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Research Article

Adsorptive Removal of Methylene Blue from Aqueous Solution Using Sawdust

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Abstract

In the present study, modified sawdust was used for the removal of an azo dye Methylene Blue (MB) from aqueous solutions. The study was carried out in batch mode. Effects of various important parameters such as pH, concentration, temperature, dose, and agitation speed on the removal of the dye were investigated for optimization of the process. It was observed that the maximum removal of 99.5% was achieved at the lowest dye concentration of 75PPM. The process of removal was found to be endothermic. Adsorption of Methylene Blue on modified sawdust was rapid and in accordance with pseudo-2nd -order kinetics. The Langmuir isotherm model agrees well with the sorption isotherm data and also confirms that adsorption took place on the homogenous surface of modified sawdust. The adsorption capacity ($Q_{max.}$) determined from Langmuir isotherm was found to be 5.464 mg g^{-1}. The thermodynamics parameters like ΔG, ΔH, ΔS are found to be 30.057 $kJmol^{-1}$, 44.089 kJ mol^{-1}, and 0.0514 $kJmol^{-1}K^{-1}$ respectively, revealing that the adsorption process is spontaneous, endothermic, and feasible Therefore, the study recommends that modified sawdust is a promising candidate for the efficient removal of dye-contaminated wastewater.

Keywords: Adsorption; Sawdust; Methylene Blue; Kinetics; Thermodynamics

Introduction

Dyes are colored organic substances that chemically bond and impart color to the substrate to which it is being applied and are mostly used in textile, leather, pharmaceuticals, varnishes, and paper industries. After textile, the leather industry is the second largest industry, more than 800 tanneries are working in Pakistan. The dyes contaminations when discharged into freshwater cause severe water pollution, harmful to humans and aquatic life. (Padda & Asim, 2019) [18].

Therefore, the removal of dyes from wastewater is very essential. Several purification techniques have been used for the removal of dyes from wastewater, for example, adsorption, electrolysis, membrane separation, chemical coagulation, biological treatments, oxidation, and some other methods. Though, these methods diverge in their efficiency, environmental impact, and cost (Bilal et al., 2017) [5]. Adsorption is preferred over other methods due to its benefits, such as being simple in operation, cost-effective, and environmentally friendly. A wide range of adsorbents such as clays, activated carbons, functionalized tannin, nanotubes, and metal nanoparticles had been studied for dyes removal from wastewater (Bilal et al., 2017) [5]. Nowadays scientists search for adsorbents that are low cost, environmentally friendly, cost effective and easily available. Adsorption is an important operation in several natural and industrial systems such as fundamental biological studies, separation and purification processes, recovery of chemical compounds and wastewater treatment processes. It can replace with other separation processes and contribute efficiently to the removal of contaminants from an aqueous solution. However, adsorption is the most popular physicochemical treatment for the removal of dissolved organic substances from water (Lokesh & Sivakiran, 2014) [14].

The adsorption process is one of the efficient methods for dyes removal (Ramachandran, Vairamuthu, & Ponnusamy, 2011) [19]. The process of adsorption has an edge over the other methods due to its sludge-free clean operation and complete removal of dyes even from dilute solutions.

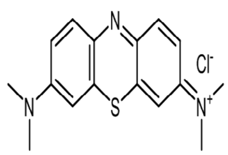
Adsorption of dyes on activated carbon is quite popular, but its high cost restricts its widespread application and researchers are working to search for low-cost adsorbents for this purpose (Salvador & Jiménez, 1996) [21]. In recent years, more attention has been focused on the utilization of several non-conventional adsorbents for the removal of dyes from aqueous solutions. Materials such as sugar beet pulp, hen feathers, modified rice straw, date stones, peat, coal, zeolites, silica gel, orange peel, coir pith, rice husks, coffee husks, barley husks, bagasse fly ash and bamboo (Mall, Srivastava, & Agarwal, 2006; Sajab, Chia, Zakaria, & Khiew, 2013) [16, 20] have been reported for the removal of dyes from aqueous solutions. The present study activated sawdust (ACSD) as an adsorbent for the removal of "methylene blue (MB)" from the aqueous solutions. Raw sawdust was activated by simple and low-cost adsorption. The study reveals that activated sawdust dust is an environmentally friendly, low cost and alternative adsorbent for the removal of methylene blue from industrial wastewater.

Materials and Methods

Sawdust of oak plant was taken from Kohistan Dir upper, Analar grade chemicals (KCl, HCl, CH_3COOH, CH_3COONa) and per Chloric acid were used in this study without any further purification and processing.

The instruments used in this study were UV-vis spectrophotometer (UVD-2960 Labomed. Inc.), wrist action shaker, pH meter, electronic balance, etc.

Methylene blue was used as adsorbate. Their molecular formulas are $C_{16}H_{18}ClN_3S$. The molecular weight of methylene blue is 319.85g/ml. The chemical structures are given below.



Structure of methylene blue

Results and Discussion

Adsorption studies

Batch experiments were performed in glass culture tubes. A specific quantity of nano sorbent was mixed with 6 ml of dye solution and shaken in a wrist action shaker for a specified time. After shaking of dyes were removed from the culture tube and its concentration was determined by a UV -spectrophotometer.

The elimination percentage of dyes was determined by using the following equation;

$$\% \textbf{Removal} = \left(\frac{Co - Ce}{Co}\right) \times \mathbf{100} \qquad (1$$

Where Co is the initial dyes concentration in ppm and Ce is the equilibrium Concentration of dye in ppm.

Adsorption of Methylene Blue

The adsorption experiment was conducted in batch mode. For the pH experiments, a specific sample quantity of sawdust with 7 ml of dye solution of 100 ppm at different pH (1-7) was explored. The experiments were conducted at 273K. Tests were performed for different periods to conclude the equilibrium of adsorption. The concentration at the equilibrium of each solution was measured using a UV-visible spectrophotometer at 454 nm.

Effect of pH on adsorption of Methylene Blue

In solutions, pH has a major impact on the adsorption because it influences the adsorbent active sites and the ionization of adsorbate (Kadirvelu, Karthika, Vennilamani, & Pattabhi, 2005) [12]. The maximum adsorption was detected at pH 2 because of the acidic nature of the dye and the increase in the protonated groups like phenolic on the adsorbent surface (Nigam, Armour, Banat, Singh, & Marchant, 2000) [17]. At lower pH, it oxidizes well and it is expected that it should adsorb up to the maximum extent but this is not the situation. The reason is that H^+ ions compete with the dye. The smaller size and abundance of H^+ ion affects the sorption of dye from an aqueous solution. The abundance and H^+ ions smaller size affect the sorption of dye. Therefore, pH 2.0 was considered optimum for further experiments (Abbas & Ahmad, 2016) [1].

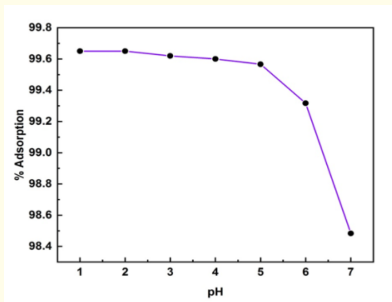


Figure 1: Effect of pH on adsorption of Methylene Blue.

Effect of shaking time on Methylene Blue adsorption

The influence of time on dye sorption was measured for an initial concentration of 25 ppm at the time ranges from 10-80 minutes. (Figure 3.2) displays that the rate of adsorption of Methylene Blue is less at the start. It is because of the availability of a small surface area at the start. Maximum adsorption was observed at about 60 minutes of shaking time (Yi & Zhang, 2008) [23]. After the optimum time, no considerable increase in adsorption was observed. At this point adsorption and desorption rate of dye become equal which is dynamic equilibrium and the time required is known as equilibration time. The extent of dye adsorbed at equilibrium reveals the adsorbent's maximum adsorption capacity.

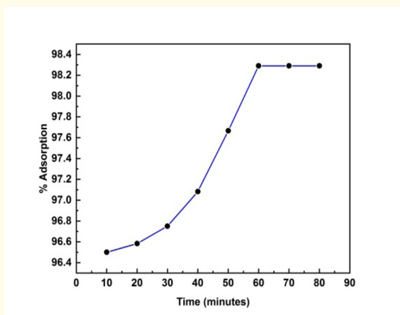


Figure 2: Shaking time effect on adsorption of Methylene Blue.

Kinetic study of Methylene Blue

The mechanisms of adsorption for sawdust were studied using Pseudo Second-order (Ho & McKay, 1998) [10]. From the kinetic studies, we can determine the nature of the adsorption and the adsorbate-adsorbent interactions.

The pseudo-second-order model was applied which can be expressed in the form:

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

Where qe is adsorption capacity (mg/g) , K_2(g mg^{-1} min^{-1}) is the pseudo-second-order rate constant.

The R^2 value for this model was found exactly equal to 0.999. This shows that the system of sawdust obeys this model for the whole range of adsorption time (Mafra, Igarashi-Mafra, Zuim, Vasques, & Ferreira, 2013) [15].

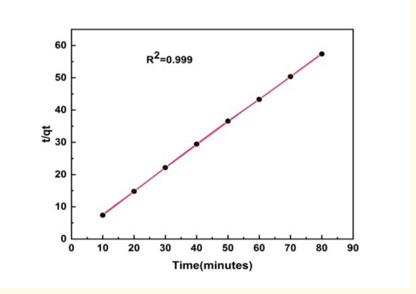


Figure 3: Pseudo second-order graph for Methylene Blue.

Concentration (ppm)	***Models***	***Parameters***	***Values***
75	Pseudo Second order	K_2 (g/mg^{-1} min^{-1})	0.815
		R^2	0.999

Table 1: Kinetics data for adsorption of Methylene Blue.

Effect of adsorbent dose

The influence of variation of the amount of sawdust was observed by increasing the amount of sorbent from 50 to 350mg/ 7 ml. Results show that % adsorption of Methylene Blue, improved with the increase in the amount of adsorbent. It is due to the increase in active sites, which helps in dyes' adsorption (Zhang, Li, Zhang, & Jing, 2008) [24]. It was found that 250 mg of sawdust adsorbed 99.35 % of 100 mg/L of Methylene Blue and consider as the optimum amount for adsorption.

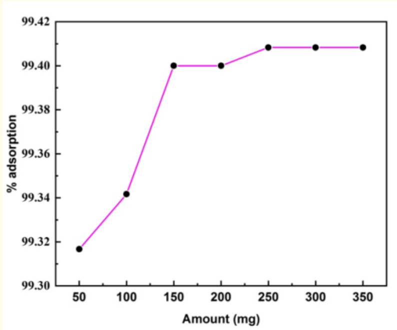


Figure 4: Influence of adsorbent amount.

Effect of concentration on the removal of Methylene Blue

Adsorption has studied a function of the concentration of Methylene Blue dye onto sawdust in the concentration range of 25 to 150 ppm. Fig 3.5 shows that at low concentrations higher percent adsorption was observed. This is because of the interaction of active sites and all dye molecules in the solution. Saturation of active sites occurred at higher concentrations (Azouaou, Sadaoui, Djaafri, & Mokaddem, 2010) [3].

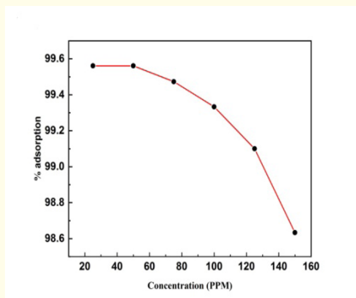


Figure 5: Effect of concentration on Methylene Blue removal.

Langmuir isotherm (Langmuir, 1918) [13] reports that on the surface of the adsorbent an adsorption monolayer will occur, the adsorption energy of solute is constant and on the surface plane, there is no adsorbate molecules migration. The equation of the Langmuir isotherm is expressed as follows:

Where K_L and Q_{max}, are constants, denotes the energy constant related with the adsorption energy and the total adsorption capacity for solid-phase loading respectively. Ce is equilibrium concentration (mg/L). The Q_{max} = 5.464 mg/g was computed from the model. Results show that sawdust had significant potential for Methylene Blue removal from wastewater.

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{\max.}} + \frac{1}{K_L Q_{\max.}} \qquad (3)$$

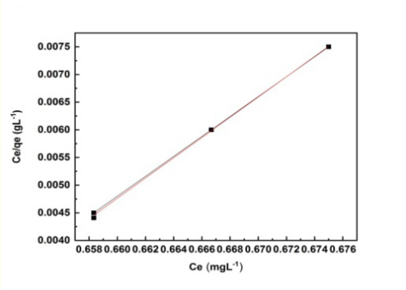


Figure 6: Langmuir Isotherm Model for Methylene Blue.

Langmuir model's important features can be defined in terms of a dimensionless constant called separation factor (equilibrium parameter) R_L is well-defined by the equation 4. Its value shows either linear (R_L = 1), unfavorable (R_L> 1), favorable (0<RL< 1) or irreversible (R_L= 0) shape of isotherm (Ahmadi & Shadizadeh, 2013) [2].

$$R_L = \frac{1}{1+K_L C_e} \qquad (4)$$

Where C_e is the initial concentration of dye in ppm and K_L is the constant of Langmuir associated with the energy of adsorption (Ahmadi & Shadizadeh, 2013) [2]. The R_L value was 0.154dm^3/mol which is between 0 and 1 for sawdust suggesting the isotherm to be favorable.

Models	Parameters	R^2
Langmuir	Q_{max}(mg/g) =5.464	0.998
	K_L(mg/g) = -1.5797	
	R_L(dm^3/mol) =0.154	

Table 2: Adsorption isotherms for Methylene Blue.

Effect of temperature on the adsorption of Methylene Blue

Temperature affects adsorption the variation in temperature changes the adsorption capacity for adsorbate. Therefore, the influence of temperature was investigated in the temperature range of 273K to 333K. Figure 3.7 indicates the influence of temperature on Methylene Blue adsorption by using sawdust. The Figure displays that the percent elimination of Methylene Blue increases with an increase in temperature. This is because the bonds amongst adsorbate and active sites of adsorbent become strong. The binding forces among the solute and the adsorbent were, therefore, greater than those between the solute and the solvent. This was therefore more difficult to adsorb solute (Iqbal & Ashiq, 2007) [11]. The noticed trend in decreased color removal capability with rising temperature indicates that an endothermic system governs the Adsorption of Methylene Blue by sawdust.

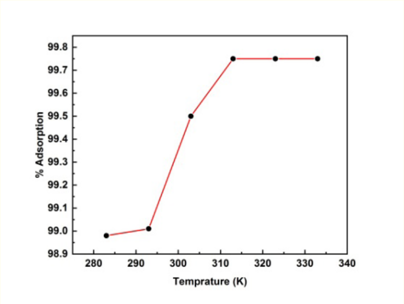


Figure 7: Effect of temperature on the adsorption of Methylene Blue.

From the temperature study of Methylene Blue adsorption on sawdust, thermodynamic parameters the Gibbs free energy (ΔG^0), enthalpy (ΔH^o), and entropy (ΔS^o) were also computed. The free energy, ΔG for adsorption system of Methylene Blue on sawdust is defined by Equation 5.

$$\Delta G^o = \Delta G + RT \ln Kc \qquad (5)$$

Where T is absolute temperature, R is gas constant, and Kc is the constant of equilibrium, where Ce is the Methylene Blue Equilibrium concentration). At equilibrium, $\Delta G = 0$, we thus obtain.

$$\Delta G = -RT \ln Kc \qquad (6)$$

The ΔG^o was -8.898 KJ mol^{-1} at the corresponding temperature of 298 K accordingly, the ΔG^0 values specify the adsorption of Methylene Blue on sawdust is spontaneous. The standard enthalpy and entropy values for Methylene Blue adsorption on sawdust were evaluated from Van't Hoff equation

$$\ln Kc = \frac{\Delta S^o}{R} - \frac{\Delta H}{RT} \ (7)$$

$$\Delta G = \Delta H - T\Delta S \qquad (8)$$

Both ΔH^o and ΔS^o were computed from the intercept and slope of the plot of lnKc vs 1/T(Figure 3.7). The results show that the enthalpy ΔH^o was 40.089 KJ mol^{-1} and ΔS ∘ was 0.0514J$mol^{-1}K^{-1}$. Values of ΔH^o and ΔS^o indicate that at the adsorption is spontaneous (Choi, Lee, & Yoo, 2011) [7] and endothermic and favored at high temperatures. The high value of entropy shows that the adsorption occurs to a greater extent.

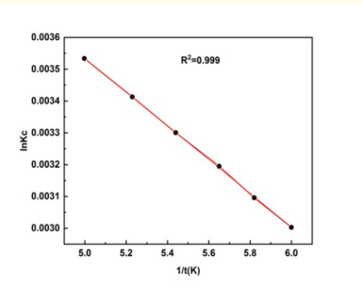


Figure 3.7: Van't. Hoff plot for methylene blue adsorption onto sawdust.

Temperature	ΔH (KJ/mol)	ΔS (J/mol/K)	ΔG (KJ/mol)
273	44.089	0.0514	30.057
283	44.089	0.0514	29.5428
293	44.089	0.0514	29.0288

Table 3: Thermodynamic parameters for the adsorption of Methylene Blue onto sawdust.

Conclusions

The removal of an azo dye, Methylene Blue, from aqueous solutions was carried out by adsorption on modified sawdust. Sawdust was modified by a simple low-cost method by using perchloric acid. Equilibrium was achieved in 60 min. Solution temperature was found to be an effective parameter, and it was observed that on increasing the temperature from 273 to 310K the dye removal percentage increased from 98.9 to 99.5%, which suggests the endothermic nature of the removal process. Dye removal was at a maximum (99.63%) at pH 2.0. The pseudo-2nd -order kinetic model was found to be more suitable for the removal of dye in the present case. The equilibrium data fitted Langmuir's model well and the Langmuir adsorption capacities were found to be 5.464 mg/g. Positive values of enthalpy (ΔH^0) and Gibbs free energy (G^0) suggest an endothermic nature and a spontaneous nature of the process of removal. Finally, sawdust modified with perchloric acid is a comparatively efficient and inexpensive alternative adsorbent material for the removal of hazardous azo dye Methylene Blue from aqueous solutions.

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