Magnetic Composite Containing Akaganeite: Synthesis, Characterization and Study of Arsenic Adsorption

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ABSTRACT

In this work, composite containing β-FeOOH and magneitic nanoparticles has been synthesized aiming at arsenic adsorption. The purpose was to combine the adsorptive capacity of akaganeite nanorods with magnetic nanoparticles, obtaining a material that can be easily separated from aqueous media under magnetic field. Akaganeite presents a tunnel structure that makes this material especially interesting in the areas of catalysis, electrode materials, ion exchange, adsorption and other applications. Several studies have verified the efficiency of akaganeite for adsorption of a large number of pollutants such as arsenic, chromium, uranium, fluoride, phosphate, and many other oxyanions. The synthesis of akaganeite was performed based on the hydrolysis of $FeCl_3.6H_2O$. The product was characterized by TEM, Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction. The adsorption tests were performed for As (III) and As (V) under different pH conditions. The TEM images revealed nanorods of Akaganeite with about 200-300 nm length. The diffraction data were used to identify the crystalline phase, and evaluate the crystallinity. Infrared results revealed the characteristics bands of Akaganeite. After the adsorption experiments, it was observed the average capacity of 92 % removal for both As(III) and As(V). A very good magnetic adsorbent has been easily synthesized by co-precipitation of magnetic nanoparticles akaganeite nanorods. This material can be used to remove arsenic species from water and liquid hazardous wastes with potential application in water decontamination processes.

INTRODUCTION

Arsenic (As) is a metalloid, widely distributed in the environment, with geogenic or anthropogenic sources. It has organic and inorganic forms in the atmosphere, hydrosphere, biosphere and troposphere (Hanusch et al., 1985). The organic species appear in the environment as a result of microbiological activity and in wastewater containing organoarsenical pesticides. The inorganic species result from natural mineral dissolution and mining activity. In the last case, arsenic can be a waste from the treatment of ores of copper, lead, cobalt and gold, to which arsenic is associated. These activities contaminate surface water and groundwater, which is a big risk to human health and to environment, due to its high toxicity. Arsenic exposure causes various diseases including skin disorders, respiratory diseases, lung and kidney disease, even cancer. Acute and chronic arsenic exposure via drinking water has been reported in many developing countries (Smedley & Kinniburgh, 2002). Especially in Bangladesh, tens of millions of people were found to be exposed to arsenic-contaminated drinking water with a concentration above the 10 mg L-1 (10 ppb), value set by the World Health Organization (WHO) guidelines for drinking water. This has led to chronic arsenic exposure and associated deaths (Argos et al., 2010; Cho et al, 2014).

Established techniques for removal of arsenic from water samples are precipitation and coagulation, ion exchange, and adsorption using various materials (Kolbe et al., 2011). Adsorption has been proven to be a promising technology for water purification for being economical and efficient. Metal oxide adsorbents have been widely reported for arsenic removal from water. Among them, iron oxides have attracted great attention owing to their low cost, natural abundance and affinity for arsenic (Bradruzzaman et al., 2004; Cavalcanti, 2012; Fagundes et al., 2008; Gimenez et al., 2007; Kolbe et al., 2011).The industry standards for arsenic removal from drinking water are iron-based adsorbents. In these industries, adsorbent replacement is responsible for 80% of the operating cost (Water Online, 2014). Therefore, using nanosized adsorbents lowers the operation costs since higher surface area adsorbents decrease the need for replacing the adsorptive media. Moreover, nanosized adsorbents could also be used instead of precipitation, which has been used to reduce arsenic concentrations from high levels (e.g., hundreds of mg/L) to moderate levels (e.g., 1 to 5 mg/L), reducing the amount of generated waste.

The nanoparticles of oxides/oxyhydroxides of iron attract the attention of the Scientists as they possess a wide range of applications such as catalytic materials, sorbents, pigments, flocculants, coatings, gas sensors and ion exchangers (Parameshwari et al., 2011).

Until now, there are 16 iron oxides/ oxyhydroxides and the mineral akaganeite (β-FeOOH) is one of these polymorphs (Cornell & Schwertmann, 2003). Akaganeite has a tetragonal structure consisting of double chains of edge-shared octahedra that share corners with adjacent chains to form channels running parallel to the c-axis, which can be occupied by chloride ions and water molecules (Figure. 1).

This tunnel structure makes β-FeOOH an especially interesting material in the areas of catalysis, electrode materials, ion exchange, adsorption and other applications (Zhao et al, 2012). Therefore the synthesis of akaganeite has been extensively investigated owing to its wide application. Zhao et al. (2012) presented a general description of different preparation methods and the adsorptive characteristics of akaganeite.
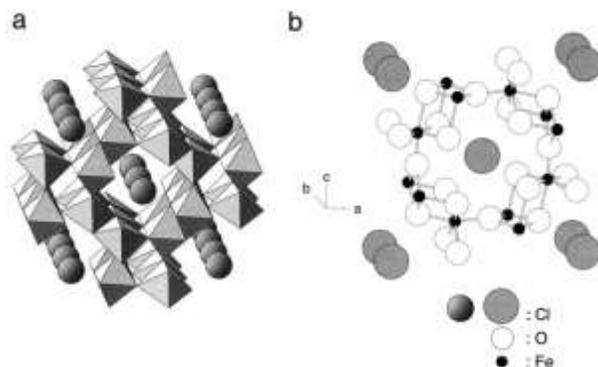
Figure 1 Structure of Akaganeite: (a) Arrangement of octahedral double chains in tunnels with chloride ions in the center of the tunnels and (b) The unit cell Model (Cornell & Schwertmann, 2003)

Akaganeite has been widely used as an adsorbent to remove contaminants from water and liquid hazardous wastes. Several studies have verified the efficiency of akaganeite for adsorption of a large number of pollutants such as arsenic, chromium, uranium, cadmium, zinc, cesium, antimony, fluoride, phosphate, and many other oxyanions (Zhao et al., 2012). In fact, many studies have shown the high arsenic adsorption capacity by akaganeite. These authors claim that the high affinity is due to the formation of a stable chemical bond (chemisorption) (Deliyanni et al., 2003; Zhang & Jia, 2014; Cho et al., 2014; Kolbe et al., 2011). However, there is still a lot of work to do to optimize the synthesis method, to enhance akaganeite adsorption properties and to improve its application form.

Recently, several methods have been used to obtain magnetic nanoparticles of different morphologies, controlled size, and high magnetization. The co-precipitation is the synthesis methodology most referenced in the literature. It is based on the co-precipitation of iron salts (ions Fe^{2+} and Fe^{3+} in the molar ratio 1: 2) in the presence of a base. The method of co-precipitation is distinguished by simplicity, efficiency, chemical homogeneity, low temperature synthesis, obtaining fine particles (average diameters less than 25 nm) with good reactivity, uniformity, low agglomeration, relatively small reaction time and the possibility of large-scale processing, forming large amount of particles (Salviano, 2014; Costa, 2013; Ferreira, 2009; Petcharoen et al., 2012; Valenzuela et al., 2009).

In this work, composite nanoparticles of β-FeOOH / Fe_3O_4 has been synthesized aiming at arsenic adsorption. The objective was to combine the adsorptive capacity of akaganeite nanorods with nanoparticles of magnetite, obtaining a material that can be easily separated from aqueous media

under magnetic field, as illustrated by Figure 2. So, an important contribution of this work is the development a magnetic adsorbent, which will make easier the solid-liquid separation operation that follows the adsorption process.
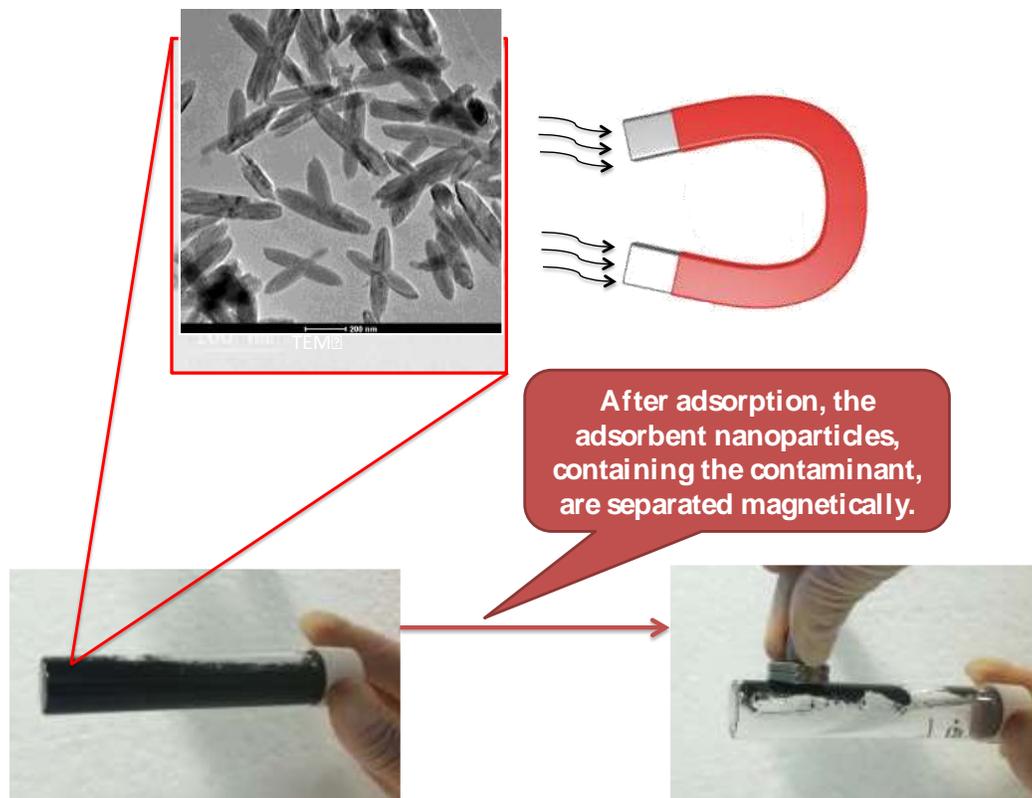
Figure 2 Magnetic separation of the akaganeite/magnetite adsorbent.

Magnetic separation is an effective technique for separating magnetic particles and it has the advantage of being rapid, easily applied in large scale operations and easily automated. Therefore, the challenge of separating high specific surface area powder adsorbents from solution could be addressed with the use of magnetic composites. These materials can be conveniently recovered by magnetic separation, avoiding the filtration steps, which may represent a barrier to the application of high performance advanced materials in environmental remediation processes and treatment of great volumes of aqueous solutions.

METHODOLOGY

The synthesis of the composite containing akaganeite (β-FeOOH) was performed based on Schwertmann & Cornell (2008) procedures, i.e., by hydrolysis of FeCl3.6H2O under temperature of 50 °C for eight days. The magnetic composite was synthesized by mixing the β-FeOOH and magnetic nanoparticles obtained by co-precipitation. The product was characterized by

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Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD).

To determine the arsenic removal capacity, the adsorption tests were conducted for As (III) and As (V) with an initial concentration of 15-20 ppm at pH 5, 7 and 8.5. In these tests, which were performed in duplicate, 100 mg of the adsorbent was maintained in contact with 50 mL of the arsenic solution for 24 hours at 120 rpm and 25 °C. These conditions were chosen based on the best results of the group for other arsenic adsorbents. The initial arsenic concentration around 20ppm was established based on the maximum adsorption capacity achieved by iron-based adsorbents in our previous works (SILVA et al.,2013; SILVA et al., 2012).

RESULTS AND DISCUSSION

As can be seen in the microscopic image shown in Figure 3, the produced akaganeite has the appearance of rods. This morphology is typical of β-FeOOH obtained by this synthesis route. The particles have length of about 200-300 nm and the width is about four times smaller.
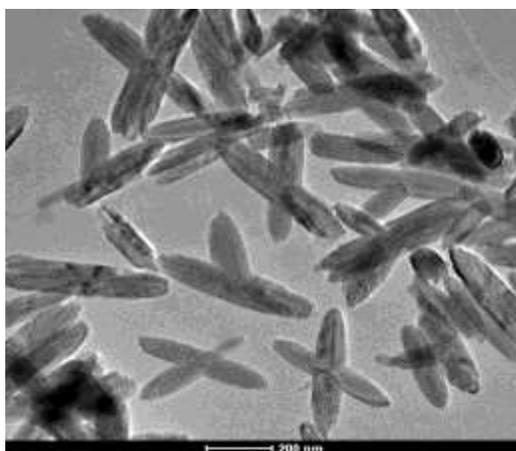
Figura 3 TEM image of Akaganeite crystals.

The infrared spectrum of akaganeite (Figure 4) shows a prominent absorption at approximately 3368 cm-1, featuring a vibrational stretch of O-H bond of the water molecules adsorbed on the surface of akaganeite nanoparticles. This band is very wide due to the great amount of water remaining in their structure. The other band located at 1628 cm-1 is attributed to the angular deformation vibration of O-H bond (Parameshwari et al., 2011).

Deliyani et al. (2007) reported that the bands near 820 cm-1 are due to the formation of OH --- Cl hydrogen bonds, which are peculiar of akaganeite containing chlorides in the structure. The bands in the range 300-700 cm-1 are attributed to the fundamental vibrations of inorganic ions in the crystal lattice (Parameshwari et al., 2011). That is, the band observed at about 399 cm-1 is attributable to symmetric stretching vibrations of the Fe-O bond at the octahedral site. Meanwhile,

the asymmetric stretching vibration of Fe-O-Fe bonds are responsible for the absorption band at 675 cm-1. In addition, the spectrum profile is fairly consistent with the literature (Schwertmann; Cornell, 2008; Parameshwari et al., 2011).
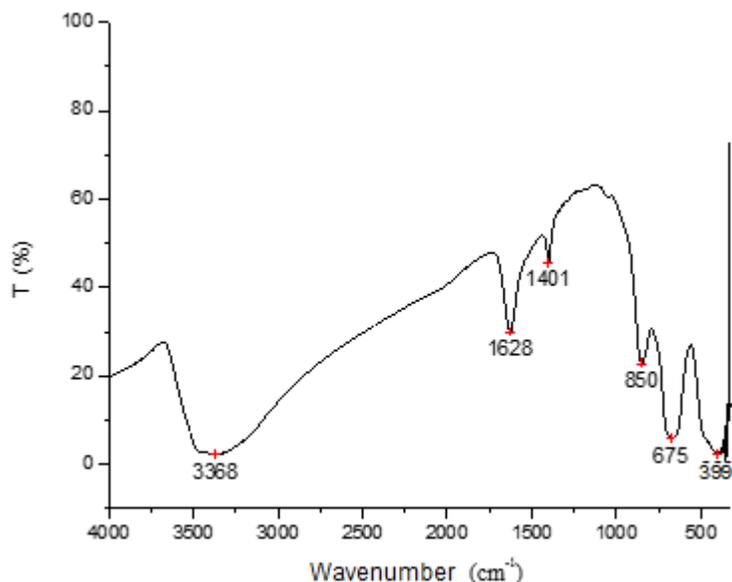
Figure 4 FTIR spectrum of Akaganeite.

Figure 5 shows the diffractogram of the akaganeite. From the X-ray diffraction data, it was determined that the crystallinity of the material obtained is 99,0. The interpretation of the X-ray diffraction data was performed by comparison with standards contained in database "Powder Diffraction File" (PDF) 34-1266 of the International Centre for Difracttion Data (ICDD) – 2003.
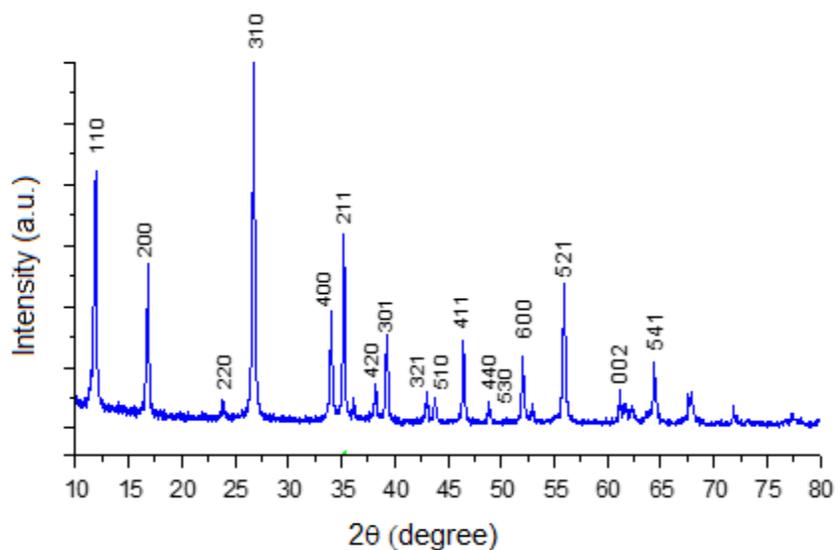
Figure 5 X-ray diffractogram of Akaganeite

From the produced akaganeite, the magnetic adsorbent was synthesized by co-precipitation of magnetite nanoparticles and akaganeite nanorods. Figure 6 shows the X-ray diffractogram of the magnetic composite. The akaganeite and magnetite diffraction peaks are clearly present in the composite. The synthesized magnetite corresponds to cubic Fe_3O_4 (ICDD, 89-0691).
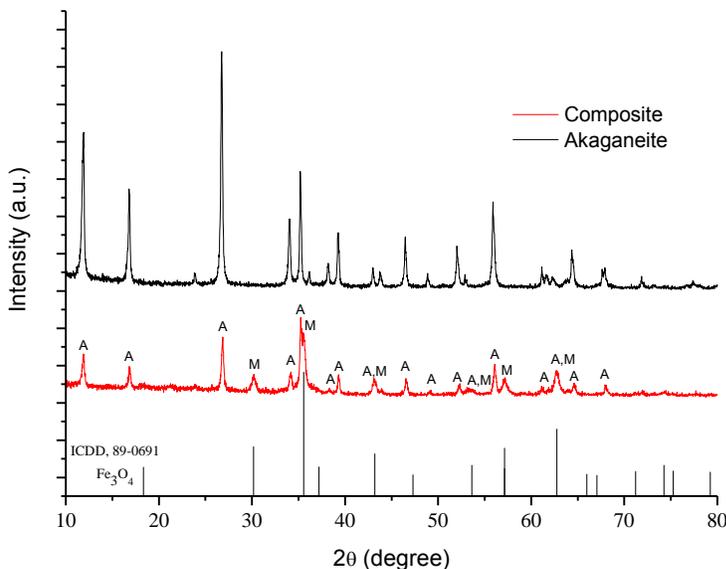
Figure 6 X-ray diffractogram of the magnetic composite. A: akaganeite; M: magnetite.

After adsorption experiments, in which the adsorbent (akaganeite and magnetic adsorbent) was maintained in contact with the arsenic solution for 24 hours at 120 rpm and 25 °C, the residual arsenic concentration was determined by Atomic Absorption Spectroscopy, then the percentage of As removal was calculated, from the initial concentration, and the results are in Table 1.

Table 1 Arsenic Removal Capacity of Akaganeite and Composite (akaganeite/magnetite)

Sample	Adsorbate	C_0 (ppm)	pH_0	% Removed
Akaganeite	As (III)	17.5 ± 1.0	5,0	85
	As (III)		7,0	83
Akaganeite	As (V)	15.8 ± 1.0	5,0	92
	As (V)		7,0	93
Composite	As (III)	17.5 ± 1.0	5,0	84
	As (III)		7,03	85
	As(III)		8,5	82

			5,0	82
Composite	As (V)	15.8 ± 1.0	7,0	81
	As (V)		8,5	42
	As (V)			

It was observed that the average capacity of removal was 84% for arsenic III in both adsorbents, pure akaganeite and composite, which is remarkable since arsenic III is more toxic, more soluble in water and less available for precipitation/adsorption reactions than arsenic V. Therefore, using the akaganeite magnetic adsorbent would also avoid the oxidation step, which is usually used in conjunction with other processes for arsenic removal. Regarding the arsenic V, it was observed 93 % removal onto pure akaganeite and 82 % removal onto composite for pH range 5 -7. At pH 8.5 the immobilization capacity decreased to 42%. According to Cornell and Schwertmann (2003), the point of zero charge (pzc) of magnetite is 6.8 and for akaganeite is between 6.7 and 7.3. That is, at the observed pH (greater than 8.0) the composite will be negatively charged, disfavoring the adsorption of anions $H_2AsO_4^-$ and $HAsO_4^{2-}$. It was possible to conclude that the presence of nanoparticle of magnetite in the composite did not compromise significantly the performance of akaganeite as adsorvbent for Arsenic and has introduced a great advantage regarding solid-liquid separation process. Therefore, the challenge of separating adsorbent with high specific surface composed of particles of 200-300 nm from solution could be addressed with the use of magnetic composites that can be conveniently recovered by magnetic separation, avoiding the filtration steps, which may represent a barrier to the application of high performance advanced materials in environmental remediation processes and treatment of great volumes of aqueous solutions. Therefore, using the akaganeite magnetic adsorbent in a batchwise operation with magnetic separation would improve arsenic removal and lower the operating costs.

What the selectivity of the adsorbent is concerned, in the work of Kolbe et al. (2011), competition reactions were studied with antimonate, arsenate, and phosphate in akaganeite. The sorption capacity of arsenate decreases up to 12.5% by adding phosphate (ratio 1:10), but the addition of antimonate did not influence the sorption of arsenate.

CONCLUSIONS

The results revealed that akaganeite has excellent tri and pentavalent arsenic removal capacity, confirming its high affinity for this harmful contaminant and noting its potential application as adsorbent in the decontamination of drinking water and/or waste.

The akaganeite/magnetite magnetic composite was obtained by a simple and efficient route. This magnetic adsorbent has a great potential application as much by high arsenic removal capacity as by the innovative possibility of magnetic separation.

ACKNOWLEDGEMENTS

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