Sorption of Arsenic and Heavy Metals Using Various Solid Phase Materials

Woosik Jung, Young Kyu Park, Ju-suk An, Ji Young Park, and Hyun Je Oh

***Abstract*—A composite adsorbent was synthesized by immobilizing ferric oxide or three different iron oxides into alginate beads (HFOAB) for the removal of arsenate [As(V)] and heavy metals from aqueous phase. Sorption studies were conducted on single and binary sorbate systems, and the effects of contact time, initial adsorbate concentration, and pH on adsorption performance of HFOAB were monitored. The sorption process for As(V) and Cu(II) reached an equilibrium state within 240 h and 24 h. The maximum sorption capacity of As(V) was 13.8 mg g^{-1} after 168 h. The effect of arsenic species on Cu(II) sorption was insignificant. The adsorption of As(III), As(V), and Cu(II) followed pseudo second order kinetics. Kinetic studies showed that adsorption process reached equilibrium within 8 h at an initial concentration of 10 mg/L. Pb(II) and Cd(II) showed a greater sorption capacity on NCBs, which might be due to sorption sites provided by the immobilized GNC. The sorption affinity of divalent metal ions on NCB was in the following order: Pb=Cu=Cd >Zn=Ni> Co>Mn. The study demonstrates that the synthesized sorbent could be useful for the simultaneous removal of both anionic and cationic contaminants from wastewater.**

***Index Terms*—Adsorption, alginate beads, hydrous ferric oxide, nano carbon, arsenic, heavy metals.**

I. Introduction

Effective removal of arsenic and heavy metals from aqueous solution is an important issue in the protection of the environment and also in public health. Because heavy metal ions are not biodegradable, must be removed from contaminated water via physical or chemical processes, such as chemical precipitation, membrane filtration, ion exchange and adsorption [1], [2]. Biological adsorbents are currently being considered as cost effective and efficient alternative materials for the removal of toxic metal contaminants [3].

Arsenic has been detected in soils, and surface and ground waters at potentially toxic concentrations due to natural sources, mine drainage, and arsenic-based pesticides [4]. Elevated and undesirable levels of arsenic in groundwater have been reported globally [5]-[7]. To avoid health issues associated with arsenic in drinking water, the World Health Organization (WHO) has recommended a maximum contamination limit of 10 μg As L-1. In view of the above issues, development of a reliable, effective, and economical treatment technology for arsenic removal from groundwater is urgently needed. Numerous studies have quantified and modeled As(V) and As(III) sorption onto amorphous iron oxides, goethite, lepidocrocite, and hematite. Both As(V) and As(III) are sorbed strongly to iron oxide; however, the sorption behavior of arsenic is dependent on its oxidation state and the mineralogy of the iron oxides [8]

Alginate is known for its metal binding properties whereby ion exchange between metal ions can occur [9]. It has been widely reported that the sorption of heavy metal ions onto biosorbents takes place via a specific ion exchange mechanism involving the replacement of protons, alkali, alkaline earth, or other cations by heavy metal ions [10]. Even though alginate has mainly been used as an immobilization agent, it plays a prominent role in metal sorption and has been reported to have excellent sorption capacity towards several heavy metal ions. In recent studies, the alginate sorption capacity has been shown to greatly exceed that of the actual sorbents immobilized in its matrix [11]. Due to this property, previous studies of alginate have not only been concerned with the mechanism of metal binding [12] and its metal sorption properties [13], [14] but also with its role as a composite membrane component [15].

Recently, nano-adsorbents such as iron oxides, titanium oxides, nickel oxide, iron-copper binary oxide, and zirconium oxides have demonstrated excellent arsenic removal efficiency [16], [17].

The aim of this study was to develop a new adsorbent by immobilizing the graphite nano carbon (GNC) or hydrous ferric oxide (HFO) on alginate matrix for the efficient removal of arsenic and heavy metals. Kinetics sorption experiments, isotherm sorption experiments, and the effect of contact time, initial adsorbate concentration, and pH on the adsorption performance of adsorbents were illustrated using the developed sorbent. The developed sorbent could be effectively utilized to simultaneously removal of contaminated water with cationic and anionic contaminants.

II. Materials and Methods

A. Chemical and Reagents

All chemicals and reagents used in the experiments were analytical grade unless otherwise specified. Sodium alginate was purchased from Sigma Aldrich and was used without further purification. Stock solutions (1000 mg L^{-1}) of As(V) was prepared by dissolving sodium hydrogen arsenate heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$, Sigma Aldrich, USA) in deionized (DI) water followed by further dilution as required. Stock solutions of Pb(II), Cd(II), Zn(II), Ni(II), Mn(II) and Co(II) (1,000 mg/L) were prepared with reagent grade in deionized (DI) water, respectively, which were further diluted

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to achieve the desired concentration. Calcium chloride ($CaCl_2$), HCl, and NaCl were purchased from Sigma-Aldrich.

B. Preparation of Adsorbents

Two grams of Na-alginate were dissolved in 1,000 mL of DI water under continuous magnetic stirring to prepare a homogeneous solution of 1 g of hydrous ferric oxide. This mixture was added dropwise into calcium chloride solution (0.05 M) using a 50 mL syringe with a 1.7 mm needle to form hydrous ferric oxide alginate beads (HFOAB). The HFOABs were washed several times with DI water to remove excess calcium ion and were finally dried at room temperature for 24 h. Graphite nano-carbon (GNC), with an average diameter of 50 nm, was prepared according to the procedure reported by Kim *et al.* [18]. In brief, electrical current with 50-60 V and 150 mA was applied using graphite cathode electrodes in a reactor containing de-ionized (DI) water for GNC preparation. A colloidal solution (pH 3) of GNC at 3,000 mg/L was obtained following 15 min of electrolysis. The calcium alginate beads employed as an adsorbent were prepared by the dropwise addition of sodium alginate (3% w/v) into 0.05 M calcium chloride solution under magnetic stirring for 12 h, to obtain a homogeneous colloidal suspension. The suspension was then added dropwise into 1,000 mL of 0.05 M $CaCl_2$ solution using a 5.0 mL syringe with a 1.7 mm diameter needle to form NCBs. Ca-alginate beads formed upon contact with the cross-linker solution and were left overnight to stabilize. The excess cross-linker solution was removed, and the beads were washed several times with deionized water. The diameters of both beads were approximately 3.0 mm.

C. Sorption Experiments

Sorption experiments were carried out in 50 mL glass vials at 25℃ and 100 rpm in batch mode. Standard solutions of heavy metals, As(V) and Cu(II) were prepared by diluting stock solution (1000 g L^{-1}), followed by adjustment of the pH to 5 with 0.1 M HCl or NaOH. Kinetic experiments of Pb(II), Cu(II), Cd(II), Zn(II), Ni(II), Co(II) and Mn(II) were performed by equilibrating 0.05 g of graphite nano carbon beads with 20 mL solutions of adsorbate containing 20 mg L^{-1} of heavy metals. The adsorption performance of NCBs with various heavy metal ions was studied in batch mode and the results were compared with ABs. The experiments were performed in 50 mL capped glass tubes. The sorbate solutions (20 mL) at desired concentrations were equilibrated with 0.2 g of sorbents (ABs and NCBs) in a shaker operated at 100 rpm. The suspensions were filtered after equilibrium has been attained.. The equilibrium time for sorption experiments was estimated from the kinetics experiments. The effect of contact time on As(V) adsorption on various solid phase iron oxides was investigated. Experiments were conducted in 20 mL of solution with initial concentrations of 10 mg L^{-1} As(V) with a mixing rate of 100 rpm at 25℃. Simultaneous As(V) and Cu(II) kinetics experiments were carried out with 20 mL solutions of 10 mg L-1 As(V), and 20 mg L^{-1} Cu(II) using 0.02 g of HFOAB. Blanks (absence of sorbent) were run to ascertain the absence of chemical precipitation in the binary system. Experiments were performed in duplicate, and the sorption capacity at equilibrium (qe, mg g-1) was determined using Eq. (1)

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

where Co and Ce are the initial and equilibrium concentrations (mg L-1), respectively, V is the volume of solution (L), and m is the mass of sorbent (g). After reaching equilibrium, the suspensions were filtered, and the residual metal concentration in the filtrate was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin Elmer 3000 DV, USA).

III. Results and Discussion

A. Effect of Contact Time with HFO Immobilized Alginate Beads

Experiments were carried out to examine the adsorption of As(V) on HFOAB, GtAB and MtAB with contact time (Fig. 1). The effect of contact time on the adsorption of As(V) onto HFOAB, GtAB and MtAB at initial concentrations of 20.0 mg L^{-1} is shown in Fig. 1. The removal efficiency for As(V) increased gradually up to 98, 86% and 41%, as the process approached the equilibrium state (168 h). The adsorption capacities of HFOAB, GtAB and MtAB for As(V) at equilibrium were 10.2, 8.4 and 2.1 ug g^{-1}, respectively. In the initial stage, the higher driving force allowed external mass transfer resistances to be overcomes, and active sites with a higher affinity were occupied [19]. Once the high affinity binding sites are occupied, residual binding sites with a lower affinity become occupied, leading to the slow attainment of equilibrium.

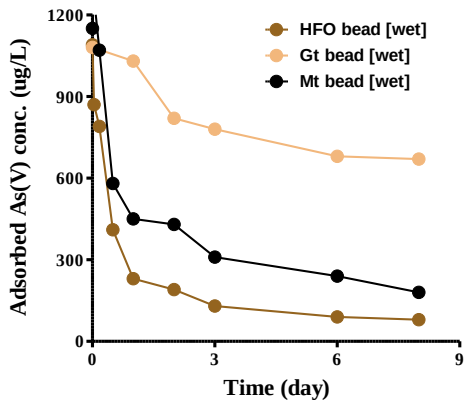

Fig. 1. Adsorption kinetics of As(V) by HFO immobilized alginate beads (HFOABs), goethite immobilized alginate beads (GtABs) and magnetite immobilized alginate beads (MtABs), respectively (Contact time: 8 d, adsorbent amount: 10 g/L, pH: 5.0).

HFO immobilized bead was one of the promising adsorbents for removal of arsenate from the aqueous phase among the three different adsorbents.

The observed sorption capacity for As(V) sorption after drying process was comparatively higher than wet HFO beads This showed that thermal activation of beads significantly influences sorption kinetics (Fig. 2).

B. Effect of Initial Concentration

The sorption capacities of As(V) on HFOAB as a function of initial sorbate concentration were evaluated. Increase in sorption was observed with the increase in initial arsenic concentration on HFOAB (Fig. 2). An increase in the initial concentrations probably provides driving forces to overcome mass transfer resistance between solid/solution interfaces. Increase in initial As(V) concentration from 10 to 500 mg/L increased its sorption on HFOAB from 0.8 to 13.8 mg/g.

C. Effect of pH

The effect of pH on As(V) sorption onto HFOAB was examined in the pH range of 4-10 (Fig. 4). As(V) species mainly exist as negatively charged, while As(III) species exist predominantly as neutral in the pH range of 2-10. The surface charge of the sorbent becomes less positive with increasing pH, and the surface of the sorbent presents negative charges at pH>pHpzc

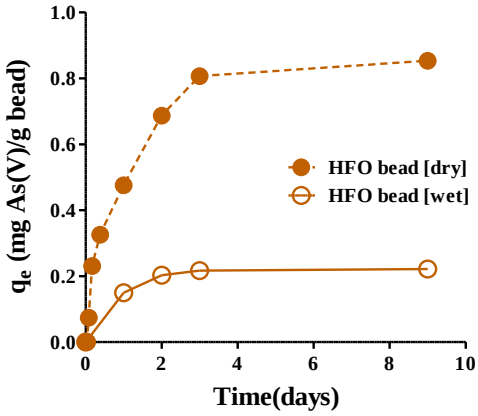

Fig. 2. Adsorption kinetics of As(V) HFO immobilized alginate beads (HFOABs) after drying process compared with wet HFOABs, respectively (Contact time: 9 d, adsorbent amount: 10 g/L, pH: 5.0).

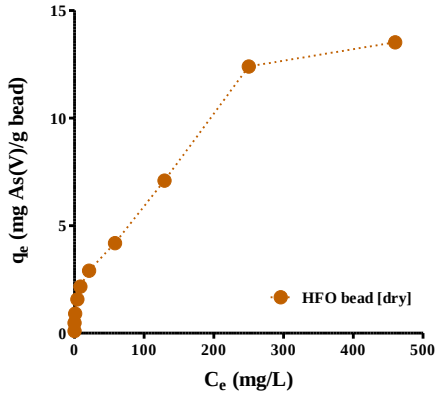

Fig. 3. Adsorption isotherm of As(V) by HFO immobilized alginate beads (HFOABs) (Contact time: 48 h, adsorbent amount: 10 g/L, pH: 5.0).

D. Effect of pH

The effect of pH on As(V) sorption onto HFOAB was examined in the pH range of 4-10 (Fig. 4). As(V) species mainly exist as negatively charged, while As(III) species exist predominantly as neutral in the pH range of 2-10. The surface charge of the sorbent becomes less positive with increasing pH, and the surface of the sorbent presents negative charges at pH>pHpzc. This phenomenon results in repulsion between sorbent and anionic sorbates. The adsorption level of As(V) was high in strongly acidic pH solution, in which $H_2AsO_4^-$ is the predominant species below pH 6.9. This result might be attributed to protonation of the hydrous ferric oxide surface with an abundant amount of protons (H^+), which would increase the adsorption of As(V) by enhancing the electrostatic attraction to negatively charged As(V) ions. By contrast, with a rise in solution pH, the number of negatively charged adsorption sites increased, and the repulsion force further increased beyond pH 7 led to a sharp decrease in the amount of adsorbed As(V) because the predominant As(V) species became $HAsO_4^{2-}$.

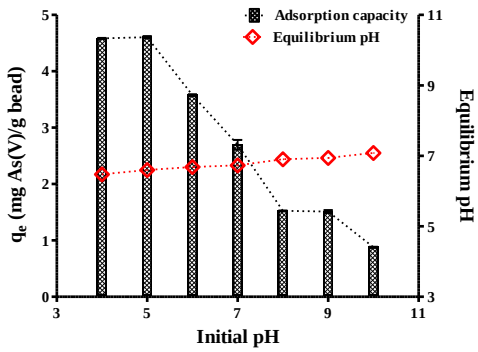

Fig. 4. Effect of pH on As(V) sorption onto HFO immobilized alginate beads (HFOABs), (Contact time: 48 h, adsorbent amount: 10 g/L).

Substantially less adsorption of As(V) was observed at higher pH values, which might be due to speciation shift of As(V) to double charged $HAsO_4^{-2}$, and change of the adsorbent surface charge to negative.

E. Sorption of As(V) and Cu(II) in a Binary System

The effect of the presence of Cu(II) on the adsorption of arsenic(V) species by HFOAB is depicted in Fig. 5. For adsorption of As(V) in the binary system, the effect of Cu(II) was negligible due to the characteristics of As(V) species being neutral in the wide pH range of 4-10. On the other hand, adsorption of As(V) distinctly increased (1.45 to 3.76) in the presence of Cu(II) ions within 168 h. Cu(II) adsorption was independent of the presence of As(V), which may be attributed to the relatively faster adsorption of Cu(II) ions than arsenic species in aqueous phase.

F. Sorption of Heavy Metals on Nano Carbon Immobilized Alginate Beads

In order to understand the sorption mechanism and to identify the equilibration time for maximum uptake, the sorption of various heavy metal ions on ABs and NCBs was studied as a function of contact time. Fig. 6 shows the adsorption kinetics of Pb(II), Cd(II), Zn(II), Ni(II), Mn(II) and Co(II) on ABs and NCBs with 10 mg/L initial heavy metal ions concentrations. Rapid Me(II) sorption on both NCB and AB was observed during the initial 4 hours contact time, accomplishing 80 to 92% metals sorption. The rapid initial phase was followed by a slower phase and finally the equilibrium phase. The adsorbents exhibited an initial rapid uptake removing 90% of Pb(II) and Cd(II) within 4 h followed by slow kinetics that reached a plateau. Pb(II) and Cd(II) showed a greater sorption capacity on NCBs, which might be due to sorption sites provided by the immobilized GNC. The sorption affinity of divalent metal ions on NCB was in the following order: Pb=Cu=Cd >Zn=Ni> Co>Mn.

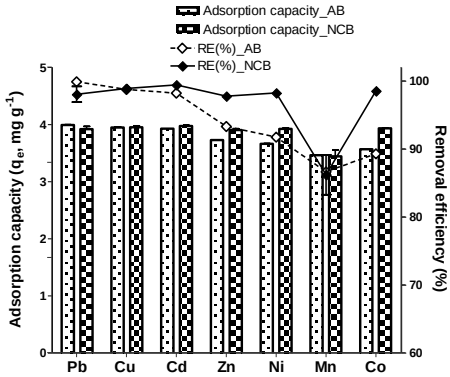

Fig. 5. Sorption equilibrium of various heavy metal ions onto nao-carbon immobilized alginate bead (Contact time: 24 h, adsorbent amount: 2.5 g/L, pH: 5.0).

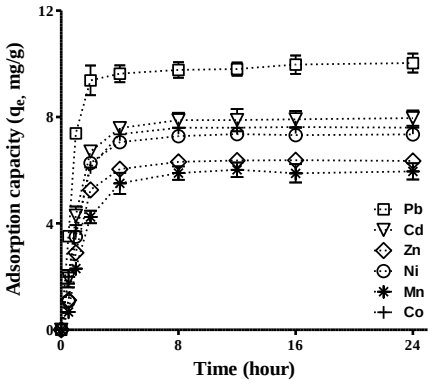

Fig. 6. Sorption kinetics of various heavy metal ions onto nao-carbon immobilized alginate bead (Contact time: 24 h, adsorbent amount: 2.5 g/L, pH: 5.0).

IV. Conclusions

An adsorbent for the efficient removal of arsenate from an aqueous phase was synthesized by immobilizing hydrous ferric oxide into alginate beads (HFOAB). The maximum sorption capacities of HFOAB for As(V) was 13.8 mg g-1. a lower pH resulted in increased adsorption of arsenic. The simultaneous removal of arsenic and copper using synthesized ZOAB was possible. As(V) and Cu(II) were sorbed onto different sorption sites. The addition of Cu(II) contributed to increased positive charge on the sorbent surface, which proved to be more favorable for As(V) sorption. In summary, an adsorbent prepared using hydrous ferric oxide and alginate beads can be an efficient material for the simultaneous removal of cations and anions from aqueous solution.

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