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Adsorption of arsenate on iron(III) oxide coated ethylenediamine functionalized multiwall carbon nanotubes

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ABSTRACT

New criteria in assessing the quality of drinking water reduced the maximum permissible concentration of arsenic from 50 μg L^{-1} to 10 μg L^{-1}, and set a requirement for the development of new technologies for arsenic removal. In this paper, ethylenediamine functionalized multiwall carbon nanotubes (e-MWCNT) were loaded with iron(III) oxide in the goethite form, by precipitation of adsorbed Fe^{3+} and oxidized Fe^{2+} using base, in that way e-MWCNT/Fe^{3+} and e-MWCNT/Fe^{2+} adsorbents, respectively, were obtained. The influence of pH on the As(V) and As(III) removal from drinking water was studied in a batch system, of pH range 3–10 and initial arsenic concentration 0.05–4 mg L^{-1}. Time dependent As(V) adsorption and adsorption data can be described by pseudo-second-order kinetic model and by Freundlich isotherm, applying linear and non-linear fitting methods. The maximum adsorption capacities obtained from Langmuir model for As(V) on e-MWCNT/Fe^{2+} and e-MWCNT/Fe^{3+} were 23.47 and 13.74 mg g^{-1} at 25 °C, respectively. Thermodynamic parameters showed that the adsorption of As(V) was spontaneous and endothermic for both e-MWCNT/Fe^{2+} and e-MWCNT/Fe^{3+}. Influences of the pH, iron(III) oxide loading and interfering ions were modeled by MINTEQ program, and good agreement between experimental and modeling data was obtained.

1. Introduction

Arsenic has been considered as one of the most hazardous element for the living organisms and its presence in natural waters, can result in serious environmental problems. The World Health Organization (WHO) established that even a low concentration of arsenic produces negative effects on the human health; therefore a maximum concentration level of 10 μg L^{-1} of arsenic in community water systems was proposed [1]. This value is related to the total concentration of arsenic, but it was recognized that arsenic toxicity for humans depends strongly on its chemical form [2–7]. Many wells spread all over the world excess a maximum concentration level, especially in some parts of Europe – Hungary, Romania, Serbia, Croatia and Montenegro [8,9]. Heightened awareness of arsenic toxicity and regulatory changes has prompted considerable research efforts towards developing methods for arsenic removal from drinking water [10].

The common used techniques for arsenic removal include oxidation/precipitation, coagulation/coprecipitation, nanofiltration, reverse osmosis, electrodialysis, adsorption, ion exchange, foam flotation, solvent extraction, and bioremediation [10]. Generally, adsorption is a promising process, because it is a simple, economic and suitable operation method. Several iron(III) oxides, such as granular ferric hydroxide [11], amorphous hydrous ferric oxide [12–15], crystalline hydrous ferric oxide [16], goethite [13,17–19] and magnetite [13], iron based granular materials [20–23], are well-known adsorbents used for efficient removal of arsenic from water. The granular ferric hydroxide is the most effective with high adsorption capacity although its robustness and mechanical strength need further improvement [24,25]. Novel metal modified adsorbents have demonstrated superior performance [26,27]. Ferric hydroxide was incorporated into matrix materials such as sand [28] or biomass [29] to overcome its collapsing nature. Treating of activated carbon and graphene oxide (GO) with various iron compounds significantly increased arsenic adsorption [30–33].

Due to a large surface area, small, hollow and layered structure, carbon nanotubes (CNTs) have already been investigated as promising adsorbents for various organic pollutants and metal ions and can be easily modified by chemical treatment to increase their

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adsorption capacity [34]. Recent years have witnessed impressive breakthroughs towards practical application of nanostructured materials such as carbon nanotubes in the field of water purification owing to their unique thermal, electrical and mechanical properties [35–37]. The potential for surface modification make them attractive support for composite adsorbent preparation; recently appeared a few articles dealing with the preparation, characterization and application of nanocomposites [38–40]. Oxidation of CNTs has been widely reported [36,37,41], although amino functionalities play an important role to construct complex structures in combination with other functional groups [37,42]. Many kinds of metals have been successfully supported on CNTs [43,44], as well as implementation of a fabric supported magnetite MWCNT composite [45]. Composites of MWCNT/nano-iron oxide were prepared, characterized and used for the removal of Cr(III) [46]. Oxidized MWCNTs were employed as supports for iron(III) oxide [47] and used for trace arsenic removal; relatively low adsorption capacity (Table S4), indicate necessary development of the more effective MWCNT functionalization. The encouraging news is that improved manufacture and large-scale production have already caused the price of CVD-produced CNTs to fall substantially, from around 200 $/g in 1999 to 2–50 $/g today [37].

In this work the degree of iron(III) oxide loading on pristine, oxidized MWCNT (raw- and o-MWCNT, respectively) and e-MWCNT was studied and materials were compared on the basis of their adsorption capacities. On the basis of the results obtained, iron(III) oxide modified ethylenediamine multiwall carbon nanotubes e-MWCNT/Fe^{2+} and e-MWCNT/Fe^{3+} were chosen for further experimental work. They were examined as potential adsorbent for the removal of arsenate and arsenite from water. To achieve this goal, the influence of experimental conditions such as pH, concentration, temperature and contact time on sorption behavior was investigated. The thermodynamic parameters were also evaluated. The results of adsorption experiments were used to fit intrinsic arsenic surface complexation constants obtained by Visual MINTEQ [48] program package.

2. Materials and methods

The information about chemicals and characterization methods is supplied in Supplementary material.

2.1. Adsorbents preparation

The oxidized MWCNTs were prepared according to literature method described elsewhere [37]. Subsequent modification of o-MWCNT by ethylenediamine was performed by pre-activation of the carboxylic acid residue using *N*-HATU coupling agent on that way providing highly efficient formation of amide linkage and amino terminal functionality [37]. The hydrous iron(III) oxide coated e-MWCNT were prepared by two optimized methods:

Method A: 50 mg of e-MWCNT was immersed in 10 ml of 0.1 mol L^{-1} $FeCl_3$ solution and sonicated for 2 h. Two hours were found to be sufficient to attain adsorption equilibrium at 30 °C. The e-MWCNTs after adsorption of Fe(III) ion were isolated by vacuum-filtration, dispersed by sonication in 5 ml of DI water, pH of dispersion was adjusted at 4–4.5 and mixed overnight by using magnetic stirrer. Final pH of dispersion was adjusted at 7.5–8 providing precipitation of adsorbed Fe(III) ion in the form of hydrous iron(III) oxide. After mixing for 6 h obtained e-MWCNT/Fe^{3+} were isolated by vacuum-filtration and dried in a vacuum oven at 40 °C for 8 h.

Method B: 50 mg of e-MWCNTs were immersed in 10 ml of 0.1 mol dm^{-3} $FeSO_4$ solution, sonicated for 2 h at 30 °C in inert atmosphere of nitrogen and then vacuum-filtered. The material was further dispersed in 5 ml DI water followed by addition of equimolar quantity either of 0.05 mol dm^{-3} $KMnO_4$ or 30% hydrogen peroxide (H_2O_2), with respect to moles of adsorbed Fe(II) ion, to perform ferrous–ferric oxidation. In order to avoid formation and precipitation of MnO_2, the oxidation was performed at pH∼2. After mixing for 2 h dispersion was filtered, and subsequent steps of e-MWCNT/Fe^{2+} adsorbent preparation was performed analogously to *Method A*.

Vacuum-filtration of the prepared adsorbents was performed by the use of 0.05 μm pore size polytetrafluoroethylene (PTFE) filter membrane. The pH adjustment was carried out by controllable addition of 0.1 mol dm^{-3} NaOH using peristaltic pump (Ismatec) at flow rate of 0.1 ml min^{-1}.

2.2. Batch adsorption tests

The effect of time, pH and initial arsenic concentrations were studied in a batch tests using arsenite or arsenate solution. Effect of time was studied by ultrasonic treatment, in a batch system, of e-MWCNT/Fe^{2+} or e-MWCNT/Fe^{3+} and As(V) 100 μg L^{-1} solution for 30, 45, 60 and 90 min, 2, 6 and 10 h at pH 4.0 ± 0.1. It was found that 100 min were sufficient for quantitative removal of As(V) and As(III). In order to evaluate the effect of pH on As(V) and As(III) adsorption, the initial pH values (pH_i) of solutions were varied from 3.0 to 10.0 adjusted with 0.01 mol L^{-1} NaOH and 0.1 mol L^{-1} HNO_3 at 25 ± 1 °C. Adsorption experiments were carried out at the pH_i 4.0 ± 0.1, varying initial arsenic concentrations from 0.05, 0.10, 0.20, 0.50, 1.0, 1.5, 2.0 and 4.0 mg L^{-1}, adsorbent content of 100 mg L^{-1} and ultrasonic treatment for 100 min. The influence of temperature (25, 35 and 45 °C) on arsenate adsorption was carried out at pH 4.0 ± 0.1. The adsorbent capacity was calculated according to Eq. (1):

$$q = \frac{C_i - C_f}{m} V \tag{1}$$

where q is an adsorption capacity in mg g^{-1}, C_i and C_f are initial and final arsenic concentration in mg L^{-1}, respectively, V is volume of solution in L and m is mass of adsorbent in g. The results of arsenate and arsenite adsorption on glass tube wall and filters showed negligible adsorption. Time dependent adsorption was performed with an initial As(V) concentration of 100 μg L^{-1} at pH 4. The dispersions of e-MWCNT/Fe^{2+} or e-MWCNT/Fe^{3+} in As(V) solutions were ultrasonically treated for appropriate time (Fig. 2) and samples were collected and analyzed.

In order to confirm the model fitting the adsorption data, it was necessary to analyze the data using error analysis, together with the values of correlation coefficient (r) from regression analysis. The data analysis was realized using average relative standard error (ARS) calculated according to Eq. (2):

$$\mathrm{ARS} = \sqrt{\frac{\sum [(q_{\mathrm{exp}} - q_{\mathrm{cal}})/q_{\mathrm{exp}}]^2}{(n-1)}} \tag{2}$$

where q_{exp} is the amount of arsenic adsorbed, obtained from the experimental work; q_{cal} is the amount of arsenic adsorbed, obtained using appropriate model and n is the number of experimental data. All the experiments were performed in triplicate and only mean values are reported. All kinetic, isotherm and thermodynamic parameters and their standard errors were calculated by the use of commercial software (Microcal Origin 7.0) with a linear and/or non-linear least-squares method.

2.3. Modeling of the sorption processes

MINTEQ is a computer program used for surface complexation computation combining the best features of two models