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Entrapment of powdered drinking water treatment residues in calcium-alginate beads for fluoride removal from actual industrial wastewater

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A B S T R A C T

The present study describes the preparation of drinking water treatment residues (DWTRs) based adsorptive media (DREAM) by entrapping the powdered-DWTRs in calcium-alginate beads and their application to fluoride removal from actual industrial wastewater. In order to evaluate the fluoride adsorption capability and mechanisms of DREAM, the adsorption equilibrium isotherm, kinetics, and effect of solution pH on fluoride removal by DREAM were evaluated. The batch and fixed-bed column adsorption tests confirmed that DREAM had high selectivity for adsorbing fluoride from actual industrial wastewater, which contained other co-existing anions (e.g., nitrate, chloride, and sulfate).

Introduction

The chemical properties of water are among the most important criteria that determine its usefulness and stability for practical use [1]. For instance, fluoride is recognized as an essential and beneficial nutrient for human beings at low concentrations, but this depends on its concentration in drinking water and the duration of intake. Fluoride taken within limits of between 0.5 and 1.0 mg/L is considered to be safe for the living environment and the maintenance of healthy bones and teeth, while excessive intake with long term drinking of water containing high fluoride concentration can result in health issues, such as mottling of teeth, softening of bones, structural damage to ligaments, and various neurologic damages [2–4]. According to World Health Organization (WHO) guidelines, the allowable fluoride concentration in drinking water is considered to be 1.5 mg/L [5].

Whilst fluoride is found in the environment through its natural presence in the earth's crust, the discharge of industrial wastewater containing high fluoride concentrations, including wastewater from semiconductor manufacturing, glass making industries, electroplating, and metal smelters, can accelerate fluoride contamination of aquatic ecosystems and can have a detrimental impact on biological wastewater treatment plants [6–9]. For these reasons, it is critical to investigate sustainable treatment technologies for industrial wastewater containing fluoride that effectively remove fluoride from wastewater in an inexpensive manner.

Various treatment technologies, including chemical precipitation/coagulation, electrocoagulation/electroflotation, ion exchange, reverse osmosis, nanofiltration, and adsorption processes, have been proposed to date and are currently being used for fluoride removal from water and wastewater. Among various approaches, the adsorption process is an attractive and promising method owing to its robust, simple operation, cost-effectiveness, and treatment stability for the removal of fluoride from wastewater [1,10–13]. Various synthesized adsorbents such as metal and modified metal oxide nanocomposites have been recently proposed and extensively studied, but these adsorbents are cost-prohibitive for widespread field application despite providing satisfactory performance.

In this regard, largely on the basis of environmentally friendly and financially viable aspects, considerable attention has been

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devoted to the reuse of industrial by-products, for instance, drinking water treatment residues (DWTRs), as an effective and the promising alternative low-cost adsorbents [14]. DWTRs are the main by-product generated during the production of drinking water, which contain very high concentrations of chemicals (e.g., Al^{3+} and Fe^{3+}), as such chemicals are conventionally used as coagulants to remove colloids, color, and turbidity in drinking water treatment plant [15]. In other words, DWTRs make it possible to effectively reuse them as a beneficial adsorbent owing to their unique chemical properties, typically a strong affinity toward Al^{3+} and Fe^{3+} for adsorbing fluoride from aqueous solutions [16–18]. However, the beneficial reuse of DWTRs may be hampered by the difficulty of recovering the powdered-DWTRs (PDs) after the adsorption process, which makes them even less attractive as adsorbents. Furthermore, the PDs are not suitable in column-type filtration systems due to their low hydraulic conductivity. Hence, if successful immobilization of PDs can be accomplished, this would lead toward environmental and economic benefits.

As an alternative, PDs can be immobilized into porous structured calcium-alginate beads as a particulate form. Alginate is a nontoxic, hydrophilic, and biocompatible natural polymer that is produced by brown algae, and can produce an insoluble hydrogel in the presence of divalent and trivalent cations as a gelling agent through ionic interaction between the carboxylic acid group located on the polymer backbone and the chelating cations [19–21]. Entrapment using calcium-alginate beads is widely used in immobilization of various powdered materials to remove target pollutants from an aqueous solution because it is a simple and cost effective technique [22]; however, to the best of our knowledge, there is no report focusing on the immobilization of PDs as a particulate form and their application for treatment of actual industrial wastewater containing fluoride through a fixed-bed column adsorption system.

Considering this research background, the objective of this study was to prepare a particulate form of PDs by entrapping powder into calcium-alginate beads and to apply them for fluoride removal from actual industrial wastewater. The prepared particulate adsorbents in this study are named DREAM (Drinking water treatment REsidues based Adsorptive Media). To determine the fluoride adsorption capability of DREAM, batch tests including equilibrium isotherms and kinetics were conducted using simulated fluoride wastewater. Furthermore, to evaluate DREAM for fluoride adsorption from actual industrial wastewater, adsorption tests in batch and fixed-bed column tests were also carried out.

Materials and methods

Preparation of powdered-DWTRs (PDs)

Dewatered DWTRs were collected from a drinking water treatment plant in Seoul, South Korea, where polyaluminium chloride is used as a coagulant. After drying in the oven at 80 °C for 24 h, DWTRs were ground into powder using a knife-milling Waring commercial blender; the fractions passing through a sieve (<850 μm) were then collected, and are named raw-PDs in this study. Concentrations of relevant elements detected in the PDs are summarized in Table 1. It can be seen that raw-PDs contain predominantly high levels of C, Si, and Al content of 26.1, 24.7 and 25.7%, respectively, and relatively small amounts of Fe, K, Ca, S, P, and other elements. The percentage of metal oxide forms indicates that the elements were present in their highest oxidation state.

Thermal pretreatment of raw-PDs

Raw-PDs often contain impurities, mainly organic matter and bacteria, which can hinder the adsorption capability [23]. Hence, in order to remove such impurities in raw-PDs and to enhance their adsorption capability, the effect of thermal pretreatment temperature and reaction time were separately evaluated. 50 g of raw-PDs were placed in an electric muffle furnace with a porcelain crucible at 250–650 °C for 2–6 h. The samples were then cooled in a desiccator and the weight loss of PDs was monitored in duplicate. As shown in the following supplementary data (Fig. S1), it was observed that the enhancement of fluoride removal efficiency and the weight loss of PDs after thermal pretreatment were negligible when the temperature and reaction time exceeded 450 °C and 4 h, respectively. Based on the preliminary assessment of the thermal pretreatment in terms of the fluoride removal efficiency and weight loss, the thermal pretreatment condition of 450 °C for 4 h were set as optimal conditions to prepare particulate adsorptive media. After thermal pretreatment, the samples were then cooled in a desiccator, and subsequently sealed in a container before use, and are denoted as thermal pretreated-PDs.

Table 1
Characteristics of actual industrial wastewater.

Parameters	Unit	Concentration
pH	–	2.95 ± 0.3
TCOD	mg/L	1857 ± 69
SS		28.4 ± 2.6
TP		0.077 ± 0.07
TN		39.5 ± 3.8
Fluoride		198.4 ± 32
Nitrate		3.25 ± 0.8
Sulfate		457.6 ± 28
Chloride		19,035 ± 2710

Preparation of particulate adsorptive media (DREAM)

A 2% (w/v) sodium alginate solution was prepared by mixing sodium alginate in 100 mL of distilled deionized water (Milli Q plus, Merck Millipore Co., Germany) under stirring for 1 h. Subsequently, 2% (w/v) of thermal pretreated-PDs at 450 °C for 4 h was added to the alginate solution, and the mixture was then stirred for 10 h. When the mixture became homogeneous, it was dropped through a burette into 2% (w/v) calcium chloride to form particulate under gentle stirring. The excess unbounded calcium chloride from the bead surface was removed by washing several times with distilled deionized water, and then oven-dried at 45 °C for 24 h. The prepared particulate adsorptive media using the thermal pretreated-PDs was denoted as DREAM (see graphical abstract). As a control sample, the prepared particulate adsorptive media using raw-PDs (without any thermal pretreatment) and denoted as NT-DREAM.

Performance evaluation of DREAM for fluoride adsorption from aqueous solution

The effectiveness of DREAM for fluoride removal from an aqueous solution was evaluated. Meanwhile, the effect of the solution pH on fluoride adsorption capability of DREAM and NT-DREAM were also investigated. The solution pH was adjusted to 2.0–11.0 with 1.0 intervals using 0.1 M HCl and NaOH using a LabQuest2 portable meter (LQ2-LE, Vernier, USA). A stock fluoride solution of 100 ± 1.5 mg/L was prepared by using anhydrous sodium fluoride in distilled deionized water. The reaction vessels containing 50 mL of fluoride solution was mixed with 0.5 g of the prepared adsorbents. The reaction vessels were then homogeneously shaken in an orbit shaking incubator at 200 rpm with controlled temperature at 20 °C for 12 h (WIS-20R, WiseCube®, South Korea), which is sufficient for reaching equilibrium. The samples were immediately filtered using a syringe filter with an opening of 0.45 μm; the concentrations