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Research Paper

Adsorptive desulphurization of model oil by Ag nanoparticles-modified activated carbon prepared from brewer's spent grains

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ABSTRACT

This study reports removal of dibenzothiophene (DBT) from model oil (DBT dissolved in *n*-heptane) by silver nanoparticles modified activated carbon prepared from brewer's spent grains using wet impregnation (WI) method. The removal efficiency follows the order $AgNPs^{cw}/AC > AgNPs^{kp}/AC >$ ACB. The $AgNPs^{kp}$/AC and $AgNPs^{cw}$/AC exhibit higher adsorption capacities for DBT with maximum values of 25.7 and 29.8 mg $_{DBT}/g_{Ads}$ at 25 °C respectively, than ACB with 13.9 mg $_{DBT}/g_{Ads.}$ The two-fold enhancement in the DBT uptake capacities of modified ACs can be attributed to the introduction of Ag(1) ion, a weak Lewis acid as an additional adsorption site. A significant decrease from 212.9 to 136.2 m^2/g in the Brunauer–Emmett–Teller surface area of $AgNPs^{cw}$/AC is observed following the loading of DBT. The equilibrium adsorption data is adequately represented by Freundlich isotherm. The adsorption kinetics of DBT by these adsorbents followed pseudo second-order (PSO) model and the mechanism of adsorption was controlled by film and intra-particle diffusion. The change in entropy and heat of adsorption for DBT adsorption by these adsorbents range from 0.18 to 0.19 kJ/mol K and 21.5 to 23.9 kJ/mol, respectively. The results indicate that Ag nanoparticles-modified ACs from brewer's spent grains can be used as adsorbent for the removal of DBT from model oil.

1. Introduction

In recent times, growing concerns regarding the air quality and associated deleterious effects to the environment posed by gasoline and diesel oil combustion process may have necessitated the removal of heteroatomic components from crude oil by petroleum refining industries in order to produce cleaner and environmental friendly products [81]. Many conventional approaches of desulfurization geared towards improving the removal efficiency of sulphur compounds from crude oil have been developed and reported in the literature [14,65,49]. Some of these technologies could address key questions surrounding emission quality and pollution. The current desulfurization technology in petroleum industry is heterogeneously catalyzed hydrodesulfurization (HDS). The inherent chemical limitations associated with HDS coupled with high cost make alternatives to this technology of interest attractive to the petroleum industry. Various types of techniques have been developed to reduce or remove sulphur compounds by oxidation [20,29,38], extraction [39,66], adsorption [7,54,68,84] and biodesulphurization [28].

Adsorption constitutes an attractive alternative to HDS method and is commonly employed in removing sulphur compounds from diesel oil [62,75]. Various researchers have used adsorption processes to remove sulphur compounds from fuels using different types of adsorbents [37,43,52,60,76]. Activated carbons (ACs) have been extensively studied because of their high surface area, cost effectiveness, receptivity to modification and high affinity for sulfur compounds removal from different fuels [10,16,82,86].

In the past few years, nanoparticles-modified adsorbents have attracted much interest due to high surface area to volume ratio and short diffusion rate [74,85,77]. Most previous applications of nanoparticles-modified sorbents were mainly focused on removal of dyes and heavy metal ions from environmental water samples [15,56,63,55]. However, reports on the removal of sulfur compounds from model oil by Ag nanoparticles-modified AC prepared from Brewer's spent grain (BSG) is sparse [13,36,6,42,27]. The generation of ACs from BSG is an appealing method that gives increased values to this material, which is principally utilized as

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animal feeding. AgNPs have been successfully synthesized using seed shell extract and novel biomaterial (cobweb). The synthetic method employed in this study is green and non hazardous to the environment.

In the present study, Ag nanoparticles-modified AC has been explored as an alternative method for desulfurization of model oil. Silver nanoparticles was chosen for sorbent modification because of its high activity, which has been suggested to be due to release of Ag^0 (atomic) and Ag^+ (ionic) clusters on dissolution, where the Ag^+ can form complex with electron donor groups containing sulfur such as DBT [17]. We therefore explored the strong affinity of Ag for sulphur containing compounds to synthesize Ag nanoparticles-modified ACs for subsequent applications to single component adsorption of DBT in *n*-heptane, in order to provide fundamental understanding and the effect of adsorbent modification on the removal of DBT from model oil.

2. Materials and methods

2.1. Materials

2.1.1. Adsorbent preparation

The brewer's spent grains (BSG) were supplied by the Nigerian Breweries. The material was washed with water to remove residues from wort and dried in the sun for 6 h until approximately 10% moisture content. Dried BSG was then placed in an oven maintained at 105 °C to completely eliminate the moisture. Thereafter, 10 g of moisture-free BSG was weighed in a crucible (50 mm diameter) and carbonized at 300 °C, at initial heating rate of 20 °C/min for 30 min in a muffle furnace (Carbolic Sheffied England LF4) and cooled at room temperature [1].

Precisely 5.0 g of sieved (10 μm mesh) carbonized BSG was activated by treatment with 5.0 mL of 0.3 M H_3PO_4

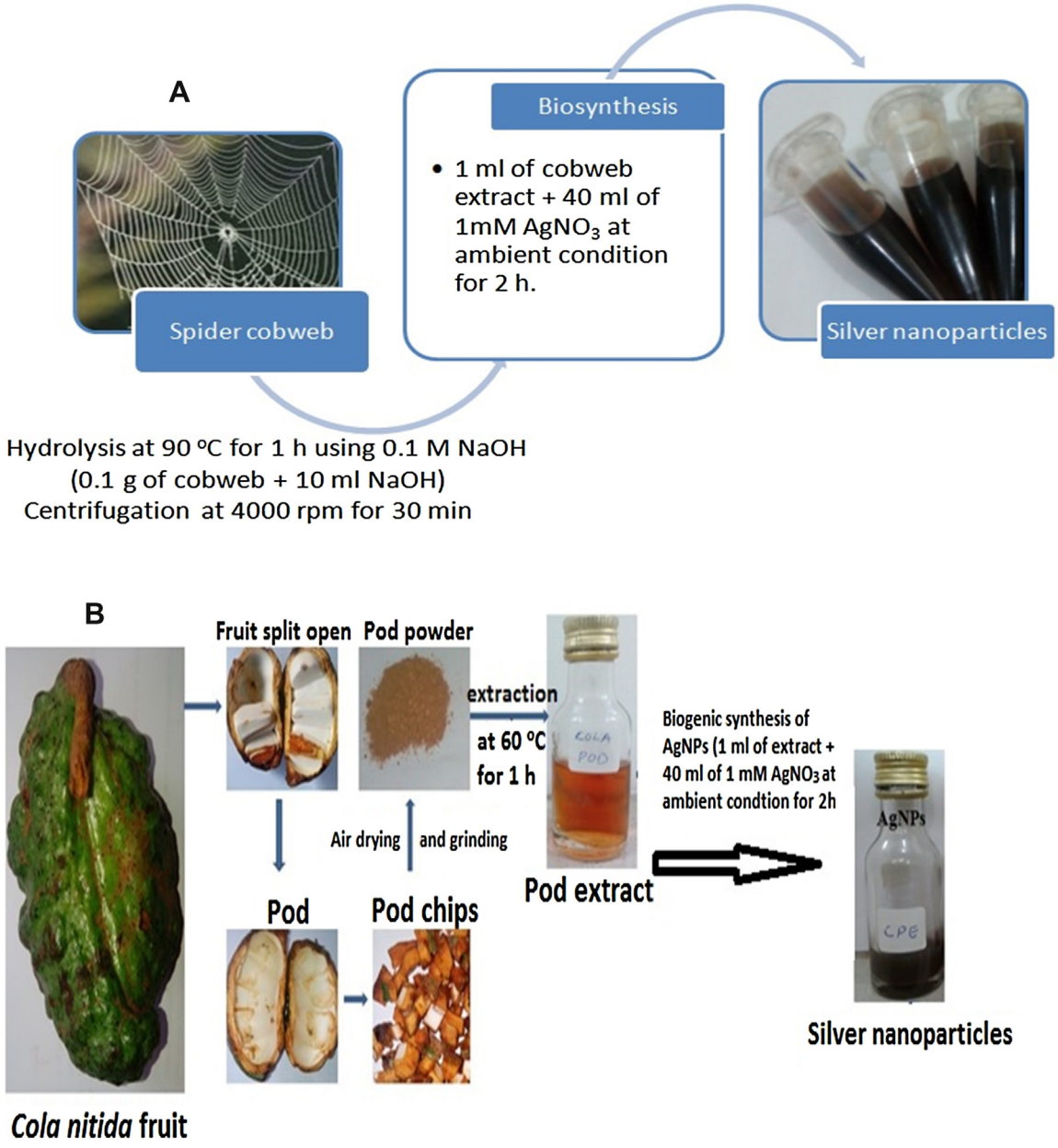

Fig. 1. Scheme for the synthesis of silver nanoparticles from cobweb (A) and *Cola nitida* fruit (B).