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# Nitrobenzene-adsorption capacity of NaOH-modified spent coffee ground from aqueous solution

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## ABSTRACT

Adsorption of nitrobenzene (NB) on the NaOH-modified spent coffee ground (NaOH-SCG) was examined and the effects of contact time and adsorbent dose were investigated. The adsorption isotherm of NB on NaOH-SCG was compared with that of untreated SCG. The results from our study showed that the removal efficiencies of NB (25 mg/L) on SCG and NaOH-SCG after 2 h were 91.8% and 98.2%, respectively. The adsorption rate was very quick with the equilibrium of adsorption being achieved within about 30 min. The values of parameters obtained for NB from the Langmuir isotherm saturated adsorption amount and adsorption equilibrium constant were 117.2 mg/g, 0.0753 L/mg for SCG and 169.4 mg/g, 0.1815 L/mg for NaOH-SCG. NaOH-SCG (0.44 mmol/g) has fewer acidic functional groups than SCG (1.49 mmol/g). Therefore, the surface polarity of NaOH-SCG is low, thus makes this material more hydrophobic. The strong hydrophobicity of the NaOH-SCG surface might explain the high adsorption capacity for NB. As a result, this study has found that the NaOH-modified spent coffee ground has high adsorption ability for NB.

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## 1. Introduction

Nitrobenzene (NB), a carcinogenic pollutant, is widely used in the production of different types of products including dyes, plastic, pesticides, explosives, pharmaceuticals, and intermediates in chemical synthesis industries for years [1,2]. After use, NB in solution is generally discharged into wastewater treatment plants where a large proportion of it cannot be removed by conventional treatment processes and is discharged into the surrounding aquatic environment [3]. The chemical structure and properties of NB is shown in Table 1. NB may present high risks to ecosystem and human health even at low concentrations [4–6]. It was reported that the tolerance limit of NB in the water and organisms was decreased from 17 to 10 µg/L in order to promote public health and environmental protection by the Office of Water, Science and Technology in the U.S. Environmental Protection Agency (EPA) in 2014 [7].

Therefore, a variety of possible treatment technologies such as bioremediation [8], chemical oxidation [9,10], catalyzed oxidation [11–13], electrochemical methods [14], and adsorption [15–17] have been adopted to remove aqueous NB. Particularly, adsorption with activated carbon materials is considered to be one of the

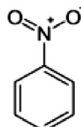
most economical and efficient methods for controlling the NB in water [18]. A large number of materials have been widely used as an adsorbent for the adsorption of NB, such as nanocrystalline HAP [1], MCM-41 [3], marine sediments [5], konjac glucomannan gel containing activated carbon [19], carbon materials released during the combustion of woody biomass [20], activated sludge modified by cetyltrimethylammonium bromide [21], and lipid adsorption material [22].

On the other hand, agricultural products, by-products and wastes are the most common raw materials being studied for this purpose, since they are renewable, usually available in large amounts and potentially less expensive than other materials to manufacture a diverse of adsorbents [23]. Among agricultural wastes, spent coffee ground is the waste residue obtained from the treatment of coffee with hot water or steam for extracting flavor substances. It has been estimated by the U.S. Department of Agriculture (USDA) that the production of spent coffee ground was approximately 4.0 million tons in 2011 in the whole world [24]. Part of it is reused as compost, fuel source and animal feed, most of the coffee grounds are burned as waste. A few studies have reported that spent coffee ground can be used as an adsorbent for the removal of organic pollutants from aqueous solutions. Hirata et al. [25] employed raw coffee grounds to produce adsorbents and compared conventional thermal treatment in an oven to microwave carbonization. The produced adsorbents were efficient for MB adsorption, with the microwave treatment improving

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**Table 1**  
Chemical structure and properties of nitrobenzene.

CAS Registry Number	98-95-3
Chemical structure	
Chemical formula	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>
Molar mass	123.06 g/mol
Density	1.199 g/cm <sup>3</sup>
Solubility in water	0.19 g/100 mL (at 20 °C)
λ <sub>max</sub>	268 nm

adsorption capacity in comparison to conventional carbonization. Namane et al. [26] employed spent coffee ground treated with zinc chloride and phosphoric acid for the adsorption of phenol and dyes (acid blue and basic yellow). The produced activated carbons were comparable to a commercial product in terms of its adsorption capacity, and the produced activated carbon presents a better affinity for basic dye in comparison to the commercial products. Franca et al. [23] studied the kinetics and equilibrium of methylene blue adsorption by spent coffee grains. The experimental saturated adsorption amount and the adsorption equilibrium constant for methylene blue were 18.73 mg/g and 0.2687 L/mg, respectively. The experimental data indicates that spent coffee grains are suitable candidates for use as adsorbents in the removal of methylene blue dye. In this research, to the best of our knowledge, the removal of NB spent coffee ground as an adsorbent have not been reported.

The objective of this research was to investigate the removal of NB from aqueous solution by using NaOH-modified spent coffee ground. The influence of several parameters, such as contact time and adsorbent dose were investigated. The kinetics and adsorption equilibrium of NB for NaOH-modified spent coffee ground were obtained from batch experiments.

## 2. Materials and methods

### 2.1. Materials

The adsorbent spent coffee ground (SCG) used in this work was obtained from Starbucks Corporation in China. SCG was produced from coffee beans of China and it was used as adsorbent to remove NB from aqueous solution. In order to investigate the effect of functional groups on the surface of SCG, NaOH-modified SCG was prepared according to the reported method [27]. SCG (10 g) was maintained for 24 h in 250 mL 20% NaOH solution with a stirring speed of 165 rpm and at ambient temperature. The modified SCG by NaOH was labeled NaOH-SCG. After decantation and filtration, the NaOH-SCG was obtained and then this adsorbent was washed by deionized water extensively before drying and storage. NB was purchased from Lingfeng Chemical Co., Shanghai, China. NB was dissolved into deionized water to prepare stock solutions. All chemicals used in this study were of analytical grade, which solutions were being prepared using deionized and distilled water. To adjust the pH, HCl (0.1 M) and NaOH (0.1 M) solutions were used.

### 2.2. Physical and chemical characteristics of SCG and NaOH-SCG

The surfaces of SCG and NaOH-SCG were observed by using a Scanning Electron Microscope (SEM), S-3400 N (Hitachi Ltd. Tokyo, Japan). X-ray diffraction (XRD) studies were carried out with an X-ray Diffractometer 1730 (Philips Ltd. Amsterdam, Netherlands) using Cu K $\alpha$  radiation. Patterns were recorded from 10° to 80° 2 $\theta$  at a scan rate 1°/min. The BET surface area and pore distribution of

SCG and NaOH-SCG were measured using a surface analyzer AUTOSORB 6AG (Yuasa Ionics Co., Osaka, Japan). The BET surface areas and the micropore surface areas were evaluated using the *t*-plot method based on N<sub>2</sub> adsorption isotherms [28]. The surface areas of mesopores and macropores were calculated by subtracting the micropore surface areas from the BET surface area. The total pore volume was calculated by using density functional theory (DFT) based on the N<sub>2</sub> adsorption isotherms [29]. The numbers of acidic functional groups and basic sites on the surface of SCG and NaOH-SCG were determined by using the method developed by Boehm [30]. Acidity was determined by mixing 0.6 g of either SCG or NaOH-SCG with 15 mL of NaHCO<sub>3</sub> (0.1 M), Na<sub>2</sub>CO<sub>3</sub> (0.05 M) or NaOH (0.1 M) solution in a well-sealed flask. The mixture was then shaken for 48 h at 25 °C and 165 rpm. An aliquot of the solution for each sample was back titrated with HCl (0.1 M). The NaHCO<sub>3</sub> neutralizes only the carboxylic groups on the carbon surface, whilst the Na<sub>2</sub>CO<sub>3</sub> does the carboxylic and lactonic, and NaOH reacts with the carboxylic, lactonic and phenolic groups. Accordingly, the difference between the groups neutralized by NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> are lactones, whereas the difference between those neutralized by Na<sub>2</sub>CO<sub>3</sub> and NaOH are the phenolic groups. The same procedure was carried out for the mixtures of 0.5 g of either the SCG or NaOH-SCG and 15 mL of HCl (0.1 M) solution to determine the basic sites of the sample surface. The remaining HCl solution was titrated with NaOH (0.1 M) after neutralization. The point of zero charge (pH<sub>pzc</sub>) for the SCG before and after treatment of NaOH was determined using the pH drift method [31]. A 0.01 M NaCl solution was aliquoted (50 mL) into a series of flasks. The initial pH (pH<sub>i</sub>) was adjusted from 1.98 to 13.25 by the addition of 0.1 M NaOH or HCl. A 0.1 g sample of either SCG or NaOH-SCG was added to each flask, followed by agitation for 48 h. Then, the final pH (pH<sub>f</sub>) of the mixtures was measured. The pH<sub>pzc</sub> was defined as the point at which the curve determined by pH<sub>f</sub>–pH<sub>i</sub> crossed the axis pH<sub>i</sub> = pH<sub>f</sub>.

### 2.3. Procedure of adsorption experiment

The adsorption features of the adsorbents (SCG and NaOH-SCG) were investigated as a function of contact time, initial pH and adsorbent dose. The adsorption equilibrium and kinetics were obtained from batch experiments, using 100 mL flasks with a stopper containing 25 mL of NB solutions. After shaking the flasks for pre-determined time intervals, the mixture was filtered using a silica filter, and the concentration of NB in the filtrate was determined from the absorbance at 268 nm measured with an ultraviolet visible spectrophotometer V-550 (Jasco Co., Tokyo, Japan). Three replicate runs were carried out for each experimental treatment. The NB amounts on the adsorbents were calculated by difference between the initial and the equilibrium NB concentrations in the solution. The removal ratio was calculated by dividing the amount of NB adsorbed on SCG and NaOH-SCG by the initial amount of NB in the solution.

### 2.4. Adsorption kinetics

The controlling mechanism of the adsorption process was investigated by using two kinetic models: pseudo-first-order and pseudo-second-order models. The kinetic rate equations can be written as:

$$\frac{dq_t}{dt} = (q_e - q_t)^n \quad (1)$$

where  $q_e$  and  $q_t$  correspond to the amount of NB adsorbed per unit mass of adsorbent (mg/g) at equilibrium and at time  $t$ , respectively, and  $k_n$  is the rate constant for  $n$ th order adsorption ( $k_n$  units are 1/min for  $n = 1$  and g/mg min for  $n = 2$ ). The linearized integrated forms of the equations are:

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