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Alumina supported carbon composite material with exceptionally high defluoridation property from eggshell waste

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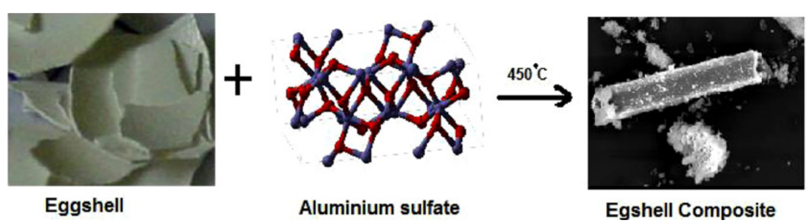
HIGHLIGHTS

- ▶ Eggshell waste has been utilized for synthesis of composite material.
- ▶ Eggshell composite has high fluoride removal efficiency at wide range of pH 3–9.
- ▶ Eggshell composite proved to be very low cost and efficient than many other reported adsorbents.

GRAPHICAL ABSTRACT



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ABSTRACT

A new alumina supported carbon composite material called "Eggshell Composite" (EC) was synthesized from eggshell waste as calcium source for selective fluoride adsorption from water. The effect of various synthesis parameters like eggshell (ES): Eggshell membrane (ESM) ratio, aluminium loading, mixing time and calcinations temperature to optimize the synthesis conditions for selective fluoride removal has been studied. It was observed that the synthesis parameters have significant influence on development of EC and in turn on fluoride removal capacity. EC synthesized was characterized for elemental composition, morphology, functionality and textural properties. Results showed that EC obtained from eggshell modified with alumina precursor is more selective and efficient for fluoride removal. Langmuir and Freundlich isotherm were used to obtain ultimate fluoride removal capacity. The calcium and alumina species in EC shows synergistic effect in fluoride adsorption process. Fluoride sorption studies were carried out in synthetic, groundwater and wastewater. EC proved to be a potential, indigenous and economic adsorbent for fluoride removal.

1. Introduction

Hen eggshell typically consists of ceramic materials constituted by a three-layered structure, namely the cuticle on the outer surface, a spongy (calcareous) layer and an inner lamellar (or mammillary) layer [1,2]. The spongy and mammillary layers form a matrix composed of protein fibers bonded to calcite (calcium carbonate) crystal. The two layers are also constructed in such a manner that there are numerous circular openings (pores). This structure permits gaseous exchange throughout the shell. The outer surface of the eggshell is covered with a mucin protein that acts as a soluble plug for the pores in the shell. The chemical composition (by weight) of by-product eggshell has been reported as follows: calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%) and organic matter (4%) 2. Notably, the by-product eggshell generated from food processing and manufacturing plants is inevitably composed of calcium carbonate (eggshell) and eggshell membrane (ESM). The ESM resides between the egg white (albumen) and the inner surface of the eggshell. There are two shell membranes around the egg, a thick outer membrane attached to the shell and a thin inner membrane [3,4]. Each of these membranes is composed of protein fibers that are arranged so as to form a

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semi-permeable membrane. Therefore, the ESM possesses an intricate lattice network of stable and water-insoluble fibers and has high surface area resulting in various applications such as adsorbent [5–11] and immobilization support [12–14]. Taking into account the sustainable utilization of eggshell and its intrinsic pore structure [15], the characterization of the biomaterial is very scarce in the literature.

Regarding water contamination, high fluoride concentration in drinking water, i.e. >1.5 mg/L [16], is still of significant concern in many countries, due to serious health consequences of its prolonged and systematic ingestion, even in minimal concentrations, i.e. parts per million [17]. Fluoride is classified by the World Health Organization as one of the human consumption water contaminant that most negatively affects water quality for human consumption, only comparable with arsenic and nitrate [16]. Removal of fluoride from water has been studied since 1930s; aluminum derivatives were mainly the first kind of compounds used for such a purpose [18]. Subsequently, different methods to eliminate fluoride from water have been developed, i.e. adsorption [19–21], chemical precipitation [22,23], reverse osmosis [24,25] and electrodialysis [26]; however, adsorption has remained as the most suitable technique [21]. Nowadays, adsorption on activated alumina is one of the most widely used methods for fluoride removal [16], due to its economical, operative and adsorption efficiency advantages. Nevertheless, there is an increasing necessity to produce more economical and environmentally sustainable adsorbents, thus promoting the increasing use of biosorbents. Supported biosorbents by synthetic materials show suitable properties for their use in high scale column adsorption processes. Therefore, the objective of this study is to determine the optimum composition parameters of an eggshell composite that enable its use in adsorption columns, and to explore its potential as an adsorbent material for contaminants present in water, such as fluoride.

2. Experimental

2.1. Materials

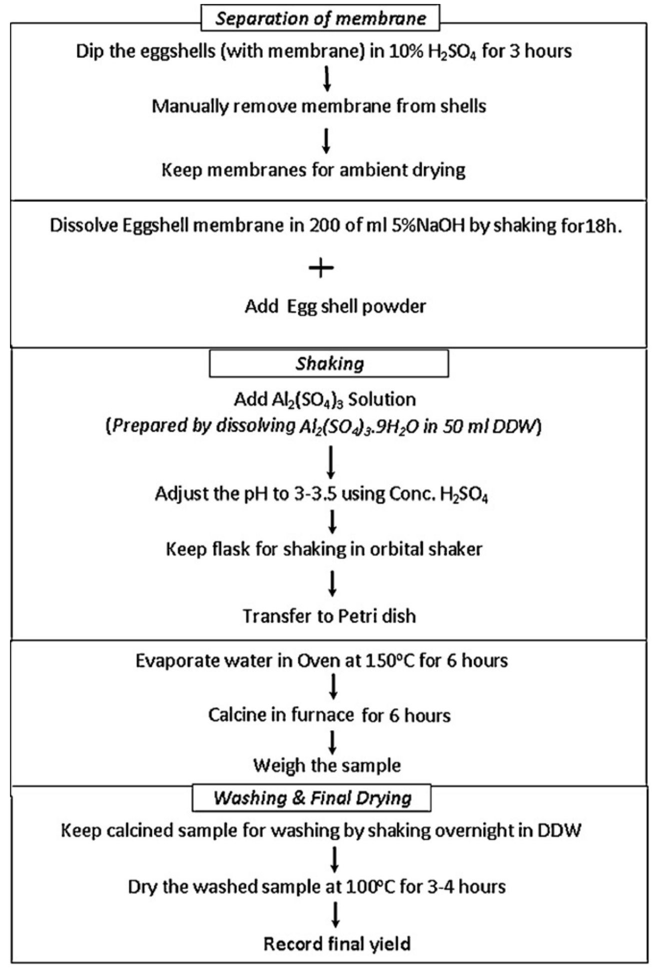
Raw eggshell was collected from local breakfast shop and hotels. Eggshell was immediately washed thoroughly with water and air dried. Hen eggshell was immersed in 5% H_2SO_4 for 1 h and then hen eggshell was manually stripped from eggshell membrane after cleaning of the raw material. The stripped eggshell and eggshell membrane was washed with water and dried at room temperature. The eggshell and eggshell membrane were further ground to prepare powder particles.

2.2. Reagents

Aluminium nitrate and all other chemicals used in this study were analytical grade obtained from E-Merck India Ltd., Mumbai, India. Total ionic strength adjustor buffer (TISAB III) solution was purchased E-Merck India Ltd., Mumbai, India. A stock solution of fluoride was prepared by dissolving NaF in RO (reverse osmosis)-deionized water and working solution was obtained by appropriate dilutions of the stock solution.

2.3. Synthesis protocol of EC

EC was synthesized using Eggshell (ES), Eggshell membrane (ESM) and aluminium sulphate. The synthesis procedure mainly involves mixing, shaking drying and calcination steps. Step by step synthesis procedure is shown in Scheme 1.



Scheme 1. Synthesis protocol of eggshell composite.

2.4. Optimization of eggshell composite synthesis

Eggshell composite was synthesized using ES, ESM and aluminium sulphate. Conditions have significant effect on Synthesis of, EC like ratio of ES and ESM, aluminum loading, shaking, calcinations temperature were optimized by varying the parameters within feasible parametric rang. The as synthesized EC samples were tested for fluoride removal at initial fluoride concentration of 15 mg l^{-1}; adsorbent dose 3 g l^{-1} and contact time of 24 h. Table 1 gives various synthesis parameters which were optimized and their variation in conditions for identifying optimal condition. Synthesis condition which brings down the fluoride concentration to minimum level was considered as optimized condition. However, the results of synthesis optimization were discussed further. The optimized synthesis protocol is given below.

2.5. Optimum synthesis of eggshell composite

The optimal conditions for synthesis of EC are as follows:

1.8 g of ESM was dissolve in 5% NaOH solution by shaking for 18 h on shaker. 1.2 g of eggshell powder was added to ESM solution followed by addition of aluminium sulphate solution prepared by dissolving 9.26 g of $Al_2SO_4{\cdot}3H_2O$ in 50 ml distilled water. The pH of the mixture was adjusted to 3–3.5 using concentrated H_2SO_4 and continuously stirred for 8 h on shaker. After shaking the mixture was transferred to Petri dish and dried at 150 °C for 6 h. Dried mass was calcined at 450 °C for 6 h in muffle furnace. The calcined product was kept for washing with distilled water (Sample (g):DDW