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Equilibrium kinetics study of electrospun polystyrene and polystyrene-zeolite fibres for crude oil-water separation

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ABSTRACT

Electrospun polystyrene, zeolite-modified polystyrene fibres and expandable polystyrene foam (EPS) were used to remove crude oil from oil-spilled water by adsorption process. Varying proportions of the adsorbent materials were used in the experiment. The polystyrene fibres were prepared from the viscous precursor solution of the expandable polystyrene foam dissolved in Xylene, using electrospinning technique. Porosimetry analyses of the adsorbents EPS foam, EPS fiber and EPS-Zeolite fiber was done using BET method. Equilibrium adsorption isotherms and kinetics were investigated. The experimental data were obtained from adsorption analyses and subsequently analyzed using Lagergren adsorption models. The kinetic data obtained were analyzed using a pseudo-first-order, pseudo-second-order equation. The experimental data were found to fit very well the pseudo-second-order kinetic model with correlation coefficient (R^2) value of 0.9994 and calculated equilibrium adsorption amount ($q_{e,expt}$) between 1.9763 and 9.4073 mg/g. EPS-zeolite fibres showed highest adsorption efficiency (9.4073 mg/g) for the removal of crude oil from oil spill more than EPS foam and EPS fibre.

1. Introduction

Oil resources in Nigeria is a great fortune to the economy of the nation. Globally, oil and gas sector contribute to the development of strong economies. Meanwhile, as oil resources provide lot of benefits on one hand, the great hazards and pollution caused by its spillage are immense and cannot be overemphasized. Oil spills in populated areas spread quickly and widely, taking out crops and aquacultures through contamination of the groundwater and soils. Nigeria has witnessed serious environmental degradation resulting from pollution related to the oil and gas industry. The Department of Petroleum Resources reports that there were over 4200 oil spill incidences in Nigeria over the last 50 years, ranging from minor spills to over half a million barrels in one single incident. Though the study of the impacts of oil spillage on the environment and human life may be important, research on a concrete solution to the menace caused by the spillage would be of greater significance. Irrespective of the source, pollutants are harmful to human, for instance, metals such as selenium, arsenic, barium, chromium, lead, mercury, zinc, cadmium etc. are responsible for hair loss, kidney damage, high blood pressure, increased cancer and neurological damage risk. Also, benzene, toluene, ethyl-benzene and xylene (BTEX) are carcinogenic. It affects the reproductive, central nervous system, respiratory and neurological components of human body [1]. Volatile organic compounds trigger respiratory diseases and cancer in human. The most popular pollutant associated with oil spill is polycyclic aromatic hydrocarbons (PAHs). PAHs are well disseminated in aquatic habitat than terrestrial environment, and it is assumed to be more bio available in water than sediments, plants and other common petroleum biomarker. Aquatic animals such as crabs, fish, etc. bioaccumulate PAHs but are resistant to the toxic effect of the pollutant [2].

Oil spill on water bodies and soils should be cleaned up or at least be reduced. There are various ways in which the effect of the spillage can be reduced. The technology of clean-up hasn't changed substantially. For the most part, the only ways to get rid of the majority of the oil are old ones – corralling it, burning it, mopping it up and letting nature break it down [3]. Different ways have been used to remove spilled oil from water; the mechanical techniques include the use of booms, skimmers, and sorbents. In another way chemicals such as detergents and other dispersants can be used, while the physical methods are being used in the form of burning of the floating oil on water. It has been

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found that burning can actually remove up to 98% of an oil spill. However, field testing is needed to check the feasibility of this technology [4], because of its attendant effects on the ecosystem.

The study and use of membranes and adsorbents for water borne pollutants had increased over the years due to selectivity of absorbents, cheap, recyclability, side effects, surface modification of adsorbent and recovery [5–7,9,10]. Several adsorbents had been reported for crude oil and other pollutants removal from water, i.e. oil palm leaves, hydrogel of chitosan based on polyacrylamide, natural ceramic [7–10], hydrophobized vermiculite with carnauba wax, polyethynylbenzene derivatives, hydrophobic aquaphyte *Salvinia* sp., hydrophobic aerogel, carbonized rice husk, black rice husk, oleic acid grafted sawdust, recycled wool-based nonwoven material, hydrophobic graphene, [6,7,11] etc. Important properties for an ideal crude oil adsorbent in water are: fast and large absorption capacity, good selectivity (oleophillic nature), reusability, high oil recovery, cheap, super hydrophobicity nature and insolubility in water [12,13]. Furthermore, huge amounts of non-biodegradable wastes are generated through various industrial activities in food and packaging sectors, these include food take away pack, plastic bottles, nylon, water sachet and common expanded polystyrene foams. Their disposal constitutes a major problem in Nigeria. Currently, there is no functioning central recycling facility for these wastes in Nigeria. Even when incinerated, the resultant problems of air pollution and conversion to soot have proven to be an unsatisfactory solution. Invariably, this has constituted major environmental hazards to the environment. Therefore, it is noteworthy that sustainable re-use of polymer wastes would serve as strategic measure toward an effective management environmental hazards.

The aim of this study is to investigate and compare the kinetics of adsorption of crude oil spill from water using expandable polystyrene (EPS) foam and electrospun EPS fibre intercalated with zeolite. The physicochemical parameters involved in the adsorption process were determined, while the kinetic data obtained were analyzed using a pseudo-first order and pseudo-second order Lagergren adsorption models.

2. Materials and methods

2.1. Materials

Expandable polystyrene (EPS) packing and insulation materials for consumer electronic devices was used in this work. Reagent grade xylene from Sigma Aldrich (St Louis, MO, USA). Zeolite was obtained from Zeochem Ltd., Slovenia and crude oil was obtained from Nigeria National Petroleum Company, Nigeria.

The surface area, porosity and pore volume were analysed using Brunauere Emmette Teller (BET) method using surface analyser of Micrometrics ASAP 2020. The EPS foam, fibre and zeolite-intercalated samples of 200 mg weight analysed by nitrogen adsorption and desorption isotherms at a degassing temperature of 120 °C for 360 min.

2.2. Polystyrene fibre preparation

The polystyrene fibres were produced by electrospinning from EPS foam wastes as shown in Fig. 1. Two types of EPS fibres were prepared; one is 100% polystyrene, while the other contained 10% zeolite. To prepare the nanofibres fibres, the EPS foam was dissolved in xylene and stirred for four hours. After adequate stirring, the viscous EPS solution was electrospinned onto an aluminium foil which served as substrate and electrode for the electrospinning set-up. Detachable lump of EPS fibre was formed on the foil which was carefully removed for the adsorption experiment. The spinning procedure in this study is according to the previous studies [14,15].

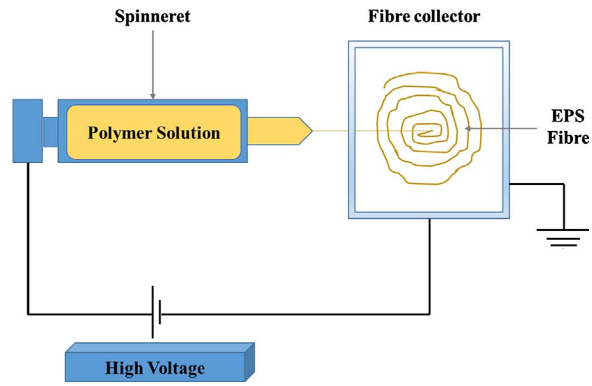

Fig. 1. Typical Electrospinning set-up.

2.3. Adsorption procedure

In this work, batch adsorption experiments were carried out using the three EPS variants, solid EPS foam, fibre polystyrene and zeolite-modified polystyrene. Crude oil spilled water was prepared in the laboratory. The step-by-step procedural route is shown as follows. For each adsorption test, empty 50 ml beaker was weighed with and without water (20 ml) on the high sensitive weighing balance (*Ohaus: Adventurer™ Pro*), and the weights were recorded accordingly. Hence, two drops of crude oil was added to each 20 ml water in the beaker using a Fischer pipette and the initial masses were determined and recorded. In the spillage, 0.01 g–0.05 g of raw and modified adsorbents were added and agitated between 5 and 10 min. At different time intervals (10–120 min), the adsorbent lump was removed. The beaker content (oil spill water) and polystyrene adsorbents were weighed in order to determine the slight change in mass of the materials.

2.4. Kinetic studies

Adsorption behavior of the polystyrene adsorbents (electrospun and foam) was determined to evaluate its potential for removal of crude oil from oil spilled water. Experiments were carried out in a 50 ml batch beakers as described in the methodology. In the present study, the adsorbate solutions were maintained under the same conditions, while the concentration of the adsorbents was varied. For a preliminary comparison, the adsorption behavior of modified and normal polystyrene fibres on spillage solutions was investigated. The amount (mg) of the remaining crude oil in the spillage and on the adsorbents was determined immediately through the use of high sensitive weighing equipment. Hence, the amounts of crude oil adsorbed at equilibrium on the adsorbents were obtained using expression (1):

$$q_t = \frac{(C_0 - C_t)V}{(W)} \tag{1}$$

where C_o and C_t are the initial and liquid-phase concentrations of spillage solution at t (min), respectively, V is the volume of solution (mL), and W is the mass of dry adsorbent used (g).

$$q_e = \frac{(C_0 - C_e)V}{(W)} \tag{2}$$

In Eq. (2), q_e is the adsorption amount of crude oil (mg g^{-1}) at equilibrium contact time, W and V are as designated in Eq. (1). Kinetic models was applied to examine the controlling mechanism of the oil adsorption from oil spill. In this study, both Lagergren first order and second order rate equations were used to describe the adsorption rate based on adsorption capacity. The pseudo first order equation [16] based on equilibrium adsorption is expressed as:

$$ln(q_e - q_t) = lnq_e - \frac{k_1 t}{2.303} \tag{3}$$