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Mesoporous carbonaceous material from fish scales as low-cost adsorbent for reactive orange 16 adsorption

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ABSTRACT

This work investigates the possibility of utilizing carbonized fish (*Labeo rohita*) scales (CFS) as low-cost materials for the adsorption of reactive orange 16 dye (RO16) through batch processing. The textural and morphological characteristics of CFS were evaluated which showed mesoporous structure with BET surface area of 213.82 m^2/g and average pore diameter of 5.116 nm. The effects of initial RO16 concentration (25–400 mg/l), solution pH (3–13), and temperature (30–50 °C) on the adsorption efficiency of the prepared CFS were demonstrated. The equilibrium isotherm data were best correlated using the Freundlich equation. The prepared CFS exhibited maximum adsorption capacities of 105.8, 107.2, and 114.2 mg/g at 30 °C, 40 °C, and 50 °C, respectively. The pseudo-second-order model well represented the adsorption kinetics. The prepared CFS had a high adsorption capacity for RO16 and could be utilized effectively for the removal of reactive dyes from wastewater.

1. Introduction

Water pollution caused by synthetic organic dyes through the discharge of common effluents from textile and dyestuff industries is a worldwide environmental problem. Commercial dyes have over 1,00,000 types and a yearly production higher than 7,00,000 tons; moreover, about 2% of the produced dyes are discharged directly in aqueous effluent [1]. Given the variety of color shades and flexibility of utilization, reactive dyes are one of the widely used colorants in the textile industry [2]. During the dying process, 10–50% of these dyes are lost, which produce highly colored effluents. The direct disposal of these effluents into the aquatic environment is extremely deleterious because most of the dyes are carcinogenic and mutagenic; therefore, from the environmental viewpoint, the efficient removal of reactive dyes from wastewaters is very significant [3].

Many technologies have been applied for removal of synthetic dyes; however adsorption appears to be the most convenient and popular method due to its simplicity and high efficiency [4,5]. Although, zeolites and activated carbon are commonly used adsorbent for treatment of dyes and other pollutants [6–9], char represents an alternative, effective, and inexpensive adsorbent, wherein the production of activated carbon requires higher temperature and additional activation process [10]. Char is a carbon-rich solid produced by the pyrolysis of organic wastes under the partial or full absence of oxygen. The favorable properties including surface characteristics, considerable hydrophobicity and aromaticity, and more surface functional groups, render char a suitable adsorbent for the treatment of organic and inorganic contaminants [11,12].

Several fish species are consumed daily in different parts of the world. Consequently, a large amount of wastes, which account for 50–70% of original materials, are generated in fish shops and processing factories [13]. The total fish output in Malaysia in 2010 was approximately 1.77 million tons at a value of RM 6.8 million; of the total production, 30% are solid wastes consisting of skin, scale, and bone [14]. The accumulation of these wastes leads to acute environmental contamination with undesirable odor and health problems. Therefore, the optimized treatment of these wastes to generate value-added products is the best solution. Solid fish wastes have been utilized for the production of a porous carbon with high performance for attraction of acid dye pollutant [15]. The high organic composition of fish scales, which are mainly of collagen fibers, provides the carbon for porous carbonaceous materials [16]. The objective of this work is to utilize carbonized fish scales as low-cost adsorbent for the adsorption of reactive orange 16 dye (RO16). In addition, the adsorption behavior of RO16 dye onto carbonized fish scales (CFS) is illustrated in terms of isotherms, kinetics, and thermodynamics.

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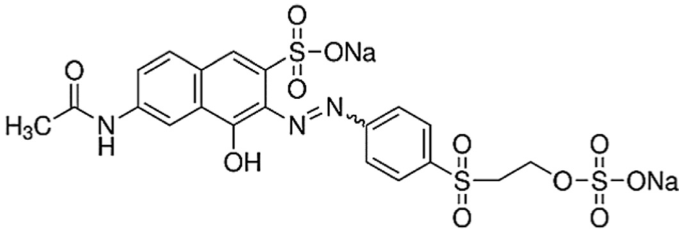
Table 1
Characteristics and structure of RO16 dye.

Structure	Formula	Molecular weight (g/mol)	λ_{max} (nm)
	$C_{20}H_{17}N_3Na_2O_{11}S_3$	617.54	492

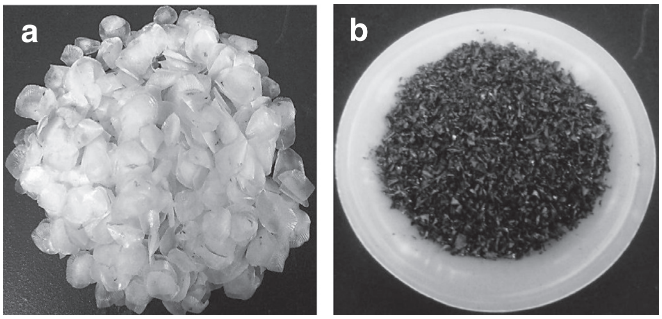


Fig. 1. Images of (a) raw and (b) carbonized FS.

2. Materials and methods

2.1. Materials

The raw fish scales (hereafter FS) were obtained from a local shop in Penang, Malaysia and repeatedly washed with distilled water to remove soluble impurities. The FS were then placed in an oven at 60 °C for 24 h and stored in tightly sealed containers until further use. RO16 dye was supplied by Sigma-Aldrich, Malaysia and was used as an adsorbate. The characteristics and chemical structure of RO16 dye are shown in Table 1.

2.2. Preparation and characterization of CFS

The carbonization of FS was conducted in an electrical furnace under N_2 (99.99%) at a flow rate of 100 cm^3/min and a heating rate of 10 °C/min. The sample was placed in a tubular stainless steel reactor and maintained at 600 °C for 90 min. After carbonization, the prepared CFS was cooled under N_2 gas flow to room temperature. To remove residual inorganic matters from the prepared CFS and to open up its pores, CFS was washed with 1 M HCl. It was then rinsed with hot distilled water until the filtrate became neutral. The CFS were then dried at 105 °C for 24 h and were subsequently ground and sieved to a fraction of fine particles through a mesh of 250–500 µm. Raw and carbonized FS are shown in Fig. 1. The yield of prepared CFS was calculated using following equation [17]:

$$\text{Yield}\ (\%) = \frac{W_f}{W_o} \times 100 \tag{1}$$

where W_f and W_o (g) are the mass of CFS and FS, respectively.

To assess the effect of carbonization temperature on FS, thermo-gravimetric analysis (TGA) of FS was conducted with a Perkin–Elmer STA 6000 TG/DTG analyzer. The elemental composition was performed using Quanta FEG 450 equipped with Oxford Instrument X-Max for energy-dispersive X-ray (EDX). The surface characteristics of CFS were measured using N_2 adsorption and desorption isotherms at 77 K over a wide range of relative pressures with an automated Micromeritics ASAP 2020 surface area analyzer. The Brunauer–Emmett–Teller (BET) surface area was calculated by the BET equation. The micropore volume and total pore volume were determined using *t*-plot method. The surface morphologies of the raw FS and CFS were imaged using Zeiss Supra 35VP scanning electron microscope. The functional groups was examined by a Fourier transform infrared (FTIR) spectrometer (Model 2000 FTIR, USA) with the wave number ranging from 4000–400/cm.

2.3. Adsorption studies

Batch equilibrium experiments were conducted by adding CFS powder (0.20 g) to a set of 250 ml conical flasks containing 200 ml of RO16 solutions with initial concentrations of 25, 50, 100, 150, 200, 300, and 400 mg/l. The sealed flasks were shaken at 125 rpm at various temperatures (*i.e.*, 30 °C, 40 °C, and 50 °C), and pH was kept natural without any adjustment until equilibrium was reached.

Solution pH was calibrated by adding a few drops of 0.1 M NaOH and 0.1 M HCl before each run to study the effect of the solution pH on the removal of RO16 by CFS adsorbent. The operating conditions were as follows: amount of CFS = 0.1 g; initial concentration of dye solution = 100 mg/l; temperature = 30 °C; and contact time = 24 h. For the point of zero charge (pHpzc) determination the initial pH (pH_i) of aqueous solutions (100 ml) were adjusted to a pH range of 2–12 using 0.1 M HCl or NaOH. Then, 0.1 g of CFS was added to each adjusted solution. The dispersions were shaken for 48 h at 30 °C, and the final pH of the solutions (pH_f) was determined. The point of zero charge (pHpzc) is the point where the curve pH_f vs. pH_i intersects the line $pH_f = pH_i$.

Aqueous samples were taken from each RO16 solutions at precise time intervals. The concentrations of the RO16 in the supernatant solution before and after adsorption were determined using a double-beam UV–visible spectrophotometer (UV-1700 Shimadzu, Japan) at maximum wavelength, $\lambda_{max} = 493$ nm. The percentage removal (%) of RO16 by the CFS adsorbent is described by the following:

$$Removal\ (\%) = \frac{C_o - C}{C_o} \times 100 \tag{2}$$

where C_o and C (mg/l) are the initial and final concentrations of RO16, respectively. The adsorbed amount at equilibrium, q_e (mg/g), was computed from the concentration of the dye solution according to following relation:

$$q_e = \frac{(C_o - Ce)V}{W} \tag{3}$$

where C_o and C_e (mg/l) are the initial and equilibrium liquid-phase concentrations of RO16, V is the volume of the dye solution (l), and W is the weight of CFS powder (g).

The experimental equilibrium data were fitted using two well-known isotherm models, namely, Langmuir and Freundlich

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