

# Adsorptive uptake of basic dyes from aqueous solution by novel brown linseed deoiled cake activated carbon: Equilibrium isotherms and dynamics



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## ABSTRACT

In present work, various process parameters for the adsorptive removal of acridine orange and azure B onto a novel activated carbon prepared from brown linseed (*Linum usitatissimum* L.) deoiled cake with phosphoric acid activation were optimized. The activated carbon was characterized using FTIR, surface area (adsorption desorption isotherm), field emission-scanning electron microscopy, and X-ray diffraction studies. Isotherm data were modeled using non-linear Langmuir, Freundlich, Temkin and D-R equations. Freundlich isotherm model best fitted the data with good correlation coefficient, suggesting heterogenous distribution of adsorption sites. The adsorbent demonstrated high Langmuir monolayer saturation capacity ( $Q_m$ ) of 213.57 for acridine orange and 136.58 mg/g for azure B. Pseudo-second-order kinetic model followed the kinetic data, with liquid-film diffusion controlling the overall adsorption rate. The negative  $\Delta G^\circ$  values (5.92–13.15 kJ/mol for AO and 10.21–20.98 kJ/mol for AzB) confirmed the feasibility and spontaneity of the process. The positive values of  $\Delta H^\circ$  (17.16–75.48 kJ/mol) indicated endothermic adsorption.

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## 1. Introduction

The release of synthetic organic dyes into aquatic streams especially from textile, leather, paper and paints industries has a serious impact on the environment and poses a health risk to humans. Acridine orange (AO) and Azure B (AzB) are water soluble cationic dyes widely used in leather and textile industries. AO ( $C_{17}H_{19}N_3 \cdot \frac{1}{2}ZnCl_2$ , molar mass: 369.96) is a dark orange solid (mp: 165 °C) belonging to xanthene class of dyes, and is soluble in water and ethanol, while AzB ( $C_{15}H_{16}ClN_3S$ , molar mass: 305.83), a thiazine dye, is a dark green crystalline solid (mp: 205 °C) soluble in water but sparingly soluble in ethanol. AO is considered mutagenic and causes skin irritation, when in contact [1], while AzB is carcinogenic and photo-toxic [2,3]. Therefore, pre-treatment of wastewater is needed before discharging into the water bodies.

Among various water treatment methods such as coagulation/flocculation [4,5], precipitation [6], advanced oxidation [7], and photo-catalytic degradation [8,9], the adsorption process is considered to be the best method due to simplicity of design

and operation, economic feasibility and reusability of adsorbents [5,10–12]. The commercial activated carbon, both granular and powdered, is an excellent adsorbent for pollutants' removal from wastewater because of its high surface area and reactivity, adequate pore size/volume distribution, and relatively high mechanical strength [13]. However, due to its high cost and consistent loss during the regeneration process, the quest for cheaper, renewable and abundant wastes biomass as precursors for activated carbon production has increased in recent years. Recently, activated carbons derived from walnut and poplar woods [14], rice straw [15], coconut shell [16], pineapple waste biomass [17], bamboo [18,19], *Loofa* *egyptiaca* [20], avocado kernel seeds [21], mango seed (*Mangifera Indica* L.), guava (*Psidium guajava* L.) and orange (*Citrus sinensis* L.) [22], rattan sawdust [23], sun flower oil cake [24], jackfruit (*Artocarpus heterophyllus*) peel [25], olive stones [26], *Flamboyant* (*Delonix regia*) pods [27], *Borassus aethiopum* (palm flower) biomass [28], and cherry stones [29] have been reported for decolourization of dyes-laden wastewaters.

Activated carbons are generally prepared by physical or chemical activations. In physical activation, the lignocellulosic precursor is first carbonized at high temperature (873–1173 K) in an inert environment, and then subjected to  $CO_2$  or steam activation [30–32]. However, chemical activation involves

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impregnation with mineral acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{H}_3\text{PO}_4$ ), salts ( $\text{ZnCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{K}_2\text{CO}_3$ ), or alkali ( $\text{KOH}$ ,  $\text{NaOH}$ ) as activating agents. Chemical activation is considered to be a superior method for activated carbon production because of its simplicity, reduced activation time/temperature, higher carbon yield and development of good pore structure [33].  $\text{H}_3\text{PO}_4$  is preferred over other activators for manufacture of activated carbons on large-scale in recent years because it has environmental benefits and several other advantages [34].

Linseed (*Linum usitatissimum* L.) is a commonly cultivated (468.0 thousand ha) oil crop in India with productivity of 349 kg/ha per annum. The deoiled cake, obtained after extraction of oil from seed, is abundant and an easily available agricultural waste biomass. The deoiled cake usually has no economic importance and is commonly used as feed for ruminant livestock or as fertilizer. The linseed deoiled cake with high carbon (53.23 wt%) and low ash (6.30%) [35] contents could be a potential renewable precursor for the production of activated carbon, which may enhance its economic utility. Activated carbon derived from some deoiled cakes have recently been reported [36,37] for the adsorptive removal of dyes/metals from aqueous solution. But to our present knowledge, the linseed de-oiled cake has not been utilized for the preparation of activated carbon for treatment of aqueous effluents.

The objectives of the present study are to utilize the brown linseed (*Linum usitatissimum* L.) deoiled cake as a precursor for preparation of the activated carbon (LCAC) by  $\text{H}_3\text{PO}_4$  activation, to evaluate its efficiency towards the adsorption of textile dyes, AO and AzB from aqueous solution, and, to optimize the process variables such as contact time, initial dye concentration, adsorbent dose, pH and temperature using batch procedure. The linear model is often used to estimate the isotherm and kinetic parameters because of its simplicity. But it is not considered an appropriate method in terms of accuracy of results. Therefore, the isotherm and kinetic coefficients were determined by non-linear regression analyses, which have a uniform error distribution. In order to understand the industrial applicability of the activated carbon, the efficiency of LCAC was evaluated using real textile industries wastewater. The reusability of adsorbent was tested for four cycles.

## 2. Materials and methods

### 2.1. Materials and chemicals

AO, AzB (Loba Chemie, Mumbai, India) (Fig. 1)  $\text{H}_3\text{PO}_4$ , NaCl, NaOH, HCl (AR grade, Merck, India) were used as such. Linseed

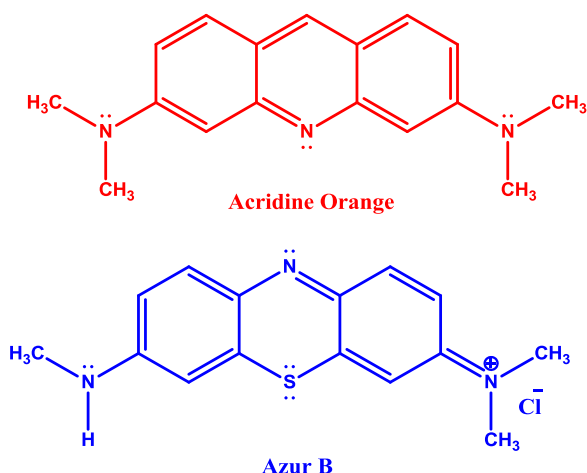


Fig. 1. Molecular structure of Acridine orange and Azure B.

deoiled cake (LC; 5 kg, moisture: 5.4%, oil content: 3%) was purchased from a local supplier at Sadar Bazar, Delhi, India, washed with distilled water to remove adhering impurities and dried in an electric oven at 50–60 °C. It was thoroughly homogenized by mechanical grinding, sieved to 0.5–1.0 mm particle size, and finally stored in a PVC food grade air-tight container.

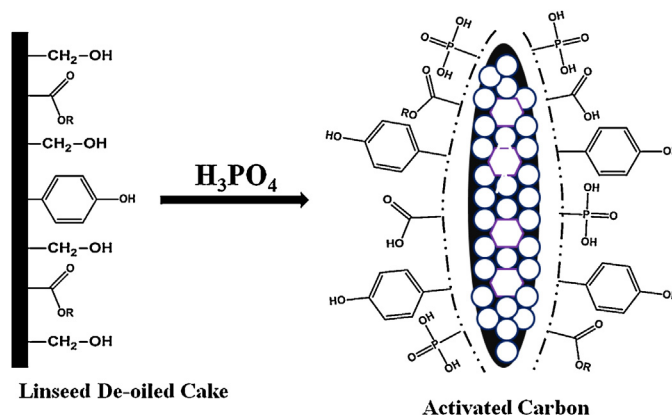
The stock solutions of AO and AzB (250 mg/L) were prepared by dissolving 62.5 mg of dyes in 250 mL of double distilled water. The solutions of respective dyes of desired concentration were prepared by diluting the stock solution with double distilled water.

### 2.2. Preparation of activated carbon

De-oiled linseed cake (LC, 100 g) was transferred into a beaker (1 L). To it, was added 500 mL of double distilled water and the content stirred for 4–5 h at 333–343 K, and the supernatant decanted to remove traces of oil/dirt. The process was repeated until the supernatant became clear, and finally the slurry was filtered using a Buchner funnel. Any organic impurities present in the biomass (LC) was oxidized with 50 mL of hydrogen peroxide (30%) at 333 K for 24 h and after washing with double distilled water, the biomass was dried in *vacuo* at 383 K for 2 h. The treated LC (80 g) was impregnated with 85% phosphoric acid in 1:1.5 ratio (w/w) according to the reported procedure [38] at 303 K for 24 h. The impregnated biomass was heated at 973 K in a programmable muffle furnace (heating rate = 283 K/min;  $\text{N}_2$  flow rate = 10  $\text{cm}^3/\text{min}$ ). The furnace temperature was maintained at 973 K for 2 h, thereafter, it was left to cool to room temperature in an inert environment. The resulting activated carbon (LCAC) was washed with 1% sodium bicarbonate solution (w/v) followed by hot double distilled water till the runoff reached neutral pH. The solid activated carbon was oven dried for 24 h at 383 K, and stored in an air-tight polypropylene bottle after sieving to < 75  $\mu\text{m}$  size. The schematic diagram for activated carbon preparation is presented in Scheme 1.

### 2.3. Characterization of LC and LCAC

The surface functional groups were determined by Boehm titration method [39]. The FTIR spectra ( $4000\text{--}400\text{ cm}^{-1}$ ) of LC (deoiled linseed cake) and LCAC (de-oiled linseed cake activated carbon) was recorded with Perkin Elmer IR spectrometer (model BX spectrum) as KBr pellets. Surface area was determined using multipoint Brunauer–Emmett–Teller (BET) method with Surface Area Analyzer (Micromeritics Instruments Corp., Gemini 2375 V5.01, Georgia, USA) by nitrogen adsorption-desorption at 773 K. Scanning Electron Micrographs (SEM) were recorded with Carl Zeiss (Sigma 5.05, Germany/FE Quatnta 200F, USA) and Energy



Scheme 1. Schematic diagram for preparation of activated carbon.

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