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# Arsenic(V) removal from aqueous solutions using an anion exchanger derived from coconut coir pith and its recovery

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## Abstract

The performance of a new anion exchanger (AE) prepared from coconut coir pith (CP), for the removal of arsenic(V) [As(V)] from aqueous solutions was evaluated in this study. The adsorbent (CP–AE) carrying dimethylaminohydroxypropyl weak base functional group was synthesized by the reaction of CP with epichlorohydrin and dimethylamine followed by treatment of hydrochloric acid. IR spectroscopy results confirm the presence of $-NH^+(CH_3)_2Cl^-$ group in the adsorbent. XRD studies confirm the decrease of crystallinity in CP–AE compared to CP, and it favours the protrusion of the functional group into the aqueous medium. Batch experiments were conducted to examine the efficiency of the adsorbent on As(V) removal. Maximum removal of 99.2% was obtained for an initial concentration of 1 mg $l^{-1}$ As(V) at pH 7.0 and an adsorbent dose of 2 g $l^{-1}$. The kinetics of sorption of As(V) onto CP–AE was described using the pseudo-second-order model. The equilibrium isotherms were determined for different temperatures and the results were analysed using the Langmuir equation. The temperature dependence indicates an exothermic process. Utility of the adsorbent was tested by removing As(V) from simulated groundwater. Regeneration studies were performed using 0.1 N HCl. Batch adsorption–desorption studies illustrate that CP–AE could be used to remove As(V) from ground water and other industrial effluents.

*Keywords:* Arsenic; Coir pith; Epichlorohydrin; Psuedo-second-order; Langmuir equation; Desorption

## 1. Introduction

The presence of arsenic in water and wastewater has been of great public concern. It is introduced into water through a combination of natural processes such as weathering reactions, biological activity, and volcanic emission as well as through a range of anthropogenic activities (Lenoble et al., 2005). Anthropogenic arsenic stems from the discharges of various industries such as smelting, petroleum refinery, fertilizers, insecticides, herbicides as well as glass and ceramic manufacturing industries. A number of technologies have been developed for the removal of arsenic from groundwater based on various principles, namely, oxidation, coagulation, precipitation, ion exchange, adsorption and reverse osmosis. Of all these, adsorption and ion exchange are the best methods for the purification of water or they are often combined. A wide range of adsorbents has been used for removing arsenic from water and wastewater and has been reviewed by Maity et al. (2005).

Lignocellulosic biomass wastes represent cheap and environmentally safe sources for the preparation of adsorbent materials that may be useful for the removal of heavy metals from solution. There have been numerous studies on the adsorption of heavy metals from water by lignocellulosic materials as reviewed by Shibi and Anirudhan (2005). Nevertheless, although they have exhibited good adsorptive capacity for metal uptake, reinforcement by chemical processing may be required for sorption process applications. A number of modifications such as chemical modification, copolymerization, cross linking and quaternisation have been used for improving physical and chemical properties of the lignocellulose materials and to increase the adsorption capacity (Nada et al., 2002;

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Orlando et al., 2002; Unnithan et al., 2004). The potential of using chemically modified lignocellulosics for cation binding has been explored. Information on the ability of chemically modified lignocellulosics to remove anions from wastewater is still restricted. Quaternised biomasses such as sugarcane bagasse (Simkovic and Laszlo, 1997), and Chineese Reed (Namasivayam and Holl, 2005) have been used as anion exchangers for nitrate and anionic dye, respectively. The present work is devoted to the preparation of an anion exchanger from coconut coir pith, a lignocellulosic residue, by its reaction with epichlorohydrin and dimethylamine followed by treatment with hydrochloric acid. The efficiency of the produced weakly basic ion exchanger towards the uptake of As(V) from aqueous solution and ground water was also investigated.

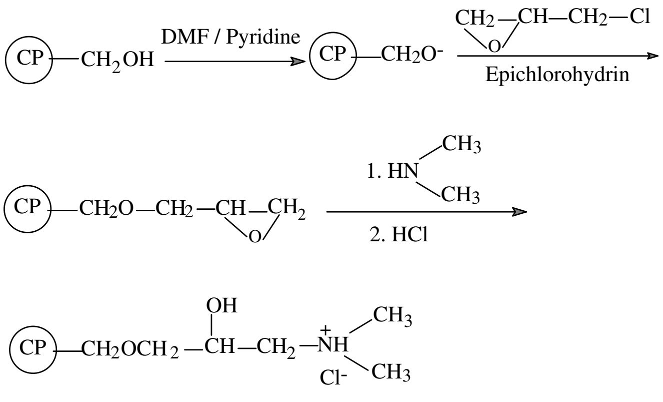
## 2. Experimental methods

### 2.1. Chemicals

All the chemicals used in this study were of analytical grade. A 1000 mg l$^{-1}$ As(V) stock solution was prepared by dissolving a weighed quantity of $Na_2HAsO_4 \cdot 7H_2O$ (Aldrich, USA) in distilled water. All solutions for adsorption and analysis were prepared by appropriate dilution of the freshly prepared stock solution. Epichlorohydrin (Fluka, Switzerland) was used as received. Pyridine, dimethylformamide (DMF), dimethylamine, $NaNO_3$, NaOH and $NaBH_4$ were obtained from M/S E.Merck, India. All other chemicals (Ascorbic acid, HCl and KI) were supplied by the Loba Chemie Ltd (Bombay, India).

### 2.2. Adsorbent preparation

Coconut coir pith (CP) was procured from a local coir industry. It was washed with distilled water to remove surface adhered particles and water soluble materials. Particles of $-80+230$ mesh size were separated after drying at 80 °C. The CP basically contains α-cellulose, hemicellulose and lignin which were determined using the standard methods described by Ott (1946) and were found to be 47.4%, 18.3% and 27.1%, respectively. For the synthesis of adsorbent, CP was first cross linked with epichlorohydrin into epoxy ether from which it was then utilized for derivatisation. The sensitive component for cross linking might be the hydroxyl groups of the cellulose unit present in CP, CP—CH$_2$OH. Scheme 1 presents the general procedure adopted for the preparation of adsorbent. Twenty grams of dried CP was reacted with epichlorohydrin (200 ml) in 240 ml of DMF at 100 °C and stirred for 1 h. Pyridine (80 ml) was added to the solution to accelerate the rate of wetting. The reaction product was washed repeatedly with diluted ethanol (1:1) at 40 °C to remove excess pyridine and epichlorohydrin. Amino groups were then introduced into the epoxy propyl by-product after reaction with 100 ml of 50% dimethylamine solution for around 3 h maintaining the temperature in the range of 70–80 °C. The reaction product was washed using distilled water till the filtrate became clear of dimethylamine. To convert into an anion exchanger (AE), the above product was treated with 500 ml of 0.2 M HCl for 4 h at room temperature, washed well to remove excess chloride ions and dried at 80 °C. The functionalized CP (CP–AE) was sieved and particles having the average diameter of 0.096 mm were used through out the study.



**CP-AE**

Scheme 1. Preparation of CP–AE.

### 2.3. Equipment and method of characterization

The FTIR spectra of CP and CP–AE were obtained using the pressed disk technique on a Schimadzu FTIR model 1801. The XRD patterns of the adsorbent samples were obtained with a Siemens D 5005 X-ray unit using Ni-filtered Cu K$_\alpha$ radiation. The specific surface area of CP and CP–AE was measured by BET $N_2$ adsorption using a Quantasorb surface area analyzer ($Q_{S/7}$). A systronic microprocessor pH meter (model, $\mu$362, India) was used to measure the potential and pH of the suspension. For kinetic and isotherm studies a Labline temperature controlled water bath shaker with a temperature variation of ±1.0 °C was used.

The point of zero charge ($pH_{pzc}$) is defined as the pH of the suspension at which surface charge density $(\sigma_0) = 0$. The $pH_{pzc}$ of the CP and CP–AE at different ionic strengths (0.001, 0.01 and 0.1 M $NaNO_3$) was determined by a potentiometric titration method (Schwarz et al., 1984). The adsorbent (0.25 g) and 50 ml of $CO_2$ free electrolyte solution were titrated in 100 ml stoppered conical flasks. Prior to the titration the solution was equilibrated until a pH value of 7.0 was observed in the suspension. Titrations were made over a pH range of 2.0–10.0 by adding 0.1 M $HNO_3$ ($C_A$) and 0.1 M NaOH ($C_B$). After the equilibrium period the pH was recorded using a pH meter. Titrations of the electrolytes in the absence of the adsorbent were also made. The $\sigma_0$ ($C\,cm^{-2}$) was calculated from the titration curve using the following equation.

$$\sigma_0 = \frac{F(C_A - C_B) + [OH^-] - [H^+]}{A} \tag{1}$$