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Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2,4,6-trichlorophenol on oil palm empty fruit bunch-based activated carbon

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ABSTRACT

The adsorption characteristics of 2,4,6-trichlorophenol (TCP) on activated carbon prepared from oil palm empty fruit bunch (EFB) were evaluated. The effects of TCP initial concentration, agitation time, solution pH and temperature on TCP adsorption were investigated. TCP adsorption uptake was found to increase with increase in initial concentration, agitation time and solution temperature whereas adsorption of TCP was more favourable at acidic pH. The adsorption equilibrium data were best represented by the Freundlich and Redlich–Peterson isotherms. The adsorption kinetics was found to follow the pseudo-second-order kinetic model. The mechanism of the adsorption process was determined from the intraparticle diffusion model. Boyd plot revealed that the adsorption of TCP on the activated carbon was mainly governed by particle diffusion. Thermodynamic parameters such as standard enthalpy (ΔH°), standard entropy (ΔS°), standard free energy (ΔG°) and activation energy were determined. The regeneration efficiency of the spent activated carbon was high, with TCP desorption of 99.6%.

1. Introduction

Cholorophenols are a group of chemicals in which chlorines (between one and five) have been added to phenol. The main pollution sources containing chlorophenols are the wastewaters from pesticide, paint, pharmaceutics, wood, paper and pulp industries as well as water disinfecting process [1]. Chlorophenols are weak acids which permeate human skin by in vitro and are readily absorbed by gastro-intestinal tract [2]. 2,4,6-Trichlorophenol (TCP) is a toxic, mutagenic and carcinogenic pollutant. It is found in the emissions from fossil fuel combustion, municipal waste incineration and chlorination of water containing phenol or certain aromatic acids with hypochlorite or during disinfection of water [3]. TCP has been also reported to cause adverse effects on human nervous system and respiratory problems such as chronic bronchitis, cough and altered pulmonary function [4]. The stable C—Cl bond and the position of chlorine atoms relative to the hydroxyl group are responsible for their toxicity and persistence in the biological environment [5]. Due to its high toxicity, carcinogenic properties, structural stabilization and persistence in the environment, the removal of TCP from the environment is crucial.

From the literature, various treatment methods have been applied to remove phenolic compounds from aqueous solutions, such as biological treatment using anaerobic granular sludge [1], catalytic wet oxidation [3], photochemical treatment [6], adsorption technology using activated clay [4], fuel oil fly ash [7] and activated carbons prepared from various precursors such as rattan sawdust, coconut shell and rice straw [8–10]. Other treatment technologies include air stripping, incineration, ion exchange and solvent extraction [4]. Adsorption on activated carbon is one of the most effective and widely used techniques in treating high strength and low volume of phenolic wastewaters [2]. Commercially available activated carbons like F300 granular activated carbons from Calgon Corp, Pittsburgh, PA are commonly used for the adsorption of chlorophenols [11]. However, the usage of activated carbon has been limited by its high cost due to the use of non-renewable and relatively expensive starting material such as coal, which is a major economic consideration [12]. This has prompted a growing research interest in the production of low cost activated carbons especially for application concerning wastewater treatment.

Recently, focus has been given on the preparation of activated carbons from agricultural by-products such as almond shell [13], bean pod [14], rice husk [15], cherry stone [16], date palm seed [17], sunflower seed hull [18], waste apricot [19], oil palm fibre [20], bamboo [21], plum kernel [22] and coconut husk [23,24]. Besides, not many studies have been reported in the literature on the adsorption of TCP using agricultural waste-based activated carbon. In practice, the feasibility of activated carbon adsorption process depends on many factors including the feasibility of regeneration and disposal of spent activated carbon. Therefore, the spent activated carbon

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should have high regeneration efficiency for wider application of carbon adsorption process. Solvent regeneration in which carbon loss by attrition is negligible has been shown to be an attractive alternative. Hamdaoui et al. [25] in their study on regenerating granular activated carbon saturated with *p*-chlorophenol revealed that the desorption rate was enhanced by the addition of ethanol. Ethanol desorption technique was also reported to be suitable for regenerating activated carbons prepared from waste tires which showed high regeneration efficiencies for phenol and reactive dyes [26].

In the present investigation, oil palm empty fruit bunch-based activated carbon prepared under optimum conditions was evaluated for its potential to remove TCP from aqueous solutions. The equilibrium and kinetic data of the adsorption process were then analyzed to study the adsorption isotherms, kinetics, thermodynamics and mechanism of TCP on the prepared activated carbon. The feasibility of regenerating the spent activated carbon using ethanol desorption was then determined.

2. Materials and methods

2.1. Activated carbon preparation

The oil palm empty fruit bunch (EFB) used for preparation of activated carbon in this study was obtained from a local palm oil mill. The activated carbon preparation procedure was referred to our previous work [24] where the pre-treated EFB was loaded in a stainless steel vertical tubular reactor placed in a tube furnace and the carbonization of the precursor was carried out by ramping the temperature from room temperature to 700 °C with heating rate of 10 °C/min and hold for 2 h. Throughout the carbonization process, purified nitrogen (99.995%) was flown through at flow rate of 150 cm^3/min. The activated carbon was prepared using physiochemical activation method consisting of potassium hydroxide (KOH) treatment followed by carbon dioxide (CO_2) gasification by applying the optimum operating conditions which gave a high activated carbon yield and TCP uptake. The char produced from the carbonization process was mixed with KOH pallets with KOH:char impregnation ratio (IR) of 2.8:1. The dried mixture was then activated under the same condition as carbonization, but to a final temperature of 814 °C. Once the final temperature was reached, the nitrogen gas flow was switched to CO_2 and activation was held for 1.9 h. The activated product was then cooled to room temperature under nitrogen flow and then washed with hot deionized water and 0.1 M HCl until the pH of the washing solution reached 6–7.

2.2. 2,4,6-Trichlorophenol

2,4,6-Trichlorophenol supplied by Sigma–Aldrich (M) Sdn Bhd, Malaysia was used as the adsorbate in this study, and was not purified prior to use. TCP has a chemical formula of $C_6H_3Cl_3O$, with molecular weight of 197.46 g/mol. The chemical structure of TCP is shown in Appendix A. Deionized water supplied by USF ELGA water treatment system was used to prepare all the reagents and solutions.

2.3. Batch equilibrium studies

Batch equilibrium tests were carried out for adsorption of TCP on the activated carbon prepared. The effects of TCP initial concentration, agitation time, solution pH and temperature on the adsorption uptake were investigated. The sample solutions were withdrawn at equilibrium to determine the residual concentrations. The solutions were filtered using syringe filter prior to analysis in order to minimize interference of the carbon fines with the analysis. The concentrations of TCP in the supernatant solutions before and after adsorption were determined using a double beam UV–vis spectrophotometer (Shimadzu UV-1601, Japan) at its maximum wavelength of 296 nm. The TCP uptake at equilibrium, q_e (mg/g), was calculated by Eq. (1).

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

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

2.3.1. Effect of TCP initial concentration and agitation time

In order to study the effect of TCP initial concentration and contact time on the adsorption uptake, 100 mL of TCP solutions with initial concentrations of 25–250 mg/L were prepared in a series of 250 mL Erlenmeyer flasks. 0.1 g of the EFB-based activated carbon was added into each flask covered with glass stopper and the flasks were then placed in an isothermal water bath shaker at constant temperature, with rotation speed of 120 rpm, until equilibrium point was reached. In this case, the solution pH was kept original without any pH adjustment.

2.3.2. Effect of solution temperature

The effect of solution temperature on the adsorption process was studied by varying the adsorption temperature at 30, 40 and 50 °C by adjusting the temperature controller of the water bath shaker, while other operating parameters such as activated carbon dosage and rotation speed were remained constant while the solution pH was original without any adjustment.

2.3.3. Effect of solution pH

The effect of solution pH on the TCP removal was examined by varying the initial pH of the solutions from pH 2 to 12. The pH was adjusted using 0.1 M HCl and/or 0.1 M sodium hydroxide (NaOH) and was measured using pH meter (Model Ecoscan, EUTECH Instruments, Singapore). The TCP initial concentration was fixed at 175 mg/L, with activated carbon dosage of 0.1 g/100 mL and solution temperature of 30 °C. The TCP percent removal was calculated using Eq. (2).

$$\text{Romoval}\,(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

2.4. Batch kinetic studies

The procedure of kinetic adsorption tests was identical to that of batch equilibrium tests, however the aqueous samples were taken at preset time intervals. The concentrations of TCP were similarly measured. The TCP uptake at any time, q_t (mg/g), was calculated by Eq. (3).

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (3)$$

where C_t (mg/L) is the liquid-phase concentration of TCP at any time, t (h).

2.5. Regeneration of activated carbon

The feasibility of regenerating the spent activated carbon saturated with TCP was evaluated using ethanol desorption technique [26]. Initially, batch equilibrium tests were performed on the fresh activated carbons prepared where 100 mL of TCP solution with initial concentration of 200 mg/L were placed in 250 mL Erlenmeyer flasks. 0.1 g of the fresh EFB-based activated carbon was added into the flask and placed in an isothermal water bath shaker at