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Adsorption of 2,4,6-trichlorophenol from aqueous solution onto activated carbon derived from *loosestrife*

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ABSTRACT

An activated carbon was prepared from the stalk of the scrap aquatic plant *loosestrife*, by H_3PO_4 activation and then was evaluated for its ability to adsorb 2,4,6-trichlorophenol (TCP). The effects of solution pH, agitation time, TCP initial concentration, and temperature on TCP adsorption were investigated. The equilibrium adsorption data of TCP on activated carbon were analyzed by Langmuir, Freundlich and Temkin isotherm models. The Temkin model gave the best correlation with the experimental data. The adsorption was found to follow the pseudo-second-order kinetics. The intraparticle diffusion model was used to determine the mechanism of the adsorption process. Thermodynamic parameters such as standard enthalpy (ΔH^o), standard entropy (ΔS^o), and standard free energy (ΔG^o) were obtained. Adsorption of TCP is exothermic with ΔH^o at −12.87 kJ/mol.

1. Introduction

Highly chlorinated phenol derivatives, such as 2,4,6-trichlorophenol (TCP), have been commonly used as pesticides, herbicides, wood preservatives, and defoliants since the early 1930 s [1]. Wastewaters from pesticide, wood, pharmaceuticals, dye manufacturing, paper and pulp industries as well as drinking water treatment are the most important chlorophenol pollution sources [2]. Adverse effects on the human nervous system and many health disorders have been reported to be caused by 2,4,6-TCP, such as respiratory effects, cardiovascular effects, gastrointestinal effects as well as cancer [3–5]. Evidence of structural chromosomal aberrations in both somatic and germ cells is also available for 2,4,6-TCP [3]. As a result of its high toxicity, carcinogenic properties, and structural stabilization in the environment, the removal of 2,4,6-TCP from the environment is an important remediation goal.

Various treatment technologies have been applied to remove chlorophenols from aqueous solutions, including biological treatment [6], photochemical treatment [7], air stripping and incineration [8], adsorption technology using activated clay [4] as well as activated carbons generated from various sources such as oil palm shell [9], polyethylene terephthalate [10], rattan sawdust, and rice straw [11,12]. Among these treatment methods, activated carbons with high surface areas are some of the most effective adsorbents in treating wastewaters containing this pollutant. However, the high cost of the raw materials such as coal used in producing activated carbons has limited the extensive use of these adsorbents, which is a major consideration before wide environmental application is feasible [13]. Recently, research interest has been transferred to using low cost activated carbons in wastewater treatment.

From the literature, activated carbons prepared from low cost starting materials, mainly agricultural by-products, include coconut shells [14–16], peach stones [17], Tamarind wood [18], olive kernels [19], bamboo [20], rice husk [21], coffee endocarp [22,23] and bean pods [24]. Although most of these materials are available for production of activated carbons, two disadvantages still limit the use of these methods: first, most of these starting materials come from xerophiles (drought-tolerant plants), the inner structure of which is compact and thus activated carbons prepared from these sources usually have relatively low surface areas as well as small pore numbers; second, none of these agricultural by-products are broadly available and many of them have seasonal limitations. Considering all these factors, new plant materials used for producing activated carbons should be hydrophytes, in order to make an adsorbent with a high surface area, and they should be widely available.

Loosestrife, which belongs to the Lythraceae, is a perennial plant which can be seen in many tropical and subtropical areas not only in China but also in many countries across the world. A hardy and beautiful plant with varieties such as purple *loosestrife* and crape myrtle, *loosestrife* is widely planted as a landscape plant. After use, most of the adult plants are simply discarded or burned, which is a waste of resources and can lead to environmental pollution. Hence, recycling of such solid waste is imperative. As a hydrophyte, the inner structure of the stems of *loosestrife* are thin and lacunose, which can be a huge advantage when used to produce quality activated carbons with high surface areas and abundant pores.

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The goal of this study was to find the optimum production conditions for making activated carbon from *loosestrife* and to investigate the adsorption potential of *loosestrife* based activated carbon (LMC) for 2,4,6-TCP. The equilibrium and kinetic data of the adsorption studies were analyzed to understand the adsorption kinetics, isotherms, and thermodynamics, as well as the mechanism of 2,4,6-TCP adsorption on the prepared activated carbon.

2. Materials and methods

2.1. 2,4,6-Trichlorophenol

2,4,6-Trichlorophenol (TCP) used as an adsorbate in this study was supplied by Tianjin Guangfu chemical reagents Co.(Tianjin, China), and was used without any purification. The molecular weight of 2,4,6-TCP is 197.45 g/mol and it has a chemical formula of $C_6H_3Cl_3O$.

2.2. Preparation of activated carbon

The *loosestrife* used for preparation of activated carbon in this study was collected from a local hydrophyte research institute in Shandong province, China. The precursor was first cut into small pieces and washed with distilled water five times to remove surface adhered particles and water-soluble impurities and then dried. The dried *loosestrife* was then crushed in a laboratory mill. After crushing, the material was dried again and immersed in 40 wt.% phosphoric acid solution at a ratio of precursor: H_3PO_4 of 1:2 (w/w). After soaking for 12 h at room temperature, the mass was then transferred to a muffle furnace and carbonized. Since mesopores together with micropores in the activated carbon will enhance its adsorption capacity, especially for large molecules of adsorbates [25], we chose to control the conditions to obtain *loosestrife* activated carbon (LMC) with a highly mesoporous structure. The formation of the carbon's porous networks was greatly influenced by process of the activation [14] and the activation temperature and time should be controlled in order to obtain the highest surface area and best pore volume. After a series of experiments to investigate different conditions, in this study the mass was heated slowly from room temperature to 450 °C and held for 1 h. Then the activated product was cooled to room temperature and washed repeatedly with hot distilled water and 0.1 mol/L NaOH until the pH of its filtrate reached 6–7. The resulting activated carbon was then dried at 120 °C for 12 h in a vacuum oven. The resulting LMC was dried at 120 °C for 2 h and the dried product was then sieved to 160–180 mesh by standard sieves (Model Φ200) before storage in a desiccator for later use.

2.3. Batch adsorption equilibrium studies

Batch adsorption equilibrium experiments were performed to investigate the effects of initial concentration, adsorbent dose, solution pH, and contact time on the adsorption uptake. The pH was adjusted with 0.1 mol/L NaOH and 0.1 mol/L HCl solutions. In each batch experiment, a 250 mL stoppered conical flask containing 100 ml 2,4,6-TCP of certain concentration was agitated mechanically at the controlled temperature in a isothermal water bath shaker to reach equilibrium, then the mixture was filtered through a syringe filter to minimize interference between the carbon fines and the analysis. The amount of 2,4,6-TCP adsorbed at equilibrium, q_e (mg/g), was calculated by the following equation:

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

where C_0 and C_e are the 2,4,6-TCP concentrations at the initial time and at equilibrium (mg/L), respectively. V is the volume of the solution (L) and W is the mass of adsorbent used (g).

2.4. Effect of solution temperature

To study the effect of temperature on 2,4,6-TCP adsorption, the experiments were studied at 20, 35 and 50 °C using different adsorption isotherms, with different concentrations, while other variables such as activated carbon dose, rotation speed remained constant and the solution pH was initial without any adjustment.

2.5. Batch kinetic studies

The kinetic experiments were similar to the batch equilibrium tests, however, the samples were taken at certain time intervals, ranging from 1 to 600 min. The amount of 2,4,6-TCP adsorbed (from initial concentrations of 50 mg/L, 100 mg/L and 150 mg/L) at time t, q_t (mg/g), was calculated as follows:

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

where Ct (mg/L) is the concentration of 2,4,6-TCP at any time t (min).

2.6. Desorption studies

Desorption studies were conducted using ethanol desorption technique. After, batch equilibrium tests were performed under the conditions: the adsorbent dose = 0.10 g/100 mL, the concentration of 2,4,6-TCP = 150 mg/L, t = 24 h, the solution pH was kept original, the adsorbent was filtered and gently washed with distilled water to remove any unadsorbed 2,4,6-TCP. Then the sample was immediately mixed with 100 mL 95 vol.% ethanol solution, and agitated at 25 ± 1 °C for 24 h. The concentration of adsorbate adsorbed at equilibrium was calculated as the difference between the initial and equilibrium concentration ($C_0 - C_e$). After desorption, the concentrations of TCP desorbed, C_{de} (mg/L) was similarly measured using the UV–vis spectrophotometer. The percent desorption was calculated using Eq. (3).

$$\text{Desorption}(\%) = \frac{C_0 - C_e}{C_{de}} \times 100 \quad (3)$$

2.7. Analytical methods

Structural characterization of the *loosestrife* activated carbon was done by N_2 adsorption isotherm at 77 K using an automated surface area and pore size analyzer (Quantachrome Corporation, QUADRASORB SI, USA). The specific surface area (SBET) was calculated by the Brunauer–Emmett–Teller (BET) method. The BET surface area, total pore volume (V_T), average pore radius (D), mesopore volume (V_{me}) and micropore volume (V_{mi}) were obtained from the N_2 adsorption isotherms. The DFT method was used in the pore size distribution determination and the t-plot method was applied to calculate the pore volumes.

The Boehm titration method was used to qualitatively and quantitatively identify the surface functional groups of the activated carbons [26]. First, 0.5 g of LAC was placed in 25 mL of 0.1 mol/L solutions of sodium hydroxide, sodium carbonate, sodium bicarbonate and hydrochloric acid. The sealed vials were shaken at room temperature for 24 h. Then each solution was filtrated and the excess base or acid was back-titrated with HCl or NaOH. The numbers of all acidic sites were calculated under the assumption that NaOH reacts with carboxylic groups, HCl reacts with basic surface functional groups, Na_2CO_3 reacts with carboxylic and lactonic groups and $NaHCO_3$ reacts only with carboxylic groups.

The pH value at the zero point of charge (pH_{zpc}) on the surface of LAC was estimated by mass titration [27].

The pH of each solution was measured with a digital pH meter (Model pHS-3C). The initial and final concentrations of 2,4,6-TCP