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Colloids and Surfaces B: Biointerfaces

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



The role of chitosan as nanofiller of graphite oxide for the removal of toxic mercury ions

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ARTICLE INFO

Article history:

Received 24 April 2013
Received in revised form 21 July 2013
Accepted 29 July 2013
Available online xxx

Keywords:

Mercury(II)
Chitosan
Graphite oxide
Magnetism
Adsorption mechanism
Characterization

ABSTRACT

The present study focuses on the role of chitosan (CS) as nanofiller of graphite oxide (GO) in order to prepare composite materials with improved Hg(II) adsorption properties. The removal of Hg(II) from aqueous solutions was studied using adsorbents as graphite oxide (GO), graphite oxide nanofilled with chitosan (GO/CS) and magnetic chitosan (GO/mCS). Many possible interactions between materials and Hg(II) were observed after adsorption and explained via characterization with various techniques (SEM/EDAX, FTIR, XRD, DTG). The adsorption evaluation was done studying various parameters as the effect of pH (both in adsorption and desorption), contact time (pseudo-second order fitting), temperature (isotherms at 25, 45, 65 °C), in line with a brief thermodynamic analysis (ΔG^0 , ΔH^0 , ΔS^0). The maximum adsorption capacity (fitting with Langmuir model) of GO at 25 °C was $Q_{\max} = 187$ mg/g, while after the CS nanofilling (formation of the composite GO/CS), Q_{\max} was increased to 381 mg/g with a further enhancement for GO/mCS ($Q_{\max} = 397$ mg/g).

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1. Introduction

Contamination of aquatic systems is a serious environmental problem given the pollution of natural waters by heavy metal ions is one of the main sources all over the world. Mercury is one of the most toxic heavy metals since it is not biodegradable and causes a lot of toxic effects in the human body [1]. Its presence is due to a combination of natural processes (volcanic action, erosion of mercury-containing sediments) and anthropogenic activities (mining operations, tanneries, metal plating facilities) as well [2]. Adsorption is considered to be one of the most effective and economical treatment methods for mercury removal of effluents [3].

Chitosan (CS), which is a deacetylated product of chitin (found in abundance in nature), was proved to be a promising material, due to its content of a large number of hydroxyl and amino groups, which can act as adsorption sites for metals [4–8]. In addition, chitosan presents high non-toxicity, biocompatibility and biodegradability [9–12]. Its adsorption performance can be further improved by cross-linking with reagents such as glutaraldehyde, tripolyphosphate salts, genipin, epichlorohydrin, ethylene glycol or diglycidyl ether, which can stabilize chitosan in acid solutions and increase its mechanical properties [13,14].

Graphite oxide (GO), a member of carbon-based nanomaterials with a lamellar structure, recently was attracted intense interest for its potential application as adsorbent material [15]. Graphite oxide can be synthesized after graphite oxidation with strong oxidizing agents such as potassium permanganate, which makes GO to have multiple oxygen containing functional groups, such as carboxyl, hydroxyl and epoxide, covalently attached to its layers. These oxygen hydrophilic functionalities make GO extensively disperse in water [16]. On the other hand, due to the presence of these oxygen functional groups, different polar substances can be easily inserted between its layers leading to formation of graphite oxide intercalated composites [17]. Recently, glutaraldehyde cross-linked chitosan was examined as an intercalating substance for the preparation of a chitosan/graphite oxide nanocomposite [18]. Taking into account that magnetic separation, compared with traditional methods (filtration or centrifugation), requires less energy and results to better separation by the application of an external magnetic field to extract the adsorbents [4,19–21], a composite of graphite oxide with magnetic chitosan was also prepared [22,23]. The two composites were tested as adsorbents for dye removal.

The novelty of the current work is the role of chitosan as nanofiller of graphite oxide in order to prepare materials (composites of graphite oxide/chitosan) presenting improved Hg(II) adsorption properties. The latter is strengthened by the lack of literature for graphite oxide/chitosan composite materials as mercury adsorbents. Carboxyl, hydroxyl and epoxy groups of graphite oxide are combined and interacted with amino groups of chitosan (or/and

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in its magnetic form) creating new sites for Hg(II) adsorption. In this attempt, after adsorption many possible interactions between adsorbents and Hg(II) were observed and explained via characterization with various techniques (SEM/EDAX, FTIR, XRD, DTG). Hg(II) adsorption onto materials was performed in batch mode, studying the effect of pH, contact time and temperature, in line with a brief thermodynamic analysis.

2. Materials and methods

2.1. Materials

Commercial chitosan powder of high molecular weight (preparation for nanofilling) was obtained from Sigma–Aldrich (St. Louis, MO, USA) was purified with organic solvent (acetone) and after 12 extraction cycles in Soxhlet at least for 24 h, it was dried at room temperature under vacuum. The average molecular weight of the final (purified) chitosan was estimated at 3.55×10^5 g/mol, calculating its degree of deacetylation at 84 wt% [24]. Glutaraldehyde (GLA) was used as cross-linker reagent (50 wt% in distilled water). $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (puriss. pa. >99.0%) was used in the synthesis of magnetic nanoparticles. For the synthesis of GO, commercial graphite powder (<150 μm) was purchased. For the preparation of stock aqueous mercury solutions, mercury(II) nitrate monohydrate was used (puriss. pa. $\geq 98.5\%$). All reagents were purchased from Sigma–Aldrich, while all solvents used were of analytical grade.

The synthesis of chitosan (CS) [25], magnetic chitosan (mCS) [23] and graphite oxide (GO) [26] were described in previous works, and given in Supporting Information section (SI1. Preparation of CS, mCS, GO). The preparation of composite nanomaterials after chitosan nanofilling (GO/CS [18] and GO/mCS [23]) is given below. The particle size of the adsorbents prepared was in the range of 75–125 μm (after sieving).

For the preparation of GO composite after chitosan nanofilling (GO/CS), chitosan solution (2%, w/v) was prepared by dissolving 0.4 g of powder chitosan into 20 mL of acetic acid solution (2%, v/v) under ultrasonic stirring for 2 h at room temperature. Also, 3 mL of GLA (50 wt% in water) were added to cross-linked chitosan. Then, 0.3 g of GO were added in the solution prepared and the mixed system was stirred continuously for 90 min in a water bath at 50 °C. The pH of the reaction system was adjusted to 9–10 with micro-additions of NaOH (0.1 M) and kept in the water bath for further 60 min at 80 °C. Black products were washed with ethanol and distilled water in turn until the pH was reached about 7 and dried in a vacuum oven at 50 °C. The final product was the CS nanofilled graphite oxide (GO/CS).

For the preparation of GO the composite after magnetic chitosan nanofilling (GO/mCS), 2 g of chitosan powder was dissolved in 100 mL of acetic solution (2%, v/v) and was sonicated for 30 min. 0.75 g magnetic particles were added in the chitosan solution and the mixture solution was stirred for 2 h. 15 mL of GLA (50 wt% in water) was added into reaction flask to mix with the solution together with 1.5 g of GO. The mixture was adjusted at pH=9–10, and was stirred at 80 °C for 1 h. The precipitate was washed with ethanol and distilled water in turn and was dried in a vacuum oven at 50 °C.

2.2. Instrumentation

X-ray powder diffraction (XRD) patterns were recorded an XRD-diffractometer (model Richard Seifert 3003 TT, Ahrensburg, Germany) with a Cu K α radiation for crystalline phase identification ($\lambda = 0.15405$ nm for Cu K α). The samples were scanned from 5° to 60°. Thermal analysis was carried out using a TA Instrument thermal analyzer (SDT) (Q500 model, TA Instruments, New York,

USA) at a nitrogen atmosphere and a heating rate of 10 K/min. About 25 mg of sample was used for each measurement. FTIR spectra of the samples were taken with a FTIR-spectrometer (model FTIR-2000, Perkin Elmer, Dresden, Germany) using KBr disks (thickness of 500 μm). The spectra were recorded from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} and presented at transmittance mode. Scanning electron microscopy (SEM) images were performed with electron microscope (model Zeiss Supra 55 VP, Jena, Germany). The accelerating voltage was 15.00 kV and the scanning was performed in situ on a sample powder. EDAX analysis was done at magnification 10 K and led to the maps of elements and elemental analysis.

2.3. Adsorption–desorption experiments

Batch experiments (all experiments were run in triplicate and the error bars in figures were given after standard deviation) were carried out using 1 g/L of adsorbent each time (0.02 g of adsorbents' mass were added to 20 mL of deionized water in a conical flask). For the pH-effect experiments, the solution pH was initially adjusted with aqueous solutions of acid or base (0.01 M HNO_3 and/or 0.01 M NaOH) to reach pH values of 2–6 (higher pH values were not studied to avoid precipitation). The agitation rate was fixed at 160 rpm for all adsorption–desorption tests using shaking incubator (Julabo SW-21 C) under a controlled temperature. Isotherms were taken running the adsorption experiments with various initial Hg(II) concentrations (0–500 mg/L) at three different temperatures ($T = 25, 45, 65$ °C) for $t = 24$ h. Kinetic tests were performed using 100 mg/L as initial Hg(II) concentration at 25 °C (the solution pH was the optimum found from the pH-effect tests) for fixed time intervals during adsorption ($t = 0$ –24 h). Desorption experiments were similarly performed in batch mode using fixed adsorption conditions (pH=5; $C_{0,\text{Hg}} = 100$ mg/L; $T = 25$ °C; $t = 24$ h). After the end of adsorption step, the materials were separated from supernatant and placed at flasks using pH-adjusted (2–12) deionized water as eluant. The desorption step was similarly lasted 24 h, where it was found the optimum desorption pH value.

After the end of each adsorption or desorption experiment series, the measurement and analysis of Hg(II) residual concentration in the liquid phase was realized. In particular, samples were collected from the supernatant and filtered in fixed pore-sized membranes (0.40 μm) purchased by Schleicher & Schuell-MicroScience. Hg(II) was measured using atomic absorption spectrophotometer (Perkin-Elmer 1100 B) at 254 nm. The absorbance was converted to concentration using calibration curve. The equilibrium amount of Hg(II) in the solid phase, expressed as Q_e (mg/g), was determined according to the mass balance equation $Q_e = (C_0 - C_e) \times (V/m)$, where C_0 and C_e (mg/L) is the initial and equilibrium Hg(II) concentration; V (L) is the volume of adsorbate (solution); m (g) is the mass of adsorbent.

3. Results and discussion

3.1. Adsorption mechanism via characterization

The XRD patterns of GO, GO/CS and GO/mCS, which were taken before and after Hg(II) adsorption, are shown in Fig. 1a–c. In the XRD pattern of GO before Hg(II) adsorption (Fig. 1a, red line), the characteristic peak of GO was appeared at $2\theta = 10.9^\circ$ indicating an interlayer distance of $D_1 = 8.11$ Å between the carbon layers, as determined by Bragg's law [27]. This was caused by the large amount of polar groups generated between the layers of graphite during oxidation [15]. After Hg(II) adsorption (Fig. 1a, blue line), the GO characteristic peak was appeared at $2\theta = 13.4^\circ$, indicating a decrease of 1.51 Å ($D_2 = 6.60$ Å) in the interlayer distance between

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