantages of having a high adsorption capacity for uranium ions, the high cost usually limits their application. There have been attempts to utilize low cost, naturally occurring adsorbents to recover uranium, such as activated carbon (Mellah et al., 2006), bentonite (Anirudhan et al., 2010) and Na-rectorite (Zhao et al., 2011).

Palygorskite (Pal) is a kind of crystalline hydrated magnesium aluminum silicate mineral present in nature with a fibrous morphology and has a large specific surface, moderate cation exchange in its framework channels and reactive OH^- groups on its surface (Zhao et al., 2009; Eduardo et al., 2011). Palygorskite used as adsorbent for the removal of heavy metal ions and organic contaminants has been intensively investigated (Galan, 1996; Chen et al., 2007; Uri et al., 2011). There are large reserves of palygorskite in South China (Jiang Su, Zhe Jiang and An Hui province) and in the USA (Florida) (Galan, 1996; Huang et al., 2007). Compared to activated carbons, palygorskite is cheaper and has chemical and mechanical stability, high surface area and structural properties such as the presence of silanol group on the external surface and of different types of water moleculars associated with the fibrous silicates (Eduardo et al., 2011). In order to enhance its adsorption capacity and selectivity, palygorskite has been widely modified by organic reagents such as octodecyl trimethyl ammonium chloride (Huang et al., 2007) and 2,2-bis(hydroxymethyl)propionic acid (Liu and Wang, 2007). Recently, much attention has been paid to organic–inorganic hybrid adsorption materials (Jiang et al., 2007; Wang et al., 2009; Jin et al., 2011a; Wang et al., 2011) because of their high adsorption capacity, mechanical strength and low cost.

In the present study, a new kind of palygorskite/amidoxime polyacrylonitrile was prepared by solution free-radical graft polymerization.

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The palygorskite surface was first modified with 3-glycidyloxypropyl trimethoxy silane (KH-560), and polyacrylonitrile was then grafted onto the KH-560-modified Pal. The palygorskite/amidoxime polyacrylonitrile composite was used to recover uranium from simulated seawater. The adsorption of uranium(VI) ions was investigated as a function of pH, contact time, initial feed concentration, as well as ionic strength. The characteristic parameters for the Langmuir and Freundlich isotherm modes, the pseudo-first and the pseudo-second order kinetic models were determined. The recovery of the composite material was also studied.

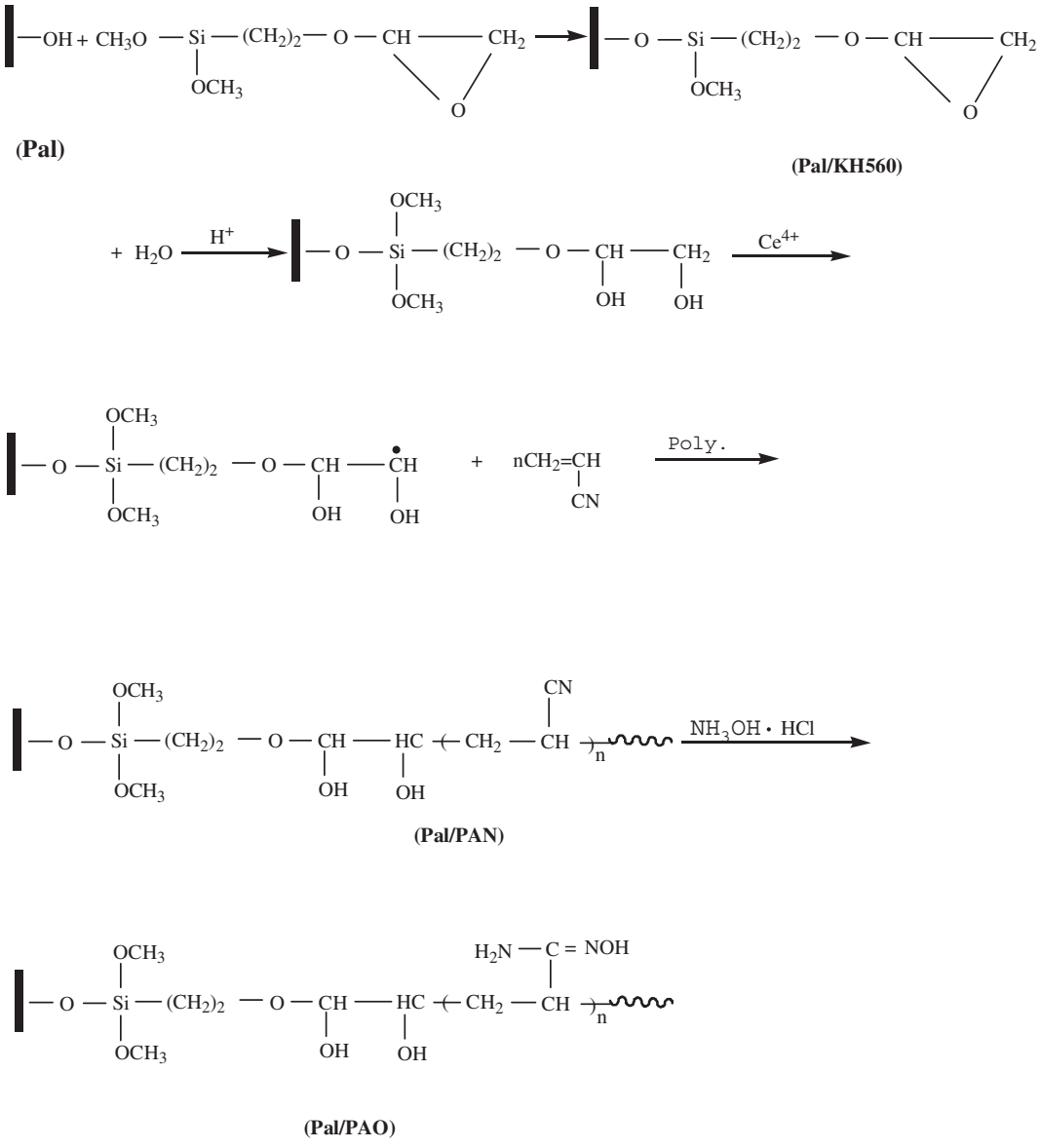
2. Experimental

2.1. Materials

All chemicals were of analytical grade unless stated otherwise. Hydroxylammonium chloride, toluene and acrylonitrile were purchased from Huadong Medicine Co. Ltd. Toluene was dried over molecular sieves for at least 24 h and acrylonitrile was distilled under reduced pressure just before use. 3-Glycidyloxypropyl trimethoxy silane (KH-560) (97%) and diethylamine (99%) were supported by Aladdin. Ammonium ceric sulfate (≥98%) was purchased from Yuejing Chemical Co. Ltd., Shanghai, China. Palygorskite, with an average diameter of 200 mesh, was obtained from Mingmei Minerals Co. Ltd., Anhui, China. Stock solutions of uranium (100 mg/L) were prepared as follows: analytical reagent grade $UO_2(NO_3)_2$, purchased from China Medicine Co. Ltd., was calcined at 900 °C in a muffle furnace for 4 h. The obtained U_3O_8 powder (0.1179 g) was dissolved in 5 mL nitric acid by heating in an electric furnace, then diluted with nitric acid solution (pH = 2) to 1000 mL, to obtain the standard solution of uranium. The stock solution was diluted to prepare working solutions. All the other reagents were used as received without any further purification. Distilled water was used to prepare all the solutions.

2.2. Preparation of palygorskite/amidoxime polyacrylonitrile composite

Scheme 1 shows the synthesis process of palygorskite/amidoxime polyacrylonitrile composite. The process was divided into four stages, introducing surface modification of Pal with KH-560, ring-opening reaction of bound KH-560, graft polymerization of acrylonitrile and amidoximated reaction. Details of the process are as follows:Surface modification of Pal with KH-560: the suspension of dried Pal (4 g) in



Scheme 1. Preparation process of the Pal/PAO composite.