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Preparation of microporous activated carbon and its modification for arsenic removal from water

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ABSTRACT

Arsenic removal from water was investigated using activated carbon. The chemical activated carbon (CAC) prepared using H_3PO_4 from jute stick largely featured micropore structure with surface functional groups, while meso- and macropore structures were mainly developed in physical activated carbon (PAC). The CAC and PAC reduced arsenic concentration to 45 and 55 $\mu g\,L^{-1}$, respectively, from 100 $\mu g\,L^{-1}$ while iron-loaded CAC reduced to 3 $\mu g\,L^{-1}$, which is lower than the upper permissible limit (10 $\mu g\,L^{-1}$). The micropore structure of CAC along with complexation affinity of iron species towards arsenic species attributed to enhanced separation of arsenic.

1. Introduction

Arsenic poisoning and its effect on human health is a serious issue in many countries in the world. The inorganic form of arsenic, especially the reduced trivalent form, As(III) is a potent poison for human health [1]. The deep aquifer in many countries in the world has recently been found contaminated by arsenic, especially in the form of As(III) [2] and created high profile of public health problems in the areas where the people are mainly depended on the underground water for drinking. Consumption of arsenic contaminated water even in a very low concentration can cause lethal diseases like cancers of skin, lung, urinary bladder as well as chronic bronchitis and cardiovascular diseases [3]. The arsenic concentration of 0.05 mg L^{-1} (50 ppb) as a drinking water standard was originally established by the Public Health Service in the United States in 1942 [4]. Later in 1980s and 1990s, the Environmental Protection Agency (EPA) further studied the effect of arsenic concentration on human health and set a new standard of 0.01 mg L^{-1} (10 ppb) to take effect from January 2006 [5]. The higher concentrations of arsenic than the upper permissible limit can cause deposition in human body and lead to serious human health problems. Therefore, the arsenic level in drinking water must be lowered than the recommended level. Different attempts have been made to remove arsenic from water such as coagulation/precipitation [6,7], coagulation/filtration [8], adsorption [9], magnetic separation [10], ion exchange [11], membrane/reverse osmosis [12] and etc.

The oxidized form of arsenic species, As(V) is negatively charged and can be more strongly adsorbed on mineral in the earth crust, while the reduced form, As(III) forms neutral species and can less strongly be adsorbed on mineral. Hence, As(III) predominantly exists in underground water, which is commonly used for drinking [13]. Because of neutral nature, As(III) is often difficult to separate from drinking water using conventional methods [14,15]. In the large scale arsenic separation, the combination of coagulation and precipitation/co-precipitation is a common practice using lime, alum, sulphide and iron species [16]. However, the alkaline sludge produced in the process creates post treatment problems. The iron-loaded chelating ion-exchange resin has been reported to be more efficient material to form stable complex with arsenic, however the cost associated with the materials and process is unaffordable in the commercial scale of arsenic separation [17,18].

Activated carbons have been extensively investigated in last couple of decades for arsenic removal from water [19–25]. Since activated carbon has wide surface area with micropore structure, it

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can adsorb arsenic and accommodate in micropore. It is fact that the quantity of arsenic adsorption largely depends on the extent of micropore surface area. Despite the advantages of the removal of arsenic from water using activated carbons, two problems are often encountered: the difficulties of the generation of required micropore structure in activated carbon and the neutrality of As(III) species. The adsorption between them is more likely attributed to physical adsorption largely because of neutral charge of As(III) species and less polarity of activated carbon surface. It could be realized that either the modification of activated carbon in order to enhance the surface affinity towards the adsorbate [26] or the oxidation of As(III) to pentavalent As(V) [27,28] could enhance the interaction of adsorbent and adsorbate.

It has been reported that around 50% of As(III) can be removed from 0.1 ppm solution using virgin activated carbon, while As(III) was completely removed when the solution was treated with a dilute solution of potassium permanganate to convert As(III) to As(V) [29]. However, it would not be feasible in practical application for drinking water purification. Many researchers have attempted to load iron species on activated carbon surface in order to enhance the affinity of the surface to arsenic species [30–33]. It is evident that the formation of different iron species on the activated carbon surface increases the net positive charge of iron-loaded activated carbon [34] and improves the arsenic adsorption capacity. This positive species of iron on activated carbon surface oxidizes the As(III) to As(V), which can easily be adsorbed by the adsorbent [35]. Some of the As(III) does not oxidize to As(V); however, they can also be adsorbed on activated carbon and iron-loaded activated carbon surface [21,36]. The particle size of iron species in nanometer range is especially required to enhance the arsenic sorption. In order to load iron species in nano-particle range, the microporosity and surface functionality of activated carbon are important.

The surface functional groups can strongly hold the iron species in dispersed state on the micropore surface, which in turn can accommodate a large number of arsenic species [21,34]. The contribution of macropore volume is less significant for arsenic separation. This is because the distance between the surface and centre of the pore is too far to form multilayer with adequate binding energy. The activated carbons prepared by physical activation using steam often possess macropore structure, and thus it is assumed to be less effective to adsorb heavy metals from water, even after loading iron.

The preparation method plays a great role in forming micropore structure with surface functional groups. In the physical activation method, steam reacts with carbon on the charcoal surface at around 800 °C to form carbon monoxide, which is then moved out, leaving behind the pores [37]. For the successive reactions in the pore, the steam would have multiple choices to react with carbons either at the wall side or at the bottom. The reaction with carbons at the bottom would lead the micro-channel through the centre of the charcoal, while the reactions with the wall side carbons progress the diameter of the pores, leading to macropore structure. In addition, the treatment at such a high temperature (800 °C) destroys most of the functional groups on the surface as observed in the FT-IR spectra in the previous work [38]. On the other hand, the chemical activation often carried out at a lower temperature (500 °C) [29], a usual carbonization temperature, compared to the temperature of physical activation. Hence, a significant number of functional groups of raw biomass can be retained on the surface as could be observed in many works [38,39]. In addition, since most of the carbons in biomass retained in the activated carbons and the pores are usually generated due to the evacuation of some small molecules like water, methanol, ethanol and etc. by dehydration and elimination reactions, most of the pores generated are micropore range.

In this work the main emphasis was given to evaluate micropore structure in the activated carbon prepared from jute stick, abundantly available in many countries in the world, using phosphoric acid as an activating agent. Iron was loaded by impregnation method on activated carbon, which was then used for arsenic separation from water.

2. Experimental

2.1. Feedstock collection and preparation

Jute (*Corchorus capsularis)* stick, which is abundantly available agricultural residue in many countries in Asia, was selected for the preparation of activated carbon in this study. After collecting jute stick from local farmer, it was washed with distilled water in order to remove any muddy soil stuck to them and then open-air dried for minimum of two days in order to remove unbound moisture. The feedstock was then cut into 1 cm size and ground using a grinding machine and sieved to obtain around 1 mm size. In our previous work, the prepared sample of jute stick was characterized by evaluating the proximate and ultimate analyses [38,40]. According to the proximate analysis, the volatile fraction, fixed carbon and ash yield of jute stick were found to be 76–78 wt%, 21.4–23.4 wt% and 0.62 wt%, respectively. From the ultimate analysis, the elemental composition of jute stick has been found to be 49.79 wt% C, 6.02 wt% H, 41.37 wt% O, 0.19 wt% N, 0.05 wt% Cl and 0.05 wt% S.

Phosphoric acid (99%, E-Merk, India) was used as an activating agent for chemical activation of jute stick. Iodine (99.5%, Loba Chemicals, India), potassium iodide (99.9%, Loba Chemicals, India), sodium thiosulphate (99.9%, Loba Chemicals, India), potassium dichromate (99.5%, Loba Chemicals, India), activated carbon (Laboratory Reagent, Thomas Baker Chemicals Ltd.) and methylene blue dye (99.9%, Aldrich) were also used in this investigation.

2.2. Preparation of activated carbon

About 100 g of dry jute stick particles was taken in a 1 L beaker, containing 166 g of 60% phosphoric acid solution. The mixture was then stirred for a while and kept undisturbed for about 15 h. The solution was completely socked into the particles. The solid mass was then transferred to a stainless steel reactor of 6 cm diameter and 30 cm length as shown in Fig. 1. The reactor was heated with a ceramic band heater equipped with a temperature controller. A thermocouple was inserted into the reactor through a thermo-well in order to control the temperature. The system ensured the precisely controlled temperature within the range of ±1 °C.

Initially, the reactor was heated to about 200 °C and kept at this temperature for about 30 min. Finally, the reactor was heated to the activation temperature, 475 °C and kept isothermal for 1 h. Nitrogen gas of 200 mL min^{-1} was continuously passed through the reactor in order to keep the inert atmosphere in the reactor as well as to facilitate faster evacuation of steam and organic vapours, so as to prevent the re-condensation of vapours in the reactor. After completing the activation, the reactor was cooled down to room temperature, opened and the product was collected. In order to remove the residual H_3PO_4, the product was washed with hot distilled water repeatedly until the pH of solution reached to 6.5. Finally, the product was washed with 0.05% NaOH solution to completely neutralize the sample. Residual NaOH was washed out by further washing with distilled water. The sample was then dried at 105 °C for 24 h and named as CAC and stored in a desiccator for