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Removal of chromium (VI) from dilute aqueous solutions by activated carbon developed from *Terminalia arjuna* nuts activated with zinc chloride

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Abstract

Different structured activated carbons were prepared from *Terminalia arjuna* nuts, an agricultural waste, by chemical activation with zinc chloride for the adsorption of Cr(VI) from dilute aqueous solutions. The most important parameter in chemical activation was found to be the chemical ratio (activating agent/precursor, g/g). Carbonization temperature and time are the other two important variables, which had significant effect on the pore structure of carbon. A high surface area of 1260 m^2/g was obtained at a chemical ratio of 300%, carbonization time and temperature of 1 h and 500 °C, respectively. The activated carbon developed shows substantial capability to adsorb Cr(VI) from dilute aqueous solutions. The parameters studied include pH, adsorbent dosage, contact time, and initial concentrations. The kinetic data were best fitted to the Lagergren pseudo-first-order model. The isotherm equilibrium data were well fitted by the Langmuir and Freundlich models. The maximum removal of chromium was obtained at pH 1.0 (about 99% for adsorbent dose of 2 g/l and 10 mg/l initial concentration).

Keywords: Pollution; *Terminalia arjuna* nuts; Activated carbon; Chemical activation; Surface area; Cr(VI) removal; Waste water treatment; Water pollution

1. Introduction

Water pollution due to toxic heavy metals has been a major cause of concern for chemists and environmental engineers. The industrial (Dwari et al., 2004) and domestic wastewater, if properly not managed, is responsible for causing severe damage to the environment and adversely affecting the health of the people. Chromium is one of the contaminants, which exist in hexavalent and trivalent forms. Hexavalent form is more toxic (Smith and Lec, 1981) than trivalent and requires more concern. Strong exposure of Cr(VI) causes cancer in the digestive tract and lungs (Kaufaman, 1970) and may cause epigastric pain, nausea, vomitting, severe diarrhoea, and hemorrhage (Browning, 1969). It is therefore, essential to remove Cr(VI) from wastewater before disposal. The main sources of chromium (VI) are tannery, paint, ink, dye, and from aluminium manufacturing industries etc.

The treatment of chromium bearing effluents has been reported by several methods, such as reduction precipitation, ion exchange, electrochemical reduction, evaporation, reverse osmosis and direct precipitation (Marshal, 1980; Patterson, 1985). Most of these methods need high capital cost and recurring expenses such as chemicals, which are not suitable for small-scale industries. The process of adsorption is by far the most versatile and widely used technique for the removal of metal ions. Activated carbon has been the water industry's standard adsorbent for the reclamation of municipal and industrial wastewater for potable use for almost three decades (Fornwalt and Hutchins, 1966). Despite its prolific use in the water and waste industries, activated carbon remains an expensive material. In recent years, research interest in the production of low-cost alternatives to activated carbon has grown.

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Activated carbons (ACs) exhibit a great adsorption capacity, owing to their highly developed pore structures characterized by large surface areas. International growing demand of this adsorbent, mainly because of their use in applications related to their environmental mitigation, has led to search for new, available low-cost feedstocks of renewable character. In practice, coal and agricultural by-products of lignocellulosic materials are two main sources for the production of commercial activated carbons. Agricultural wastes have emerged as a better choice. There are a quite large number of studies regarding the preparation of activated carbons from agricultural wastes (Kadirvelu et al., 2003; Nag et al., 1999) which include nutshells (Ahmadpour and Do, 1997), fruit stones (Lussier et al., 1994), bagasse (Mohan et al., 2002), coirpith (Kadrivelu et al., 2001), oil palm waste (Lua and Guo, 1998) and agricultural residues from sugarcane (Blanco Castro et al., 2000), rice (Srinivasan et al., 1998) and peanut (Periasamy and Namasivayam, 1996; Ricordel et al., 2001), sawdust (Marquez-Montesinos et al., 2001) and canes from some easy-growing wood species (Basso et al., 2002).

Basically, there are two different processes for the preparation of activated carbon: physical activation and chemical activation. In comparison with physical activation, there are two important advantages of chemical activation. One is the lower temperature in which the process is accomplished. The other is that the global yield of the chemical activation tends to be greater since burn-off char is not required. Among the numerous dehydrating agents, zinc chloride in particular is the widely used chemical agent in the preparation of activated carbon. Knowledge of different variables during the activation process is very important in developing the porosity of carbon sought for a given application. Chemical activation by $ZnCl_2$ improves the pore development in the carbon structure and because of the effect of chemicals; the yields of carbon are usually high (Ahmadpour and Do, 1997).

In this work it has been reported the results obtained on the preparation of activated carbons from *Terminalia arjuna* nuts with zinc chloride activation and their ability to remove hexavalent chromium from dilute aqueous solutions. Different preparation variables on the characteristics of activated products were studied to find the optimum conditions for making activated carbons with well-developed porosity. The influence of several operating parameters, such as pH, adsorbent dosage, contact time, and initial concentrations on the adsorption capacity, were investigated. Kinetic models were used to identify the possible mechanisms of such adsorption process. The Langmuir and Freundlich models were used to analyse the adsorption equilibrium.

2. Experimental technique

2.1. Preparation of activated carbon

Terminalia arjuna nuts collected from nearby locality was first washed with distilled water to remove the water-soluble impurities and surface adhered particles and then dried at 60 °C to remove the moisture and other volatile impurities. Then the precursor was ground in the ball mill and sieved to a particle size range of 150–200 μm. The proximate analysis of the precursor is presented in Table 1. Chemical activation of the powdered precursor was done with $ZnCl_2$. 10 g of dried precursor was well mixed with distilled water so that 100 ml concentrated solution contained 10 g of $ZnCl_2$. The chemical ratio is defined as the ratio of chemical activating agent ($ZnCl_2$) to the precursor. The chemical ratio (activating agent/precursor) was 100% in this case. The mixing was performed at 50 °C for 1 h. After mixing, the slurry was subjected to vacuum drying at 100 °C for 24 h.

Table 1
Proximate analysis of *Terminalia arjuna* nut used as raw material

Component	Quantities
Moisture 3%	76
Volatile matter 20%	3
Fixed carbon 76%	20
Ash 1%	< 1

The resulting chemical-loaded samples were placed in a stainless-steel tubular reactor and heated (5 °C/min) to the final carbonization temperature under a nitrogen flow rate of 150 ml/min STP. Samples were held at the final temperature (carbonization temperature) for different carbonization times of 1, 2, 3 h before cooling down under nitrogen. Nitrogen entering in the reactor was first preheated to 250–300 °C in a pre-heater. The products were washed sequentially with 0.5 N HCl, hot water and finally cold distilled water to remove residual organic and mineral matters, then dried at 110 °C. In all experiments, heating rate and nitrogen flow was kept constant. The experiments were carried out for different chemical ratio (100–300%) and carbonization temperature (300–600 °C).

Weight loss of the carbon samples was calculated on a chemical free basis and chemical recovery (CR) was estimated according to

$$CR = \frac{W_{Pi} - W_{Pf}}{W_C} \times 100, \tag{1}$$

where W_{Pi} and W_{Pf} are the weight of products before and after washing and W_c is weight of chemical used.

The BET surface areas of these activated carbons were measured in Flowsorb-2300. The Flowsorb-2300 was used to find out the surface area of activated carbon on the basis of mono-layer adsorption at or near the boiling point of gases. The monolayer formation was achieved with a nitrogen–helium of 30% by volume. The adsorbed monolayer of nitrogen were established at atmospheric pressure and at the temperature of liquid nitrogen. In this method first sample quantity is optimized after several trial runs so that surface area falls with in 0.5–2.5 m^2. The sample is dried at 105–110 °C and is free from any gases or vapours for which 200–250 °C for 15 min is adequate. Relatively adsorbing and