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New calcareous soil–alginate composites for efficient uptake of Fe(III), Mn(II) and As(V) from water

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ABSTRACT

In the present study, various grades of sodium alginates were extracted from different brown macroalgae and their characteristics were investigated using FTIR, UV–vis and EA. The alginates were used in combination with different proportions of calcareous soil to develop new composite microparticles as potential sorbents for efficient uptake of Fe(III), Mn(II) and As(V) from water. Under the investigated conditions (1 g of composite equilibrated in 100 ml of standard metal ion solution), the composites have removed almost 100% of Fe(III) in the concentration range of 0.5–16.0 mg l^{-1}. Soil, alginate and composites exhibited the highest removal (about 89%) of Mn(II) at 0.5 mg l^{-1}. Reasonable removal efficiency (50–60%) was recorded at 0.5 mg l^{-1} of As(V) whereas, increasing the initial As(V) concentration resulted in marked decrease in removal efficiency. The collected equilibrium data were also fitted to both Langmuir and Freundlich isotherms for all the developed composites.

1. Introduction

Heavy metals have a wide range of potential applications in various fields, however many of them are highly toxic even at low concentrations and being non-biodegradable tend to accumulate in living organisms and cause different diseases and health disorders (Reddy, Seshaiah, Reddy, Rao, & Wang, 2010). Hence, such heavy metals must be removed from the polluted water streams in response to environmental legislation and enforcement. Besides, polluted water streams and groundwater often contains some heavy metals such as iron and manganese, which can not only affect the color and flavor of water but also accumulate to cause hindrance in the water equipment and pipelines (Gotoh, Matsushima, & Kikuchi, 2004).

Iron, manganese and arsenic are three of the major toxic metal ions that are hazardous to life. Iron levels below 0.3 mg l^{-1} were characterized as unnoticeable, whereas iron concentrations in the range of 0.3–3 mg l^{-1} were considered acceptable (WHO, 1996).

Manganese is naturally occurring in various groundwaters and surface water sources and also in soils that may erode into these waters. On the other hand, human activities are also responsible for a significant part of the manganese contamination in water in some regions.

In higher concentrations, iron and manganese were also found to cause various problems such as staining laundry and water use fixtures, developing a metallic or vinyl type taste in the water, often appearing as a crusty sheen on the water's surface and supporting the growth of iron and manganese bacteria, which can clog strainers, valves and pumps.

Arsenic, a toxic trace element, occurs in both natural and industrial waters. Recently, arsenic contamination of surface and groundwater at toxic levels has become a growing concern on a global perspective. Besides, there have been several reports of arsenic poisoning in various countries such as India (Das et al., 1996), Bangladesh (Hoque et al., 2000), Vietnam (Berg et al., 2001) China, and Taiwan (Tseng et al., 1968). It has been found that long-term drinking of water contaminated with arsenic can cause kidney, bladder, lung, liver, skin, and nerve tissues injuries (Roberts et al., 2004; Thirunavukkarasu, Viraraghavan, & Subramanian, 2003).

Over the last few decades, a significant body of research has focused mainly on developing more effective approaches for

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removal of heavy metals from polluted water streams or improving conventional techniques such as chemical precipitation (Harper & Kingham, 1992), ion exchange, filtration, and electrodialysis (Balaji, Yokoyama, & Matsunaga, 2005). Current applied methods including ion exchange and electrodialysis have relatively high operation and maintenance costs. Chemical precipitation is, however inexpensive but still unable of removing trace concentrations of heavy metal ions. Adsorption strategy is expected to overcome such shortcomings, and used in a wide range of potential applications.

Of various widely used sorbents, naturally occurring materials, including natural polymers, soil, and their composites have been accepted as feasible sorbent materials for reducing the cost of waste water treatment (Bailey, Olin, Bricka, & Adrian, 1999). An important class of polymers that was found beneficial in metal ions removal is the class of biopolymers isolated from algae such as sodium alginates due to their ability to form complexes with metal ions (Banerjee, Nayak, & Lahiri, 2007).

Sodium alginate, a natural polysaccharide obtained from brown macro-algae, is a copolymer of varying compositions of β-1,4 linked L-guluronic and D-manuronic acids (Banerjee et al., 2007; El-Sherbiny, 2010; El-Sherbiny, Abdel-Bary, & Harding, 2010). Several alginate-based sorbents have been investigated for metal uptake from aqueous solutions for possible application in water treatment processes. For instance, alginate beads were found effective in the removal of a wide range of heavy toxic metal cations, such as Ni, Cu, Zn, Cd, Hg, Pb, Nd, Eu, Yb, and Ra (Min & Hering, 1998; Nayak & Lahiri, 2005).

In the current study, various grades of sodium alginates were extracted via a modified procedure from three different types of brown macro-algae; *Turbinaria murryana*, *Cystoseira spinosa* and *Sargassum* sp. The brown macro-algae were collected in mid-fall from a local protected area in Egypt. Selection of the algal species and the collection season was based on the relatively high content of alginate as found in our earlier study (Shukr, Azab, Abdel-Hamid, & El-Sherbiny, 2010). The various extracted alginates were characterized and then used in combination with different proportions of a locally collected calcareous soil to develop novel series of hydrogel composite microparticles. The developed composites were investigated as sorbents for efficient uptake of iron, manganese and arsenic from aqueous solutions for possible application in water treatment processes.

2. Experimental

2.1. Materials

Calcareous soil samples were collected from the Northwestern coast of Egypt at El-Alamien area between latitudes 30°44′30″–30°49′40″ North and longitudes 29°00′–29°28′ East and it is situated about 80 km to the west of Alexandria City. Analytically grade (AR) salts of iron ($FeCl_3$), manganese ($MnCl_2{\cdot}4H_2O$), arsenic ($Na_2HAsO_4{\cdot}7H_2O$), $CaCl_2$, NaCl, Na_2CO_3, ethanol, HCl, H_2SO_4, KCr_2O_7, $FeSO_4{\cdot}7H_2O$, sodium acetate, ammonium acetate, and double distilled deionized water were used as provided.

2.2. Methods

2.2.1. Collection of brown algae biomass

Biomass samples of the brown macro-algae; *T. murryana*, *C. spinosa* and *Sargassum* sp. (belonging to the order: *Fucales*, class: *Phaeophyceae*) were collected during the mid-fall 2010 from the littoral algal community of seashore of the Nabq protected area located 30 km north east of Sharm El-Sheikh city, Aqaba gulf, Red sea, Egypt. Selection of the brown algae species and the collection season was based on the relatively high content of alginate (Shukr et al., 2010).

2.2.2. Extraction of sodium alginate from algae biomass

The alginates extracted in this study were obtained in the form of water soluble sodium salts according to the procedure reported by Truus, Vaher, and Taure (2001). Briefly, a mass of 20 g of air-dried brown algae was boiled in 300 ml of distilled water for 30 min, filtered and the wet algal biomass was boiled for further 30 min in 0.5% (w/v) aqueous $CaCl_2$ solution. The mixture was then allowed to cool down to room temperature, filtered and the algal biomass was boiled for 1 h in 300 ml of 0.5% (w/v) NaCl solution. The filtration process was repeated and the algal biomass was boiled for 30 min in 3% Na_2CO_3 solution with vigorous stirring. This step involves conversion of alginic acid into soluble sodium salt, which remains in the extract. A highly viscous solution was then obtained in addition to the insoluble algal residue. The mixture was filtered through a cloth filter with squeezing and the filtrate was treated with ethanol to precipitate the sodium alginate. The obtained alginate was air-dried, collected, ground into powder and stored until further investigation. No bleaching treatment was applied to the extracted sodium alginate and therefore, the color was relatively brown.

2.2.3. Characterization of the extracted alginates

The average molecular weights (M_w) of the extracted alginates were determined using the Mancini et al. protocol (Mancini, Moresi, & Sappino, 1996) with the aid of Cannon-Fenske Routine Viscometer (Cannon Instrument Co., State College, PA 16801, USA). Different dilutions of sodium alginate samples were prepared in 0.1 M NaCl solvent. During viscosity measurements, alginate solutions and the solvent, as a control, were maintained at 20 °C (±0.1 °C) via immersing in a temperature-controlled circulating water bath. The elution times of both solvent and the different alginate solutions were measured in triplicates. Then, the reduced viscosities (η_{red}) were calculated from the average values of elution times according to the following relationship:

$$\eta_{\text{red}} = \frac{t - t_o}{C} \times t_o$$

where t and t_o are the average elution times of alginate solutions and the solvent (NaCl 0.1 M), and C is the concentration of alginate solutions. The curves of reduced viscosity versus concentration were then built, and the intrinsic viscosity, $[\eta]$ (L.g^{-1}) was obtained by extrapolating η_{red} when concentration tends toward zero by means of linear regression. The average molecular weight, M_w (Da) was then obtained using the following equation (Mancini et al., 1996):

$$[\eta] = 1.228 \times 10^{-4} \times M_w^{0.963}$$

The UV–vis spectra of 0.1% aqueous solutions of the alginate samples extracted from different brown algae were recorded in the range of 200–800 nm using Unicam UV–vis spectrometer (UVII) with the aid of ATI Unicom UV–vis. vision software V 3.20. The analysis was performed at room temperature using quartz cuvets (1 cm optical path). FTIR characterization of solid samples of alginates was carried out with a Mattson 5000 FTIR spectrometer. The dried samples were pressed with KBr and their FTIR spectra were recorded at 25 °C in the range of 400–4000 cm^{-1}. Also, the viscosities of the alginates extracted from different algal species were measured with Brookfield DV-III Ultra Programmable Rheometer. Three different concentrations of the aqueous alginate solutions (0.5%, 1% and 1.5%, w/v) were prepared and measured at different velocities from 20 to 500 rpm.