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Evaluation of AC/ZnO composite for sorption of dichloromethane, trichloromethane and carbon tetrachloride: kinetics and isotherms

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ABSTRACT

The present work reports on the efficiency of activated carbon loaded with zinc oxide nanoparticles (AC/ZnO) for removing dichloromethane, trichloromethane and carbon tetrachloride from aqueous solutions. Waste tires were used as a raw material for the production of activated carbon (AC) by thermo-chemical process. Zinc oxide nanoparticles were loaded into AC by using $Zn(NO_3)_2.6H_2O$. The AC/ZnO composite has been characterized by BET analyzer, scanning electron spectroscope, energy dispersive X-ray spectroscope, FTIR spectrophotometer, and X-ray diffraction. Batch experiments were conducted under various adsorbent dosages, initial concentrations and contact time. Rapid adsorption was observed with adsorption capacity of 6.67 mg/g for dichloromethane, 11.91 mg/g for chloroform and 16.10 mg/g for carbon tetrachloride. The equilibrium was obtained in 20 min of contact time. The adsorption of these pollutants onto AC/ZnO was described well by the pseudo second-order model, and the hydrophilic fraction adsorption fitted the intraparticle diffusion model. Freundlich and Langmuir models were used to evaluate the process, and the Langmuir adsorption isotherm model fitted the data better than other models. The reusability of the composite was proved when no significant decrease in its adsorption capacity was observed even after several times of regeneration.

1. Introduction

Hazardous volatile organic compounds (VOCs) are usually used as solvents, cleaning agents, coating agents, and extractants in different industries. They are released from various pharmaceutical, chemical, petrochemical and allied industries [1]. Chloromethanes are the most common environmental contaminants of worldwide concern. They are commercially produced, and used for purposes including the manufacture of herbicides, plastics, and solvents. Uses outside the chemical industry include solvent degreasing in the automotive and aerospace industries, dry cleaning solvents in the garment industries and precision solvent cleaning in the electronic industries [2]. These compounds, when emanated into the environment from the industrial exhaust gases or wastewater streams, present direct and serious hazards to all living organisms. Chlorinated hydrocarbons are considered hazardous pollutants due to their harmful effects on the environment and health. They contribute to the pollution of soil, water bodies and air, to the decaying of the stratospheric ozone layer and to smog formation besides generating harmful odors leading to chronic toxicity in humans, animals and vegetation [3,4]. Thus, it is important to eliminate these compounds before discarding the wastewater into the environment.

Techniques such as air stripping, thermal oxidation, catalytic oxidation, photocatalytic degradation, ultraviolet (UV) oxidation, biofiltration, absorption, adsorption, condensation, biological treatment, and membrane separation have been developed for chloromethanes and their recycling treatment [5,6]. Among them, adsorption technology is widely considered the most applicable technique for the removal of VOCs. However, an appropriate cost-effective material for VOCs capture is important. The most widely used adsorbent among the various adsorbents for VOCs adsorption is activated carbon because of its low cost, high surface area, and unique microporosity [7]. ACs with micropores showed high adsorption performance [8]. Adsorption with activated carbon (AC) has been widely used for the removal of vapor organic pollutants [9]. Transition metal oxide such as copper oxide (CuO and Cu_2O), iron oxide (FeO, Fe_2O_3 or Fe_3O_4) and zinc oxide (ZnO) nanoparticles have special physicochemical properties which have arisen from the quantum size effect and high specific surface area [10,11]. Zinc oxide nanoparticles impregnated on activated carbon is considered a non-toxic and green adsorbent [12]. Production of activated carbon from waste rubber tires for liquid phase treatment has received more interest recently [13,14].

The aims of the study were to evaluate the sorption activity of zinc oxide-loaded activated carbons (AC/ZnO) for simultaneous removal of dichloromethane, trichloromethane and carbon tetrachloride from

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aqueous liquids. As the activated carbon was derived from waste rubber tires, the study is considered a doubly effective solution for environmental pollution. It represents a cleaning way to dispose the waste tires and an economic source of carbonaceous material. With this in mind, a composite of zinc oxide nanoparticle loaded on activated carbon AC/ZnO was prepared and characterized for the structural properties and surface morphology. The composite was evaluated for its sorption activity toward dichloromethane, trichloromethane and carbon tetrachloride.

2. Experimental

2.1. Preparation methods

2.1.1. Preparation of activated carbon from rubber tires

The activated carbon (AC) was derived from waste rubber tires as described in an earlier publication [15, 16]. Briefly, waste rubber tires were cleaned and steel was removed. Then, it was heated to 500 °C for about 6 h. The derived gas products were carried by the carrier gas and condensed downstream and the non-condensable gases were collected. The residual char was collected and treated with hydrogen peroxide solution for 1 day to oxidize adhering organic impurities. Then, it was washed with deionized water, and dried in vacuum oven. The material was then treated with nitric acid solution to remove ash contents and was then washed with deionized water and dried.

2.1.2. Preparation of activated carbon/zinc oxide

Activated carbon loaded with zinc oxide nanoparticles (AC/ZnO) was prepared via thermal coprecipitation. In a typical preparation, 6.0 g of AC was dispersed in 150 mL of deionized water by the use of sonicator. A 50 mL solution containing 6.975 g of Zn $(NO_3)_2.6H_2O$ was slowly added. The mixture was stirred for 120 min. The pH of the mixture was maintained at 8–9 followed by reflux, heating up to 90 °C for 6 h under stirring. The precipitate was allowed to cool and then filtered and washed. The produced material was dried at 110 °C overnight and then calcined at 350 °C for 4 h.

2.2. Characterization

Scanning electron microscopy micrographs were recorded by TESCAN LYRA 3 (Czech Republic) equipped with an energy-dispersive X-ray spectroscopy (EDX) detector model X-Max with 10 kV accelerating voltage. X-ray analysis was performed on Rigaku Rint D/max—2500 diffractometer using Cu Kα radiation (wavelength = 1.5418 A) in a scanning range $2\theta = 10$–80°. A nitrogen adsorption isotherm (Brunauer–Emmett–Teller) was obtained to determine the specific surface area. The IR spectra of the samples were recorded on a MATTSON FTIR-100 spectrophotometer using KBr pellets over the range 4000–400 cm^{-1}. BET surface area measurements were made by measuring N_2 adsorption at 77 K using a MICROMERITICS 2000 instrument. Pore volumes were subsequently determined from the cumulative nitrogen adsorption by the BJH method. A JASCO, V-670, UV–vis–NIR spectrophotometer was used for recording the solid-state absorption and diffused reflectance spectra (DRS) of the synthesized AC/ZnO using BaSO$_4$ pellet as a reference.

2.3. Sorption procedure

The equilibrium adsorption isotherm was studied by using batch mode adsorption. Batch equilibrium studies were carried out by using the prepared AC/ZnO composite conducted with a solution of chlorinated hydrocarbons in a series of conical, airtight Pyrex glass flasks. Different parameters were studied. The effect of the composite dosage was investigated in a range between 0.25 and 5 g/L. Other experimental parameters such as the effect of initial concentration, pH and

contact time were also studied. Each flask was loaded with a 50 mL solution of chlorinated hydrocarbons. A predetermined amount of the composite was added to each flask and preserved in an isothermal shaker at 150 rpm until equilibrium was achieved. It is worth mentioning that preliminary results indicated that AC/ZnO has a higher adsorption capacity than the pristine AC.

2.4. Adsorption and kinetic studies

All the batch adsorption experiments were performed by using 150 mL conical hermetically sealed flasks. The liquid phase of chlorinated hydrocarbons solution (dichloromethane, chloroform and carbon tetrachloride) was prepared in distilled water. The adsorption capacity of the synthetic composite was estimated by contacting 50 mL of chlorinated hydrocarbons solution with different amounts of suspended composite. At different predetermined time, intervals the supernatant liquid were filtered by using a syringe connected to a filter. Then, the chlorinated hydrocarbons concentration was monitored by using gas chromatography–mass spectroscopy instrument (Agilent, model 7890A).

The chlorinated hydrocarbons adsorption at a certain time t (q_t, mg/g) was identified by Eq. (1):

$$q_t = (C_o - C_t) \times \frac{V}{m} \tag{1}$$

where V is the volume of chlorinated hydrocarbons solution in liters, C_o (mg/L) and C_t (mg/L) are the initial and final concentrations at time t of chlorinated hydrocarbons in solution respectively and m (grams) is the weight of the adsorbent.

The percent removal of chlorinated hydrocarbons in solution is calculated by Eq. (1) as follows:

$$\% \, \text{Removal} = \frac{C_o - C_e}{C_o} \times 100 \tag{2}$$

2.5. Analysis

The chlorinated hydrocarbon concentration was monitored by using the Headspace Gas Chromatography Mass Spectrometer (HS–GC/MS). Sample analysis was performed using Agilent 7890A GC interfaced with an Agilent 5975C Network Mass Selective Detector. Direct headspace automated injection was performed using a 2.5 mL-HS syringe. 250 μL of the headspace vapor was injected. The incubation temperature was optimized in the range of 40–70 °C for 1–20 min. The optimum temperature and time were found to be 60 °C and 15 min respectively. 10 mL vials were used and the optimum volume was found to be 1 mL. The agitation speed of 250 rpm, syringe temperature of 50 °C and injection speed of 500 μL/sec were adjusted.

Optimal GC–MS conditions were adjusted, as measured by maximum sensitivity, the baseline separation of the analyte and Gaussian peak shapes. The GC inlet was operated in split 50:1 mode at 180 °C to permit the trapping of the analytes at the head of the column. The oven temperature program was as follows: 35 °C for 10 min, then increased at the rate of 5 °C/min to 40 °C for 1 min, then 15 °C/min to 120 °C for 2 min, then 20 °C/min held at 120 °C for 11 min (total run time 17.33 min). Helium was used as a carrier gas at a constant flow of 1.4 mL/min by using capillary column HP-5 (5% phenyl methyl siloxan) 30 m x 320 μm x 0.25 μm. Determination of analytes was carried out using a mass spectrometer in electron impact (EI) ionization mode at 70 eV. The mass spectrometer quadruple temperature was set at 150 °C and the mass spectrometer source at 230 °C. Optimization experiments were conducted in total ion chromatogram (TIC) mode between m/z 40 and 550. Quantification of dichloromethane, trichloromethane and carbon tetrachloride was performed in selected ion monitoring (SIM) mode. Five different acquisition windows were defined taking into account the retention times and suitable fragments of the compounds: 49, 84, 86, 88 for