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Utilization of esterified sago bark fibre waste for removal of oil from palm oil mill effluent

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A B S T R A C T

With oil and grease content of 4000–8000 mg/l in palm oil mill effluent (POME), the commonly used ponding system often fails to produce treated effluent that meets the minimum standard of treated effluent. The present study investigates the efficiency of sago bark (SB) and esterified sago bark (ESB) for removal of emulsified oil from POME. Oil removal experiments were conducted at different batch experimental conditions: namely adsorbent dosage, contact time, temperature and pH. In overall, the oil removal efficiency of both SB and ESB increased with the increasing of sorbent dosage and contact time. 24-h oil adsorption test afforded oil removal efficiency of 57.77% (SB) and 80.23% (ESB).On the other hand, the oil removal efficiency of both SB and ESB decreased with the increasing temperature. Acidic pH was favorable pH condition for high oil removal efficiency in POME. There was a good correlation ($R^2 > 9.5$) between experimental data and the intra-particle diffusion model for both SB and ESB. The adsorption of oil in POME using SB was best described by Freundlich isotherm ($R^2 = 0.998$), indicating heterolayer adsorption of oil on SB. The adsorption of oil in POME using ESB was better represented using Langmuir isotherm ($R^2 = 0.992$), indicating a monolayer adsorption of oil onto the ESB surface. In conclusion, ESB showed better potential for use as sorbent for removing emulsified oil from wastewater, particularly POME.

1. Introduction

One of the main sources of industrial oily wastewater in Malaysia is palm oil mill effluent (POME). POME is generated at significant level as a by-product during palm oil processing. In year 2008 alone, at least 44 million tonnes of POME was generated in Malaysia [38]. The oil concentration in POME ranges between 4000 and 8000 mg/l [3,22]. Most of the palm oil mills use conventional ponding system to treat POME. However, ponding system requires long treatment time and large area [38]. Malaysian Department of Environment (DOE) has set a value of 50 mg/l as the maximum allowable limit for oil and grease content in the effluent to be discharged in waterways. The ponding system quite often fails to produce treated effluent that meets the DOE standard [12]. Thus, it is crucial for the palm oil industries to adapt an efficient treatment for oil removal.

Many technologies have been suggested for oil removal from water. Although ultrafiltration has a higher efficiency for the removal of oil, it is not suitable to be used in treating wastewater with high solid content such as POME due to the risk of premature membrane fouling [39,41]. Other treatments like coagulation, flotation and biological treatment are either expensive, complex in operation or required highly skilled operators. Adsorption is the most preferred method due to its feasibility and effectiveness, provided an appropriate sorbent is used.

Natural fibres are potential sources of natural sorbent for removal of oil from POME. Raw natural sorbents generally has excellent adsorption capacity, comparable density with synthetic sorbent, chemical free and highly biodegradable [7,37]. Natural fibres comprise cellulose, hemicellulose, and lignin [42], which is known responsible for oil adsorption [33,36,40]. Examples of natural fibres used as oil sorbent are rice husk [6], kapok [1], barley straw [19], sugarcane baggase [28], sawdust [10] and grass [32].

Despite of their advantages, many natural fibres suffer low hydrophobicity and buoyancy, therefore are only suitable for oil removal in the absence of water [6]. This is because most of the

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cellulose hydrophobic portions are covered by the hydroxyl groups, causing cellulose to behave more hydrophilic than hydrophobic [28]. To improve the oleophilicity and hydrophobicity of natural fibres, hydrophobization can be conducted by means of alkalization [1], chloroform treatment [1,20], acetylation [2,26], salt treatment [37], surfactant treatment [18], combination of chemical-biotechnological treatment [17], polymerization followed by ion-exchange process [24], and esterification [9,28].

Sago, known scientifically as *Metroxylon sagu* Rottboll, comes from genus metroxylon and family palmae [30]. It is one of the potential natural fibers abundantly found in tropical lowland forest and freshwater swamps. In 2009, nearly 59,000 ha of Sago is planted in Sarawak [14]. Sarawak is currently one of the world largest exporters of sago products with annual export of approximately 43,000 t [15,16].

Every tonne of sago flour produced generates approximately 0.75 t of sago bark (SB) as a solid waste [34]. With this regards, SB is a potential source of natural fibre for oil removal. More than 85% of SB is left unutilized in sago processing mill. Common disposal of SB is via incineration, direct dumping into nearby rivers and natural degradation, which gives rise to environmental problems [35].

In the work of Ngaini et al. [21] and Noh et al. [23], the SB was esterified using fatty acid derivatives to improve the oleophilicity and hydrophobicity of SB. It was found that the esterified SB (ESB) showed a good adsorption capacity on engine oil in water. Wahi et al. [35] studied the optimization of the esterification process using stearic acid (SA). The optimum ESB synthesis conditions were at 1:1 SB: SA, 15 wt% CaO as catalyst and 8 h refluxing time. The application of ESB for removal of oil from POME, is however, a complex process. The high suspended solids and COD values, acidic pH, and moderate temperature (between 40 and 80 °C) of POME could affect the oil removal efficiency. The aforementioned factors made it crucial to carefully study the performance of ESB in removing oil from POME at various adsorption parameters before it could be applied at larger scale. Thus, this present study aims to investigate systematically the oil removal efficiency of ESB in POME via batch adsorption system at various adsorption parameters, namely the adsorbent dosage, contact time, POME temperature, and POME pH.

2. Material and methods

2.1. Preparation of ESB and POME

Shredded SB was collected from sago processing mill in Mukah, Sarawak. SB was ground and sieved into particle size range of 0.5 mm to 1.5 mm. Esterification of SB with fatty acid derivative was carried out using stearic acid (SA). SA was chosen due to the reason that it is a long-chain fatty acid with 18 carbon chains, with highly hydrophobic properties. Fig. 1 shows the experimental set up for esterification of SB with SA. The ground SB (5 g) was placed in a round bottom flask containing ethyl acetate (50 ml). In this study, the SB to SA mass ratio was 1:1. Calcium oxide (0.75 g) was added to the mixture, to expedite the esterification process [35]. The mixture was heated under reflux for 8 h. The resulting ESB was cooled down to room temperature, filtered, washed with ethyl acetate and dried in a desiccator prior to use. The hydrophobicity of ESB was measured based on Ribeiro et al. [27]. The degree of esterification was estimated by calculating the ratio, R, between the intensity of C=O (ester peak) and C—O (cellulose backbone) in infrared spectra, as described in Adebajo and Frost [2]. Total pore volume was measured using BET Analyser (Quantachrome® ASiQwin™). The hydrophobicity, average C=O:C—O intensity ratio, and total pore volume of ESB was 50.2 ± 9.7%, 1.251 ± 0.213, and 0.012 cm^3/g, respectively. Full physicochemical characteristics of ESB including the surface functional groups and surface morphology has been described in detail in our previous work [35].

POME was collected from FELCRA palm oil mill in Kota Samarahan, Sarawak. The POME sample was collected from the drain coming from the mill before entering the first treatment pond, whereby the temperature was around 40 °C (raw POME). The POME was filtered through a muslin cloth strainer to remove solid particles of millimeter size. The oil and grease content, total suspended solid content and pH of the POME sample was 4850 mg/l, 15,200 mg/l and 4.18 respectively. The POME sample was stored at 4 °C before use.

2.2. Oil adsorption study

The batch adsorption study was conducted using SB and ESB at different sorbent dosage, contact time, pH and temperature using rotary shaker (Luckham R100/TW). The effect of sorbent dosage

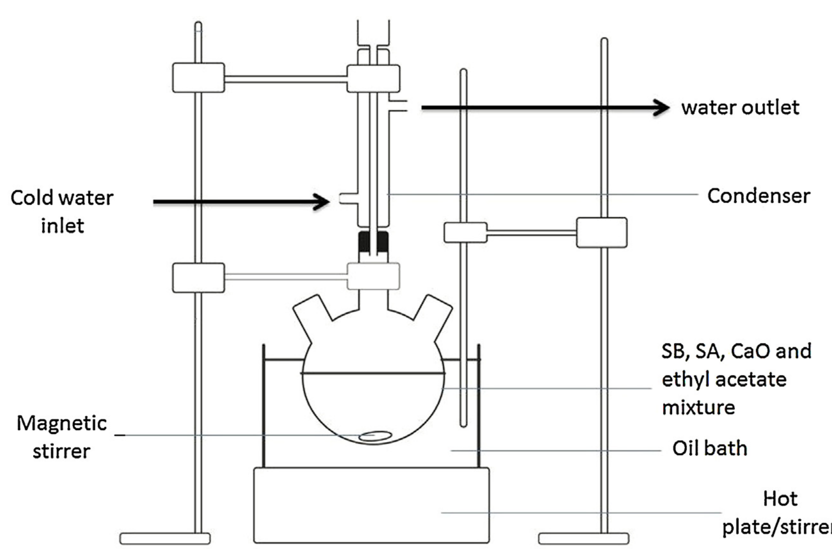

Fig. 1. Experimental set up for ESB preparation.