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Removal of crude oil from aqueous medium by sorption on hydrophobic corncobs: Equilibrium and kinetic studies

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Abstract

Crude oil released to the marine environment through accidental spillage or drainage from land causes serious damage to the environment and marine life. The treatment of an oil spill remains a challenge to environmental scientists. Sorption is a popular technique for clean-up of oil spills. In this study, corncobs, which are an abundant, biodegradable agricultural waste, were treated with acetic anhydride to increase their hydrophobic properties and improve their sorption effectiveness in aqueous environments. The crude oil absorption behaviour has been discussed, and the employed kinetic models suggest that the sorption process occurs via a surface reaction and intraparticle diffusion mechanism. Equilibrium isotherm data were analysed using the Langmuir and Freundlich isotherms. Based on the regression coefficients, the Langmuir isotherm provided the best fit to the experimental data. The maximum monolayer sorption capacities were 0.0768 mg/g and 0.0043 mg/g for the acetylated and raw corncobs, respectively. The results presented and discussed in this study indicated that acetylated corncobs are suitable sorbents with the potential for further development for oil spill treatment.

Keywords: Oil spillage; Acetylated corncob; Hydrophobic; Sorption capacity; Kinetics

1. Introduction

Oil is the lifeblood of our modern industrial society. Oil is one of the most important energy and raw material sources for synthetic polymers and chemicals worldwide [1,2]. However, when this vital resource is out of control, it can destroy lives and devastate the environment and economy of a particular region [3].

When oil is explored, transported and stored and its derivatives are used, there is risk for spillage with the potential to cause significant environmental impact [1]. Due to its destructive properties, the entire character of the area is damaged once an area has been contaminated with oil. In addition, when oil encounters something to cling to (e.g., beach, rocks, feathers of a duck or a bathers hair), it is difficult to remove [3]. Therefore, pollution by petroleum oils affects sea life, economy, tourism and leisure activities due to the coating properties of these materials [1].

When oil is spilled in water or on land, the physical and chemical properties of oil change progressively. The spilled oil contributes an undesirable taste and odour to

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drinking water and causes severe environmental damage. Contaminated water cannot be used as a municipal water supply, in industry, or for irrigation [1,4]. Oil settles on beaches and kills organisms that lie there. In addition, oil settles on ocean floors and kills benthic (bottom dwelling) organisms, such as crabs. Oil endangers fish hatcheries in coastal areas as well as contaminates the flesh of commercially valuable fish [1,4].

Effective decontamination and clean-up are necessary after a spill for the protection of the environment and human health. Sorption techniques are one of the most effective approaches for the treatment of oil spills. Among the various sorbents that have been employed for oil spill remediation, synthetic materials, such as polypropylene and polyurethanes, are the most commonly used commercial sorbents due to their oleophilic and hydrophobic properties [5]. However, these materials are not biodegradable, which is a major disadvantage. Landfill disposal is environmentally undesirable, and incineration is expensive [6,7]. Therefore, there is a renewed interest in natural sorbents and a wide variety of organic vegetable products, such as rice straw, peat moss, wood, and cotton, which have been employed as sorbents in oil spill clean-up [6,7]. The main drawbacks of these plant-derived sorbents are their relatively low oil sorption capacity, low hydrophobicity and poor buoyancy compared to synthetic sorbents, such as polypropylene [2,8]. Once plant-derived sorbents are applied to saturated environments, preferential water sorption is favoured over the sorption of oil because the sorbents are typically hydrophilic in nature. Agricultural by-products have well-documented problems with water sorption and a lack of dimensional stability due to their associated hydroxyl functionalities. These groups are abundantly available in all three major chemical components of plant-based materials and are responsible for their hydrophilicity [9]. Hydrophobicity (oleophilicity) is one of the major disadvantages of sorbent properties that influences the effectiveness of oil sorption in the presence of water [9]. The effectiveness of the sorbents in saturated environments would be enhanced when the density of the hydroxyl functionalities is decreased [9,10]. The hydroxyl functionality of these fibres can be reduced by chemical modification, such as acetylation, methylation, cyanoethylation, benzoylation, acrylation, and acylation [11,12].

The acetylation reaction is one of the most common techniques employed for hydrophobic treatment of lignocellulosic materials (e.g., wood), which involves a substitution reaction of a hydroxyl group (hydrophilic) into an acetyl group (hydrophobic). This reaction is typically carried out by heating lignocellulosic material in the presence of acetic anhydride with or without a catalyst [11]. In addition, for the efficient application of sorbents, data on the sorbent sorption capacity and a good understanding on the basic mechanism behind the sorption capabilities are required [13].

Corncobs are an agricultural waste abundantly found in Enugu metropolis, Enugu State, Nigeria. Due to its abundance and easy accessibility, this material can be used as a cheap adsorbent for crude oil sorption in aqueous medium.

To the best of our knowledge, no studies on the sorption of oil using acetylated corncobs and the mechanism of the sorption process have been reported. In this study, the influence of acetylation on the oil sorption capacity of corncobs was investigated. The equilibrium and kinetic parameters were also determined to provide a better understanding of the mechanism of the sorption process.

2. Materials and methods

2.1. Material preparation

The corn cobs were collected from a local market (Ogbete main market) in Enugu metropolis, Nigeria. The corncobs were thoroughly washed with water to remove dust, fungus, foreign materials and water soluble components. The washed cobs were dried in sunlight for 12 h (4 h for three days) and then left to dry at 65 °C in an oven. They were size reduced and sieved through 20 and 25 British standard sieves (BSS Sieves). The other reagents and chemicals were obtained from the British Drug House (BDH) and included acetic anhydride, N-bromosuccinimide (NBS), acetone, ethanol and n-hexane, which were used without further purification.

2.1.1. Soxhlet extraction

To reduce the influence of the fibre extract on acetylation, 10 g of the sieved materials were extracted with a mixture of acetone and n-hexane (4:1, v/v) for 5 h. The extracted samples were dried in a laboratory oven for 16 h. The extracted content was calculated as a percentage of the oven-dried test samples.

2.2. Acetylation of corncobs

The acetylation of the corncobs under mild conditions in the presence of NBS using acetic anhydride was carried out using the method reported by Sun et al. [12] which involved acetylation in a solvent-free system. The amount of substrate and reactant were combined in a ratio of 1:20 (g dried corncob/mL acetic