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Research Article

STUDY OF DIFFERENT PARAMETERS ON ADSORPTION OF METHYLENE BLUE DYE FROM AQUEOUS SOLUTION USING NERIUM OLEANDER AS BIOADSORBENT

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ABSTRACT

A Bio adsorbent nerium oleander has been used as a low cost adsorbent and its efficiency in methylene blue adsorption was comparatively greater than other adsorbent. The influence of various factors such as adsorbent dose, adsorbate concentration, particle size, temperature, contact time and pH was studied. The adsorption of the dye over bio adsorbent was found to follow Langmuir and Freundlich adsorption isotherm models. Based on these models, various useful thermodynamic parameters have been evaluated. The adsorption of methylene blue over nerium oleander follows first order kinetics and the rate constants for the adsorption processes decreases.

Keywords: Adsorption, Industrial effluents, Methylene blue, Adsorbent, Dye.

1. INTRODUCTION

Environmental contamination has been identified as a serious issue in the modern world. Industrial pollution is caused by dyes, detergents, grease, sulphates, solvents, heavy metals, and other inorganic salts, as well as fibers. Industrial dye effluent has a bright color, a high pH, a high temperature, a high COD, and a low biodegradability.

The color of effluent dumped into receiving waterways has become a severe environmental issue in recent years. Woolen, carpet, pulp, paper, and textile effluents can add color to receiving waterways kilometers downstream from the source. The hue is unappealing to the eye, and it also inhibits light penetration into the water, lowering photosynthetic efficiency in aquatic plants and hence limiting their development.

Textiles, paper, food, cosmetics, plastics, and pharmaceuticals are among the sectors that employ synthetic dyes to add color to their goods. Large amounts of colored effluents are discharged in to fresh water supplies by these enterprises. These colored effluents impair sunlight penetration, photosynthetic activity, and oxygen dissolution in water, posing serious dangers to aquatic biodiversity and rendering them unsuited for living in polluted water. Carcinogenesis, mutagenesis, teratogenesis, and respiratory toxicity are among the concerns connected with dyes. Toxic amines are produced by inadequate degradation of the dyes, which are detrimental to the aquatic environment [1]. Although traditional waste water treatment methods such as sedimentation, flocculation, aeration, precipitation, ultra filtration, and disinfection are available, the adsorption technique outperforms them due to the easy availability of adsorbent, the simplicity of the method, and the high adsorption efficiency. Synthetic colors, which are highly poisonous, allergic, and carcinogenic, are employed more than natural dyes. The content of these colors combines with metal ions to generate compounds that are extremely poisonous to aquatic flora and wildlife and cause a variety of ailments. Hair temporary coloring, coloring paper, wool and cotton dying all utilize Methylene Blue (MB). It is a poisonous color that has negative health consequences on both humans and animals [2].

Methylene Blue is a heterocyclic basic ionic thiazine dye. The presence of MB dye in wastewater is undesired, thus methylene blue dye treatment is more important [3]. Remove colors from industrial and residential effluents, a variety of procedures have been explored, including chemical oxidation, coagulation, filtration with coagulation, precipitation, adsorption, and biological treatments. However, each of these separation processes has advantages and downsides. Coagulation, for example, is the most widely used process in the industry since it does not result in the development of hazardous or poisonous intermediates. The most significant disadvantage is the development of sludge and the disposal of that sludge. Furthermore, operating expenses influence technique selection. As a result, the adsorption technique is regarded as one of the most successful and cost-effective methods for removing colors from wastewater. As a result, the current study provides an overview of the adsorption technology for dye removal from polluted water.

The bioadsorbent is utilized as a cheap precursor for adsorbent. It not only reduces costs but also finds a solution to the waste management issue. Because commercially available adsorbents are more expensive and have less effective adsorption, scientists are more interested in adopting bio-sorbents. Researchers have employed apricot stones [4], oil palm shells [5], vetia peruviana [6], mahogany saw dust [7], rice husk [8], and other biomaterials for color adsorption from aqueous media.

A flowering plant known as Nerium Oleander (NO) with needle-like leaves can be found in tropical climates. To prepare activated carbon for the elimination of the methylene blue dye from aqueous solution, these leaves are utilized as a precursor. Oleander is an evergreen shrub of the Apocynaceae family, also known as Al Defla in Jordan and "the desert rose" in ancient literature. It grows dense and green in hilly conditions, has naturalized on practically every continent, and is widely employed in tropical and subtropical climates on roadsides, parks, and landscapes. For Methylene blue dyes, the effects of various operational factors such as adsorbent dosage, dye concentration, pH, temperature, particle size, adsorption kinetics, and thermodynamic parameters were investigated.

2. MATERIAL AND METHOD

2.1. Preparation of dye solution

Methylene Blue is a cationic dye with the chemical formula $C_{16}H_{18}N_3SCI.3H_2O$. Because of its well-known strong adsorption onto solids, it was chosen for this investigation. Figure 1 depicts the structure of this dye. Although the dye is not considered acutely poisonous, it can cause a variety of side effects. Methylene Blue, a basic dye, was utilized without additional purification. Before usage, Methylene Blue was dried for 1 hour at 383 K. Distilled water was used to make the entire Methylene Blue solution. 1 gm Methylene Blue was dissolved in 1000mL distilled water to make a stock solution. When necessary, the experimental solution was made by diluting the stock solution with distilled water.

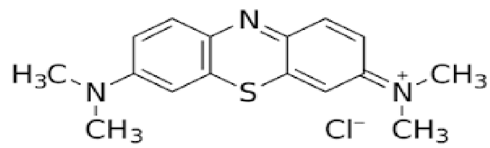

Fig. 1: Structure of Methylene Blue

2.2. Preparation of adsorbent plant samples

Mature healthy plant leaves were selected. Leaves were separated and washed separately with normal clean tap water first and then with distilled water and finally were rinsed with deionized water to remove any sediment particles that may be attached to the plant tissue surfaces. Leaves were first air dried for five days and then were kept overnight in an oven at 50°C until constant weight is reached. Leaves were ground separately into powder and sieved through proper mesh to obtain experimental particle size range of 0.125-0.250 mm. The samples were stored in clean 250 mL plastic jars to be used later in the experiments.

2.3. Batch adsorption method

Batch adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 100mL of MB concentrations ranging from 1 PPM to 9 PPM and adsorbent. An orbital shaker was employed at the necessary temperature and pH. A 180-minute time contact was employed in all tests to establish steady-state adsorption. After 180 minutes, the dispersion was filtered and the filtrate was analyzed with UV/visible spectrophotometry at 650 nm. Equilibrium tests were conducted for various lengths of time while the pH of the solution was progressively adjusted by introducing small amounts of diluted HCl or NaOH solutions. The amount of MB adsorbed at equilibrium was calculated using the following equation:

$$q_e = (C_0 - C_e) \times V/m \quad \text{(i)}$$

Where qe (mg/g) is the MB adsorbed per gram equilibrium adsorption capacity, C_0 and Ce (mg/L) are the initial and equilibrium MB concentrations, V is the MB solution volume (L), and m is the mass (g). Each experiment was repeated at least twice under the same conditions in two different ways. The adsorption percentage (percent removal) of MB from an aqueous solution may be calculated using the formula below:

$$\text{Removal percentage} = 100 \times (C_0 - C_e)/C \quad \text{(ii)}$$

2.4. Instrumentation

For all degradation analysis, a spectrophotometer with a 1.0 cm light path quartz cells (systronic spectrophotometer 166 spanning the wavelength range 325-900 nm) was utilized, digital pH metre was used for pH readings. Thermostatic mechanical orbit shaker (Neolab, India), Analytic digital balance, and Bevision D2 particle size analyzer were used.

3. RESULTS AND DISCUSSION

3.1. Effect of initial concentration

The dye solutions of various initial concentrations (C_0: range = 1 - 9 ppm) were prepared. Exactly 50 ml of each of the dye solution with different required initial concentration of dye was treated with a known dose of adsorbents 0.75 g/L of fixed particle size (0.250MM) at the solution pH, and equilibrated for 180 min. with constant shaking at 200 rpm in a thermostatic mechanical orbit shaker (Neolab, India) at 300 K (fig. 2). The equilibrium concentrations (C_e) are determined using the filtrates. The percentage removal of dye and the amount of dye adsorbed (in mg g^{-1}) are calculated.

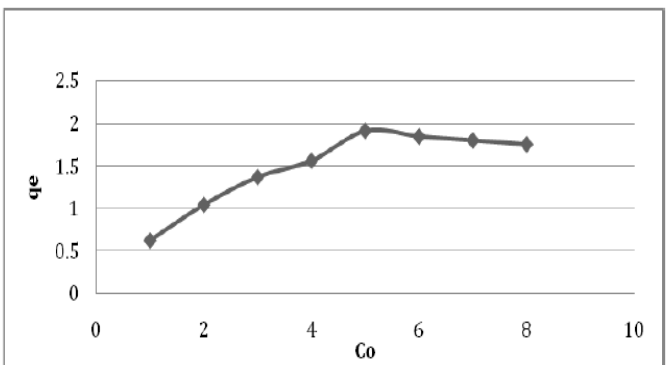

Fig. 2: Effect of concentration of the dye for the removal of Methylene blue by Nerium oleander at pH 7 and 300 K temperature

3.2. Effect of adsorbent dosage

From the stock solution, standard dye solutions of 5 mg/l were produced once again. Adsorbent was added to each of these solutions in varying amounts of 0.15gm, to 1.15gm (fig. 3). These solutions, each having a different quantity of adsorbent dosage, went through the identical shaking, centrifuging, and spectrophotometer examination technique. The findings were then utilized to investigate the influence of adsorbent dose on dye removal at different temperature. It is observed that at 0.75 gm dose of adsorbent maximum adsorption of MB dye occur. So 0.75 gm per 100 mL is optimum dose of adsorbent.

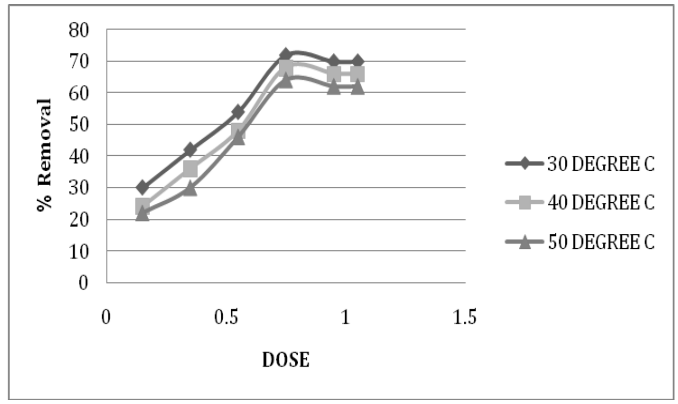

Fig. 3: Effect of amount of adsorbent for the removal of Methylene blue by Nerium oleander at pH 7 and different temperatures

3.3. Effect of pH

Different workable solutions, each with a concentration of 5 mg/l, were made on adding different amount of adsorbent. By adding 0.1N HCl or NaOH, they were maintained at varying pH levels ranging from 2 to 9, they were shaken for 2 hours at room temperature at 120 rpm. After two hours, the solutions were centrifuged and tested in a UV spectrophotometer to compare the effects. It is observed that optimum pH is 7 (fig. 4).

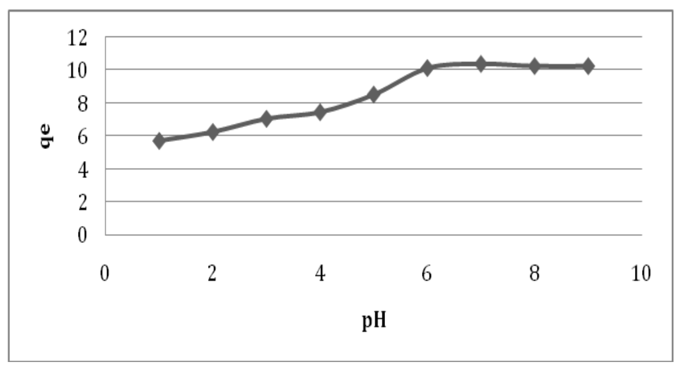

Fig. 4: Effect of pH for the Removal of Methylene blue by Nerium oleander at dye concentration 5 ppm and 300K temperature

3.4. Effect of contact time

At a temperature of 30°C, an adsorbent dose of 0.75 g per 1000 mL, and a pH of 7, dye adsorption was measured at given contact times for different initial dye concentrations. Fig. 5 depicts the influence of initial dye concentration on adsorption rate. As the contact duration increased, the rate of color loss rose significantly. The contact time for the adsorbent to attain saturation with an initial dye concentration of 1 to 8 (PPM) mg L^{-1} was 240 minutes, and the contact time was varied for each concentration, demonstrating that the equilibrium period is independent. Due to surface mass transfer, the dye was rapidly absorbed at low concentrations.

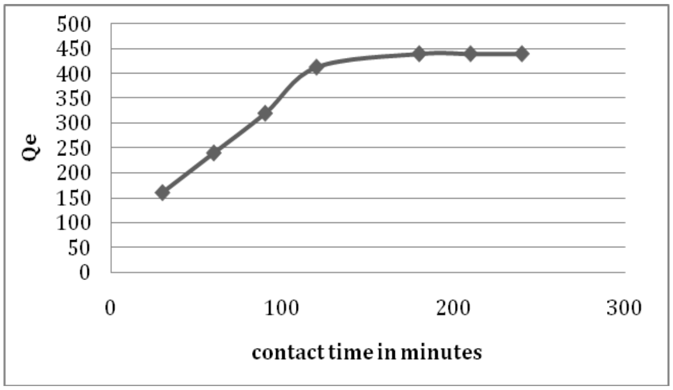

Fig. 5: Effect of time for the removal of Methylene blue by Nerium oleander at pH 7 and 300K temperature

3.5. Effect of particle size

The fig. 6 depicts the relationship between the amount of dye absorbed and the passage of time (min). Over the saturation period, the amount of dye adsorbed rise as the particle size of the adsorbent decreased. This finding corroborated the postulated process. When a bigger particle is broken, microscopic fissures and channels appear on its surface, offering more surface area. In the early phases of the adsorption process, the huge exterior surface area removes more dye than the big particles. Figure 6, shows that the adsorption of dye from a solution concentration increased when the particle size of the adsorbent was reduced.

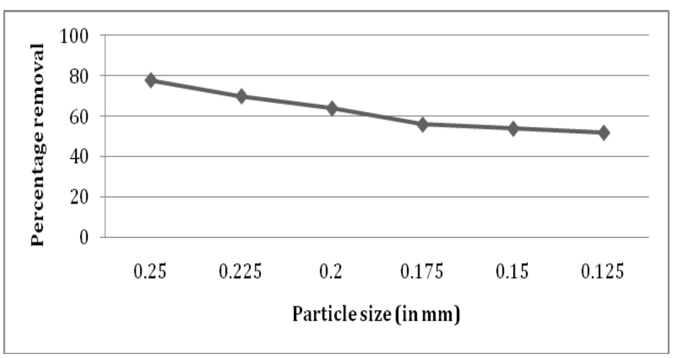

Fig. 6: Effect of Particle size for the removal of Methylene blue by Nerium oleander at 300 K temperature

3.6. Effect of temperature

Temperatures of 300, 310, and 320 K were used to investigate the influence of temperature on color removal (Fig. 7). The graph's curves show a significant increase as temperature rise, with the maximum removal rates. The amount of dyes adsorbed decreases as the temperature rises, indicating an exothermic adsorption mechanism. This might be owing to the dye molecules proclivity to escape from the solid phase and enter the bulk phase when the solution's temperature rises. MB Dye removal by NO adsorbent was confirmed.

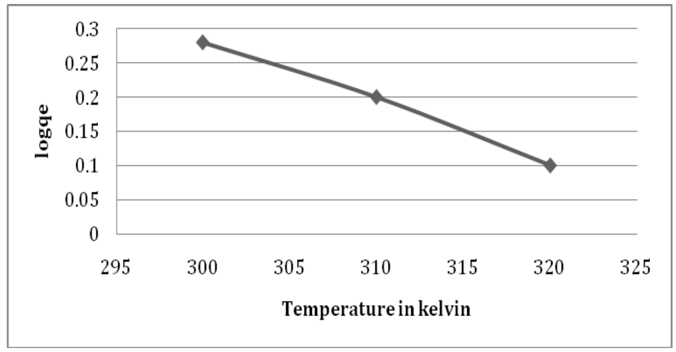

Fig. 7: Effect of temperature for the removal of Methylene blue onto Nerium oleander at pH 7 and different temperatures

4. ADSORPTION ISOTHERMS

The percentage of adsorbate molecules that are evenly distributed across the liquid and solid phases at equilibrium is referred to as an adsorption isotherm. Adsorption isotherms were used to simulate the dye sample adsorption data onto NO particles. Tempkin, Dubinin-Radushkevich, Freundlich, and Langmuir isotherms were used to assess the adsorption data. These isotherms are useful for determining the total quantity of adsorbent needed to adsorb a required amount of adsorbate from solution.

4.1. Freundlich Isotherm

The well-known original connection explaining the adsorption process is the Freundlich isotherm model. When the sorption centre of an adsorbent are fully developed, according to this model, which applies to adsorption on heterogeneous surfaces and includes interactions between adsorbed molecules and the use of the Freundlich equation, adsorption energy should exponentially decrease [9].

This isotherm, which has the following linear form and may be used to characterize heterogeneous systems, is an empirical equation.

$$\log q_e = \log KF + 1/n \log C_e \qquad \text{(iii)}$$

Where, KF is bonding energy-related Freundlich constant. The heterogeneity factor is 1/n, and the adsorption divergence from linearity is measured by n (g/L). The plot of log q_e vs logC_e in Figure 8 was used to calculate the Freundlich equilibrium constants. If n = 1, then adsorption is linear; if n<1, then adsorption is a chemical process; and if n > 1, then adsorption is a physical process, the n number shows the degree of non-linearity between solution concentration and adsorption. Freundlich equation's n value was determined to be between 1.24 and 1.89 (Table 1). Since n is a number between 1 and 10, it may be deduced that Methylene blue has adsorbed onto NO. Regression coefficient R^2 values are used to gauge how well experimental data fit isotherm model predictions.

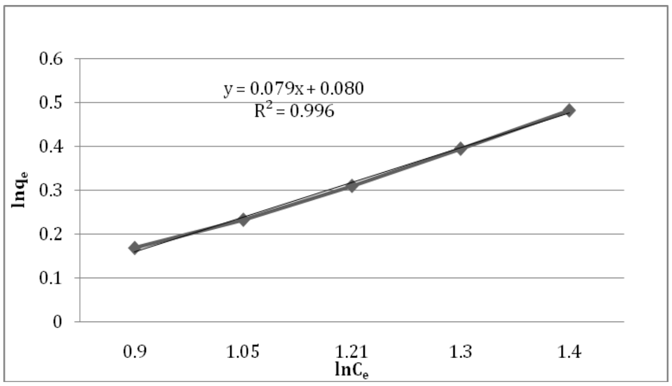

Fig. 8: Freundlich adsorption isotherms for adsorption of the methylene blue over Nerium oleander at pH 7 and 300K temperatures

Table 1: Freundlich constants for the methylene blue over Nerium oleander

Intercept	Slope	1/n	KF	R^2
0.08	0.079	0.079	1.202264	0.987

4.2. Langmuir Isotherm

According to the Langmuir isotherm, monolayer adsorption occurs on a surface that is uniform and has a limited amount of adsorption sites [10]. No more adsorption may occur at a spot once it has been filled. As a result, the surface will ultimately reach a point of saturation at which it will attain its maximum adsorption. The Langmuir isotherm model's linear form is defined as follows:

$$1/q_e = 1/Q_0 + 1/bQ_0\, C_e \qquad \text{(iv)}$$

where Q_0 and b are Langmuir constants relating to maximal adsorption capacity and relative adsorption energy, and qe is the quantity adsorbed (mol/g), C_e is the equilibrium concentration of the adsorbate (mol/L), and A straight line with a slope of $1/bQ_0$ is formed when $1/q_e$ is plotted against $1/C_e$ (Fig. 9), demonstrating that the Langmuir isotherm is followed by the adsorption of Methylene blue. Calculated values of the Langmuir constants at various temperatures are provided in (Table 2). By applying the separation factor or dimensionless equilibrium parameter, R_L, and the fundamental properties of the Langmuir isotherm parameters, it is possible to determine the affinity between the adsorbate and adsorbent:

$$R_L = 1/\ (1 + bC_0) \qquad \text{(v)}$$

Where C_0 is the starting dye solution concentration and b is the Langmuir constant. Important details regarding the adsorption's nature are revealed by the value of the separation parameter R_L. The Langmuir isotherm type is determined by the value of R_L, which can be irreversible (R_L=0), favourable, linear (R_L=1), or unfavourable (R_L>1). For concentrations of 1–9 mg/L, the R_L was shown. They fall between 0 and 1, which denotes good biosorption.

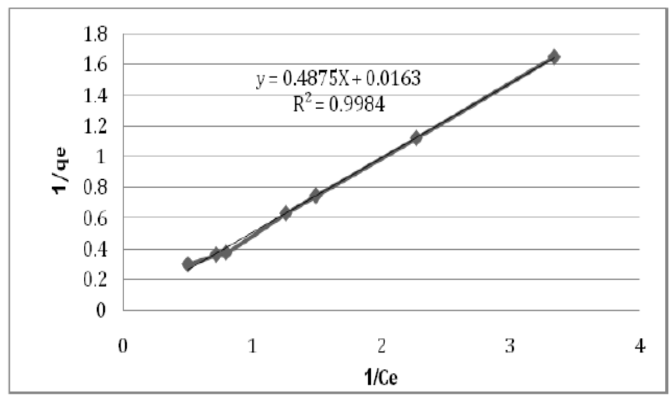

Fig. 9: Langmuir adsorption isotherm for the adsorption of methylene blue over Nerium oleander at pH 7 and 300K temperatures

Table 2: Langmuir constants for methylene blue over Nerium oleander

Slop	R^2	q_{max}	K_L	R_L
0.487	0.99	62.5	128.3368	0.001112

5. ADSORPTION THERMODYNAMICS

The idea behind thermodynamics is that entropy change acts as the driving force in an isolated system where energy cannot be obtained or lost. The following equations were used to calculate the following thermodynamic quantities: change in free energy (G°) (kJ mol-1), enthalpy (H°) (kJ mol-1), and entropy (S°) (J K 1 mol-1).

$$\Delta G^o = -RT \ln b \qquad \text{(vi)}$$

$$\Delta H^o = -R\ (T_2T_1)/\ (T_2\text{-}T_1) \ln (b_2/b_1) \qquad \text{(vii)}$$

$\Delta S^o = (\Delta H^o - \Delta G^o)/T$ (viii)

Where R (8.314 J mol K $^{-1}$) is the universal gas constant, b, b_1, and b_2 are the equilibrium constants at various temperatures, which are determined from the slopes of straight lines derived for Langmuir adsorption isotherms at various temperatures, and T (K) is the absolute solution temperature [11].

Table 3: Thermodynamics parameters of Methylene blue over NO

Adsorbent NO	$\Delta G°$(kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (KJk^{-1}mol^{-1})
	-12.1067	24.992×10^3	40.439×10^3

6. ADSORPTION KINETIC STUDIES

The adsorbent material's physical and/or chemical properties, as well as the adsorbate species that also have an impact on the adsorption process, are highly dependent on adsorption kinetics. Several models, including pseudo first-order kinetic, pseudo second-order, Elovich, intraparticle diffusion, and liquid film diffusion kinetic, have been put forth to explore the governing mechanism of sorption processes including mass transfer and chemical reaction [12]. Lagergren [13] proposed the pseudo-first-order kinetic model, which is expressed by Equation (ix), for the sorption of solid/liquid systems:

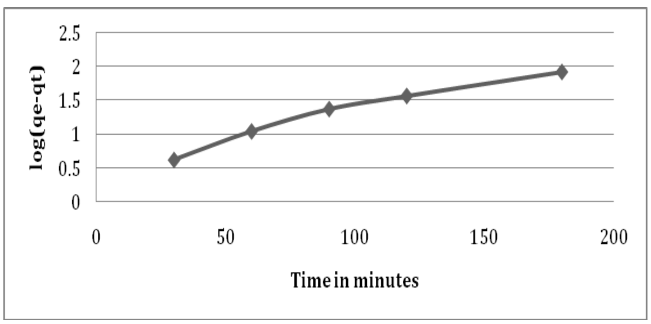

Fig. 10: **Lagergren pseudo first order plots for adsorption of methylene blue over NO at pH 7 at 300K temperature**

$\log (q_e - q_t) = \log q_e - k_{ad} \times t/2.303$ (ix)

Where k_{ad} (1/h) is the adsorption rate constant and q_e and q_t (mg/g) are the quantities of adsorbate adsorbed at equilibrium and at any time, respectively. Where, respectively, qe and qt stand for the quantity adsorbed at equilibrium and any time t. At 300K, 310K, and 320K with various contact periods, the adsorption kinetics was assessed. It is one of the crucial elements in defining adsorption efficiency. To further understand the behaviour of this inexpensive adsorbent, the kinetics of dye removal was investigated in the current work. The graph of log (q_e - q_t) with time shows straight lines, which is evidence that the adsorption process in each case follows first-order rate kinetics (Fig. 10). Table 4 displays the k_{ad} values calculated for system from the corresponding Lagergren graphic.

Table 4: Rate constant k_{ad} for Methylene blue over NO

Intercept	Slope	Kad	R2
0.502	0.008	0.018428	0.955

7. CONCLUSION

Nerium Oleander powder was used as a productive bio adsorbent material in a practical adsorption approach to decontaminate MB dye from industrial aqueous effluents. The existence of active binding sites of tiny particle size increased with surface area. The best conditions for adsorption of MB onto the biosorbent were determined to be 180 min. of contact time, 0.75 g biosorbent dosage, and 300K temperature. Isotherm models (Langmuir model, Freundlich model,) were investigated to determine the mechanism of adsorption, and the results were best matched in the Langmuir and Freundlich isotherms. The utilization of adsorbent as a viable bio-sorbent for the removal of MB dye from wastewater is a rapid, environmentally friendly, and cost-effective method that may likely be applied to remove other hazardous dyes from water as well. This study will not only enhance existing adsorption procedures but will also seeking cost-effective, environmentally friendly and hazardous dye's removal compound.

Conflict of interest

None declared

Source of funding

None declared

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