Applied Clay Science xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Applied Clay Science

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

Research paper

Assembling polypyrrole coated sepiolite fiber as efficient particle adsorbent for chromium (VI) removal with the feature of convenient recycling

Qi Zhou[a,*], Junlong Huang[a], Xing Zhang[a], Yun Gao[b]

[a] School of Environmental and Chemical Engineering, Shanghai University, 333 Nanchen Road, Shanghai 200444, PR China
[b] Anhui Electric Power Construction Second Engineering Co. Ltd., China Energy Construction Group., 12600 Prosperity Road, HeFei, PR China

ARTICLE INFO

Keywords:
Polypyrrole
Sepiolite fiber
Cr(VI) removal
Surface modificaiton
Floatation

ABSTRACT

To overcome the inherent defect of particle adsorbent that difficult to be recycled from waterbody, a new adsorbent was successfully prepared based on the surface polypyrrole (PPy) functionalized sepiolite fiber (SEP), with properties of magnetism and floatation. This adsorbent can be recovered easily from water surface by a magnet. The resultant MSEP/PPy retains the feature of sepiolite fiber template, along with a large surface area to have more surface adsorption sites. Batch experiment shows the experiment data is in good agreement with the pseudo-second order kinetic and Langmuir isotherm model. The adsorption mechanism reveals that the ion exchange occurs between Cl^- and Cr(VI), followed by the reduction of Cr(VI) to Cr(III) via the surface PPy moiety. Additionally, most of the adsorption capacity of the adsorbent can be maintained in the cyclic regeneration, ranging from 87.93 to 58.36 mg/g even in the incomplete desorption.

1. Introduction

Chromium and its compounds, as an important raw material, are widely used in industrial production, but the discharged wastewater is one of the main sources of heavy metal pollution. In the aquatic environmental medium, Cr(III) and Cr(VI) are the mainly existing forms for chromium. Cr(III) is an essential micronutrient in humans, plant, animal metabolism and much less toxic than Cr(VI) (Sedman et al., 2006; Aroua et al., 2007). But Cr(VI) is thought to be one of the extremely hazardous heavy metal ions, because of the highly toxicity, carcinogenicity and mutagenicity (Alqadami et al., 2013; Shahat et al., 2015).

As recommended by US Environmental Protection Agency (EPA), the threshold value for Cr(VI) is 0.05 mg/L in drinking water and 0.1 mg/L in surface water, respectively (Setshedi et al., 2015). Therefore, it is significantly meaningful to reduce the Cr(VI) concentration in wastewater to an acceptable level before being discharged for environment protection and health concern. To achieve the purpose, many approaches including adsorption, membrane filtration, chemical precipitation and biological method were adopted to reduce/remove Cr (VI) ions from solutions (Guo et al., 2006; Carriazo et al., 2007; Li et al., 2008; Korus and Loska, 2009; Dultz et al., 2012; Beheshti et al., 2016). Among them, adsorption is believed to be an effective, economically viable, environmentally friendly and cost-effective technique for removing Cr(VI) from wastewater. Wherein, the development of excellent Cr(VI) adsorbents with the features of high adsorption capacity, low cost and good affinity has been a practical key factor.

Recently, polypyrrole (PPy) has been received considerable attention as famous conducting polymers toward environmental remediation field due to its unique redox chemistry, nontoxicity and environmental stability (Zhao et al., 2011; Bhaumik et al., 2013; Muliwa et al., 2016), especially the dopants incorporated into the PPy framework to balance the positively charged nitrogen atoms would lead to an anion exchange capability for PPy (Ansari, 2006). However, PPy have high tendency to form self-agglomerates and low dispersion in water phase, exhibiting low surface area and adsorption capacities. Loading of PPy onto a suitable substrate is regarded as an effective approach to improve its dispersion.

Sepiolite (SEP) is a natural hydrated magnesium silicate clay minerals with a one-dimensional fiber-like morphology. The SEP consists of two layers of tetrahedral silica and a central octahedral magnesium layer, exhibiting considerable surface area (theoretical largest surface area in clay minerals) and rich pore (Chen et al., 2014), which has attracted a lot of attention to be used in environment remediation (Li et al., 2018; Ouyang et al., 2018; Zhang et al., 2018). Hence, the SEP is thought to be an excellent substrate template to fabricate PPy coated nano-composite adsorbent. Previously reports have shown that pyrrole can be chemically polymerized on the solid substrates surface with

* Corresponding author.
E-mail address: superbzhou@shu.edu.cn (Q. Zhou).

https://doi.org/10.1016/j.clay.2018.09.031
Received 21 June 2018; Received in revised form 28 September 2018; Accepted 30 September 2018

ferric chloride as an oxidant at room temperature, while Cl^- ions are incorporated into the polymer as a counter ion (Babel and Kurniawan, 2004; Li et al., 2012). The obtained MSEP/PPy composite adsorbent could be used as an efficient adsorbent in Cr(VI) removal based on the mechanism of anion exchange of the polymer layer formed as PPy^+/Cl^-.

Always, the separation and collection of particle adsorbent from the waterbody is one key challenge for its practical application. Much attentions have been paid to magnetic adsorbent, such as magnetic polymer beads, magnetic nanoscale zero-valent iron, magnetic nanoparticles and so on (Lin et al., 2012; Peng et al., 2017), because they can be easily separated from water by simple magnetic field after adsorption. However, the underlying problem remained unsolved that the particle adsorbent would sink to the bottom to be used in open water area. Here, a new recycling strategy is proposed to endow both features of magnetism and floatation to the MSEP/PPy nanoparticle adsorbent to achieve the effective and convenient recycling from the water surface directly. Two aspects were improved in the material synthesis: in advance, magnetic nanoparticles (Fe_3O_4) was deposited on sepiolite (SEP) fibers template to bring the magnetism, besides, organic hydrocarbon chain was introduced via doping sodium dodecyl sulfate (SDS) into the surface coated PPy framework during the polymerization of pyrrole (Py) to achieve the hydrophobic surface for floating. The adsorption performance is investigated systematically with the kinetic and isotherm as well as thermomechanical analysis, and the mechanism of Cr (VI) adsorption on to MSEP/PPy was revealed by combining the results of X-ray photoelectron spectroscopy (XPS) analysis.

2. Materials and methods

2.1. Chemicals and materials

Nature SEP was obtained from the Hunan Xiang Tan group Co. Ltd. (Hunan, China). Pyrrole (≥99.7%), sodium dodecyl sulfate (SDS) (≥99.0%), ammonium hydroxide ($NH_3{\cdot}H_2O$) (22–25%), ferric chloride ($FeCl_3$) (≥99.0%), ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$) (≥99.0%), ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) (≥99.0%), and Potassium dichromate ($K_2Cr_2O_7$) (≥99.8%) were purchased from Sinopharm Chemical Reagent (Shanghai, China). All chemicals were of analytical reagent grade and used without further purification.

2.2. Preparation of the MSEP/PPy

Firstly, the magnetic sepiolite (MSEP) particles was prepared through the co-precipitation of Fe^{2+} and Fe^{3+} ions with the molar ratio of 1:2, the procedure described as follows: 0.4 g (4 mmol $FeCl_2{\cdot}4H_2O$) and 2.16 g (8 mmol) of $FeCl_3{\cdot}6H_2O$ were dissolved in 40 mL of deionized water in a flask, then 2.0 g SEP was dispersed in the solution under vigorous stirring for 30 min. Subsequently, 40 mL dilute ammonia solution (10 wt%) was also added into the mixture dropwise under stirring by passing through a nitrogen gas flow for depositing Fe_3O_4 on SEP surface. After 3 h reaction at room temperature, the obtained product was collected by magnet, washed with deionized water and ethanol repeatedly and then dried at 60 °C under vacuum for 6 h.

Afterwards, the MSEP/PPy was obtained via in situ chemical oxidative polymerization method (Bhaumik et al., 2011a). Typically, 1.0 g of MSEP, 0.5 mL pyrrole and 40 mL of deionized water were added into a 100 mL flask. Then 20 mL of SDS solution (5.85 wt%) was introduced into mixed solution. After stirring for 10 min, 60 ml of $FeCl_3$ solution (0.2 M) was added into the mixture as oxidant, the reaction was kept for 4 h at room temperature. The resultant black MSEP/PPy were collected by a magnet, rinsed with distilled water and ethanol, and dried at 60 °C under vacuum. The illustration for preparation process is given in Fig. 1.

2.3. Characterization

Surface morphologies of MSEP/PPy were observed with scanning electron microscopy (SEM) using Hitachi SU8010 field emission scanning electron microscope. Fourier-transform infrared (FT-IR) spectra measurements were performed on a Nicolet AVATAR360 instrument using the standard KBr disk method. X-ray diffraction (XRD) was performed at room temperature by a Germany Bruker D8-FOCUS powder diffraction system with Cu Kα radiation operating at 40 kV and 40 mA. The surface area, pore size and pore volume of the samples were analyzed by N_2 adsorption/desorption method using automatic surface area analyzer (NOVA-2200e, USA) at the boiling point of liquid nitrogen, the SSAs were calculated using the Brunauer–Emmett–Teller (BET) method. The pore size distributions were derived from the adsorption branches of the isotherms based on the Barrett–Joyner–Halanda (BJH) model. The total pore volume was estimated from the amount absorbed at a relative pressure (P/P_0) of 0.99. Hysteresis loops were measured on a VSM-100 vibrating sample magnetometer (VSM) at room temperature. X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI 5300x multi-technique system with a Mg-Ka X-ray source (Perkin-Elmer Physical Electronics). Information about the surface charge of this material in the pH range of 2–12 was obtained by zeta potential measurements using a nano ZS90 instrument (Malvern Co. Ltd., UK).

2.4. Batch adsorption experiments

In a typical adsorption experiment, 7.5 mg adsorbent was added into 15 mL 100 mg/L Cr(VI) solution at pH 2.0, and the mixture was shaken under 200 rpm for 24 h at 25 °C. Then, the solid particles were separated from the solution and Cr(VI) concentration was determined by a UV–visible spectrophotometer (Perkin Elmer Lambda 35, USA) at 540 nm with 1,5-diphenylcarbazide color developing agent (Yan et al., 2017).

The adsorption amount of Cr(VI) is calculated by the following equation.

$$q_e = (C_0 - C_e)\frac{V}{m} \quad (1)$$

where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of Cr(VI) in aqueous solution, respectively, m (g) is the mass of the adsorbent and V (L) is the volume of the solution.

2.5. Regeneration experiment

Adsorption–desorption experiments were carried out to regenerate the MSEP/PPy after adsorbing Cr(VI) for further use. Initially, saturated adsorbent was added into 0.5 M NaOH solution for shaking 24 h with the dosage of 0.5 g/L. Thereafter, the composite was put into 2.0 M HCl solution for 0.5 h to regenerate the adsorption sites and rinsed with distilled water to neutral for next adsorption cycle.

3. Results and discussion

3.1. Characterization of materials

SEP, a hydrated magnesium silicate clay mineral, has a theoretical molecular formula of $Mg_8(Si_{12}O_{30})(OH)_4(OH_2)_4{\cdot}8H_2O$ (Table 1). It consists of SiO_2, MgO, Al_2O_3, and a trace amount of Fe_2O_3, CaO, Na_2O, K_2O and TiO_2, etc. The results indicated that the original SEP had a number of impurities such as calcite ($CaCO_3$), talc ($Mg_3Si_4O_{10}(OH)_2$) and dolomite ($CaMg(CO_3)_2$).

As depicted in Fig. 2a, the surface area and pore structure of the SEP and MSEP/PPy are obtained according to the N_2 adsorption–desorption isotherms. The linear contours of both original SEP and MSEP/PPy exhibit IV type isotherms with an evident H_3 hysteresis loop in the