Research article

Phenol adsorption on biochar prepared from the pine fruit shells: Equilibrium, kinetic and thermodynamics studies

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ABSTRACT

Biochar samples were prepared from pine fruit shell (PFS) biomass using slow pyrolysis for 1 h at three different temperatures (350, 450 and 550℃). Batch experiments were carried out for the biosorption of phenol onto these biochars. The effect of biosorption experimental parameters such as adsorbent dosage, ionic strength, initial solution pH, contact time and temperatures has been investigated. Experimental equilibrium data were fitted to Langmuir, Freundlich, and Dubinin−Radushkevich (D-R) isotherms by non-linear regression method. The experimental kinetic data were also fitted to Lagergren pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion models by non-linear regression method. Determination coefficient (R^2), chi-squared (χ^2) and error function ($F_{error\%}$) were used to determine the optimum isotherm and kinetic by non-linear regression method. Kinetics results were best described by pseudo-second order model for phenol onto three biochars. Thermodynamic parameters were estimated and implied that the adsorption process is spontaneous and exothermic in nature.

1. Introduction

Phenol has many industrial and non-industrial applications. It is water-soluble, therefore can easily get into wastewater through different types of industrial operations. It is difficult to be eliminated via biological degradation and categorized as a highly toxic organic contaminant to the environment (Podkoscielny and Laszlo, 2007). Therefore, different techniques were adopted to remove phenol from wastewater such as chemical oxidation, biodegradation, membrane filtration and solvent extraction, in addition to the adsorption process, which is preferred over the aforementioned methods for phenol removal due to its high uptake capacity, low cost, and the possibility of regeneration (Alkaram et al., 2009; Yang et al., 2016).

Different materials, either natural or synthetic, have been investigated for the removal of phenol from aqueous solutions via biosorption; which represents the ability of biological materials to remove pollutants from aqueous effluents. Bio-sorbents have high efficiency, selectivity and natural affinity to pollutants. In addition, biosorption is widely used due to their natural availability in environment at low-cost. The biochar derived from agricultural waste such as fruit wastes, coconut shell, scrap tires, bark and other tannin-rich materials, sawdust, rice husk, etc …, could be used as a bio-sorbent (Zhang et al., 2014). Recently, pinecone-derived activated charcoals (Shen et al., 2018) and

magnesium-pretreated cypress sawdust (Haddad et al., 2018) also used as bio-sorbent for removal of Tetrabromobisphenol A and phosphorus, respectively from aqueous solution. These wastes are not used in any industrial area and most probably exploited as fertilizers.

Some studies have focused on biochars prepared from pine trees wastes such as: pine cone shell to remove nickel (Almendros et al., 2015), copper and lead (Almendros et al., 2015; Martín-Lara et al., 2016), pine cone powder for the removal of textile dyes (Mahmoodi et al., 2011), Pinus pinaster to remove phenol (Vazquez et al., 2006, 2007), pine fruit shell for the removal of dyes (Calvete et al., 2010; Fatih, 2015) and pine cone activated carbon to remove lead, hexavalent chromium, phenol and methylene blue (Momoilovic et al., 2011; Duman et al., 2009) from aqueous solutions. Since this waste is available in great quantities in the Mediterranean area, and is of no market value, PFS may constitute promising low-cost adsorbent among biomaterials.

This work, focuses on exploring the ability of PFS (as an environmental-friendly agricultural by-product) to prepare biochar for the removal of phenol from aqueous solutions using batch method. The influence of several variables, such as pyrolysis temperature, adsorbent dosage, ionic strength, pH, contact time and temperature has been investigated. In addition, the kinetics and adsorption isotherms were analyzed.

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2. Experimental

2.1. Biochar preparation

PFS was manually separated from the fruit seeds, and extensively washed with water to remove any dirt or impurities from the surface, dried at $100°C$ for 24 h and then grounded to ≤1 mm size. 50 g of grounded samples were placed in covered crucibles and heated in a tube furnace at different temperatures (350, 450 or $550°C$) under oxygen-limited conditions for duration of 1 h and labeled as: BC350, BC450 and BC550, respectively. The prepared materials were stored in air tight containers for further uses.

2.2. Characterization equipment

Samples preparation was carried out using tube furnace model Protherm-PC 402, (Turkey). Thermal gravimetric analysis (TGA) was conducted using a Netzsch sta 409 PC instrument (Selb Bavaria, Germany). Elemental analysis of carbon, hydrogen and nitrogen was carried out using a Perkin-Elmer model 2400 instrument (Tokyo, Japan). Weighing of samples was carried out using the Precisa 410AM-FR analytical balance (Camlab UK). The pH of the solution was measured using a HI9025 pH-meter (Hanna Instrument, USA). FT-IR spectrum was recorded using Thermo Nicolet NEXUS 670 FTIR spectrophotometer (Tokyo, Japan). The samples were examined by X-ray powder diffractometer with Cu Kα radiation (λ = 1.5418 Å) using PANalytical's X'Pert PRO X-ray diffraction system (Malvern Panalytical, Netherlands) at 40 kV and 30 mA with a step of 0.02° over the range 4–60°. The shape and surface morphology of the samples were examined using FEI inspect F50 scanning electron microscopy (SEM) (Tokyo, Japan). Shaking of samples was carried out using the GFL 1083 shaker equipped with a thermostat. Phenol concentrations were determined using UV–Vis Cary 100 Varian spectrophotometer (Varian, UK).

The physicochemical parameters: yield%, ash content, moisture%, pH and pH zero-point charge (pH$_{zpc}$) of biochars were determined according to the procedures given by our previous publication (El Hanandeh et al., 2016).

2.3. Specific surface area determination

Pore structure and biochar surface area of the samples were measured with a Nova 2200 e Surface Area and Pore size Analyzer (Quantachrome Corp. Boynton Beach, FL, USA), from analyses of nitrogen gas adsorption isotherms at 77 K. Each sample was degassed for 8 h at $105°C$.

The specific surface area was determined by Brunauer, Emmett, and Teller (BET) equation, and the total pore volume was calculated from the near saturation uptake (P/Po = 0.99). The mesopore volume, mesopore surface area, and pore size distribution were calculated by the Barret, Joyner, and Halenda (BJH) method.

2.4. Biosorption experiments

The effects of adsorbent dose, ionic strength, contact time, initial pH, and adsorbent temperature, were investigated. To determine the effect of adsorbent dosage on the adsorption of phenol, concentrations of 0.05–0.50 g/50 mL adsorbent were used while keeping other experimental conditions constant, (phenol initial concentration of 50 mg/L, pH 6.5, at 25 °C). The effect of ionic strength was determined by using different NaCl concentrations of 0.01, 0.05, 0.10, 0.15 and 0.20 M (0.5 g/50 mL adsorbent, pH 6.5, at 25 °C). Time was varied from 5 to 270 min in order to optimize the contact time, while other experimental conditions were kept constant (phenol initial concentration of 50 mg/L, 0.5 g/50 mL adsorbent, pH 6.5, at 25 °C).

The effect of the pH on phenol adsorption was studied at different pH values (2.0, 6.5 and 10.0), at phenol initial concentration of 50 mg/L, and adsorbent dose of 0.5 g/50 mL, at 25 °C. The pH of the solution was adjusted using 0.1M HCl or 0.1M NaOH. For the determination of the effects of initial phenol concentration, 20,40, 50, 60, 70, 80 and 100 mg/L phenol solution concentrations were studied at pH 6.5, 0.5 g/50 mL adsorbent, at 25, 35 and 45 °C. Temperature effect experiments were performed using a concentration of 50 mg/L phenol solution and 0.5 g/50 mL of biochar at temperature of 25, 35 and 45 °C, for a period of 24 h.

In batch experiments, stock phenol solution (1000 ppm) was used to prepare seven different phenol solutions of 20, 40, 50, 60, 70, 80 and 100 mg/L, each solution was added separately to a stoppered volumetric flask containing 0.5 g of biochar (BC350, BC450 or BC550). Volumetric flasks were kept in an electrically thermostatic reciprocating shaker at 250 rpm at different temperatures (25, 35 and $45°C$) for 24 h. The pH of the solution was monitored by adding 0.1 M HCl or 0.1 M NaOH solution as required. After that, solutions in the flasks were allowed to settle for a while and the clear aqueous was withdrawn, centrifuged and filtered by micro filter. Absorbance was measured at the corresponding (λ_{max} = 296 nm) wavelength.

All experiments were performed in triplicates. The amount of adsorbed phenol at equilibrium, q_e (mg/g) and the percentage removal of adsorption (%R) was calculated as follows:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

$$\%R = \frac{(C_o - C_e)}{C_o} \times 100 \tag{2}$$

Where C_o and C_e are the initial and equilibrium concentrations of phenol (mg/L), V = volume of the solution (L), and m = weight of the adsorbent (g).

2.5. Analysis

The time dynamics of adsorption process was studied to understand how the mechanism of adsorption depends on the physical and/or chemical characteristics of adsorbents as well as on the mass transport process. Adsorption kinetic of adsorption is one of the most important characteristics to be responsible for the efficiency of adsorption diffusion. The kinetic parameters are helpful for the prediction of adsorption rate, which gives important information for designing and modeling the processes (Ahmed and Theydan, 2013). Pseudo-first order and pseudo-second order, Elovich and intraparticle diffusion kinetic models were tested to investigate the best-fit of the experimental data obtained from phenol biosorption.

Lagergren pseudo-first-order model (Lagergren, 1898):

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{3}$$

Pseudo-second order model (Ho, 2006):

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{4}$$

Elovich equation ((Low, 1960):

$$q_t = \left(\frac{1}{\beta}\right)ln(\alpha\cdot\beta) + \left(\frac{1}{\beta}\right)ln(t) \tag{5}$$

Intraparticle diffusion equation (Weber and Morris, 1963):

$$q_t = k_{id}t^{0.5} + C \tag{6}$$

Where q_t is the amount of phenol adsorbed at time t (mg/g), k_1 is the pseudo-first-order rate constant (min^{-1}), k_2 is the equilibrium rate constant of pseudo-second order adsorption (g/mg·min), α is the initial adsorption rate (mg/g· min), β is the desorption constant (g/mg) during any one experiment, (mg/g· min), k$_{id}$ is the intraparticle diffusion rate