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Preparation, characterization and adsorption potential of the NH_4Cl-induced activated carbon for the removal of amoxicillin antibiotic from water

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HIGHLIGHTS

- ▶ NH_4Cl-induced activated carbon (NAC) was prepared from a waste biomass.
- ▶ The prepared NAC was a mesoporous material with a BET surface area of 1029 m^2/g.
- ▶ NAC had a high density of hydroxyl, carbonyl, carboxylic, and carboxylate surface functional groups.
- ▶ NAC had an amoxicillin adsorption rate of up to 4.3 times greater than the standard AC.
- ▶ NAC had an amoxicillin adsorption capacity of 2 times of that of the standard AC.

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ABSTRACT

The preparation, characterization and application of NH_4Cl-induced activated carbon (NAC) for amoxicillin removal from the contaminated water were studied. The prepared NAC had a specific surface area of 1029 m^2/g and a mean pore volume of 2.46 nm. Over 99% of 50 mg/L amoxicillin (AMX) was adsorbed using 0.4 g NAC/L at the optimum solution pH of 6; while standard activated carbon (SAC) could only adsorb around 55% of AMX under similar experimental conditions. Kinetic analysis revealed that adsorption experimental data for both NAC and NAC were best fitted by the pseudo-second-order model, with the greater rate for NAC than for SAC. Results of equilibrium experiments indicated that adsorption of AMX onto SAC and NAC were better described by the Langmuir model. The maximum adsorption capacity of AMX onto SAC and NAC was 262 and 437 mg/g, respectively. AMX adsorption onto SAC increased from 76.8% to 92% with increased temperature from 10 to 35 °C. However, a further increase of temperature to 50 °C led to declining AMX removal to 78.1%. Overall, these results indicate that developed NAC was an efficient adsorbent that presents an attractive adsorbent method for application in treating contaminants in water.

1. Introduction

Pharmaceuticals present class of health care products that are intensively used worldwide to promote human health and well being as well applications in animal care and agriculture. Among pharmaceuticals, antibiotics are the most widely used drug for the prevention or treatment of bacterial infections in humans, animals and plants [1]. Antibiotics are released into bodies of water mainly through effluent of municipal wastewater treatment plants, as well as through effluent from pharmaceutical manufacturing plants. Pharmaceuticals are gaining recognition as being environmental contaminants, classified as recalcitrant bio-accumulative compounds and are thus regarded as hazardous chemicals. The release of pharmaceuticals into the environment thus results in contamination of aquatic or terrestrial ecosystems [2]. Effluent containing antibiotics needs to be treated chemically or physically to prevent the adverse effects from contaminated water. Although chemical processes, especially advanced oxidation processes, can often degrade and decompose antibiotics' molecules into simple compounds and/or mineralize them, these processes are very expensive and difficult to operate for complete elimination of recalcitrant compounds including antibiotics. Physical techniques remain the most appropriate treatment option and adsorption is among the most efficient of these techniques for removing organic compounds from industrial effluent [2,3]. Adsorption is efficient, simple to design and operate and it is unaffected by toxicity as well as being inexpensive [4]. Adsorption therefore presents an efficient

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and economical technique widely used to accumulate organic compounds from contaminated streams onto solid material [2]. A saturated adsorbent is easily separated from a treated stream for regeneration or disposal in an environmentally acceptable way. The performance of an adsorption process is affected by an adsorbent's characteristics as well as by the composition of a waste stream (mainly by the structural properties of the contaminant(s) and the composition of the waste stream) [5].

Several materials including activated carbon, waste material and minerals either plain or modified have been examined so far as adsorbents for organic contaminants. Due to its porosity and very high specific surface area and capacity, activated carbon is the most widely used adsorbent to remove various classes of compounds from contaminated streams [6]. However, the main disadvantages of activated carbon are high production and regeneration costs [5]. Interestingly, it has been found that adsorption of antibiotics onto activated carbon is significantly influenced by characteristics of the activated carbon [7]. Therefore, the method of carbon activation aimed at improving its adsorption capability and thus reducing the rate of activated carbon consumption to reduce the cost of activated carbon adsorption making more it cost-effective.

Several chemicals have been used in the process of microwave assisted activation of carbon, and the best activation has been obtained with the presence of alkaline hydroxide of KOH [8]. However, the main challenge with this technique of microwave-assisted modification of activated carbon using metal salts is the metal compound formed during the activation process [8]. These metal compounds are deposited in the internal structure and pores of the activated carbon, thereby reducing its pore volume and specific surface area. Accordingly, non-metal hydroxides might be used as an alternative chemical to activate carbon.

This study was set up to examine the NH_4Cl-induced activation of carbon prepared from pomegranate wood, an agricultural waste, to compare the capability of NH_4Cl-induced activated carbon (NAC) with that of standard activated carbon (SAC) in adsorption of amoxicillin (AMX) as a model of an antibiotic, from contaminated water. AMX, a β-lactam antibiotic, is the drug of choice prescribed for the treatment of a number of human bacterial infections, as a growth promoter for animals and in agriculture to prevent infections [9]. Influences of the following basic variables were evaluated in the tests on adsorption of AMX; pH of the solution, activated carbon concentration, AMX concentration, reaction time and solution temperature. The equilibrium, kinetic, mechanism and thermodynamics of AMX adsorption onto SAC and NAC were also evaluated.

2. Materials and methods

2.1. Material

Analytical grade AMX (chemical formula: $C_{16}H_{19}N_3O_5S$, molar mass: 365.4 g/mol) was purchased from Sigma Aldrich Co., and used as received. As stated above, two types of activated carbon were used in this study, NAC and SAC. The NAC was prepared from pomegranate wood waste according to the procedure explained in the following section. Activated carbon obtained from Merk Co. was used as the SAC to make a comparison with and to highlight the adsorption potential of the NAC prepared in this study. The contaminated water used in the experiments was prepared from mixing aliquots of AMX stock solutions (1000 mg/L) with distilled water. A stock solution of AMX was made by dissolving 1 g of analytical grade AMX in distilled water.

2.2. Activated carbon preparation and characterization

Dried pomegranate wood was used as the base material for the preparation of activated carbon. The pomegranate wood was obtained from a local farm as discarded agricultural waste and was first debarked, then crushed into small parts and ground. The wood particles were carbonized at 700 °C for 1 h in an oven under a N_2 gas stream. The carbonized granules were then soaked in the NH_4Cl solution with different concentrations (NH_4Cl to char ratio was 0–10 w%); each solution was shaken for 24 h at room temperature. The mixture was then sieved to separate the char, and the separated char was then oven-dried at 105 °C for 24 h. Pre-treated char was finally activated by oven-heating at various temperatures ranging from 500 to 900 °C and activation time between 0.5 and 2.5 h under N_2 atmosphere. Accordingly, the prepared NH_4Cl-induced activated carbon (NAC) was ground to particles according to a mesh size of 20/16 for use in the adsorption experiments.

The SAC and NAC were characterized for surface morphology, specific surface area, pore volume and size, pH of point of zero charge (pHpzc) and surface functional groups. The surface morphology of the adsorbent was observed using the scanning electron microscopy (SEM) technique (Philips-XL30 Electron Microscope). Evaluations for BET (Brunauer–Emmett–Teller) specific surface area and pore volume and size were determined by a nitrogen gas adsorption analyzer (BELSORP-miniII instrument). The pHpzc of adsorbents was determined according to the pH drift procedure. Surface functional groups of the selected adsorbents were determined using Fourier Transform Infrared (FTIR) spectroscopy with a Nicolet spectrometer.

2.3. Adsorption experiments

2.3.1. Parametric and kinetic experiments

Parametric experiments were conducted in the stirred (100 rpm) glass reactor in a temperature-controlled incubator. In each test, 50 mL of contaminated water containing given concentrations of AMX was transferred into the reactor, its pH was regulated (with 0.1 N HCl or NaOH) at the desired level, the predetermined amounts of activated carbon (NAC or SAC) were added to the reactor and the suspension was mixed at 100 rpm. When the predetermined mixing time was up, the suspension was filtered using a cellulose acetate filter with 0.2 μm pore size and the filtrate was analyzed for residual AMX. The concentration of AMX in a solution was measured using a Knauer HPLC (C18 ODS column; 250 × 4.6 × 5) with a UV detector 2006 at a wavelength of 190 nm. The mobile phase was a mixture of buffer phosphate with pH = 4.8 and acetonitrile with a volumetric ratio of 60/40 with an injection flow rate of 1 mL/min. The pH level of samples was measured using a pH meter (Sense Ion 378, Hack). The temperature of solutions was measured using a mercury thermometer. Parameters at this stage were as follows; water pH (2–9), initial AMX concentration (10–100 mg/L), solution temperature (10–50 °C), and reaction time (0.3–100 min) in kinetic experiment and 6 h in equilibrium tests). Experimental runs and conditions are given in Table 1. All tests were performed in duplicate to ensure reproducibility of the results; the mean of these two measurements was taken to represent each evaluation. Calculations of amounts of adsorption of AMX onto prepared NAC and SAC were based on removal percentages (Eq. (1)) and adsorption capacity (Eq. (2)).

$$\text{Amoxicillin removal } (\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{1}$$

$$\text{Adsorption capacity } (\text{mg/g}) = \frac{V(C_0 - C_t)}{m} \tag{2}$$

where C_0 and C_t represent AMX concentration at initial and time t of the contact time, respectively. V is the volume of the AMX solution and is the mass of adsorbent added.