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Original Research Paper

Neem (*Azadirachta indica*) Leaf Powder: A Plant-Based Adsorbent for Removal of Textile Acid Azo Dye from Aqueous Solution

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ABSTRACT

A plant-based adsorbent was prepared from Neem (*Azadirachta indica*) leaf and adsorption of two textile acid azo dyes, Acid Red 18 and Acid Orange 7, from aqueous solution was examined. Batch adsorption test showed that extent of dye adsorption depended on contact time, pH and adsorbent dose. Equilibrium adsorption was attained in 5 h and maximum adsorption occurred at pH 2. Dye adsorption followed pseudo second-order kinetics. Equilibrium adsorption data were described by the Langmuir and Freundlich adsorption isotherm models. Acid dye adsorption capacity of the Neem leaf powder was compared with that of other plant-based adsorbents and activated carbons. Neem leaf powder is effective in adsorptive removal of acid dyes from aqueous solution and textile dye waste.

INTRODUCTION

Acid dyes are water soluble anionic dyes that are typically used to dye acrylics, wool, nylon, and nylon/cotton blends from acid dye bath. Azo dyes, characterized by their typical azo bond (R1-N = N-R2), are more popular group of acid dyes used in the textile industry (Somasiri et al. 2006). More than one million tons of dyes annually produced in the world are azo dyes representing 70% by weight (Hao et al. 2000). Due to their poor exhaustion properties, as much as 30% of initial dye applied remains unfixed and ends up in the dye waste (Manu & Chaudhari 2003).

Adsorption by activated carbon is an effective treatment method that is widely used in the removal of contaminants from water and wastewater. This method has also been proven to be effective in the treatment of coloured textile dye waste (Gerçel et al. 2009). However, the use of coal-based commercial activated carbon is limited because of relatively high price and non-renewable feedstock. Low-cost, renewable, and easily available plant-based materials need to be explored as adsorbents for removing dyes from textile dye waste. Effectiveness of Neem (*Azadirachta indica*) leaf in adsorption of reactive dye Remazol Blue RR and basic dyes, Brilliant Green and Methylene Blue, has been studied (Bhattacharyya & Sarma 2003 & 2005, Immich et al. 2009).

In the present study, adsorption of two acid azo dyes, Acid Red 18 and Acid Orange 7, from aqueous solution by Neem leaf powder was examined. Acid dye adsorption capacity of the Neem leaf powder was compared with that of other plant-based adsorbents and activated carbons.

MATERIALS AND METHODS

Neem leaf powder: Mature Neem (*Azadirachta indica*) leaves were washed repeatedly with distilled water to remove dust and soluble impurities, and allowed to dry first at room temperature (22°C) and then in an air oven at 80°C till the leaves became crisp that could be crushed into a fine powder in a blender. The Neem leaf powder (NLP) was sieved and the 200-300 mesh fraction was separated. This fraction was again washed number times with distilled water till the washings were free of colour and turbidity. After drying for several hours at room temperature, the NLP was stored in a capped bottle for use in adsorption test. Fourier transform infrared (FTIR) spectrum of the NLP (Fig. 1) indicated presence of functional groups –OH, $-NH_2$, ≡CH, >C=N-, ≡C-C≡, ≡C-N<, ≡C-O-, >C=O, >C=C<, >C=S and asymmetric stretching of C-O-C in cellulose and hemicellulose.

Acid azo dye: Acid azo dyes, Acid Red 18 and Acid Orange 7, were obtained from Euro Chemo-Pharma Sdn. Bhd., Penang, Malaysia. Concentration of dye was determined by measuring the absorbance at the wavelength of maximum absorbance (Acid Red 18: 505 nm; Acid Orange 7: 485 nm) against a standard curve.

Adsorption test: Batch adsorption test was carried out by shaking 100 mL of dye solution with 0.5 g of NLP in a

Table 1: Reaction rate constants.

Dye	Pseudo first-order k_1 (h^{-1})	R^2	Pseudo second-order k_2 (g/mg·h)	R^2
Acid Red 18	1.687	0.968	1.465	0.999
Acid Orange 7	0.023	0.923	3.613	0.999

Table 2: Langmuir and Freundlic constants.

Dye	Langmuir constant Q^o	b	Freundlich constant K_f	$1/n$
Acid Red 18	11.23	0.205	3.23	0.275
Acid Orange 7	9.61	0.249	3.47	0.288

stoppered glass bottle placed on an orbital shaker at 150 rpm and room temperature (22°C). After a predetermined contact time, the bottle was removed from the shaker and the supernatant was filtered through 0.45 µm membrane filter and analysed for dye concentration. The effect of pH (2-8), contact time (0-6 h), dye concentration (20 and 40 mg/L) and NLP dose (2-10 g/L) on adsorption were evaluated. Adsorption isotherm was determined by batch equilibrium test at the optimum pH and contact time for adsorption with 100 mL of 10-100 mg/L of dye solution and 0.5 g of NLP.

RESULTS AND DISCUSSION

Effect of pH: The effect of pH on adsorption of Acid Red 18 and Acid Orange 7 by NLP from a 20 mg/L solution in 12 h is shown in Fig. 2. Adsorption was high at low pH and maximum adsorption occurred at pH 2. Since pH of acid dye bath and textile dye waste is usually 2-3, adsorption at pH lower than 2 was not considered. At low pH, electrostatic attraction between the negatively charged dye anions and positively charged surface sites on NLP resulted in high adsorption of the anionic acid dyes (Hashemian et al. 2008). Maximum adsorption of acid dyes on orange peel, peanut hull and rice bran was observed at pH 2 (Sivraj et al. 2002, Gong et al. 2004, Hashemian et al. 2008). All subsequent adsorption tests were conducted at pH 2.

Effect of contact time and dye concentration: The effect of contact time and dye concentration on adsorption of Acid Red 18 and Acid Orange 7 by NLP is shown in Figs. 3 and 4, respectively. Extent of dye adsorption increased with decrease in dye concentration and increase in contact time. Equilibrium adsorption was attained in 5 h. A contact time of 5 h was used in all subsequent adsorption tests.

Effect of NLP dose: Fig. 5 shows the effect of NLP dose on adsorption of Acid Red 18 and Acid Orange 7 from a 20 mg/L solution. Adsorption increased with NLP dose and attained complete removal at 8 g/L NLP dose.

Adsorption kinetics: To identify the kinetics of dye adsorption by NLP, two commonly used kinetic models i.e., pseudo first-order (Lagergren 1998) and pseudo second-order (Ho et al. 2000) were employed.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad ...(1)$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad ...(2)$$

Where, q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g), q_t is the amount of solute adsorbed at time t per unit weight of adsorbent (mg/g), and k_1 and k_2 are reaction rate constants. The following linearised time dependent functions were obtained by integrating and rearranging equations (1) and (2) for the boundary conditions $t = 0$ to > 0 and $q = 0$ to > 0.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad ...(3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad ...(4)$$

Figs. 6 and 7 show the pseudo first-order and pseudo second-order kinetic plots for adsorption of Acid Red 18 and Acid Orange 7 by NLP. The reaction rate constants calculated from equations (3) and (4) are given in Table 1. The R^2 values as well as Fig. 6 and 7 indicate that kinetics of acid dye adsorption by NLP is better expressed by the pseudo second-order kinetic model. Compliance to the pseudo second-order kinetic model strongly suggests chemical adsorption or chemisorption.

Adsorption isotherm: In adsorption in a solid-liquid system, the distribution ratio of the solute between the liquid and the solid phase is a measure of the position of equilibrium. The preferred form of depicting this distribution is to express the quantity q_e as a function of C_e at a fixed temperature, the quantity q_e being the amount of solute adsorbed per unit weight of the solid adsorbent, and C_e the concentration of solute remaining in the solution at equilibrium. An expression of this type is termed an *adsorption isotherm* (Weber 1972). The Langmuir adsorption isotherm is

$$q_e = \frac{Q^o b C_e}{1 + bC_e} \qquad ...(5)$$

where, $Q°$ is the number of moles of solute adsorbed per unit weight of adsorbent in forming a monolayer on the surface (monolayer limiting adsorption capacity) and b is a constant related to the energy of adsorption.

The Freundlich adsorption isotherm is

$$q_e = K_f C_e^{1/n} \qquad ...(6)$$

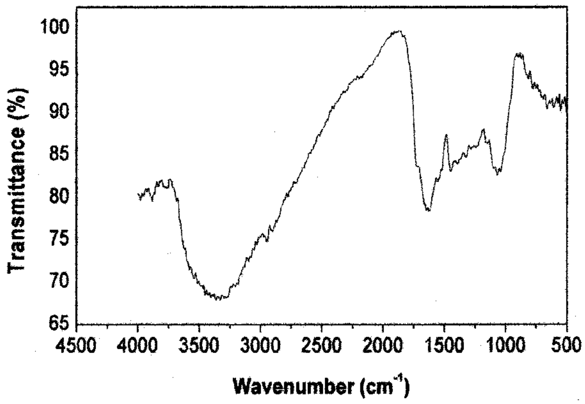

Fig. 1: FTIR spectrum of Neem leaf powder.

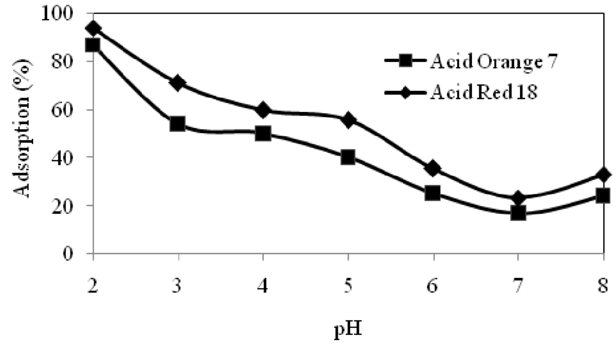

Fig. 2: Effect of pH on adsorption of Acid Red 18 and Acid Orange 7.

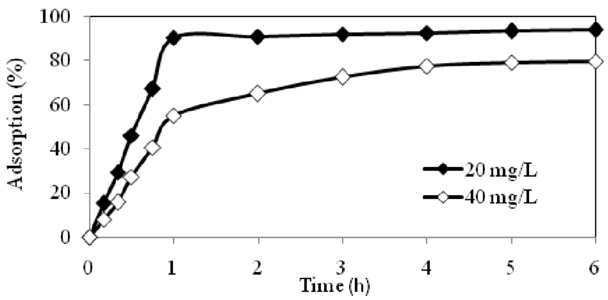

Fig. 3: Effect of contact time and dye concentration on adsorption of Acid Red 18.

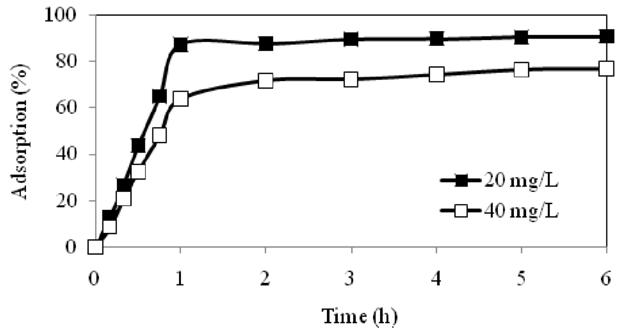

Fig. 4: Effect of contact time and dye concentration on adsorption of Acid Orange 7.

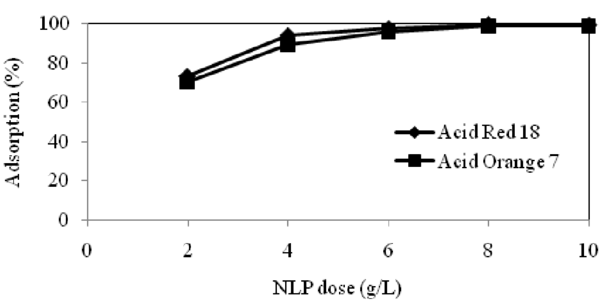

Fig. 5: Effect of NLP dose on adsorption of Acid Red 18 and Acid Orange 7.

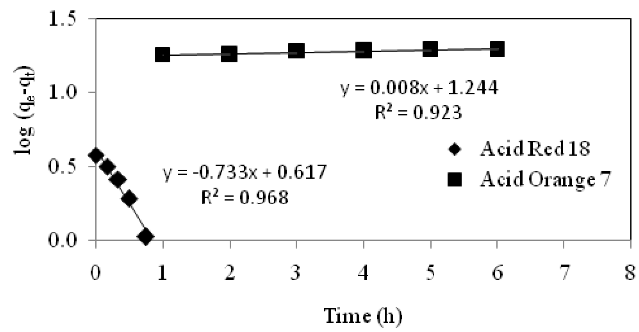

Fig. 6: Pseudo first-order kinetic plot.

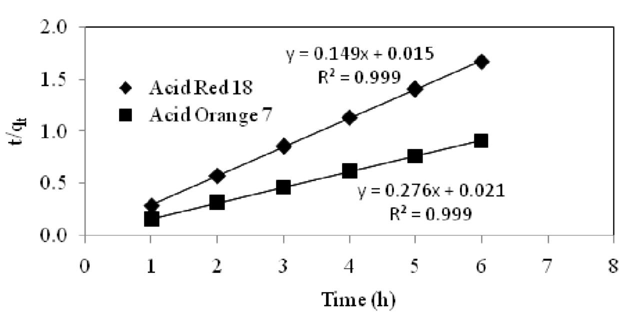

Fig. 7: Pseudo second-order kinetic plot.

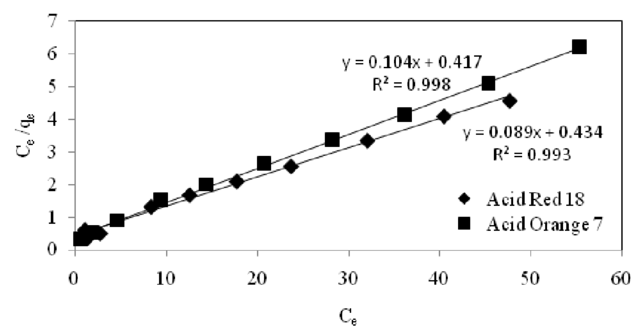

Fig. 8: Langmuir adsorption isotherm.

Table 3: Acid dye adsorption capacity of plant-based adsorbents and activated carbon.

Adsorbent	Dye	Adsorption capacity (mg/g)	pH	Reference
Neem leaf powder	Acid Red 18	11.23	2.0	This study
	Acid Orange7	9.61	2.0	
Rice bran	Acid Red 138	0.85	2.0	Hashemian et el. (2006)
Orange peel	Acid Violet 17	19.88	2.0	Sivraj et al. (2001)
Peanut hull	Amaranth	14.90	2.0	Gong et al. (2004)
	Sunset Yellow	13.99	2.0	
Commercial activated carbon	Acid Red 18	13.70	3.0	Zaid (2009)
	Acid Orange 7	17.24	3.0	
Coconut coir activated carbon	Acid Red 18	10.99	3.0	Zaid (2009)
	Acid Orange 7	13.16	3.0	

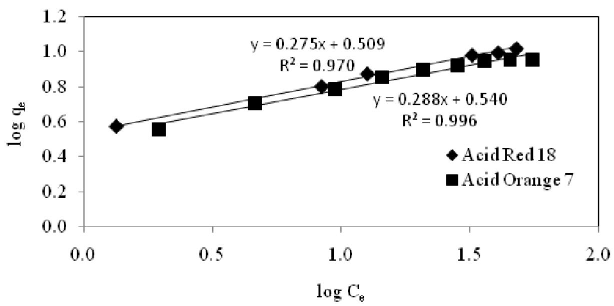

Fig. 9: Freundlich adsorption isotherm.

where, K_f is the Freundlich constant (adsorption capacity) and *1/n* represents the adsorption intensity.

Adsorption isotherm for adsorption of Acid Red 18 and Acid Orange 7 by NLP were determined by batch equilibrium test using optimum contact time and pH (5 h and pH 2) for adsorption. The isotherms were fitted to the linear form of the Langmuir equation [$C_e/Q_e = 1/(bQ^o) + C_e/Q^o$] (Fig. 8) and Freundlich equation [$\log q_e = \log K_f + (1/n)\log C_e$] (Fig. 9). The values of Langmuir constants $Q°$ and b, and Freundlich constants K_f and *1/n* are given in Table 2. Acid dye adsorption capacity of NLP is compared with that of other plant-based adsorbents and activated carbons (Table 3). NLP is effective in the removal of acid dyes from aqueous solution.

CONCLUSIONS

Maximum adsorption of acid dyes, Acid Red 18 and Acid Orange 7, by Neem leaf powder occurred at pH 2 and equilibrium adsorption was attained in 5 h. Dye adsorption followed pseudo second-order kinetics. Equilibrium adsorption data were well described by the Langmuir and Freundlich adsorption isotherm models. Neem leaf powder is effective in adsorptive removal of acid dyes from aqueous solution and textile dye waste.

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