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Cationic and anionic modifications of oil palm empty fruit bunch fibers for the removal of dyes from aqueous solutions

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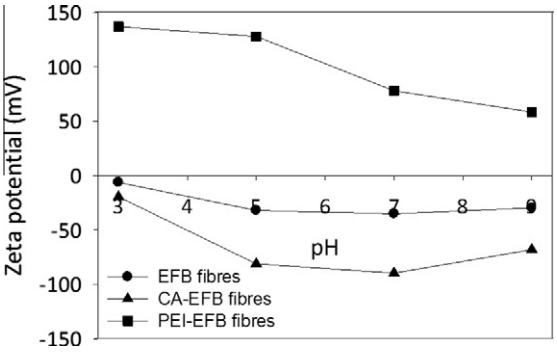
HIGHLIGHTS

- Oil palm empty fruit bunch (EFB) fibers were using as adsorbent for dye removal.
- Modifications were carried out using citric acid (CA) and polyethylenimine (PEI).
- CA-EFB adsorbed methylene blue up to 130 mg/g.
- PEI-EFB adsorbed phenol red up to 171 mg/g.
- Both EFBs can be reused up to seven cycles of adsorption/desorption processes.

GRAPHICAL ABSTRACT



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ABSTRACT

Oil palm empty fruit bunch (EFB) fibers were employed to remove dyes from aqueous solutions via adsorption approaches. The EFB fibers were modified using citric acid (CA) and polyethylenimine (PEI) to produce anionic and cationic adsorbents, respectively. The CA modified EFB fibers (CA-EFB) and PEI-modified EFB fibers (PEI-EFB) were used to study the efficiency in removing cationic methylene blue (MB) and anionic phenol red (PR) from aqueous solutions, respectively, at different pHs, temperatures and initial dye concentrations. The adsorption data for MB on the CA-EFB fitted the Langmuir isotherm, while the adsorption of PR on the PEI-EFB fitted the Freundlich isotherm, suggesting a monolayer and heterogeneous adsorption behavior of the adsorption processes, respectively. Both modified fibers can be regenerated up to seven adsorption/desorption cycles while still providing as least 70% of the initial adsorption capacity.

1. Introduction

Water pollutants from dyes industries, including textile, leather, paper, printing, and cosmetic, have caused environmental problems in water ecosystem. Release of dye compounds into water system without proper treatment will harm aquatic life due to toxicity, interrupt aquatic food chains, prevent sunlight into water ecosystem, and reduce photosynthesis (Almeida et al., 2009).

Synthetic dyes usually possess complex molecular structure and are stable in water. Dyes can be classified according to their chemical structure and application, for example, anionic (direct, acid, and reactive dyes), cationic (basic dyes), disperse, solvent, sulfur, vat, etc. (Gupta and Suhas, 2009; Srinivasan and Viraraghavan, 2010).

There are many physical and chemical techniques for removing dyes from industrial effluent, including chemical coagulation/flocculation, ozonation, cloud point extraction, oxidation, nano-filtration, chemical precipitation, ion-exchange, reverse osmosis, adsorption, and ultra-filtration; however, these techniques possess several limitations such as high cost, requirement of activating

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agents and generation of sludge. Biological treatment is advantageous in the removal of suspended solid, but is not helpful for removing dye compounds from wastewater (Dogan et al., 2009; Robinson et al., 2001).

Adsorption is one of the most economic and widely used methods. Among many adsorbents that are available, activated carbon has been proven to be the most promising due to its high adsorption efficiency, which can be explained by its large surface area, micro-porosity structure and high surface reactivity (Mohan and Karthikeyan, 1997). Several studies also proved that by converting natural adsorbent materials into activated carbon, the adsorption capacity of the materials can be increased significantly (Crini 2006; Gupta and Suhas, 2009). However, there are several problems when it comes to the regeneration of activated carbon, which requires tedious procedures to remove the adsorbate molecules from the inner pores of activated carbon. There are three main regeneration processes for activated carbon, i.e., thermal, chemical, and biological methods (Salvador and Jimenez, 1996). Each method possesses its own limitations, including high heat energy requirements, loss of carbon, use of expensive chemicals, and being time consuming.

Many efforts have focused on developing inexpensive alternative natural adsorbents such as minerals, bio-adsorbents, and agricultural residues that are inexpensive, have low processing costs and are abundantly available (Cengiz and Cavas, 2008; Cheung et al., 2007). Many efforts have also been done to increase the adsorption capacity of bio-adsorbent materials using physical (Chun et al., 2004) and chemical (Gong et al., 2006; Sajab et al., 2011) methods.

Malaysia is one of the world largest palm oil exporters, and about 3.0 million tons of oil palm empty fruit bunch (EFB) fibers are produced every year, which have been used as solid fuel in boilers of processing mills, as organic fertilizer, and as reinforcing fibers for composite making (Mohammed et al., 2012; Rozman et al., 2004). Therefore to further maximize the utilization of the EFB fibers, oil palm EFB fibers were employed in the present study for removal of dyes from aqueous solutions. The EFB fibers, particularly cellulose fraction, were chemically-treated using citric acid (CA) and polyethylenimine (PEI) to obtain anionic and cationic adsorbents, respectively. The CA-EFB and PEI-EFB fibers were used to adsorb methylene blue (MB) and phenol red (PR), respectively, at different pHs, dye concentrations, and temperatures. The regeneration performance of the fibers was also investigated.

2. Methods

2.1. Preparation of EFB fibers

EFB fibers were obtained from Szetech Engineering Sdn. Bhd. (Malaysia). The fibers were milled and sieved to collect fibers with a size ranging from 106 to 150 μm. Prior to modification, the fibers were pre-treated with 0.1 M NaOH (Sigma–Aldrich) at 65 °C for 1 h with agitation of 500 rpm to remove contaminants (oil and waxy substances). The pre-treated EFB fibers were rinsed with deionized water until the pH of the filtrate dropped to ~7. The washed fibers were dried overnight at 50 °C.

2.2. Chemical modifications of EFB fibers

The CA modification of the EFB fibers was performed according to Sajab et al. (2011). Briefly, 10 g of EFB fibers was added to 100 ml of 0.6 M CA (Sigma–Aldrich) at room temperature. The liquid was decanted and the wet fibers were dried in an oven at 50 °C for 24 h. The temperature of the oven was raised to 120 °C and maintained at this temperature for 90 min. The modified EFB fibers were washed with hot water to remove excess CA. The fibers were then dried in the oven at 50 °C for 24 h and stored in a desiccator.

The PEI modification was carried out according to a previously reported procedure (Deng and Ting, 2005). Briefly, 10 g of EFB fibers was treated with PEI solution (5% (w/v) ($M_W \sim 750{,}000$, 50 wt.% in H_2O) at 65 °C for 6 h. The mixture was transferred to 500 ml glutaraldehyde (1% v/v) and left to stir at room temperature for 1 h. The mixture was washed several times with deionized water and dried in the oven at 50 °C for 24 h and stored in a desiccator.

2.3. Characterization of the EFB fibers

Changes in the functional groups on EFB fibers after CA treatment were verified using a Perkin Elmer GX Fourier transform infrared (FTIR) spectrometer. The surface charge of the raw and modified EFB fibers was examined using a Malvern Zetasizer Nano ZS.

2.4. Preparation of dye solutions

Methylene blue (MB) trihydrate (Mallinckrodt, ⩾99%) and phenol red (PR) (Sigma–Aldrich) solutions were prepared and diluted accordingly to the required initial concentrations. The concentrations of MB and PR in working solutions were measured using a UV–Vis spectrophotometer (Jenway 7315 Spectrophotometer) at a λ_{max} of 665 nm and 430 nm, respectively. Standard calibration curves were prepared from the MB and PR solutions with different concentrations that yielded absorbances ranging from 0.1 to 1.

2.5. Adsorption studies

Adsorption experiments were carried out to determine the effect of pH of the dye solutions on the adsorption performance of the modified fibers at room temperature. Briefly, 0.1 g of EFB fibers was added into a flask containing 100 ml of dye solution (100 mg/l) at different initial pH, ranging from pH 3 to 9. The initial pH was adjusted using 0.01 M HCl or 0.01 M NaOH. The mixture was stirred at 250 rpm for 6 h. The concentration of dye in the supernatant solution (C_e) was measured using the spectrophotometer. The amount of dye adsorbed per unit mass of fibers (q_e) was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of dye (mg/l), respectively. V is the volume of the dye solution (l) and m is the mass of adsorbent (g). The percent of dye removal was calculated using the following equation:

$$\text{Percentage of dye removal } (\%) = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (2)$$

2.6. Adsorption kinetics

A similar procedure as described in Section 2.5 was employed to investigate the adsorption kinetics of the modified fibers towards MB and PR at different dye concentrations (50–300 mg/l) and temperatures (20–60 °C). The temperature of the solution was controlled using a water bath shaker (Lab Companion BS-06) with a temperature regulator. Aliquots of solution (~0.1 ml) were withdrawn at various times, centrifuged at 4000 rpm for 10 min and the concentration of MB was determined (Eq. (2)). The amount of dye adsorbed per unit mass of fibers at time t, q_t (mg/g) was calculated using the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (3)$$