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Effective removal of Amoxicillin, Cephalexin, Tetracycline and Penicillin G from aqueous solutions using activated carbon nanoparticles prepared from vine wood

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ABSTRACT

The present study shows the applicability of carbon nanoparticles made from vine wood as an inexpensive adsorbent for the removal of Amoxicillin, Cephalexin, Tetracycline and Penicillin G from aqueous solutions. The activation of carbon nanoparticles was studied by aqueous solutions of NaOH, KOH, $ZnCl_2$, NaCl and HNO_3. The removal efficiency ($R\%$) of pollutants showed that NaOH can be used as an efficient, low-cost and environmentally friendly activator ($R\%$ = 74–88). Infrared spectroscopy, XRD pattern, BET and BJH methods and scanning electron microscope (SEM) images were used to characterize the prepared carbon. The area and pore volume of activated carbon were obtained as 13.397 m^2/g and 54.79 cm^3/g, respectively. The SEM images showed a high porosity for activated carbon. Removal of antibiotics from aqueous samples was carried out using a modular method. The optimized parameters of pH 2, an amount of adsorbent of 0.4 g/L, a concentration of antibiotic solution of 20 mg L^{-1}, a contact time of 8 h and a temperature of 45 °C were obtained in a modular way. Kinetic studies confirmed that the adsorption followed second-order reaction kinetics. Thermodynamic studies revealed that the process was spontaneous and endothermic. The reusability of sorbent was achieved by using of NaOH (5 w/w%) solution and recovery time of 4 h.

1. Introduction

The occurrence of antibiotic compounds in the aquatic environment is considered to be an emerging issue, which derives mainly from the pharmaceuticals industry as well as from veterinary and human medication uses [1,2]. About 30–90% of the given dose can remain un-degradable in the human or animal body, and is largely excreted as an active compound [3,4]. Many antibiotics have a toxic nature toward algae and other lower organisms which can lead to an indirect effect in the long term on ecological sustainability. The emergence of multi-resistant bacteria is perhaps the biggest challenge, because it makes treatment especially difficult, costly, and in the end may be even impossible [5–9].

The major reason for the increasing trend is a continuing overuse and mis-use of antibiotics worldwide. Resistance is mainly considered to be a clinical problem because antibiotic use is not restricted to clinical settings. At least half of all antibiotics are consumed in the farming and agricultural arena [10]. Removal of antibiotics involves high cost because the pharmaceutical industry in particular must treat their wastewater properly prior to environmental discharge. Thus, antibiotics residue removal from the environment is considered to be important and serves as an attractive case study [11–13].

Activated carbon has been widely used to remove organic contaminants from water and wastewater in industrial scale applications [14–16]. High porosity, high adsorption capacity and high specific area are the main features of activated carbon, which promote it as a good sorbent for the removal of various compounds [17–20]. The commercially available activated carbons are expensive, rendering their use infeasible for large scale operations [21–23]. Therefore, inexpensive and naturally available adsorbents are of interest. During recent years, low-cost and locally available adsorbent materials with high adsorption capacities have gained increasing attention [24–27].

The purpose of this work is to study the use of activated carbon nanoparticles from vine wood as an inexpensive and economical new sorbent in the removal of Amoxicillin, Cephalexin, Tetracycline and Penicillin G from aqueous solution. Methods of chemical

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activation of carbon nanoparticles with NaOH, KOH, $ZnCl_2$, and HNO_3 have been studied in order to compare the improvement of the carbon surface features. Different approaches for increasing removal of antibiotics from aqueous solutions have also been investigated.

2. Experimental

2.1. Materials and equipment

All chemicals used in this study were analytical grade reagents from Merck. The vine wood was obtained from Meymeh city. Antibiotics, viz. Amoxicillin, Cephalexin, Tetracycline and Penicillin G (Farabi pharmaceutical company, Isfahan, Iran) were the target analyses. Stock solutions and other solutions were prepared in distilled water.

2.2. Adsorbent

The wood was cut into pieces of 0.5 cm. Then they were washed several times with double distilled water to remove dust and impurities and dried at room temperature for 24 h. The wood was put inside the cruise and its openings were covered with aluminum foil. Then the cruise was placed in an electric furnace for 2 h at 600 °C. In the next step, the produced carbon was powdered and kept in glass containers for the subsequent investigations.

2.3. Carbon activation

For the making of activated carbon, the obtained carbon was mixed separately with NaOH, KOH, HNO_3, $ZnCl_2$ and NaCl solutions [22–25]. The activators of NaOH and KOH were used with a concentration of 5 w/w%. Then, during mixing, the mixtures were gently heated. Activated carbon was washed several times with double distilled water to reach a neutral pH. The absorber was placed inside the vacuum oven for 24 h at 70 °C.

The carbon absorbent and activator solution of $ZnCl_2$ (1, 2 and 3 M) and/or NaCl (2 and 3 M) were kept for 24 h at room temperature. Then, the activated carbon was washed several times with double distilled water. The obtained adsorbents were dried and kept in a vacuum oven at 80 °C for 24 h at room temperature and in sealed glass containers, respectively.

Prior to oxidation with HNO_3, to remove impurities from the adsorbent activated carbon, it was washed with 50 mL HCl (2 M) for 24 h at $<$100 °C. The activated carbon was washed with distilled water and dried in a vacuum oven for 15 h at 150 °C, respectively. Purified activated carbon was added into 30 mL of 5 M HNO_3 solution, which was refluxed for 8 h at 90–95 °C. The mixture was filtered off, and washed with deionized water to become neutral. It was dried in vacuum at 100 °C for 15 h to obtain the carboxylic derivative of activated carbon (AC-COOH).

2.4. Determination of point of zero charge (pH_{pzc}) of adsorbent

Verification on the point of zero charge (pH_{PZC}) was carried out. Initial pH values (pH_i) of 25 mL of 0.1 M NaCl solutions were adjusted in a pH range of 1–8 using HCl or NaOH. Then, 0.2 g of activated carbon was added to each solution. The obtained suspensions were shaken for 24 h. The dispersions were then filtered. The final pH of the solutions (pH_f) was also determined. The value of pH_{PZC} of activated carbon was found from the intersection of the curve of pH_f vs. pH_i with the abscissa.

3. Adsorption experiments

The wavelengths of maximum absorption of Amoxicillin, Cephalexin, Tetracycline, and Pnicillin G are 228, 276, 261 and 290 nm, respectively, which were determined by a UV–vis spectrophotometer (Model 70T-PG Instruments Company). A stock solution of the antibiotics (1000 mg L^{-1}) was prepared by dissolving 0.25 g of the antibiotic in double distilled water. The other antibiotic concentrations were prepared by diluting the stock solution with suitable volumes of double distilled water.

The removal percentage ($R\%$) of antibiotics on activated carbon was calculated using Eq. (1). Also, Eq. (2) was used to calculate the mass of the adsorbed antibiotic per gram of the sorbent (q_e, mg g^{-1}).

$$R\% = \left[\frac{(C_o - C_e)}{C_0}\right] \times 100 \quad (1)$$

$$q_e = \left[\frac{(C_o - C_e)}{m}\right] \times V \quad (2)$$

where C_o is the initial antibiotic concentration (mg L^{-1}), C_e is the equilibrium antibiotic concentration in solution (mg L^{-1}), V is the volume of the solution (L), and m is the weight of the activated carbon in grams [26,27].

HCl and NaOH were used for adjusting the initial pH of samples in order to study of pH effect on the removal efficiency. The pH measurements were made using a pH meter during all the experiments. The activated carbon (0.2 g) was added to 20 mL of 20 mg L^{-1} antibiotic solution in Erlenmeyer flasks. The pH values of the solutions were pH 1–12. The flasks were stirred at room temperature in a digital incubator shaker at 150 rpm. After 24 h, removal of antibiotics was measured by UV–vis spectrophotometer. The effect of activated carbon dosage was investigated in the presence of 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 g L^{-1} of adsorbent modified with NaOH. The pH of the samples was adjusted to pH 2. To determine the effect of initial concentration of the antibiotic in solution, 20 mL of aqueous solutions with concentrations of 20, 30, 50, 80, 100, 150 and 200 mg L^{-1} were prepared. The $R\%$ values were obtained at optimum conditions of 0.4 g L^{-1} sorbent and pH 2.

The contact time of adsorbent and adsorbate plays an important role in the adsorption process. Hence, the effect of contact time on the removal extent of antibiotics by activated carbon was studied in batch experiments at an agitation time of 120, 240, 360, 480, 600, 720 and 840 min. The experimental results were used for kinetic studies.

The effect of temperature on adsorption equilibrium was studied by shaking the mixture of activated carbon for 8 h at temperatures of 35, 45, and 55 °C. The experimental results were used for thermodynamic studies.

3.1. Adsorption isotherms

Adsorption isotherms at a constant temperature 25 ± 2 °C were obtained using 0.4 g L^{-1} of activated carbon in 20 mL antibiotic solution and pH 2 by varying initial concentrations of antibiotic: 20, 30, 50, 80, 100, 150 and 200 mg L^{-1} for 8 h. Eqs. (3) and (4) show Langmuir and Freundlich isotherms, respectively, which are the most common equations to represent the adsorption equilibrium data [28,29]:

$$\frac{C_e}{q_e} = \frac{1}{(q_{max} \times b)} + \frac{C_e}{q_{max}} \quad (3)$$

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \quad (4)$$

where C_e is the equilibrium concentration of antibiotic in solution (mg L^{-1}), q_e is the amount of antibiotics absorbed by activated carbon at equilibrium (mg g^{-1}), q_{max} and b are the Langmuir constants related to adsorption capacity and the energy of adsorption, respectively. A plot of C_e/q_e vs. C_e indicates a straight