International Journal of Chemistry and Chemical Engineering.
ISSN 2248-9924 Volume 3, Number 2 (2013), pp. 107-112

http://www.ripublication.com

Removal of Arsenic and Copper Metals from Contaminated Water using Iron (III) Oxide Nanoparticle

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Abstract

In this paper, the removal of heavy metals like As (V) and Cu (II) from the contaminants in municipal water supply by the process of adsorption to make it safer for domestic purpose is discussed. For this magnetite (Fe_3O_4) nanoparticles are assigned for separating and removing contaminants in wastewater by applying external magnetic fields. It is synthesised by co- precipitation method obtained by an aging stoichiometric mixture of ferrous and ferric salts in aqueous medium. The precipitation of Fe_3O_4 is expected at a pH between 8 and 14. Magnetite (Fe_3O_4) nanoparticles with size less than 30 nm have a large surface area and remain non-magnetised under external magnetic field. The size and shape of the nanoparticles can be controlled by adjusting pH, ionic strength, temperature and nature of the salts. At optimized pH the obtained Fe_3O_4 nanoparticles are coated with coating agents which develops surface functionalized groups. These form miniature aggregates in aqueous suspensions. The sorption of metals like As(V) and Cu(II) take place on these aggregates which are removed with help of external magnetic field leaving the supernatant free from Copper and Arsenic.

Keywords: Contaminants; Nanoparticle; Heavy metals; Purification; Particle size.

1. Introduction

The presence of Arsenic and copper in high concentrations in domestic water supply is a major hindrance to public health. These heavy metals are discharge into the ground and surface water from the improperly treated toxic wastes from industries. Water

from these sources is inadequately treated for removal of As in the form of As(III)/As(V) and Cu before supplying it for domestic usage. The As and Cu concentration more than 0.01mg/l and 0.13mg/l respectively has been proved toxic in the long run(W.H.O) which causes arsenicosis, skin lesions and internal cancers. Arsenic may be present in two oxidation states as arsenate As(V) or arsenite As(III). Prevailing arsenic species are a function of pH and redox potential. Copper is stable in its metallic state and forms monovalent (cuprous) and divalent (cupric) cations. The removal of Arsenic(V) and Cu(II) is discussed in this paper. Adsorption is widely used for their removal treatment due to its simplicity and cost-effectiveness. The recent advancements in Nano technology gave rise to many nanoparticle adsorbents. The smaller the size of these nanoparticles, the larger the surface area provided for the contaminants to get adsorbed. Magnetite nanoparticles are being extensively used due to high surface area favoring adsorption and simple removal with the help of an external magnetic field. Several disadvantages like extensive agglomeration and poor morphology are also associated with it. There are several methods for the synthesis of Fe_3O_4 nanoparticles(Luciano carlos, et al) such as thermolysis of precursors, reverse micelle and micro-emulsion technology. Co-precipitation method is simplest and efficient method to synthesize magnetite nanoparticles. Particles with sizes ranging from 5 to100 nm are obtained. These nanoparticles are coated with solvents to adsorb As and Cu. Badruddoza et al. fabricated carboxymethyl-β-cyclodextrin modified Fe_3O_4 nanoparticles (CM-β-CD-MNPs) for removal of Cu(II) from aqueous solution by grafting CM-β-CD onto the magnetite surface via carbodiimide method. These CM-CD nanoparticles are later desorbed and are grafted with Zn2+ ions to enhance the adsorption of Arsenic in the obtained Cu(II)-free supernatant.

2. Material and Methods

2.1 Materials

In this method the following chemicals are used: Arsenic (III) oxide (As_2O_3) and arsenic (V) oxide hydrate (As_2O_5.3H2O). stock solutions of Zn2+,iron(II)chloride tetrahydrate($FeCl_2.10H_20$), iron(III)chloride hexahydrate($FeCl_3.6H_20$), ammonium hydroxide(NH_4OH), cyclodextrin (-CD 99%), cyanamide(CH_2N_2), copper (II) nitrate $Cu(NO_3)_2$, chloroacetic acid (CH_3COOCl), sodium hydoxide(NaOH)

2.2.1 Preparation of Magnetite nanoparticles

The nanoparticles required for the removal process are obtained by the method of co-precipitation

This method is the simplest and most efficient chemical pathway to obtain magnetic particles. Magnetite is prepared by an aging stoichiometric mixture of ferrous and ferric salts in aqueous medium. The precipitation of Fe3O4 is expected at a pH between 8 and 14.

2.2.2 Preparation of carboxymethyl-β-cyclodextrin

CM-β-CD was prepared following the procedure of literature[E. Furusaki,et al], in which 16.3% CH3COOCl (27 mL) at 50 ◦C for 5 h is treated with a mixture of β-CD (10 g) and NaOH (9.3 g) in water (37 mL). After the reaction mixture was cooled to room temperature, HCl is used to adjust the neutral pH(6–7). It is then poured to superfluous methanol solvent and white precipitates were produced. The solid precipitation was then filtered and dried under vacuum to give carboxymethylated _-CD (CM-β-CD) 6 g

2.2.3 Preloading CM-β-CD and Zn^{2+} over the magnetite nanoparticles

100mg of magnetic nanoparticles were first added to 2mL of buffer A (0.003M phosphate, pH 6, 0.1M NaCl). 0.5mL of carbodiimide solution (0.025 gmL−1 in buffer A) and 2.5mL of CM-β-CD (10–120mg/mL in buffer A) was added and the reaction mixture was sonicated for 90 min s. The resulting nanoparticles were recovered using a permanent magnet and washed 2–3 times with buffer A and then dried in a vacuum oven.

Zn is preloaded by mixing the magnetite nanoparticles suspension (5g in 450 mL solution containing 0.01MNaNO3 and 0.005 M Tris buffer at pH 8.0) with the Zn^{2+} stock solution (2000 mg/L). This was stirred for 6 h continuously by supplying with a syringe pump at a rate of 4 mL/h to avoid the formation of (zinc hydroxide) precipitate on the magnetite surface. Due to the thorough mixing and the slow rate, the Zn^{2+} stock solution was homogenized instantaneously. At the end of the loading experiment, the suspension was left undisturbed overnight, the supernatant was removed, and the slurry was kept for future use.

2.3 Characterization of magnetite nanoparticles

The size distribution and morphology of magnetic nanoparticles is analyzed with a TEM. The zeta potentials of as-synthesized nanoparticles were measured at different pH using aMalvern ZEN2600 Zetasizer Nano ZS.

2.4 Adsorption and Desorption process

The adsorption of Cu^{2+} by the CMCD-MNPs 120mg of wet magnetic nano-adsorbent was added to 10mL of $Cu(NO_3)_2$of various concentrations and shaken in a thermostatic Water-bath shaker operated at 230 rpm. After equilibrium was reached the magnetic nano-adsorbents were removed using a strong permanent magnet made of Nd–Fe–B and the supernatant was collected. The solution pH was adjusted by NaOH or HCl. The concentrations of copper ions were measured using atomic absorption spectrometer. Desorption was then carried out by adding 10mL of either acid solution to the Cu2+-sorbed CMCD-MNPs. After shaking at 200rpm for 3 h, the CMCD-MNPs were removed and the concentration of copper ions was measured.

Zn^{2+} is now grafted on the desorbed nanoparticles. Adsorption kinetics experiments were carried out in 1-L glass containers. In a typical arsenic adsorption experiment, 1 L aqueous solution of approximately 100 mg/L arsenic was added to the

glass container. The solution contained 0.01M of NaNO3 background solution; it also contained 0.005 M Tris buffers for the pH 8.0 solution (Jin et al). The pH values were adjusted with trace amount of HNO_3 or NaOH, 4 mL of Zn-preloaded magnetite nanoparticles slurry, collected under vigorous stirring, was used as the adsorbent in a 1-L glass reactor. After 28.5 h, an additional 1.0 mL Zn^{2+} stock solution was added into the reactor to increase the aqueous Zn^{2+} concentration to 2 mg/L and arsenic concentration was monitored for an additional 19.5 h.

3. Results and Discussion

3.1. Synthesis and characterization of magnetic nanoparticles Typical TEM image and size distribution of CMCD-MNPs.

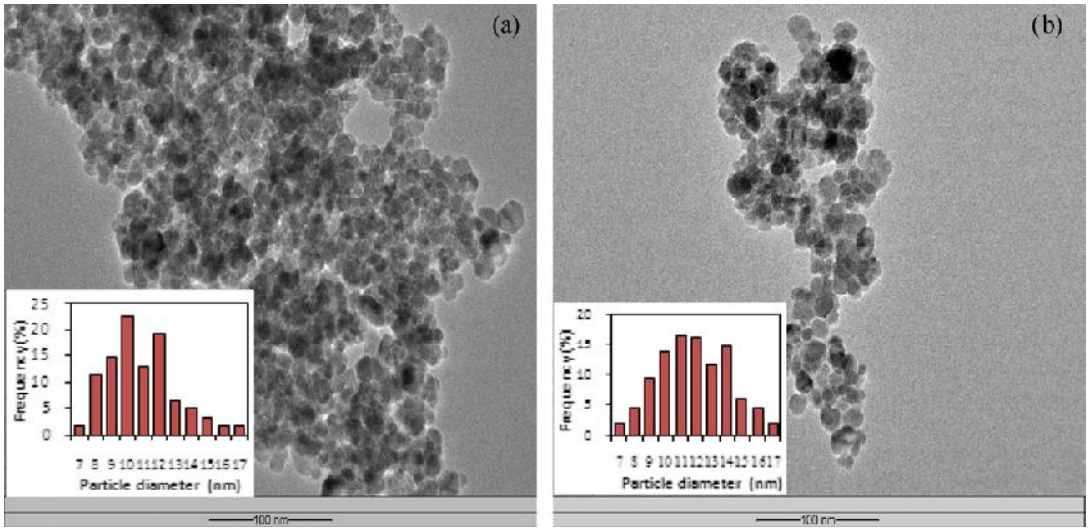

Figure 1: TEM micrographs and size distributions of (a) uncoated and (b) CM-β-CD bound Fe3O4 magnetic nanoparticles. (A.Z.M. Badruddoza et al.).

Zeta potentials of uncoated and CM-β-CD coated magnetic nanoparticles (0.1 mg/ml) were measured in 10−3M NaCl aqueous solution at different pH. The solution pH was adjusted by NaOH or HCl. The pH value of point of zero charge (pHpzc) after being grafted with CM-β-CD has been shifted from 6.8 to 4.7, indicating that the grafting of CM-β-CD onto uncoated MNPs is successful. Moreover, magnetic nanoparticles modified with CM-β-CD yields acidic surface since pHpzc is lower than that of uncoated MNPs and this surface acidity is due to the introduction of several oxygen-containing functional groups (M.H. Kalavathy, et al).

3.2. Adsorption of Cu2+ ions onto CMCD-MNPs

Atomic mass for CM-β-CD is determined as 1312 amu(A.Z.M. Badruddoza et al).CM-β-CD was covalently bonded onto the surface of magnetic nanoparticles via

carbodiimide activation. Here, the–COOH functional groups on CM-β-CD reacted with surface –OH groups to form metal carboxylate

3.2.1. Effect of initial pH in Cu2+ adsorption

The pH of the aqueous solution is an important controlling parameter in the adsorption process (Y.T. Zhou, et al). The adsorption capacity of Cu2+ ions increases with the solution pH (S.H. Huang et al). This might be due to the less insignificant competitive adsorption of hydrogen ions (Y.C. Chang, et al). At a lower initial Cu2+ concentration (50 mg/L), the adsorption capacity increases with increasing the solution pH and then remains almost unchanged at pH 4–6. This might be due to the fact that almost all Cu2+ ions are adsorbed.

3.2.2. Adsorption kinetics of Cu^{2+}

The kinetics of Cu2+ adsorption follows the pseudo-second-order model

3.3. Zn-enhanced arsenic removal by magnetite Nanoparticles

3.3.1 Adsorption kinetics

All adsorption kinetics data was biphasic, i.e., adsorption was rapid in the beginning, but after a few hours became very slow. Biphasic patterns have been reported for arsenic adsorption on mineral oxides and soils (Zhang, H. et al). At pH 8.0, the adsorption of As(V) is more pronounced than As(III) due to the enhancement effect caused by the addition Zn^{2+}

3.3.2 pH-dependency of Zn-enhanced arsenate removal

Adsorption-enhancement effect of Zn was only significant under neutral or basic conditions, and was negligible under acidic conditions

4. Conclusions

In this paper the method of removal of Copper and Arsenic metals using Iron(III)oxide nanoparticles is discussed.

These magnetite nanoparticles that are synthesized by co-precipitation method and are grafted with carboxymethyl-β-cyclodextrin (CM-β-CD) and these nanoparticles adsorb the Cu^{2+} in the contaminated water and can be separated with help of external magnetic field. The adsorption follows pseudo-second order mechanism. The Supernatant is retained for Arsenic removal. The Cu^{2+} containing nanoparticles are then desorbed. Now the Zn+ metal is grafted on the surface of recovered nanoparticles, the supernatant is now treated for the removal of As(V). The adsorption of Arsenate is biphasic. The nanoparticles are removed with help of external magnetic field and the nanoparticles can be desorbed for further use to remove As(V) or Cu(II) based on concentration level by Grafting with appropriate solvent. The same nanoparticles are hence used for the removal of Cu(II) and As(V) from contaminated water.

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