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Highly mesoporous K_2CO_3 and KOH/activated carbon for SDBS removal from water samples: Batch and fixed-bed column adsorption process

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ABSTRACT

This manuscript evaluates the behavior of activated carbon (AC) prepared from the cones biomass of Iranian pine trees, with high mesoporosity and a large specific surface area, as a high potential adsorbent for sodium dodecylbenzene sulfonate (SDBS) in batch and continuous systems. The AC samples were prepared from pine tree cones by chemical activation with different impregnation ratios of K_2CO_3 and KOH. The materials were characterized by Boehm titration, approximate elemental, SEM, FT-IR, TGA, XRF analyses and BET surface area measurement. In a batch process, the effects of various parameters such as adsorbent dose, pH, contact time and initial SDBS concentration and temperature were considered. Six different adsorption isotherms were applied to equilibrium data. Pseudo-first-order, pseudo-second-order and intraparticle diffusion models were used to estimate the adsorption kinetic data. The experimental data resulted in excellent fits with the Redlich-Peterson isotherm and that the pseudo-second-order described the best description of adsorption data. Thomas and Yan models were used in describing the experimental data in a continuous system. The thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy (ΔH°), entropy (ΔS°) and activation energy (E_a) were analyzed. The contrasting negative and positive values of ΔG° and ΔH°, respectively, indicated that adsorption was spontaneous and endothermic in nature, and the obtained E_a confirmed chemisorption of SDBS adsorption onto AC. The adsorptive behavior of AC was also investigated with different bed heights, flow rates and the initial concentrations of SDBS. These results, by the recovery of 88% after five successive cycles, indicated that the combination of sulfuric acid and ethanol with a ratio of 4:6 is suitable for desorbing SDBS from AC.

1. Introduction

Wastewater effluents that contain surfactants are common and one of the major causes of environmental pollution. Use of excessive amounts of surfactants, if released into the environment, has widespread negative effects on human health such as diarrhea, emaciation, skin irritation, necrosis, respiratory problems and eventually death. The treatment of surfactants is usually difficult and expensive, having become a challenge, as a significant amount of surfactants is released into the environment, creating serious environmental problems due to their extensive applications (Taffarel and Rubio, 2010).

The prevalent method for surfactant removal from the water environment is an adsorption process using different adsorbents. Investigations of surfactant adsorption have been carried out on AC (Gurses et al., 2003). It is widely used in water and wastewater treatment due to its porous structure and high adsorption capacity, However, adsorption of ABS's by AC been studied, although it has an extensive practical potential such as use in waste water treatment, chemical recovery, medical applications, removal of organic contaminants from drinking water and industrial purification. However, the most important feature of AC is the selective removal of contaminants (Williams and Reed, 2006). Also, it is resistant to interactions with acidic substances and environmental toxins (Chen et al., 2002). The ultimate functioning of AC in pollution control depends on the carbon content of the raw material, thermal stability of oxygen-containing functional groups, surface functional groups, the chemical composition of the raw material (Kruk et al., 2005), type of activated agent (AA) and different activation methods.

The combination of the chemical and physical activation processes was employed to produce specific activated carbons.

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Physical activation (PhA) includes the preliminary carbonization of a carbonaceous precursor (below 700 °C) and subsequent activation of the obtained char with oxidizing gases such as air, CO_2 or steam at high temperature, in the range of 700–1100 °C (Heidari et al., 2014a; Heidari et al., 2014b). Chemical activation (ChA) consists of the impregnation of raw material with chemical agents such as alkali metal hydroxides (KOH and NaOH), carbonates, alkali metal oxides (Li_2O_3, Na_2CO_3, K_2CO_3, Rb_2O_3, Cs_2O_3) and metal salts ($ZnCl_2$) along with carbonization at temperatures between 400 and 800 °C under inert gas such as nitrogen or argon atmosphere (Heidari et al., 2014a). The priority of ChA rather than PhA is in that it is done in a single step at a relatively low temperature, which increases the development of pores in the carbon structure due to chemical effects (Moreno-Castilla et al., 2001). Furthermore, the yield is higher from ChA than PhA, while the use of ChA results in drift in time and energy (Moreno-Castilla et al., 2001). The use of agricultural and forest waste as raw material for the production of AC has increased substantially in recent years because, besides being renewable, these materials are inexpensive and easily available (Timur et al., 2010). A few reports have been published on the production of AC from different parts of various pine species (Momčilović et al., 2012) such as from cones of the European Black Pine using H_3PO_4 (Berglund et al., 2004), from humus of Scots pine (*Pinus sylvestris* L.) (Ntuli and Hapazari, 2013) and from cone of *Pinus contorta*, using steam as the AA. To the best of authors' knowledge, no study seems carried out on the abstracted topic which makes the present study first of its kind.

The main objective of this study was to prepare AC from cones of Iranian pine trees (*Pinus eldarica*) with high mesoporosity and a large specific surface area, considered as a high potential adsorbent for SDBS adsorption in batch and continuous systems. However, to our knowledge, there is scarce information in the literature about the preparation of AC from cone of pines by chemical impregnation using K_2CO_3 and KOH as activating agents nor about their application for SDBS as an adsorbent.

2. Materials and methods

2.1. Materials and chemicals

Iranian pine tree cones (*Pinus eldarica*), as a precursor for the preparation of ACs, were collected from a park near Dargaz city in northeastern Iran. The raw material was crushed to 2–3 mm diameter in a mechanical sieve shaker, and sieved with 60 μm mesh, then washed entirely with distilled water to remove foreign material and oven-dried at 105 °C until constant weight was attained. Sodium dodecylbenzene sulfonate ($C_{18}H_{29}SO_3Na$) was purchased from Acros, America. Sodium hydroxide (NaOH), hydrochloric acid by 37% (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4), ethanol (C_2H_6O), acetone (C_3H_6O), 2-propanol (C_3H_8O), sodium carbonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$) were purchased from Merck, Germany. Potassium carbonate (K_2CO_3) and potassium hydroxide (KOH) were purchased from Scharlo, Spain, besides commercial AC from Loba Chemie, India.

2.2. Preparation of AC

For preparation of AC from the biomass of cones, two AAs, consisting of K_2CO_3 and KOH with different ratios, were used. First, 10 g of dried precursor was impregnated with K_2CO_3 and KOH in impregnation ratios of 0.2:1, 0.5:1, 0.75:1, 1:1, 1.5:1, 2:1 g AA. g^{-1} precursor. Then the mixture was stirred continuously at ambient temperature for 1 h to allow penetration of the AA into the precursor. After mixing, it was oven-dried at 110 °C for 48 h and weighed. Pyrolysis of the cones biomass impregnated with K_2CO_3 and KOH was carried out in a stationary horizontal tube furnace under pure nitrogen gas and atmospheric pressure. The heating rate of the nitrogen gas was 8 °C/min. The pyrolysis temperature and retention time were 750 °C and 3 h, respectively. After the activation step, the samples were cooled in a nitrogen atmosphere and removed from the reactor at the end of each experiment and weighed. The pyrolysis product was washed sequentially with distilled water to remove residual organic compounds and AAs until the pH neutral range (6–7) had been reached. Then the samples were dried at 110 °C.

2.3. Characterization of AC

The cones were characterized by approximate analysis (ASTM D5832-98), elemental analysis (CHNOS) (Vario EL III), compound analysis (TAPPI methods), and TGA (Netzsch STA 409) analysis. The synthesized AC was characterized by SEM, BET, FT-IR, XRF and Boehm titration. Also the surface morphologies of the ACs were characterized by scanning electron microscopy (SEM, KYKY, model; SBC 12, EM3200, China). Characterization of textural properties of the ACs was done by N_2 adsorption isotherm at 77 K by using the Brunauer–Emmett–Teller method (Quantachrome NovaWin2, American). To determine the micropore volumes and the external area, the t-plot approach was applied. Mesopore volumes and areas were determined by subtracting micropore volumes and areas from total pore volumes and areas. Boehm's titration and Fourier transform infrared (FT-IR) analysis was performed using Boehm method and a spectrophotometer (Shimadzu, FTIR1650 spectrophotometer, Japan) (Boehm, 1994), respectively, to identify the surface functional groups of the ACs. The major elements of the synthesized AC were determined by X-ray fluorescence (XRF) analysis (Philips XPert MPD, Netherlands). The yield is usually defined as the final weight of the AC produced after activation, washing, and drying, divided by the initial weight of the raw material, both on dry weight basis. The following relationship was used for calculating the yield of the AC:

$$Yield = \frac{W_i}{W_{ac}} \times 100 \quad (1)$$

where W_i is the mass of impregnated sample and W_{ac} the mass of the dried AC after washing.

2.4. SDBS analysis

The SDBS concentration was determined by using UV–vis spectrophotometer at 224 nm wavelength (PerkinElmer, Lambda 25). The calibration curves were prepared for several standard solutions of SDBS at concentrations ranging between 1–50 mg/L. The solutions were measured in a quartz glass cell (Suprasil; Hellma, Mulheim/Germany) with a path length of 10 mm at 25 °C.

2.5. Batch experiment

Batch experiments were carried out in glass flasks (250 mL) and agitated on a shaker at a constant agitation rate of 50 rpm. In the batch system the different parameters, i.e., impregnation ratios, pH, temperature, contact time, adsorbent dosage and initial concentration of SDBS, were investigated. First, the ability of AC samples, produced by K_2CO_3 and KOH, was investigated in SDBS adsorption. These adsorption experiments were performed under constant conditions, i.e., pH = 7, solution volume of 100 mL, SDBS concentration of 50 mg/L and 0.5 g/L AC, at temperature of 25 °C for 120 min. The supernatant aliquots were collected and filtered through a 0.45 μm filter before chemical analysis. To investigate effects of the AA on the properties of AC, an AC sample was produced without an AA (w/o AA). Then the performance in the removal of SDBS of its commercial AC (CAC) was compared with the ACs pro-