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Iron-oxide modified sericite alginate beads: A sustainable adsorbent for the removal of As(V) and Pb(II) from aqueous solutions

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ABSTRACT

Sericite powder was used as a substrate to immobilize the iron-oxide particles and it was encapsulated into beads using Na-alginate and Fe(III) ions by a simple cross-linking method to obtain iron-oxide modified sericite alginate beads (IMSA). The presence of iron oxide particle and other functional groups of alginate allows interaction of anionic arsenic species as well as the cationic Pb(II) ions with the IMSA beads; therefore, the material possess enhanced affinity towards these two highly toxic pollutants. The surface morphology and chemical composition of the beads were characterized by SEM-EDX analysis. Various functional groups present in the beads were identified by FT-IR analysis. Moreover, the iron content in the beads was obtained by US EPA 3050B method and the stability of immobilized iron was evaluated as a function of pH. The batch experiment showed that an increase in solution pH facilitate the uptake of Pb(II) whereas the As(V) removal found to decrease at higher pH. The simultaneous adsorption study showed that the As(V) removal was significantly high even at basic solution, which is perhaps, due to the presence of $Pb(OH)_2$ precipitates. The adsorption capacity of IMSA beads is evaluated using Langmuir adsorption isotherm and found to be 21.61 mg/g and 133.73 for As(V) and Pb(II), respectively. The adsorption kinetic data of As(V) fit well to pseudo second order kinetic model whereas Pb(II) showed a better fit to the pseudo first order kinetic model. Moreover, 100 times increase in the ionic strength of the solution did not show significant effect in the uptake of As(V) whereas Pb(II) removal was slightly suppressed. This study demonstrates that IMSA beads obtained by exploiting natural sericite, iron oxide and alginate are efficient and sustainable adsorbent for the removal of arsenic and lead from the aquatic environment.

1. Introduction

Human exposure to toxic heavy metals is widespread in many countries as a result of their exponential exploitation in various industrial, agricultural, domestic and technological applications [1]. Wastewater produce from several industrial processes such as electroplating, metallurgical operations, metal finishing and electronic industries, etc. usually contain significant amount of heavy metals and cause detrimental impact on living organisms [2]. Unlike organic pollutants, heavy metals are non-biodegradable and they have a tendency to accumulate in living tissues, causing various biological disorders. Among heavy metals, cadmium, lead, mercury and arsenic are the major elements which cause severe threats to human health [3]. Arsenic is one of the most toxic element and consumption of water contaminated with arsenic is a serious health concern in many countries around the globe. Arsenic is released into human environment due to natural weathering reactions, biological activity, geochemical reactions, volcanic emissions and various anthropogenic activities, etc. The most common anthropogenic sources are mining, combustion of fossil fuels, pesticides, herbicides, livestock feed additives, and agricultural wastes [4,5]. Arsenic usually enters human body through drinking water and the acute toxicity includes gastrointestinal discomfort, vomiting, bloody urine, anuria, convulsions, coma, and even death. Moreover, chronic exposure to inorganic arsenic is able to cause skin lesions, blackfoot disease, peripheral neuropathy, hepatomegaly, heme metabolism problem, bone marrow depression, diabetes and renal disorder in human body [6]. The inorganic arsenic compounds are classified as Group 1 carcinogen (human carcinogenic) by International Agency for Research on Cancer (IARC), and lung, kidney, bladder and skin cancers were reported to be linked with inorganic arsenic exposure [7,8]. Lead is another toxic heavy metal, which is extensively used in process industries such as battery manufacturing, metal plating, industries engaged in lead–acid batteries, paint, oil, metal, phosphate fertilizers, electronic, and wood production. Other main sources are combustion of fossil fuels and smelting of

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sulphide ore. Among the toxic heavy metals, lead contamination is the most prevalent in human environment. Long term exposure to lead is also known to cause severe damage to kidney, nervous system, reproductive system, liver and brain. Pb^{2+} has high affinity towards the thiol (-SH) and phosphate (PO_4^{3-}) containing enzymes, ligands and biomolecules, thereby inhibiting the biosynthesis of heme units, affecting membrane permeability of kidney, liver and brain cells [9]. Due to all these threats towards human health, the removal of arsenic and lead from water is very important.

Iron oxide is known to have high affinity towards arsenic; therefore, various types of iron impregnated or iron modified adsorbents have been developed and employed for effective removal of arsenic from aqueous solutions [10–12]. Use of iron oxide in water treatment technology has advantages since iron-oxide is abundant in nature and is relatively inexpensive. However, use of fine particles of iron oxide is sometime not suitable in water treatment plant since the separations of spent smaller oxide particles is a tedious job and sometimes requires the sophisticated instrumentation [13]. Therefore, iron is usually immobilized on the substrate or other adsorbent and then employed in water treatment system. Previously, iron oxide particles were incorporated on the surface of solid substrate such as sand [14], activated carbon [15], silica [16], zeolites [17] and clay [18] etc. and then applied for the removal of various toxic metal ions from aqueous solutions. Previously, we have reported the facile process for preparing Fe-sericite alginate beads in which calcium is used as a cross-linking ion and the material was successfully employed for the removal of As(V) and phosphate from aquatic environment [19]. In this research, previous study is extended in such a way that the iron oxide modified clay was encapsulated into beads using sodium alginate and Fe(III) as a cross-linking agent. The cross-linking of alginate with Fe allows interaction of anionic arsenic species with the alginate moiety; therefore, the IMSA beads are expected to possess significantly high efficiency for removal of arsenic from aqueous solutions. Meanwhile, various functional groups of alginate have a high tendency to adsorb Pb(II) ions. Therefore, the synthesized composite beads were used as an efficient adsorbent for the removal of As(V) and Pb(II) from aqueous solutions.

2. Materials and methods

2.1. Materials

The naturally abundant sericite clay was collected from a Dongyang deposit, Gagokmyun, Kangwon province, Korea. Initially, sericite rock was crushed and grinded, and the fine powder (0.075–0.053 mm) was separated using a mechanical sieve. Disodium hydrogen arsenate heptahydrate was obtained from Wako Pure Chemical Industries ltd. Lead nitrate and Ferric chlorides were purchased from Junsei Chemical Co. Ltd., Japan. Nitric acid, sodium hydroxide, and sodium chloride were procured from Duksan Pure Chemicals Co. Ltd., Korea. The water used in all the experiments was purified by Millipore water purification system (Milli-Q^+).

2.2. Modification of sericite

The modification of sericite by iron was carried out by a simple wet method. Initially, 0.1 mol/L $Fe(NO_3)_3 \cdot 9H_2O$ solution was prepared in 1000 mL beaker and 6 mol/L NaOH was added drop wise with continuous stirring until the pH was adjusted to ~8.5. Then, 40 g of sericite powder was added into this solution and continuously stirred for 15 h. The slurry was separated and washed with purified water for several times, and then kept in a hot air oven at 120 °C until completely dried. The iron-oxide modified sericite powder was further used for the preparation of IMSA beads.

2.3. Preparation of IMSA beads

For preparation of beads, 4 g of Na-alginate was dispersed in 300 mL of distilled water under continuous stirring. After homogeneity, 20 g of iron oxide modified sericite powder was homogeneously mixed with the alginate suspension. The mixture was then kept in a separatory funnel and it was slowly drop into an aqueous coagulation bath containing 1000 mL solution of 2% $FeCl_3$ which was continuously stirred. The stable beads obtained were separated and kept in 0.5% $FeCl_3$ solution for overnight to complete the Fe cross-linking reaction. And then, the beads were washed with pure water for five times and kept for further use. This material is named as IMSA beads. The beads have uniform spherical shape with the diameter ranges from 2 to 4 mm and the macrograph is shown in Fig. 1.

2.4. Characterization of materials

The micrograph of IMSA bead was taken by scanning electron microscope (SEM; FE-SEM-Model: SU-70, Hitachi, Japan) and the elemental composition were collected using an energy dispersive X-ray spectroscopy (EDX) system. The functional groups present in the IMSA beads were identified by the Fourier transform infra-red (FT-IR) machine (Bruker, Tensor 27, USA by KBR disk method). In addition, the iron content in the IMSA bead was evaluated by US EPA 3050B method.

2.5. Stability test of immobilized iron and pH_{PZC} measurement

In order to determine the iron leach from the beads, the stability test for IMSA beads was conducted between pH 2.0 to 10.0. For this experiment, 50 mL of purified water was taken in a polyethylene bottles and the pH of each bottle were adjusted to various pH between 2.0 and 10.0 by adding of drops of 0.1 mol/L HNO_3/NaOH solutions. 0.8 g of IMSA beads (=0.1 g of dry beads) was added in the water samples and kept in an automatic shaker overnight at 25 °C. The solutions were filtered and subjected for measuring the total iron concentrations using atomic absorption spectrometer.

The pH_{PZC} (point of zero charge) of the IMSA beads was determined by following previously reported method [20]. In brief, N_2 gas was purged into 500 mL of distilled water for 20 min to expel the dissolved CO_2. The flask was capped with cotton to avoid re-absorption of atmospheric CO_2 and then CO_2 free water was utilized to prepare 0.01 M NaCl solution. 50 ml of this solution was taken out in six different plastic bottles. The pHs of solution in each flask were adjusted to pH values of 2, 4, 6, 8, 10 and 12 by adding 0.1 M HCl/NaOH solutions. Subsequently, 0.10 g of the IMSA bead was added in each bottles and agitated at 25 °C for 24 h.

Fig. 1. Macrograph of IMSA beads.