Removal of Arsenic from Drinking Water by Hydroxyapatite Nanoparticles

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ABSTRACT

Arsenic(As) contained in drinking water can cause adverse effects on human health. This study investigated the effect of hydroxyapatite nanoparticles (nano-HAp) on sorption of As(V) ions in aqueous solution. The amounts of arsenic ion,nano-HAp and pH on removal efficiency were also investigated. Results showed that the removal of arsenate from water using hydroxyapatite nanoparticles, improved with increasing pH. The optimum amount of nano-HAp for As (V) removal is found to be 0/6 g/L with the removal efficiency of 88 %. The sorption data were then correlated with the Langmuir, Freundlich, adsorption isotherm models. The results indicated that nano-HAp can be used as an effective adsorbent for removal of As(V) from aqueous solution.

Key words: Arsenic, Water filtration, Hydroxyapatite nano particles, Adsorption, pH.

INTRODUCTION

Arsenic compounds are common contaminants in the environment. Because of arsenic toxicity and induced carcinogenetic agents (Eblin *et al.*, 2006; Hughes.,2002), higher arsenic concentration in the environment represents serious problems for human health, especially for populations in Bangladesh, Western Bengal, Vietnam,China, Mexico and Chile. The danger of elevated arsenic concentration in waters in these countries was under lined by WHO, which estimated the recommended limit for arsenic concentration in drinking waters up to10 μg/L Arsenic-contaminated drinking water can cause adverse health effects in human beings. Arsenic plays crucial role in making disturbance in RNA and DNA synthesis, which consequently lead to cancer. Increasing birth of exceptional child, low birth weight, malformed child and dead births were reported due to Arsenic compounds (Jain *et al.*, 2000; Kiping *et al.*,1997; Ng *et al.*,2001; Bissen *et al.*,2003; Penrose *et al.*,2009; Ng *et al.*,2003; Burkel *et al.*,1999; Smedley *et al.*,2002). The conventional technologies for arsenic removal from waters are based on processes of coagulation, sorption, ion-exchange reactions or methods of reverse osmosis. Materials used in these processes are Fe^0, Fe (III) oxyhydroxides, Mn (II), Al(III), apatite, silicate sands, carbonates, sulphides, ashor various types of coal (Chmielewská *et al.*,2008; Daus *et al.*,2004; DeMarco *et al.*,2003; Hiller *et al.*,2007; Lin *et al.*,2001; Sato *et al.*,2002; Song *et al.*,2006). Now a days, there is a trend to use the alternative and low-cost materials for arsenic removal from the waters in laboratory or medium-scale experiments, too. Effectiveness of chemically modified or native biomass in processes of arsenic removal was evaluated and proved by various authors (Abdel-Ghani *et al.*,2007; Boddu *et al.*,2008; Cernansky *et al.*,2007; Loukidou *et al.*,2003; Malakootian *et al.*,2009; Murugesan *et al.*,2006; Rahaman *et al.*,2008; Seki *et al.*,2005). Calcium hydroxyapatite (HAp), $Ca_{10}(PO_4)_6(OH)_2$, has also been used for the removal of heavy metals from contaminated soils, waste water and fly ashes (Omar *et al.*,2003; Takeuchi *et al.*,1990).Calcium hydroxyapatite (Ca-HAp) is a principal component

of hard tissues and has been of interest in industry and medical fields. Its synthetic particles find many applications in bioceramics, chromatographic adsorbents to separate protein and enzyme, catalysts for dehydration and dehydrogenation of alcohols, methane oxidation, and powders for artificial teeth and bones paste germicides (Elliott *et al.*,1994). These properties relate to various surface characteristics of HAp, e.g., surface functional groups, acidity and alkaline, surface charge, hydrophilicity, and porosity. It has been found that Ca-HAP surface with to P–OH groups acting as sorption sites (Tanaka *et al.*, 2005). The sorption properties of HAp are of great importance for both environmental processes and industrial purposes. Hydroxyapatite is an ideal material for long-term containment of contaminants because of its high sorption capacity for actinides and heavy metals, low water solubility, high stability under reducing and oxidizing conditions, availability, and low cost(Krestou *et al.*,2004). HAP has been utilized in the stabilization of a wide variety of metals (e.g., Cr, Co, Cu, Cd, Zn, Ni, Pu, Pb, As, Sb, U, and V) by many investigators (Omar *et al.*,2003; Ramesh *et al.*,2012; Vega *et al.*,1999). They have reported the sorption is taking place through ionic exchange reaction, surface complex with phosphate, calcium and hydroxyl groups and/or co-precipitation of new partiallysoluble phases. In this study, the effect of Hap nanoparticles on removal efficiency of arsenic ions in different conditions investigated.

MATERIALS AND METHODS

The hydroxyapatite nanoparticles previously have prepared (Montazeri and Biazar., 2011)and characterized by using the different analyses. The pH values of the solution were roughly adjusted from 2 to 12 by adding HNO_3 and NaOH respectively. The pH of the solutions was then accurately noted. Hydroxyapatite nanoparticles with different concentrations were added to each flask and securely capped, immediately. The suspension was then manually agitated. The pH values of the supernatant liquid were noted.Metal salt of ($HAsNA_2O_4.H_2O$) was used to prepare metal ion (As(V)) solution. Sorption studies were carried out by shaking aseries of bottles containing different amounts of HAp-nano in 50 mL of metal ions solution with different concentrations and pH. Suspensions were exposed toultrasonic waves (50W,20 min;), to disperse nanopaticles. The samples were stirred at room temperature at 250 rpm for 1 h (Equilibrium time), then centrifuged for 5 min and the supernatant liquid was analyzed by an atomic absorption spectrometer(S-series, Thermo Scientific; USA).

RESULTS AND DISCUSSION

Effect of pH

The pH is a significant factor for determining the form of the metallic species in aqueous media. It influences the adsorption process of metal ions, as it determines the magnitude and sign of the charge on ions (Gupta *et al.*,2005). The effect of solution pH on the sorption of As(V) ions from the aqueous solution by Hap-nanoin different concentrations was investigated in the pH range of 2–12 with the As(V) concentrations of 0/6 g/L. The result is shown in Fig 1. It was found that the adsorption capacity of HAp increases with increase in pH in acidic

Table. 1: Comparison of contact time for As(V) removal

No. Adsorbent	Equilibrium time	References
Activated Aluminasupported iron Oxid	4, 8, 12 and 36 h, corresponding to Pb(II)initial concentrations of 0.1, 0.2, 0.4 and 0.8 mM, respectively	Huang et al. (2007)
Rice husk, maize cobs and sawdust	90 min	Abdel-Ghani et al. (2007)
Syzygium cumini L.	10 min	King et al. (2007)
Bamboo dust carbon	45 min	Kannan and Veemaraj (2009)
Commercial activated carbon	35 min	Kannan and Veemaraj (2009)
Calcite	10 min	Yavuz et al. (2007)
HA	60 min	Present study

medium. But in alkaline conditions, the removal efficiency remains constant, approximately. The effects of pH on arsenate removal by HAp-nano suggest that electrostatic attraction is not a major mechanism responsible for the arsenate sorption under our experimental conditions; otherwise the apparent arsenate sorption would decrease with increasing pH. The sorbent dissolution can result in a decrease of sorbent mass and an increase of phosphate concentration in water, both of which can inhibit arsenate sorption. Lowering pH can favor the dissolution HAp-nano, and thus suppress arsenate sorption (Sneddon *et al.*,2005; Valsami-Jones *et al.*,1998; Mohan *et al.*,2007).

Effect of Arsenic concentration

For study the effect of solution arsenate amount on the sorption of As(V) ions from the aqueous solution by HAp-nanoin different concentrations was investigated in the range of (0/1,0/2, 0/4,0/6 g/L in pH:8).The result is shown in fig 2. increase arsenate absorption occurred with increasing arsenaterate. Arsenate adsorption, in different concentrations of arsenate in water, investigated in nano-hydroxyapatite, showed a similar increase approximately, As a result, absorption levels for these different amounts of arsenate are significant.

Effect of contact time

The time-dependent behavior of As(V) dsorption was measured by varying the contact time between adsorbate and adsorbent in the range of 5–120 min. The percentag adsorption of As(V) with different contact time is shown in Fig. 3. From Fig. 3, it can be observed that the rate of removal of As(V) ions was higher at the initial stage, due to the availability of more active sites on the surface of HA and became slower at the later stages of contact time, due to the decreased or lesser number of active sites (Kannan and Karrupasamy 1998). It is apparent from Fig. 3 that until 1 h, the percentage removal of As(V) from aqueous solution increases rapidly and reaches up to 85 %. A further increase in contact time has a negligible effect on the percentage removal. Therefore, a 1 h shaking time was considered as equilibrium time for maximum adsorption. The decrease in rate of removal of As(V) with time may also be due to aggregation of As(V) around the HA particles. This aggregation may hinder the migration of adsorbate, as the adsorption sites become filled up, and also resistance to diffusion of As(V) molecules in the adsorbents increases(Mittal *et al.* 2010).

Table. 2: Isotherm parameters for sorption of As(V) by HA

Langmuir isotherm constants			Freundlich isotherm constants		
xq_{max}	*b*	*r²*	*k*	*n*	*r²*
526	0/053	0/938	6/683	0/207	0/975

Table. 3: Comparison of As (V)) adsorption capacities of different adsorbents

Adsorbents	Freundlich parameters K (mg/g)	Author and the source are credited References
Magnetiteemaghemite nanoparticles	10.6	24
TiO2 at pH 9	16	43
Akaganeite	69.7	44
Ce(IV)-doped iron oxide	60.4	45
Laterite soil	0.055	46
Granularferric hydroxide (GFH)	10.3	47
Magnetite	10	48
HA	526	Present Study

Effect of mass of adsorbent on As(V) removal

The effect of HA dosage on As(V) removal was analyzed by varying the dosage of HA and the result is shown in Fig. 4. It was observed that the removal efficiency increases with the increase in HA dosage. This reveals that the instantaneous and equilibrium sorption capacities of As(V) are functions of the HA dosage

Adsorption isotherms

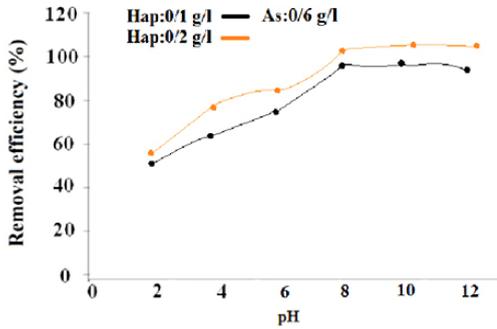Equilibrium isotherm is described by a sorption isotherm,characterized by certain constants

Fig.1: Effect of pH on removal of As(V) ions with concentration of 0/6g/LAs
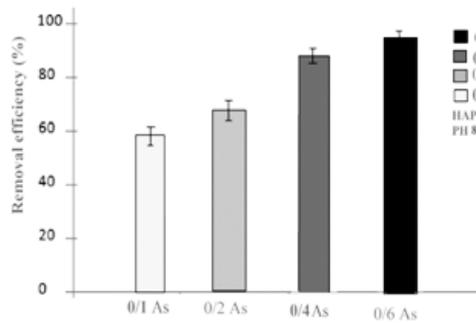

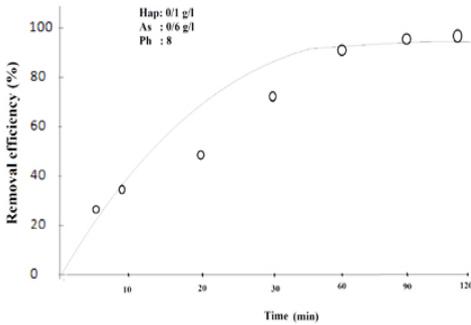**Fig.2: Effect of As on removal of As(V) ions with pH = 8**

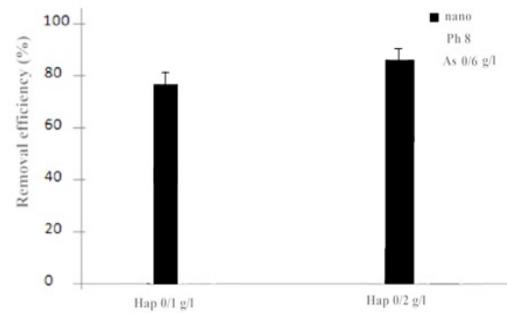**Fig.3: Effect of time on removal of As(V) ions with pH = 8**

Fig. 4: Effect of dosage on removal of As(V) ions with pH = 8 and As= 0/6 g/l
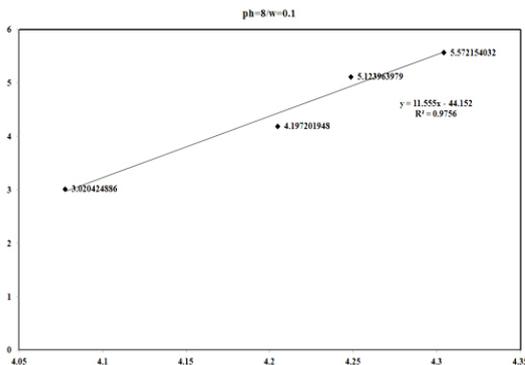

Fig.5: freundlich Isotherm plots for sorption of As (V) by HA
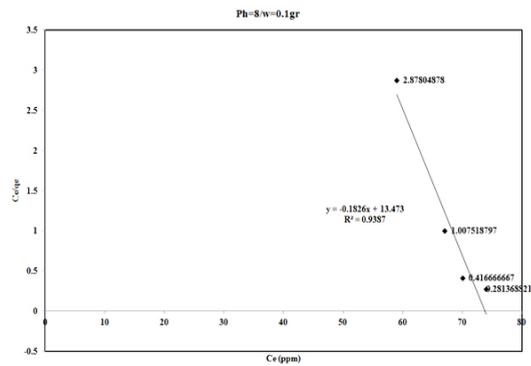

Fig.6: longmuir Isotherm plots for sorption of As (V) by HA

whose values express the surface properties and affinity of the sorbent sorption equilibrium is established when the concentration of sorbentin the bulk solution is in dynamic balance with that at the sorbent interface (Oladoja *et al.*,2008). The adsorption isotherm study is carried out on well-known isotherms such as Langmuir Langmuir .,1915).

$$\frac{1}{x/m} = \frac{1}{q_{max}} + \frac{1}{q_{max}} \frac{1}{bc_e}$$

Where b is the constant that increases with increasing molecular size, q_{max} is the amount adsorbed to form a complete monolayer on the surface (mg/g), X is weight of substance adsorbed (mg), M is weight of adsorbent (g), and Ce is the concentration remaining in solution (mg/L). The

essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter RL, which is a dimensionless constant referred to as separation factor or equilibrium parameter (Weber and Chakkravorti, 1974).

$$RL = \frac{1}{1 + bc_o}$$

The value of RL indicates the type of the isotherm to be either unfavorable (RL[1]), linear (RL = 1), favorable (0\RL\1) or irreversible (RL = 0). The Freundlich isotherm is expressed as (Freundlich, 1906) .

$$lnq_e = lnk_f + \frac{1}{n} \times lnc_e$$

Where K_f and n are the constants depending on temperature An isotherm plot for sorption of As (V) by HAp-nanois shown in Fig 5 and 6 The diagram indicates that the Freundlich isotherm is favorable for removal of As (V) by HAp-nano. The value of Ralso indicates that Langmuir isotherm is favorable. It can be concluded that Freundlich isotherm is the best fit langmuir isotherms. The adsorption capacity of HAp-nanofor As (V) adsorption is compared with other adsorbents (Table 3). The value of As (V) uptake by HAp-nanofound inthis work is significantly higher than that of other adsorbents.

Three types of reactions may control As(V) immobilization by HAp-nano: surface adsorption, cation substitution orprecipitation. The first mechanism is the adsorption of As(V) ions on the HAp-nanosurfaces and following ion exchange

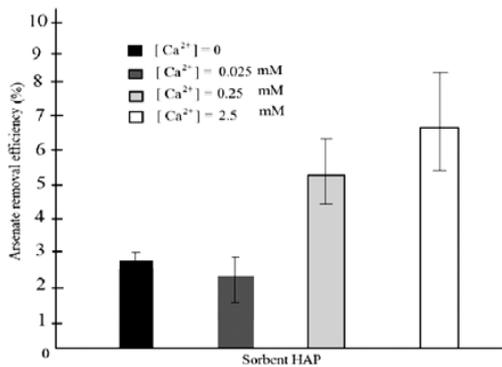
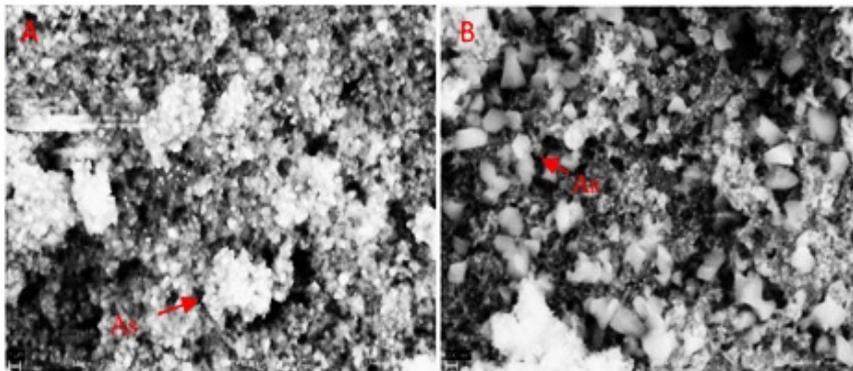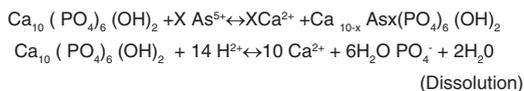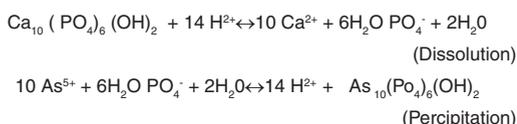**Fig.7: Metal disappearance for removal of As(V) by HAp**

Fig.8: SEM image of adsorbed As by Hydroxyapatite nanoparticles in optimum condition: As : 0/1g/L, HAp : 0/6g/L and pH: 12) at different magnifications A) 5000 X, B) 15000 X

reaction between As(V) ions adsorbed and Ca ions of HAp-nano(Suzuki *et al.*,1984). This ion exchange reaction mechanism (Ma *et al.*,1994) is expressed as:

$$Ca_{10} (PO_4)_6 (OH)_2 + X As^{5+} \leftrightarrow XCa^{2+} + Ca_{10-x} Asx(PO_4)_6 (OH)_2$$
$$Ca_{10} (PO_4)_6 (OH)_2 + 14 H^{2+} \leftrightarrow 10 Ca^{2+} + 6H_2O PO_4^- + 2H_2O$$

(Dissolution)

Showed that HAp-nano dissolution and hydroxypyromorphite (HP) precipitation were the main mechanisms for As(V) immobilization by HAp-nanoin the absence of other metals. These chemical reactions can bedescribed as follows:

$$Ca_{10} (PO_4)_6 (OH)_2 + 14 H^{2+} \leftrightarrow 10 Ca^{2+} + 6H_2O PO_4^- + 2H_2O$$

(Dissolution)

$$10 As^{5+} + 6H_2O PO_4^- + 2H_2O \leftrightarrow 14 H^{2+} + As_{10}(Po_4)_6(OH)_2$$

(Percipitation)

Information about the sorption mechanisms have been inferred by the values of molar ratios (Qs) of cations bound by HAp-nanoto Ca desorbed from HAp-nano (Aklil *et al.*, 2004). Fig 7 presents the effect of calcium concentration on arsenate removal by HAp-nano. For all sorbents tested, increasing calcium level appeared to assist arsenate sorption. When calcium concentration increased from 0 to 2.5 mM, the arsenate removal efficiency increased from 2.4% to 5.4% by using HAp-nano. The calcium effects on arsenate sorption to HAp-nanoare to be due to two reasons. First, according to increasing calcium concentration in water can inhibit HAp-nano, which can inhibit arsenate sorption to the sorbents. Second, Ca^{2+} in water can complex with phosphate on HAp-nano surface, resulting in an increase of sorption sites and subsequently an increase of arsenate sorption (Czerniczyniec *et al.*,2007; Sneddon *et al.*,2005). SEM image of absorb As(V) by nanoparticles of HAp-nanoshown in figure8.

CONCLUSION

The result shows that hydroxyapatite nanoparticle (HAp-nano) is a powerful adsorbent for removing As(V) from aqueous solution. The optimum dose of HAp-nanofor As(V)removal is found to be 0.2 g/L with the removal efficiency of 88 %. Freundlich isotherm had best fit than Langmuir, for experimental data. The adsorption capacity of HAp-nano was found to be 526 mg/g HAp-nano dissolution and hydroxy pyromorphite precipitation were the main mechanisms for As(V) immobilization by HAp-nano.

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