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The use of low-cost adsorbent (Canola residues) for the adsorption of methylene blue from aqueous solution: Isotherm, kinetic and thermodynamic studies

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ABSTRACT

The batch adsorption was carried out to study and investigate pH, initial concentration of MB, adsorbent dosage and contact time. The best efficiency of MB removal by Canola residues were obtained at pH alkaline, dose adsorbent of 3.5 g/L, initial concentration of MB of 25 mg/L and contact time of 75 min. The maximum dye removal was obtained to be 97.5%. As the Canola concentration was increased from 0.5 to 5 g/L, the equilibrium adsorption capacity of Canola (q_e) decreased from 16.7 to 4.87 mg/g, whereas, the MB removal efficiency increased from 33.4% to 97.5%. The adsorption kinetics and equilibrium data were in good agreement with the pseudo-second-order kinetic model and Sips adsorption isotherm respectively. Thermodynamic parameters suggest that the adsorption is a typical physical process, which is spontaneous and endothermic. The study demonstrated that biomass is effective to remove MB under a wide range of experimental conditions.

In recent decades, water pollution has become one of the major environmental problems due to the releasing of toxic and hazardous chemicals from various industrial activities [1–3]. The dye-contained effluents are supposed to be a significant concern due to the adverse effects of dye in various parts of the life cycle [4–6]. The toxicological and aesthetical problems associated with releasing of dyes into the environment are the main reasons of these worries [7,8]. Methylene blue (MB) is one of the widespread materials in dye which is used for cotton and silk painting [9,10]. Eye burn is one of the most harmful effects of MB because it is considered as a permanent injury of the eyes [6,11]. It can also create breathing problems, nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia [8,12].

Canola stalk is considered as easily-available lignocellulosic wastes all over the world because the production and use of vegetable oil are increasing and Canola is extensively used for this purpose; therefore, Canola stalk can be easily founddue to its characteristics and it has been used in several studies to remove pollutants [13–15].

In addition to the abovementioned properties, several other adsorbents such as combination of nanoparticles (loaded on AC) help the researchers to remove the high quantity of various dyes in a short time [16–20].

The aim of the present work was: (i) to determine maximum removal of MB in different conditions such as pH, contact time, adsorbent dose and initial concentration of MB, (ii) to estimate linear and nonlinear methods of the isotherm and kinetic model parameters, and (iii) to study the thermodynamic of the process.

The Canola residues were collected in agricultural fields during the harvesting season, which was later followed by washing with distilled water to remove dust impurities, and then dried completely in natural sunlight. The dried materials were crushed into fine particles with the help of an electric mill. In order to eliminate the color and contaminants, the fine particles were then mixed with distilled water in a ratio of 1 to 5 and then heated at 100 °C for 5 h. The prepared particles were treated with 0.1 M HCl for 5 h and then washed with distilled water and were

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dried in a shed. After drying, the adsorbent was milled again to smaller particles with an electric mill [21].

Methylene blue (MB, basic blue 9, C.I.52015; chemical formula ($C_{16}H_{18}N_3ClS$; MW, 373.90 g mol^{-1}) was used as the model impurity in the present study. The obtained chemical formula is shown in Fig. S1.

The specific surface area of dried Canola was determined by the BET-N_2 method using an ASAP 2000 apparatus based nitrogen adsorption–desorption isotherms at 77 K. (Fig. S2a and b).

The pH value of the solution was an important influential parameter that plays a key role during the adsorption process and it was found that the initial pH value of the solution has more influence than the final pH. The percentage sorption of MB at every concentration was minimum at the initial pH 3, then increased and became almost constant over the initial pH ranges of 3–11 (Fig. 1). The reason for such type of behavior is due to the fact that MB is a cation dye, and this can also be attributed to the fact that at higher pH value the surface charges of the adsorbent have become more negatively charged, which led to higher electrostatic interaction between negatively charged adsorbent and positively charged MB. The percentage sorption of methylene blue was not significantly altered ($P > 0.05$) when the initial pH was increased from 3 to 11. So pH 7 was chosen for the study on the effect of contact time.

Fig. S3 depicts the effect of contact time on the removal efficiency of MB at various initial concentrations (25–200 mg/L). The saturation curves increase sharply in the initial stages, indicating that there are plenty of readily accessible sites. Eventually, a plateau is reached in all curves indicating that the adsorbent is saturated at this level. However, for MB solutions with higher initial concentrations, larger equilibrium times were required. It was also seen that an increase in initial MB concentration resulted in increased MB uptake. The adsorption capacity at equilibrium (q_e) increased from 6.09 to 32.2 mg/g with an increase in the initial MB concentrations from 25 to 200 mg/L. Three consecutive mass transport steps are associated with the adsorption of solute from the solution by porous adsorbent.

The effects of Canola biomass concentration on the removal of MB from aqueous solutions were investigated by using ten different Canola concentrations in the range of 0.5–5 g/L and initial MB concentration of 25 mg/L at pH 7. As the Canola concentration was increased from 0.5 to 5 g/L, the equilibrium adsorption capacity of Canola (q_e) decreased from 16.7 to 4.87 mg/g, whereas, the MB removal efficiency increased from 33.4% to 97.5% (Fig. 2). The increase in adsorption percentage of MB was probably due to the increased more availability of active adsorption sites with the increase in Canola concentration.

According to the kinetic data obtained from the experimentation, the pseudo-first-order and pseudo-second-order and intraparticle diffusion mechanisms have been used to elucidate the mechanisms of adsorption and potential rate controlling steps [22,23].

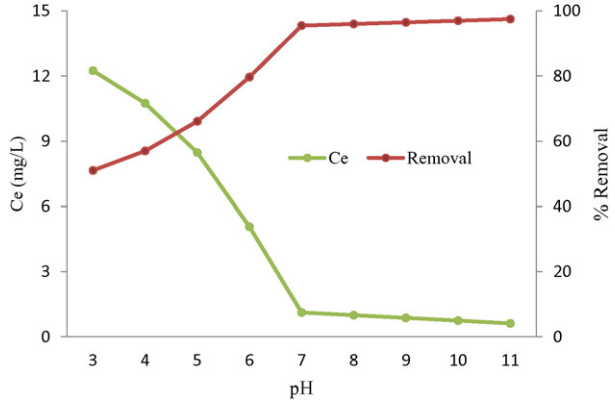

Fig. 1. Effect of pH on MB removal efficiency ($C_0 = 25$ mg/L, adsorbent dose of 3.5 g/L, contact time = 75 min).

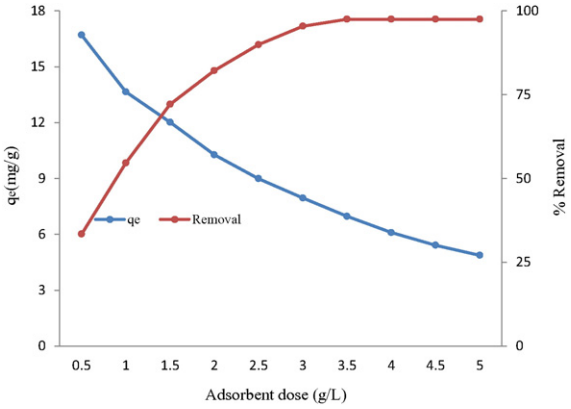

Fig. 2. Effect of adsorbent dose ($C_0 = 25$ mg/L, pH: 7, time: 75 min, temp: 25 °C).

Three kinetic models, pseudo-first order, pseudo-second order and intraparticle diffusion, were used to fit the experimental data to examine the adsorption kinetics. The kinetic parameters of MB under different conditions were calculated and are given in Table 1. It is seen that the pseudo-second order model well represented the experimental data ($R^2 > 0.995$).

The Langmuir adsorption isotherm has been the most widely used in many pollutant adsorption processes and is a successfully applied sorption isotherm for the sorption of a solute from a liquid solution. The saturated monolayer isotherm can be expressed as [24]:

The Freundlich isotherm can be represented as [25]: The derivation of the Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm can be represented as [26]:.

The Sips isotherm is derived from the limiting behavior of the Langmuir and Freundlich isotherms. The model is valid for localized adsorption without adsorbate–adsorbate interactions. When C_e approaches a low value, the Sips isotherm effectively reduces to Freundlich, while at high C_e, it predicts the Langmuir monolayer sorption characteristic. The Sips linear equation model is expressed as [27]:

$$\frac{1}{q_e} = \frac{1}{q_{max} k_s}\left(\frac{1}{C_e}\right)^{1/n} + \frac{1}{q_{max}} \quad (1)$$

where K_s (1/mg) and q_{max} (mg/g) are the Sips equilibrium constant and maximum adsorption capacity values respectively, The Sips isotherm equation is characterized by the dimensionless heterogeneity factor, n, which can also be employed to describe the system's heterogeneity when n is between 0 and 1. When $n = 1$, the Sips equation reduces to the Langmuir equation and it implies a homogeneous adsorption process.

Table 2 summarized the coefficients of the isotherms at different doses. It can be seen from this table that most R^2 values exceed 0.9 and ARE values are smaller than 22% for all isotherm models, suggesting that all models closely fitted the experimental results. However, the regression results show that the Sips isotherm fitted the experimental data better than the others. Based on the coefficients of the Langmuir isotherm model, R_L values, for methylene blue adsorption onto Canola biomass, were less than 1 and greater than zero indicating favorable adsorption.

Table S1 lists some of the low cost materials used as adsorbents for the removal of MB and their sorption capacity values.

The effect of temperature on MB dye adsorption was investigated at (293–328 K). The thermodynamic parameters of Gibb's free energy change, ΔG°, enthalpy change, ΔH°, and entropy change, ΔS°, for the adsorption processes are calculated.