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RESEARCH ARTICLE

Coleus Root Spent as New Adsorbent for Efficient Removal of Methylene Blue from Aqueous Solution: Kinetics and Isotherm Study

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Abstract: *Coleus* root spent (CRS) was used as an efficient adsorbent for the removal of methylene blue (MB). Morphological properties of the adsorbent were studied using SEM and FTIR. The adsorption parameters such as initial dye concentration, contact time, pH and temperature were studied. Langmuir and Freundlich isotherm models were used to explain the adsorption behaviour. Pseudo first order and second order kinetic models were used to study adsorption kinetics. The maximum adsorption capacity value (q_{max} = 66.66 mg g^{-1}) for Langmuir isotherm was near to the experimental value (Q_{max} = 58.00 mg g^{-1}). It is confirmed that, CRS is an efficient adsorbent for removal of MB from aqueous solution.

Keywords: Methylene blue, *Coleus* root spent, Biosorbent, Adsorption isotherms, Kinetics

Introduction

Most of the industries, such as textile, leather tanning, paper, food and plastic use synthetic dyes to colour their products. Textile industry alone consumes 10^7 kg per year[1]. A large quantity of the dye will be released with the wastewater of industries during its synthesis, dying process and washing. Dyes are highly coloured compounds and most of them have aromatic structure with low biodegradability. Presence of these dyes in water will harm both aquatic life and human being[2,3]. Dyes in water bodies not only impart colour and toxicity but retard the photosynthetic capacity of the autotrophs by blocking sunlight into aquatic system[4]. It is very necessary to remove dyes from the polluted water to obviate health, ecological and environmental problems. The removal of these dyes from the water has become a challenging task. Several methods have been reported from the researchers, which includes, photo degradation[5], biodegradation[6], chemical degradation[7] and adsorption[8]. Among these methods adsorption is the simple, environmental friendly and economical. Many research papers have been published on the adsorption method for the removal of dye from aqueous solution. Authors have tried different class of adsorbents which includes, inorganic[9], agricultural waste[10], biological waste[11], polymers[12] and industrial waste.

In the present research work, an attempt has been made to use *Coleus* root spent (CRS) as effective biosorbent for the removal of methylene blue (MB) from aqueous solution. MB is a hazardous dye which causes heart related issues, cyanosis, vomiting, jaundice and quadriplegia in humans[13]. Because of these ill effects of MB it is imperative to remove from water bodies. CRS is found to be cheap and effective adsorbent for the removal of MB from aqueous solutions. *Coleus forskohlii (Lamiaceae)* is a perennial herb, 1-2 ft. high with a thick root stalk, distributed Kumaon and Nepal and in Deccan peninsula[14]. After extraction of forskolin from the roots of C. *forskohlii* a large quantity of waste is generated and this has no commercial/fertilizer value. Hence, an attempt has been made to use CRS as an efficient adsorbent for dye removal. Various factors affecting adsorption capacity like initial concentration of dye, temperature and pH was evaluated.

Experimental

Analytical grade Methylene blue (LobaChemie, Mumbai, India) was used in this work. Stock solution of 1000 ppm of dye solution was prepared in distilled water and solution of required concentration was prepared by diluting stock solution.

Adsorbent

The *Coleus* spent used in this work was supplied from nutraceutical industries. Industrially processed spent material was ground to fine powder and washed thoroughly with distilled water to remove chemical and other impurities. Washed spent was dried in sunlight and passed through sieve again dried in hot air oven at 60^{o} C for 24 hours and stored in air tight containers.

Characterization of adsorbent

Coleus was characterized using scanning electron microscope (Hitachi S3400N, Japan). Absorption spectra were obtained and the spectra of the samples were recorded using Fourier transform infrared spectroscopy (FTIR, PerkinElmer-Spectrum, USA) over the range 4000-400 cm^{-1}.

Adsorption studies

Dye removal experiments with CRS were carried out by batch experiments in 250 mL flasks in an orbital shaker incubator at 140 rpm. In each batch experiment, 50 mL dye solution of known concentration (10-100 mg L^{-1}) and known amount (0.05 g) of spent was taken in 250 mL flask at constant temperature. Kinetic studies were carried out at three different initial dye concentrations 25, 50 and 100 mg L^{-1} using 0.05 g dose of spent and agitated for the fixed time intervals. The effect of the solution pH on MB removal was investigated over a pH range of 4-11. The solution of pH was measured by pH meter (Systronics 802). The pH was adjusted using dilute HCl and NaOH solution. After adsorption, the pH of the dye remains in the solution was adjusted to pH 4 and measured at the maximum wavelength of MB (λ_{max}= 618 nm) using double beam UV-Vis spectrophotometer (Systronics 166). The adsorbed amount of MB at equilibrium q_e (mg g^{-1}) was determined.

$$q_e = (C_0 - C_e)V / W$$

All tests were performed in triplicate to ensure the reproducibility of the results, the mean of the measurements was reported.

Results and Discussion

Scanning electron microscopy (SEM)

The SEM images of CRS before and after adsorption are presented in Figure 1 and 2 respectively. Morphology of CRS is complex with porous structure which has changed significantly with adsorption.

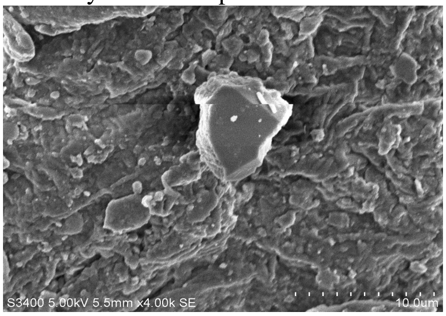

Figure 1. SEM image of CRS before adsorption

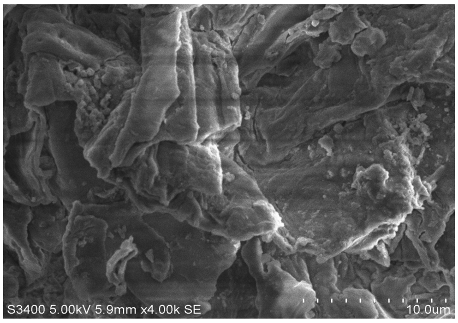

Figure 2. SEM image of CRS after adsorption

Fourier transform infrared spectroscopy (FTIR)

IR spectra of CRS (Figure 3) give the information about the functional groups present. A band at 3423 cm^{-1} is due to stretching of hydroxyl groups of cellulose, hemicelluloses and lignin that are present in CRS. It shows a prominent C–H stretching absorption around 2926 cm^{-1}. Absorption bands due to C=C stretching were found at 1627 cm^{-1}, 1638 cm^{-1} and 1652 cm^{-1}. The bands at 1374 cm^{-1} and 1246 cm^{-1} are due to C-O vibrations and O-H bending. Bands at 1325 cm^{-1} and 1160 cm^{-1} are due to OH bending and C-O vibration respectively. The bands of C-O-H and C-O-C stretching were found at 1103 cm^{-1} and 1031 cm^{-1} respectively[15].

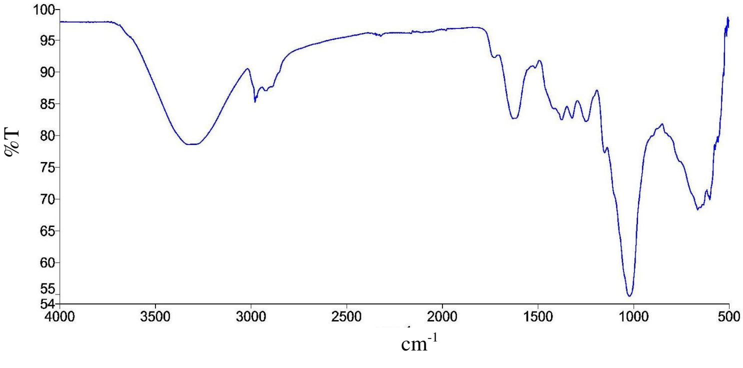

Figure 3. IR spectra of CRS

Effect of initial concentration

The adsorption of dye was increased from 8-58 mg g^{-1} for CRS with the increase in dye concentration from 10 to 80 mg L^{-1}. This may be related to an increase in the driving force of the concentration gradient with the increase in the initial MB concentration[16]. Further increase in the initial concentration of dye above 80 mg L^{-1} will not change the q_e considerably because of the saturation of the adsorbent (Figure 4).

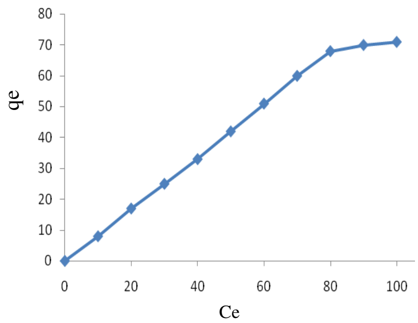

Figure 4. Effect of initial MB concentration

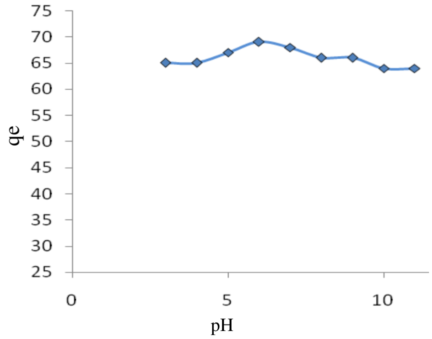

Figure 5. Effect of pH

Effect of initial pH

The pH is an important parameter that affects adsorption. To study the effect of pH on the adsorption of MB onto CRS, the experiments were performed at initial dye concentration of 80 mg L^{-1} and adsorbent dosage of 0.05g/ 100 mL for equilibrium time of 2 hours at 25 C. The amount of dye adsorbed in the pH range of 3-11 was shown in the Figure 5. The solution pH affects both aqueous chemistry and binding sites on the surface of the adsorbents. It is observed from the experiments that, the adsorption increases from pH 5, reaches maximum at pH 6 and again decreases gradually. It is clear that, pH range 5-7 is favourable for the adsorption of MB onto CRS. Decrease in adsorption at lower pH may be due to competition of H^+ ions with cationic dye molecules[17]. Some authors have reported the increase in adsorption of MB above the pH 5[18].

Effect of time

The amount of MB adsorbed as a function of contact time is represented in Figure 6. It shows that the MB adsorption was fast at the initial stage of the contact time and then became slower near the equilibrium time. This phenomenon was due to the availability of large number of vacant sites on the surface of adsorbent. Near the equilibrium, rate of the adsorption decreases due the slow pore diffusion of the MB molecules into the adsorbents[19].

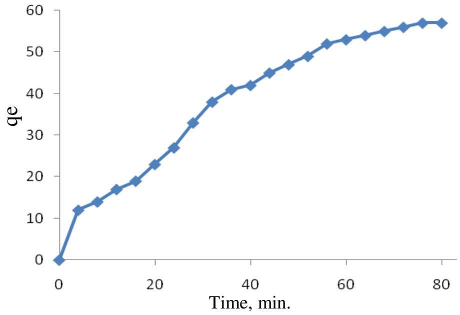

Figure 6. Effect of time

Adsorption isotherm

Two commonly used adsorption isotherms, Langmuir and Freundlich isotherms were used to explain the interaction of adsorbate and adsorbent (Figures 7 & 8). Langmuir isotherms explain the monolayer adsorption on surface containing limited number of sites. Freundlich isotherms describe adsorption on surface having heterogeneous energy distribution.

Langmuir isotherm: $Ce/q_e = (1/bq_{max}) + (1/q_{max})\ Ce$

Freundlich isotherm: $\ln q_e = \ln KF + (1/n) \ln Ce$

Where *C*e is the equilibrium concentration of the adsorbate (mg L^{-1}), q_e is the amount of dye at equilibrium in unit mass of adsorbent (mg g^{-1}), q_{max} and b are the Langmuir constants related to adsorption capacity (mg g^{-1}) and adsorption energy (L mg^{-1}), respectively. KF and n are the Freundlich constants related to adsorption capacity (mg g^{-1} (mg $L^{-1})^{-1/n}$) and adsorption intensity of adsorbent, respectively.

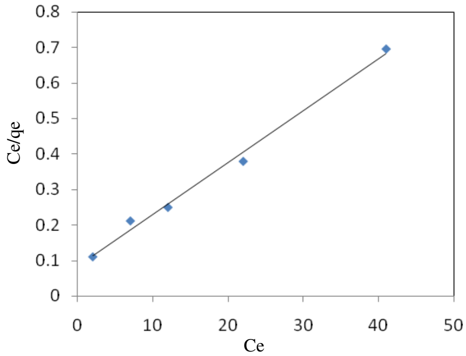

Figure 7. Langmuir isotherm

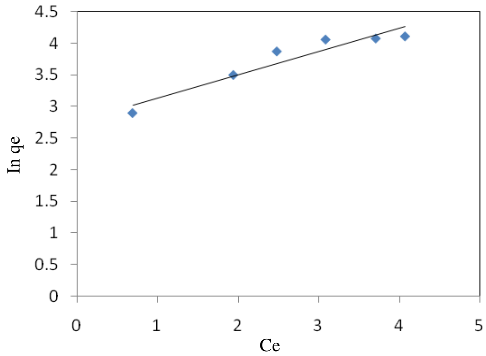

Figure 8. Freundlich isotherm

Langmuir model fits best for the obtained experimental data with regression coefficient (R^2) 0.996, which indicates the adsorption of MB onto CRS is monolayer, in which all molecules have equal enthalpies and activation energies[20]. Feasibility of this isotherm could be understood from the value of R_L, which indicate the shapes of isotherm to be either favourable ($0 < RL < 1$), unfavourable ($RL > 1$) or irreversible ($RL = 0$)[21]. The calculated *R*L value (0.0426) indicates that the adsorption of MB onto CRS is favorable.

Kinetic Models

Kinetics of adsorption

Analysis of the kinetic data is important in any adsorption processes, since the kinetics describes the rate of adsorption which helps to predict the mechanism of the process and rate controlling steps.

In the present study, Pseudo-first order and pseudo-second order kinetic models have been used to test the experimental data.

Pseudo-first order kinetic model

The differential rate equation is

$$dq_t /dt = k_1 (q_e - q_t) \quad (1)$$

Where q_t and q_e are the amounts of dye adsorbed at time t (mg/g) and at equilibrium (mg/g), respectively and k_1 is the pseudo-first order rate constant (min^{-1}). Integrating the above equation using the boundary condition, $q_t = 0$ at $t = 0$ leads to:

$$\log (q_e - q_t) = \log q_e - (k_1/2.303)\ t \quad (2)$$

The values of k_1 and q_e were calculated from the slopes and intercepts of the linear plots of $\log (q_e - q_t)$ *vs*. t (Figure 9), respectively and presented in Table 2.

Pseudo-second order kinetic model

The pseudo-second order kinetic model is represented as:

$$dq_t /dt = k_2 (q_e - q_t)^2$$

Where q_t and q_e are the amount of dye adsorbed at time t (mg/g) and at equilibrium (mg/g), respectively and k_2 is the pseudo-second order rate constant (g mg^{-1} min^{-1}). Integrating the above equation using the boundary condition, $q_t = 0$ at $t = 0$ leads to:

$$t/q_t = 1/k_2 q_e^2 + t/ q_e \quad (3)$$

The values of k_2 and q_e were calculated from intercepts and slopes of the linear plots of t/q_t *vs*. t (Figure 10), respectively and presented in Table 1. Table 1 shows that the calculated q_e values are very close to that of experimentally obtained q_e and the values of correlation coefficients (R^2) are closer to unity confirms that adsorption of MB on CRS follows pseudo-first order kinetics. From the kinetic constants (Table 2), it is clear that pseudo first-order is better fits with the experimental data than pseudo second-order.

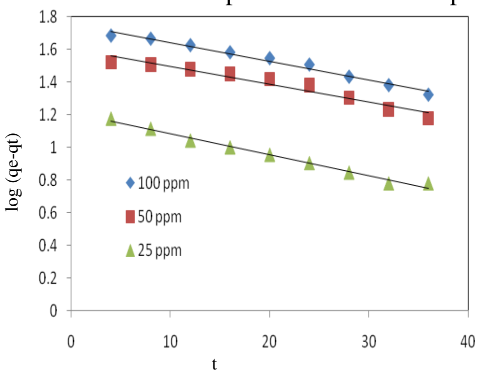

Figure 9. Pseudo-first order kinetics

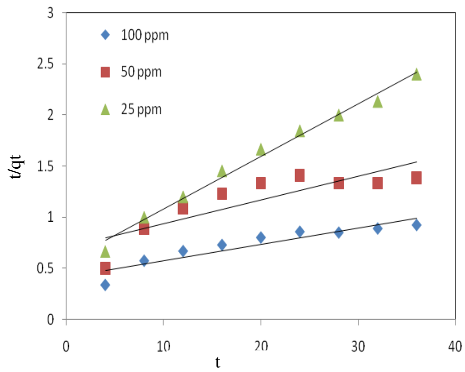

Figure 10. Pseudo-second order kinetics

Table 1. Isotherm parameters for the adsorption of MB onto CRS

Langmuir constants				Freundlich constants		
q_{max}	b	R_L	R^2	K_F	n	R^2
66.66	0.187	0.0426	0.996	15.9	2.392	0.908

Table 2. Kinetic parameters

Initial dye Concentration, mg/L	q_e exp	Pseudo-first order			Pseudo-second order		
		q_e cal	k_1	R^2	q_e cal	K_2	R^2
25	21	19	0.0506	0.0.963	1.838	7.046	0.946
50	41	43	0.0276	0.919	1.416	21.671	0.707
100	59	73	0.0253	0.917	2.392	11.648	0.849

Conclusion

In the present study *Coleus* root spent, has been used as an eco-friendly and cost-effective biosorbent for the remediation of Methylene Blue, a toxic dye. Maximum adsorption capacity was q_{max} = 58.00 mg/g and it is close to what obtained by Langmuir (q_{max} = 66.66 mg/g) with correlation coefficient (R^2) of 0.996. The experimental data fitted perfectly well with pseudo-first order kinetic model. Possible mechanisms of interactions that can occur in MB-CRS system have been discussed. It has been proved that, CRS can be used as a fast and effective adsorbent for the removal of MB from aqueous solutions.

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