Applied Surface Science 364 (2016) 620–627

Contents lists available at ScienceDirect

Applied Surface Science

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

Comparison of Pb(II) adsorption onto graphene oxide prepared from natural graphites: Diagramming the Pb(II) adsorption sites

Weijun Peng, Hongqiang Li, Yanyan Liu, Shaoxian Song*

School of Resources and Environmental Engineering, Wuhan University of Technology, Luoshi Road 122, Wuhan, Hubei 430070, China

ARTICLE INFO

Article history:
Received 26 October 2015
Received in revised form
29 November 2015
Accepted 28 December 2015
Available online 29 December 2015

Keywords:
Natural graphite
Crystalline morphology
Graphene oxide
Lead ion
Adsorption sites

ABSTRACT

Comparative study has been performed on the adsorption of Pb(II) on graphene oxides (GOs) prepared from flaky, lump and amorphous graphites with the Hummers method in this work. The GOs were characterized by X-ray diffraction spectroscopy, Fourier transform infrared spectroscopy, Chemical analysis, Raman spectroscopy and Atomic force microscope. The results indicated that GO prepared from amorphous graphite had lower C/O ratio and more thin layers (less than 2 nm in thickness) than those prepared from the other two natural graphites. The adsorption process was well described by the pseudo-second-order kinetics model, and the equilibrium data agreed precisely with the Langmuir model. The hydroxyl and carboxyl located at the edges of GO sheets mainly participated in the complexation of Pb(II), and different GO sheets were bridged by Pb(II) through simultaneously bonding the marginal oxygenous groups.

1. Introduction

Lead is recognized as a persistent contaminant, which mainly generated from acid battery, printing, painting, ceramic and glass manufacturing and production of lead additives for gasoline [1–3]. Long-term drinking of lead polluted water will cause anaemia, cancer, kidney disease and metal retardation, etc. [2,3]. Therefore, the removal of Pb(II) ions from aqueous solution is very crucial.

GO is considered as the oxidized form of graphene, decorated with a range of reactive oxygenous functional groups, such as epoxy, hydroxyl, ketones and carboxyl groups which closely related to its hydrophilicity and high negative charge density [4,5]. Compared to other carbonaceous adsorbents, GO is regarded as the most promising adsorbent for multivalent metal ions due to its large theoretical surface area, surface hydrophobic π–π interaction, hydrophilicity, high negative charge density and easily obtained from the abundant nature graphite in large scale, which has been used to remove Au(III) and Pt(IV) [4], Pb(II) [6], Cu(II) [7], Zn(II) [8], Cd(II) [9] and Co(II) [10], etc. It had been confirmed that the adsorption of Pb(II) on GO was dominated by the strong surface complexation between Pb(II) and the oxygenous functional groups on the surface [2]. Thus, the oxygenous functional groups on the surface of GO play an important role in the adsorption of Pb(II) from aqueous solution [9].

In general, natural graphite could be classified as flaky, lump and amorphous graphites based on the difference of crystalline morphology [11]. Flaky graphite (FG) and lump graphite (LG) are crystallized clearly. Crystal size in LG is larger than 0.1 mm, while that in the FG is of 0.001–0.5 mm. In contrast, amorphous graphite (AG) is crystallized poorly with crystal size less than 1 μm [12]. Conventionally, GO is prepared from graphite and its derivatives via oxidation and exfoliation process. The factors, such as the pristine graphite, oxidant dose, oxidation time and temperature during the GO preparation may affect the characteristics of GO had been reported in numerous literatures [13–15]. Botas et al. [15,16] confirmed that the crystal size of synthetic graphite significantly affected the oxidation process and the functionality and sheet size of the resulting GO. Wu et al. [17] found that both the lateral size and crystallinity of the starting graphites notably influenced the number of graphene layers obtained by chemical exfoliation. Consequently, the crystalline morphology of the natural graphites may also have an effect on the structural features of the prepared GOs, and then directly influence the adsorption capacity of heavy metallic ions. But scarce literatures have been focused on this.

In this paper, the comparison of Pb(II) adsorption onto GO prepared from different kinds of natural graphites was investigated. The focuses were centred on: (1) to study the influence of crystalline morphology of natural graphites on the characteristics of synthesized GOs; (2) to compare the adsorption behavior of Pb(II)

---

* Corresponding author.
E-mail address: shaoxian@uaslp.mx (S. Song).

http://dx.doi.org/10.1016/j.apsusc.2015.12.208
0169-4332/

on the GOs based on experimental equilibrium adsorption capacities, adsorption isotherm and kinetics studies; (3) to discuss the adsorption mechanism and diagram the Pb(II) adsorption sites on the surface of GO sheets.

2. Experimental

2.1. Materials and chemicals

Three kinds of natural graphite, FG, LG and AG with the particle size of 45–38 μm and purity of more than 99% were used as the starting materials to synthesize GO. Potassium permanganate ($KMnO_4$), sodium hydroxide (NaOH) and sodium nitrate ($NaNO_3$) in analytical purity, 30% hydrogen peroxide aqueous solution were purchased from the Sinopharm Chemical Reagent Co., Ltd (China). 0.0501 mol/L lead nitrate standard solution was gotten from Shenzhen Carbon Twelve technology Co., Ltd (China). 98% sulfuric acid (H_2SO_4) and 36% hydrochloric acid (HCl) were obtained from the Xinyang chemical reagent (China). Deionized water with the resistivity of 18.25 MΩ cm was used in this work.

2.2. Preparation of graphite oxide (GrO) and GO

GrOs were prepared with the Hummers method [18] in this work. First, 46 mL of H_2SO_4 was placed in a conical flask with magnetic stirring in an ice-water bath. Then, 2.0 g of graphite and 1.0 g of $NaNO_3$ were added. After stirring for 10 min, 6 g $KMnO_4$ was slowly added over about 20 min, and the mixture was maintained stirring for 1 h at the temperature less than 10 °C. Subsequently, the mixture was transferred to a pre-heated water-bath at 35 ± 3 °C and kept stirring for 2 h. Next, 92 mL of water was dropwise added into the mixture to avoid a rapid increase of the temperature. After that, the mixture was transferred again to a pre-heated water-bath at 95 ± 3 °C and kept stirring for 30 min. The reaction was terminated by adding 280 mL of water to dilute the mixture, and 25 mL of 30% H_2O_2 aqueous solution to neutralize the residual $KMnO_4$ until no bubble appeared. Finally, the mixture was centrifuged at 2520 × g for 20 min. The sediment was washed using first 5 wt% hydrochloric acid solution and then warm water until the pH value in the supernatant reached near 7 and no $SO_4{}^{2-}$ was detected. The washed sediment was dried at 60 °C for 48 h in vacuum, which was the GrO. The GrO prepared from FG, LG and AG were termed as GrO-FG, and GrO-LG and GrO-AG, respectively.

The as-prepared GrO powder was dispersed in deionized water (0.67 mg/ml) and ultrasonically exfoliated by a Cole Parmer ultrasonic processor (750 W and 20 kHz) with the 60% amplitude for 9 min. Then the colloidal suspension was centrifuged at 2520 × g for 20 min to remove the unexfoliated GrO, and the supernatant was achieved, which was the GO. GOs obtained from GrO-FG, and GrO-LG and GrO-AG were termed as GO-FG, GO-LG and GO-AG, respectively.

2.3. Measurements

X-ray diffraction (XRD) patterns were obtained using an advance diffractometer (D8, Bruker, Germany) with Cu Kα radiation (k = 0.15406 nm) at 40 kV and 100 mA. The patterns were recorded in the range of $2\theta = 5°–80°$ at steps of 0.01° and intervals of 6 s per step.

Fourier transform infrared spectra were detected by a Fourier transform infrared spectrometer (Vector-22, Bruker, Germany) at room temperature, for which 1 mg GOs and Pb(II)-loaded GO-AG powder were mixed with 200 mg of KBr in an agate mortar, respectively, and then pressing the mixture at a pressure of 10 MPa for 3 min. The spectra were scanned from 400 to 4000 cm^{-1} at the rate of 4 cm/s.

Element analysis of carbon, oxygen and hydrogen of the as-prepared GOs powder was performed by a Vario EL cube ANALYZER (Germany). In this, 5.0 mg of GO was weighed by a electronic balance with the accuracy of one of millions and placed in a tin boat and packaged. Then, the test was carried out after the tin boat was placed in the autosampler.

A Renishaw INVIA Raman microscope (England) was used to obtain the Raman spectra of GOs powder with the Raman shift range of 500–3000 cm^{-1}. The laser probe was Ar laser tuned in the 514.5 nm mode.

The atomic force microscope (AFM) images of GOs were obtained by using a Bruker MultiMode 8 AFM with peak force tapping-mode. The sample for AFM measurement was prepared by dropping GO dispersion on a freshly cleaved mica surface. The mica substrate with GO on was dried at 60 °C for 2 h in an automatic thermostatic blast air oven. In order to obtain the distribution of sheet thickness, 400 sheets of each GO in the AFM images were determined for the topographic height.

Zeta potential analyses of the GOs were carried out on a Malvern Zetasizer Nano ZS90 (UK) equipped with a rectangular electrophoresis cell. The conductivity and pH value of the suspension solution were monitored continuously during the measurement and the environmental temperature was maintained at 25 °C. The range of initial pH was 2.0–10.0, adjusted by dilute HCl or NaOH aqueous solutions.

2.4. Pb(II) adsorption

Batch tests of Pb(II) adsorption on GO were carried out in a conical flask, in which given amounts of GO suspension and aqueous Pb(II) solution were added. The pH value of the mixed suspensions in each conical flask was adjusted to 5.0 by adding negligible volumes of NaOH solution, at which the predominant lead species was Pb^{2+} [3,19,20]. Then, the suspension was shaken thoroughly by a mechanical shaker (HZQ-C, Hangzhou Chincan Trading Co., Ltd, Hangzhou, China) at an agitation speed of 150 rpm for a pre-determined time intervals at 30 °C. Finally, the suspension solution was filtered by 0.22 μm filter membrance, and Pb(II) concentration in the filtrate was immediately examined using atomic absorption spectrophotometry (ZEEnit700, Analyjena, Germany).

All the adsorption experiments were conducted at the initial GO concentration of 60 mg/L. The adsorption isotherm studies were performed by ranging the initial Pb(II) concentration from 10.37 mg/L to 259.25 mg/L. The kinetic experiments were carried out at different time intervals (5–180 min) in an initial Pb(II) concentration of 103.7 mg/L.

All the tests were carried out in triplicate, and the average values were reported. The amount of adsorbed Pb(II) was calculated using the following expression:

$$q_t = \frac{C_0 - C_t}{m} V \qquad (1)$$

where C_0 and C_t (mg/L) are the liquid-phase concentrations of Pb(II) at initial and final concentrations, respectively. V is the volume of the solution (L) and m is the mass of adsorbent used (g).

3. Results and discussion

3.1. Characterization of GOs

Fig. 1 illustrates the XRD patterns of the GrOs prepared from the FG, LG and AG. The GrOs patterns all showed a characteristic (002) plane reflection peak near $2\theta = 10°$, corresponding to an average d-spacing of 0.80 nm. The increase in d-spacing was due to the intercalation of water molecules and the formation of oxygenous functional groups between the layers of graphite [21]. It was