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Equilibrium, kinetic and thermodynamic studies for adsorption of As (III) on coconut (*Cocos nucifera* L.) fiber

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ABSTRACT

Contamination of drinking water due to arsenic poses severe health problems. Investigation of Arsenite [As(III)] removal from water by adsorption on coconut fiber (*Cocos nucifera* L.) adsorbent was conducted in the present study. Surface area of the adsorbent was determined by the Brunauer–Emmett–Teller (BET) method and scanning electron microscopy (SEM) was used to analyze surface morphology of coconut fiber adsorbent before and after adsorption process. Equilibrium study revealed that the uptake increased almost linearly with increase in initial As(III) concentration. The data was analyzed for Freundlich and Langmuir isotherm models at varying initial adsorbate concentration (0.5 mg/L to 2.0 mg/L) and found that the adsorption of As(III) on coconut fiber adsorbent followed Freundlich isotherm. Freundlich isotherm constants 'k' and 'n' were found to be 0.118 mg/g and 3.571, respectively at adsorbent respectively at adsorbent dose of 10 g/L and ambient temperature 25 °C. Kinetics study showed that the equilibrium approached at contact time of 8 h. The data fitted well with the pseudo first order kinetic model. Estimated kinetic rate constant (k_1) was 0.0069 min^{-1}. Thermodynamic study indicated spontaneous and endothermic nature of As(III) adsorption.

1. Introduction

Trivalent (+3) arsenite or Pentavalent (+5) arsenate are the most commonly found toxic and carcinogenic compounds in drinking water [1]. Trivalent arsenic is about 60 times more toxic than oxidized pentavalent state [2]. Because of its toxicity, various regulatory agencies have revised the maximum contaminant level of arsenic in drinking water from 0.05 mg/L to 0.01 mg/L [3].

Arsenic can be removed by various conventional techniques such as chemical precipitation, coagulation, adsorption, ion exchange and membrane processes. Coagulation, precipitation, oxidation, etc. are chemical intensive methods. Treatment using alum lime, aluminum sulphate, polyaluminum chloride, poly-aluminum silico sulphate, iron chloride, soda ash and synthetic polymers causes several serious health problems such as Alzheimer's disease [4]. Ion-exchange resins are costly. The main disadvantages of membrane filtration process are the high capital and operating costs, membrane fouling and scaling by organic matter, iron and manganese in raw water [5]. Many commercial adsorbents such as activated carbon [6,7], activated alumina [8] have been used for arsenic removal. But, these adsorbents are costly. The adsorption of arsenic by hydrous oxides of Fe, Mn and Al has also been extensively studied. These methods again becomes chemical intensive and hence expensive.

Study of natural or non-conventional materials for removal of metal ions is a new field of research. The use of natural or non-conventional adsorbents is advantageous than conventional adsorbents because they are much cheaper, locally available, require less transportation costs and environmentally favorable [9]. Agricultural or plant products such as Shelled Moringa Oleifera Lamarck Seed powder [4], Cupressus Female Cone [10], Maize Leaves [11], and biomass such as Heat-resistant Fungi [12], Bacterium Acidithiobacillus Ferroxidants [13] have been studied as natural adsorbents for arsenite [As(III)] removal from water. Coconut fiber have been used for removal of some heavy metals such as cadmium, chromium and lead [14] and dyes [15]. But, still the detailed adsorption study for arsenic removal on coconut fiber has not been performed

Hence, in the present investigation a new low cost biosorbent developed from coconut (*Cocos nucifera* L.) fiber, which is a natural waste material was used to study As(III) ion removal through adsorption process. Adsorption equilibrium, kinetic models and thermodynamics were evaluated from experimental data.

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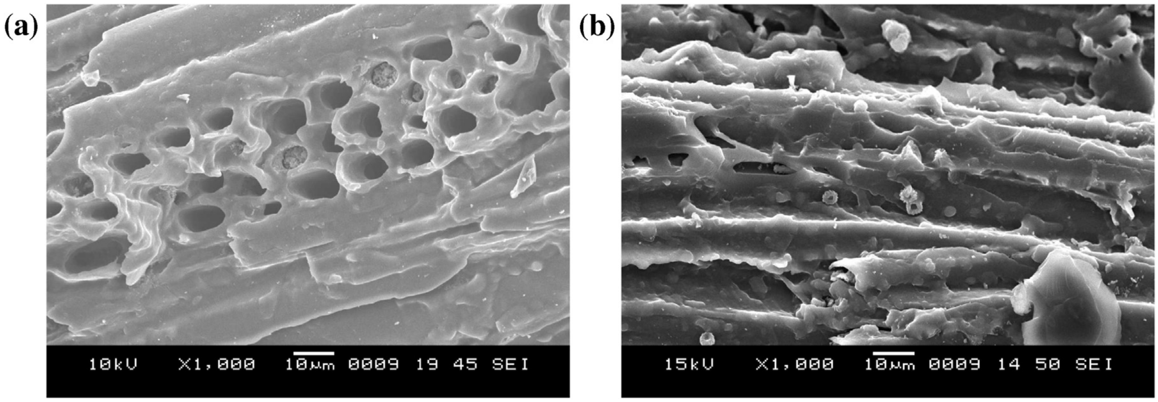

Fig. 1. SEM image of coconut fiber adsorbent (a) before adsorption (b) after adsorption.

2. Materials and methods

2.1. Reagents and apparatus

Stock solutions having concentration 1000 mg/L of As(III) was prepared by dissolving As_2O_3 (SD Fine Chem.) in distilled water. Working solutions were freshly prepared from the stock solution as per the experimental requirements. As(III) concentration was measured using UV–vis spectrophotometer (Elico, Model no. SL 210) at a wavelength of 535 nm, by silver diethyl dithiocarbamate method [16].

2.2. Preparation of adsorbent

Adsorbent was prepared using coconut fibers. Coconut fibers were air dried and crushed by grinder. The material was sieved through 2 mm copper sieve. 40 g of crushed material was taken in a beaker and mixed with 400 ml of 1 N nitric acid. The content was heated on hot plate maintaining a temperature of 70°–80 °C for 20 min, cooled and washed with distilled water till the dirty color was removed. Washed material was mixed with 400 ml of 1 N sodium hydroxide, again heated at 70°–80 °C for 20 min and washed thoroughly. This material was air dried, grinded, sieved through 600 μm sieve and stored [17]. The surface area of the adsorbent was measured using Horiba SA- 9600 series (Japan) BET surface area analyzer by Nitrogen gas adsorption. The surface morphology of the adsorbent before and after adsorption was observed by scanning electron microscopy (SEM).

2.3. Adsorption experiments

Batch experiments were performed to determine the kinetic, equilibrium and thermodynamic parameters for As(III) adsorption on coconut fiber adsorbent. All the experiments were conducted at room temperature. Variable doses of adsorbent (1–20 g/L) were added to beakers containing 250 ml of water sample and having concentration 0.380 mg/L at room temperature (26 ± 1 °C) to determine optimum adsorbent dose for As(III) removal. The suspensions were stirred at 100 rpm for 10 min and then 80 rpm for remaining time. The stirring was carried out for 6 h. For isotherm study, 10 g/L of the adsorbent was stirred with 250 ml of As(III) solutions having initial concentrations of 0.2, 0.5, 1.0, 1.5 and 2.0 mg/L for 8 h at room temperature (26 ± 1 °C). The kinetic study was performed by varying time from 1 h to 10 h 10 g/L of the adsorbent was added to 250 ml of As(III) solutions having concentration of 0.40 mg/L in series of beakers and stirred as mentioned above at room temperature (26 ± 1 °C). Thermodynamic study was conducted by varying temperature from 10 to 50 °C at adsorbent dose of 10 g/L contact time of 8 h, pH 4, mixing speed of 80 rpm and initial adsorbate concentration of 0.5 mg/L. In every experiment, suspensions were allowed to settle for 30 min after stirring, supernatant were filtered and residual As(III) concentration in filtrates were measured. The adsorption capacity ‘q’ of coconut fiber adsorbent i.e. amount of As(III) adsorbed per unit mass of adsorbent was estimated using the equation:

$$q = (C_o - C_t) \times \frac{V}{m}$$

where, C_o and C_t are the initial and final As(III) concentrations respectively in mg/L, V is the volume of solution and m is the mass of adsorbent.

3. Results and discussion

3.1. Characterization of adsorbent

The SEM image of coconut fiber adsorbent before adsorption of As(III) ions is shown in Fig. 1a. It reveals that the adsorbent had porous structure. BET surface area of the adsorbent was 226.83 m^2/g. It exists in clustered, aggregated shapes and their actual size could not be determined. Fig. 1b shows SEM image of the adsorbent after adsorption of As(III). It is observed that a coating of adsorbed layer of arsenite is formed over the coconut fiber particles after adsorption.

3.2. Optimization of adsorbent dose

The effect of adsorbent dose on adsorption of As(III) is illustrated in Fig. 2. It is observed that the amount of As(III)

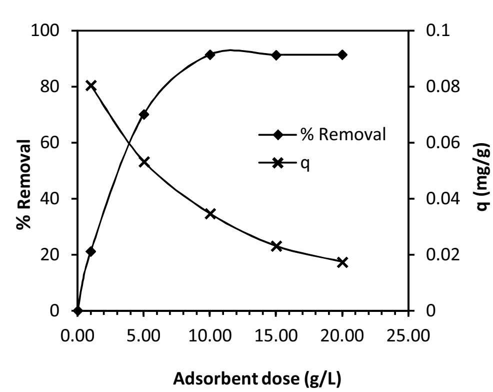

Fig. 2. Effect of adsorbent dose on As(III) adsorption initial As(III) conc.: 0.380 mg/L, time of contact: 6 h, mixing speed: 80 rpm, room temperature: 26 ± 1 °C).