TOMSK POLYTECHNIC UNIVERSITY

Research paper

Waste walnut shell valorization to iron loaded biochar and its application to arsenic removal

Xinhui Duan [a,b,c,]*, Chengcheng Zhang [a,b,c], C. Srinivasakannan [d], Xin Wang [e]

[a] *Institute of Power Source and Ecomaterials Science, Hebei University of Technology, Tianjin 300130, China*
[b] *Key Laboratory of Special Functional Materials for Ecological Environment and Information, Hebei University of Technology, Ministry of Education, Tianjin 300130, China*
[c] *Key Laboratory for New Type of Functional Materials in Hebei Province, Hebei University of Technology, Tianjin 300130, China*
[d] *Chemical Engineering Program, The Petroleum Institute, P.O. Box 2533, Abu Dhabi, United Arab Emirates*
[e] *School of Environmental Science and Engineering, Hebei University of Science and Technology, Shijiazhuang, Hebei 050018, China*

Abstract

Iron loaded biochar (ILB) was prepared from waste walnut shell by microwave pyrolysis and its application for arsenic removal was attempted. The ILB was characterized using X-ray diffraction, scanning electron microscopy and BET Surface area analyzer. The adsorption isotherm of As (V) in ILB covering a temperature range of 25 to 45 °C, as well as the kinetics of adsorption at 25 °C were experimentally generated. The adsorption isotherms were modeled using Langmuir and Freundlich isotherm models, while the kinetics of adsorption was modeled using the pseudo-first-order, pseudo-second-order kinetic models, and intra particle diffusion model. The ILB had a surface area of 418 m^2/g with iron present in the form of hematite (Fe_2O_3) and magnetite (Fe_3O_4). The arsenic adsorption isotherm matches well with Langmuir isotherm model with a monolayer adsorption capacity of 1.91 mg/g at 25 °C. The adsorption capacity of As (V) well compares with other porous adsorbents widely reported in literature, supporting its application as a cost effective adsorbent.

Keywords: Biochar; Water treatment; Adsorbent; Kinetics; Thermodynamic

1. Introduction

Presence of arsenic in natural water sources has been a serious concern worldwide. In many parts of the world, the underground water is contaminated with arsenic. The arsenic contaminated tube-wells are the only viable source for drinking water in most of the underdeveloped countries, even today. In most of these cases, the groundwater is potable, excepting the presence of unacceptable level of arsenic. Arsenic is a carcinogen and its ingestion may deleteriously affect the gastrointestinal tract, cardiac, vascular system and central nervous system. Due to its high toxic effect on human health, the USEPA has lowered the maximum contaminant level in drinking water to 10 µg/l. Arsenic contamination of the ground water occurs through natural processes such as weathering of arsenic containing minerals, anthropogenic activities such as uncontrolled industrial discharge from mining and metallurgical industries, and application of organo-arsenical pesticides [1–4].

Literature survey reveals that there are number of approaches for arsenic removal from water. The most commonly used treatment techniques for arsenic removal include coagulation with iron and aluminum salts; ion-exchange, reverse osmosis and electro-dialysis; adsorption onto activated alumina/carbon, activated bauxite, clay minerals and iron oxides, et al. [5–7]. The treatment methods such as ion exchange and reverse osmosis are expensive, which hinder the further application in large scale. The chemical precipitation with lime/ferric salt reported to be effective, but yields large quantities of solid sludge, which demands further treatment. Due to simplicity of the process as well as being re-generable, the adsorption technology has been widely used to remove arsenic.

---

* Corresponding author. Institute of Power Source and Ecomaterials Science, Hebei University of Technology, Tianjin 300130, China. Tel.: +86 60204850.
  E-mail address: dxh1191984@aliyun.com (X. Duan).

Biochar is a black carbon prepared through thermal or hydrothermal conversion of biomass, which is highly recommended for soil amendment due to its ability to reduce greenhouse gases as well as to enhance soil fertility by improving moisture and nutrients retention [8]. Its application for utilization as adsorbent for removal of containments such as heavy metals and organic compounds in water and soil has also been reported [9]. Large varieties of renewables such as agriculture waste, forestry and animal husbandry are utilized for production of biochar at low cost. With certain modifications, either physical or chemical treatment the biochar utility can be enhanced, rendering it suitable for different environmental application.

Pyrolysis is a thermochemical method in the absence of oxygen to convert biomass into biochar, usually refers to conventional heating for long duration that virtually increases cost of biochar produced. Microwave assisted pyrolysis is being increasingly utilized to produce biochar as it is energy efficient and is a clean method of heating in addition to producing biochar that possesses higher surface area than conventional heating [10]. Iron oxide coated over variety of porous precursors such as alumina, activated carbon, cloth fibers, aerogels, fly ash, membranes is of recent research interest for removal of As (V). As compared to popular iron coated porous adsorbents, ILBs are cost effective alternatives [11]. Pyrolysis of iron salt solution impregnated biomass to prepare ILB is a popular method as it is a single stage process.

Walnut in China is a cash crop, processing of which was reported to produce more than 0.5 million ton of walnut shell as byproduct per year. Common way of utilization of this carbon rich waste is to use it as fuel through combustion, which causes serious environmental problems. Toward this, the present study attempts to prepare a microwave pyrolyzed ILB from walnut shell and assess its potential as a low cost adsorbent for arsenic removal. The adsorption isotherms as well as the kinetics of adsorption data are generated and appropriately modeled.

2. Experimental

2.1. Materials

The waste walnut shell collected from local market washed thoroughly using deionized water to remove impurities, crushed and sieved into size fractions about 2 mm, dried at 105 °C overnight and stored in desiccators for later utilization, its proximate analysis along with the ultimate analysis is reported in Table 1.

All chemicals used in this study, including ferric chloride ($FeCl_3/6H_2O$), sodium arsenate ($Na_2HAsO_4/7H_2O$) were of analytical grade. Synthetic arsenate contaminated solution was prepared with sodium arsenate in deionized water with different initial concentrations.

2.2. Preparation of ILB

The microwave assisted pyrolysis is carried out in a microwave tubular furnace with microwave frequency of 2.45 GHz and maximum microwave output power of 1200 W, the schematic diagram of the microwave heating system can be seen elsewhere [12]. First an iron contained solution was prepared by dissolving 30 g $FeCl_3$ in 70 ml deionized (DI) water, and the dry walnut shell was impregnated with the solution for 4 h, then the solid was separated and dried at 105 °C for 2 h. The pretreated sample was loaded in a quartz reactor and pyrolyzed in the microwave tubular furnace at microwave power of 800 W for 20 min, in N_2 atmosphere. The samples were repeatedly rinsed with DM water, dried at 100 °C, and stored in sealed container for further experimentation.

2.3. Adsorption of arsenic

Batch adsorption experiments are performed in a set of Erlenmeyer flasks (250 ml), each containing 100 ml of different initial concentrations of As(V) (0.1–5 mg/L), together with 0.1 g of ILB, the pH is adjusted to 7 by addition of HCl and NaOH solution (0.1 mol/L). A gas bath thermostatic oscillator utilized to maintain the desired temperature for desired duration of adsorption. The concentrations of As(V) in the supernatant solutions are measured by an Atomic Absorption Spectrophotometer (ZA2000 Hitachi, Japan), before and after the adsorption process.

The adsorbed amount of As(V) at equilibrium, q_e (mg/g), is calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)\,V}{W} \tag{1}$$

where C_0 and C_e are the initial and equilibrium As(V) concentrations(mg/L), respectively. V is the volume of solution (L) and W is the dry weight of the added adsorbent (g).

The procedure for estimation of adsorption kinetics of As(V) is basically identical to that of equilibrium tests, except for the fact that the liquid samples were taken at intervals of time, with the zero time corresponding to the time that the adsorbent is charged into the dye solution. The total volume of the liquid samples withdrawn is less than 5% of the total volume of the solution. The amount of adsorption by adsorbent at time t, q_t (mg/g), is calculated by the following equation:

$$q_t = \frac{(C_0 - C_t)\,V}{W} \tag{2}$$

Table 1
Proximate and ultimate analysis of walnut shell.

Sample	Proximate analysis (Wt. %)				Elemental analysis (Wt. %)			
	Fixed carbon	Volatiles	Ash	Moisture	C	H	O	N
Walnut shell	22.07	76.98	0.67	13.60	46.80	3.41	43.11	0.28