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Modified composites based on mesostructured iron oxyhydroxide and synthetic minerals: A potential material for the treatment of various toxic heavy metals and its toxicity

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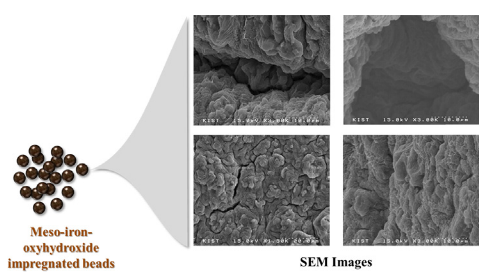
HIGHLIGHTS

- Meso-iron-oxyhydroxide was found to be efficient for anion heavy metal adsorption.
- The composite bead can simultaneously remove the cations and anions of heavy metals.
- Powdered form had stronger cytotoxicity than did the granular form.
- Adsorbent recovery is facilitated by granulation process of powder-type.

GRAPHICAL ABSTRACT



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ABSTRACT

The composites of mesostructured iron oxyhydroxide and/or commercial synthetic zeolite were investigated for use in the removal of toxic heavy metals, such as cadmium, copper, lead and arsenic, from aqueous solution. Four types of adsorbents, dried alginate beads (DABs), synthetic-zeolite impregnated beads (SZIBs), meso-iron-oxyhydroxide impregnated beads (MIOIBs) and synthetic-zeolite/meso-iron-oxyhydroxide composite beads (SZMIOIBs), were prepared for heavy metal adsorption tests. Laboratory experiments were conducted to investigate the removal efficiencies of cations and anions of heavy metals and the possibility of regenerating the adsorbents. Among these adsorbents, the MIOIBs can simultaneously remove cations and anions of heavy metals; they have high adsorption capacities for lead (60.1 $mg\,g^{-1}$) and arsenic (71.9 $mg\,g^{-1}$) compared with other adsorbents, such as DABs (158.1 and 0.0 $mg\,g^{-1}$), SZIB (42.9 and 0.0 $mg\,g^{-1}$) and SZMIOIB (54.0 and 5.9 $mg\,g^{-1}$) for lead and arsenic, respectively. Additionally, the removal efficiency was consistent at approximately 90%, notwithstanding repetitive regeneration. The characteristics of meso-iron-oxyhydroxide powder were confirmed by X-ray diffraction, Brunauer–Emmett–Teller and transmission electron microscopy. We also performed a comparative toxicity study that indicated that much lower concentrations of the powdered form of mesostructured iron oxyhydroxide had stronger cytotoxicity than the granular form. These results suggest that the granular form of meso iron oxyhydroxide is a more useful and safer adsorbent for heavy metal treatment than the powdered form. This research provides promising results for the application of MIOIBs as an adsorbent for various heavy metals from wastewater and sewage.

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1. Introduction

Heavy metals, elements having atomic weights between 63.5 and 200.6, have become major compounds in many industrial processes, such as metal finishing, painting, dying, surface treatment and electroplating, since the industrial revolution began in the 18th century [1]. These compounds occur naturally at various concentrations in ecological systems. However, recently, heavy metals have been introduced into the environment from anthropogenic sources [2]. Pollution of aquatic ecosystems by heavy metals originated from many sources, such as metal purification [3]. These elements, such as cadmium, copper, lead, arsenic and chromium, are very harmful to both humans and the environment and persist in organisms when consumed [4,5]. They can also accumulate in internal organs, such as the brain, liver and kidney, and their high levels of toxicity result in acute poisoning or chronic addiction [6]. The maximum contaminant levels determined by the Environmental Protection Agency for cadmium, copper, lead, arsenic and chromium in drinking water are 0.25, 1.30, 0.05, 0.01 and 0.10 mg L^{-1}, respectively [7–11].

Therefore, various methods, including precipitation, coagulation, ionic exchange and biological methods, have been suggested to treat heavy metals in aqueous solution [12–14]. However, each of these methods has limitations. For example, precipitation requires efficient control of pH, and coagulation produces toxic sludge. Additionally, biological methods require strict controls, and it is difficult to obtain stable removal efficiencies with biological methods because heavy metals are not biodegradable [15,16]. Adsorption has been widely used to treat aqueous pollutants due to its selectivity, simplicity and ease of application, and it is the most common method of heavy metal treatment in aqueous solution [17]. However, the more effective adsorbent materials have some disadvantages, such as relatively high capital costs and regeneration, which are required to comply with new, rigorous regulations [18].

In the past few years, alginate has been widely used to immobilize microorganisms, along with some powder-type adsorbents, such as synthetic zeolite and activated carbon, in the treatment of organic and inorganic aqueous pollutants [19,20]. Because it is a salt of unbranched copolymers with β-D-mannuronic and α-L-guluronic acids, alginate irreversibly produces a gel by associating with most divalent cations [21]. Additionally, some research studies have quantified a strong adsorption of anionic heavy metal ions onto iron oxides due to oxidative adsorption [22,23].

Mesoporous structures possess high internal surface areas and a pore size distribution ranging from 2 to 50 nm. They have been widely investigated for their potential application as adsorbents and catalysts. Among these applications, the mesostructure-type adsorbents offer a more dependable method of adsorption due to their special characteristics, such as extremely large reactive surface area. In particular, mesostructured iron oxyhydroxides are known to have a high degree of coordinative unsaturation in their iron complex [18]. However, these nano- or meso-scale adsorbents must be separated from sewage or wastewater after the heavy metals are treated because the adsorbents can act as a secondary contaminant. One method to solve this problem is to immobilize the powder-type adsorbent into or onto alginate gel beads to enable the straightforward separation of the adsorbent from aqueous phase.

In this study, we developed effective adsorbents for the removal of toxic heavy metal cations and anions and performed experiments related to their application. The adsorption equilibrium and kinetics of single and mixed heavy metal solutions were determined, and the obtained results were adequately described by adsorption models. Additionally, the regeneration efficiency was estimated, and the toxicity of the developed adsorbents was also investigated.

2. Material and methods

2.1. Chemicals

Iron(III) oxide (95%, Aldrich, Korea), iron(II) chloride (98%, Aldrich, Korea), hydrogen peroxide (Fluka, Korea), sodium dodecylsulfate (Sigma–Aldrich, Korea) and ethanol (99.5%, Sigma–Aldrich, Korea) were used to synthesize of meso iron oxyhydroxide. Alginic acid (Viscosity 20,000–40,000, Aldrich, Korea) and calcium chloride (KANTO Chemical, Japan) were used to produce alginate gel beads. Each heavy metal solution was prepared with a standard solution (KANTO Chemical, Japan).

2.2. Synthesis and characterization of various modified adsorbents

Meso-iron-oxyhydroxide (meso-FeO(OH)) was prepared under ambient conditions. Meso iron oxyhydroxide was synthesized at an iron-to-surfactant molar ratio of 6:1. Fifty milliliters of 0.1 M iron(II) chloride was mixed with 10 mL of 0.05 M sodium dodecylsulfate, followed by 10 mL of 0.2 M hydrogen peroxide added dropwise. The solution was stirred for 2 h. In the next step, the mixture was centrifuged and washed with deionized water, and then the seal-brown powder of meso iron oxyhydroxide was obtained. The powder was washed and heated again with ethanol using a Soxhlet extractor, and the color of the meso iron oxyhydroxide powder changed to that of rust. The powder was collected by filtration, washed with distilled water and dried at 70 °C for 4 h.

The next steps were followed to form alginate gel beads immobilized with powder-type adsorbents, such as synthetic zeolite or meso iron oxyhydroxide. First, 4.0% sodium alginate solution was prepared by mixing 16 g of alginic acid powder with 400 mL of distilled water. After adding 4 g of the synthetic zeolite and/or mesostructured iron oxyhydroxide into 400 mL of the alginate solution, the solution was mixed homogeneously for 16 h to yield 1% (w/v) alginate solution mixed with these powder-type adsorbents. The 1% alginate solution in a 50-mL buret was added dropwise to a solution of 4% calcium chloride solution, thus forming 3–4 mm spherical alginate composite beads. For comparison, alginate gel beads were formed using the same procedure but the synthetic zeolite and mesostructured iron oxyhydroxide were not added to the alginate solution. Each type of bead formed through the procedures mentioned above was dried in an oven at 60 °C for 10 h until the diameter of the beads had reduced to approximately 1 mm. The size reduction enhanced the adsorption capacity and specific surface area of the activated sites. The final synthesized composite beads contained 0.13 g of the synthetic zeolite and/or meso iron oxyhydroxide powder, respectively.

2.3. Equilibrium adsorption experiments

Equilibrium batch tests were conducted to determine the adsorption capacity of the various alginate composite beads for cations and anions of heavy metals. One hundred milligrams of adsorbent was allowed to react with 50 mL of cadmium, copper or lead solution (cations) or arsenic solution (anion) (pH 3.6–4.4) with initial concentrations of 1, 5, 10, 30 and 50 mg L^{-1} using an air shaker (120 rpm, 25 °C). The experiments were performed under low pH to eliminate the influence of pH on adsorbent performance.

To compare the adsorption capacities of different adsorbents, an equilibrium adsorption model, the Langmuir adsorption isotherm model (Eq. (1)) was used [24]:

$$S = \frac{\alpha\beta C}{1 + \alpha C} \quad (1)$$