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Kinetic Studies of Wastewater Purification Using Local Sand Samples in Erbil, Kurdistan

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Abstract

This research describes a straightforward procedure for extracting the pigment of Methylene Blue (MB) dye from aqueous solutions by utilizing a low-cost, safe, natural, and national source. Batch adsorption experiments were carried out to determine contact time, adsorbent dose, and the starting concentration of the adsorbate. For the analysis, a UV spectrophotometer was employed. Dye adsorption equilibrium was obtained after 120 minutes of contact time. Temkin, Langmuir, and Freundlich isotherm adsorption were used at solution concentrations of (3, 4, 6, and 8) mg/l. Adsorption data is used to predict the pseudo first and pseudo second order kinetic equations, Elovich kinetic models, and intra-particle diffusion using pseudo first and pseudo second order kinetic equations. The Langmuir adsorption model fits the MB adsorption data better than other isotherm models, with the MB capacity at 8 mg/l equal to 0.992 mg/g. The pseudo-second-order model and the adsorption kinetic data are satisfactorily related.

Keywords: Adsorption isotherm, Kinetics, Methylene Blue, Sand, Wastewater

دراسة حركية لاستخدام عينة الرمل المحلية لتنقية مياه المجاري في إقليم كوردستان – أربيل

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الخلاصة

يقدم هذا البحث طريقة سهلة لازالة صبغة الميثيلين الزرقاء من محلول مائي باستخدام مادة رخيصة وامنة ومتوفرة طبيعيا ومحليا وهي الرمل. تم استخدام هذه المادة لمعالجة مشكلة اللون في المياه المصرفة لاحتوائها على صبغة المثيل الازرق. وأجريت تجارب الامتزاز كدالة لوقت الامتزاز ، و دالة للتركيز الابتدائي للممتز و وزن الماز. تم استخدام الأشعة فوق البنفسجية الطيفية للتحليل . تم تحقيق التوازن الكيميائي لعملية امتزاز الصبغة بعد 120 دقيقة من وقت التلامس ، وطبقت النتائج على نماذج الامتزاز بثبوت درجة الحرارة : تيمكن ، لانكماير و فريندلج على مدى التراكيز التالية (3 ، 4 ، 6 و 8) ملغم/لتر ولدراسة الحركية الكيميائية لعملية الامتزاز طبقت بيانات الامتزاز على النماذج الحركية. أن بيانات امتزاز المثيل الازرق دلت على ان

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نموذج لانك ماير افضل من نماذج الايزوثيرم الاخرى. وان سعة المثيل الازرق لتركيز 8 اجزاء من المليون تساوي 0.992 ملغم / غرام . ترتبط البيانات الحركية للامتزاز بشكل معقول بنموذج الدرجة الثانية الكاذبة.

1. Introduction

The rapid growth of industry and urbanization throughout the world has led to a better knowledge of the link between pollution and human health. The largest one, which originates from dye-based businesses and acts as the primary cause of water pollution, is one of the most connected to environmental pollutions that are harming our biodiversity and producing water pollution [1]. Various companies generate contaminants in water media by discharging various types of dyes. Because of its negative impacts on the environment and public health, it has sparked global attention as a global environmental concern [2]. Methylene Blue [3,7bis (dimethyl amino) phenazothionium chloride] is a dye that is used to color cotton, silk, and wool [3]. Methylene Blue creates a slew of issues. It causes eye burn in both people and animals, which can be irreversible. When inhaled, it can produce short bouts of difficult or fast breathing, while ingested through the mouth causes a burning sensation and can result in sweating, vomiting, nausea, and mental disorientation [3]. The major motivation for investigating Methylene Blue is because of its high adsorption onto solids. Methylene Blue is a model chemical that eliminates colorful bodies and organic impurities from aqueous solutions [3]. Dyes have been removed using a variety of methods, including biological, chemical, physical, and related technologies. Adsorption is one of the greatest strategies for getting the best results since it may remove many types of dyes at once. When a fluid or a known gas is used as the adsorbate, a molecular film is created on the surface of a solid adsorbent [4]. At this time, activated carbon (AC) adsorption is considered the most popular and effective physical approach [5,6]. Natural sands include active components that adsorb organic molecules with a positive charge from an aqueous solution with vigour. It is most commonly utilized as a filter media in wastewater-treatment facilities for the physical and microbiological removal of numerous factors such as turbidity, suspended particles, chemical oxygen demand, and biochemical oxygen demand, as well as coliform bacteria [7]. The inexpensive cost of natural sand is one of the reasons for its use as an adsorbent. Sand has also been employed as an adsorbent in the past in laboratory size research to remove inorganic ions [8] and dyes [9] from water.

The need of executing several techniques for the purpose of treating dye wastes has previously been mentioned in previous studies. Biodegradation, photolytic, photocatalytic, and advanced oxidative degradation of various dye solutions are all involved [10]. The adsorption of dyes on various adsorbent surfaces, such as fly ash, sand, clays, and activated carbon, has been studied extensively. Nonetheless, no research on sand surfaces has been undertaken to my knowledge [11].

The focus of this research is to see if it is possible to remove Methylene Blue (MB) from aqueous solutions using locally available sand in Iraq. This sand is inexpensive and widely available in developing countries.

2. Materials and Methods

2.1Adsorbent

The use of sand as an absorbent in this investigation was made possible by the fact that it is abundantly available in the region. A sample of sand was retrieved from the Bastoura Valley in Erbil province, Iraq's Kurdistan Region. The sand had no treatment other than sifting to separate the distinct sections. To execute the test, a sufficient sample of the aggregate should be obtained from the source. To obtain a homogenized sample, the aggregate would need to be completely mixed and reduced to an adequate size. Allowing 250 grams of sand to pass through a 250 micron screen produced a sample of 250 grams of sand.

2.2 Adsorbate

Fluka was used to supply Methylene Blue (MB), which had a purity of roughly 99 percent and was used as a dye. In order to prepare the dye solutions with the desired concentration, deionized water was used. At 664 nm , this dye solution appears as an intense absorption peak in the visible region. In an adsorption operation, removing the dye from solution is carried out by an alteration in the intensity of the peak.

2.3 Experimental Methods

A particular concentration of dye solution was applied to 0.08 g of sand in a 10 ml of glass-test tube at 25 0.1 ^{0}C in each adsorption experiment. The mixture was then agitated for 150 minutes in a water bath shaker. The samples were analyzed while swirling at predetermined intervals. The adsorbent was satisfactorily separated from the solution by centrifugation at 1500 rpm for 5 minutes (Research Centrifuge, HERMLE (Z200A)). The concentration of the leftover dye was thought to be controlled by the absorbance process of the supernatant solution. The concentration of leftover dye was measured using a spectrophotometer (CECIL (CE 3021, 3000, SERIES) Spectrophotometer before and after the procedure. The studies were conducted out twice. As a result, the concentrations given are averages. The starting dye concentration and adsorbent dose were changed in the test solution to see how they affected the adsorption kinetics. The following formula was used to compute the amount of sorption at time t, qt (mg/g):

$$q_t = \frac{(C_0 - C_t)V}{(W)}$$

As C_0 (mg/l) is the initial concentration of the dye in solution, Ct (mg/l) stands for the liquid phase concentrations of dye at any time throughout the experiment. Finally, *V* is the volume of the solution (l), whereas *W* is the mass of dry adsorbent (g).

In order to calculate the amount of equilibrium adsorption, *qe (mg /g)*, the following formula was used [12] :

$$q_e = \frac{(C_0 - C_e)V}{(W)}$$

Where Ce (mgl^{-1}) stands for the liquid-phase concentration of the dye at equilibrium .

3. Results and Discussions

3.1 Impact of Adsorbent Dose

The effect of adsorbent dose is depicted in Fig. 1 (below). This graph shows that as the weight of the adsorbent grew, the absorbent capacity increased as well, peaking at 0.08g of sand at 25°C, mg/l. As a result, the optimal sand adsorbent dose was 0.08g. The adsorption effectiveness is determined by chemical and physical features, namely the surface area and distribution, as well as the size of pores on the surface, which rises as the weight of the adsorbent particles increases.

The adsorption drift is the result of growth in surface area and, consequently, the number of active sites.

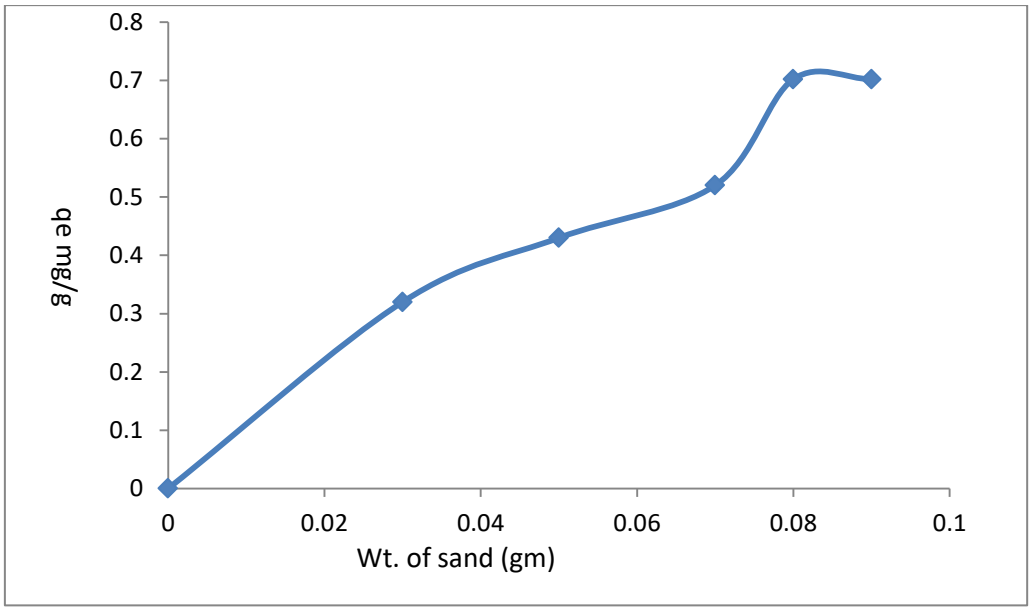

Figure 1-Methyl Blue removal as a function of adsorbent dosage

3.2 Impact of Contact Time

In determining the size of an adsorption plan, contact time is critical. The variation in concentration with contact time varies depending on the starting concentrations, which range from (3 to 8) mg/l. Figure 2 illustrates this. The dye absorption was rapid over the first 40 minutes. Later on, the uptake slowed until it reached a point of equilibrium. The maximum capacity at this time is at a concentration of 8 mg/l, while the equilibrium period for methyl blue dye is 120 minutes. The solute molecules approach the adsorbing surface and begin to bind with the adsorbent surface as the concentration rises, followed by migration of the solute molecules from the adsorbent surface sites into the Adsorbent Pores. The amount of adsorbed dye was minimal after that. With increasing initial dye concentrations, the equilibrium adsorption of sand increased [13 and 14].

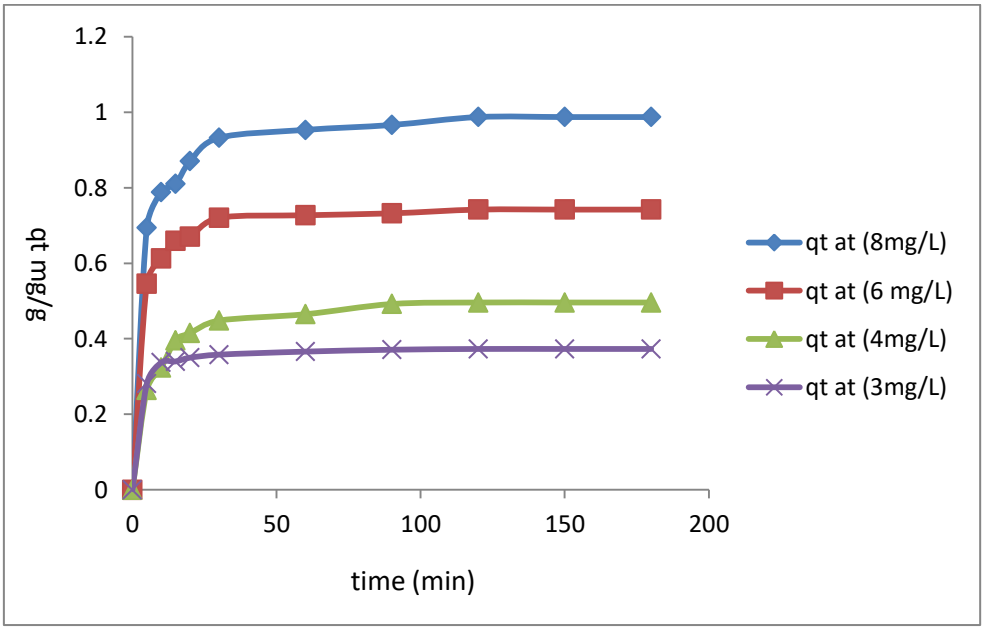

Figure 2-Effect of initial dye concentration vs. time

3.3 Adsorption Isotherms

For elucidating experimental sorption equilibrium parameters, many isotherm equations are appropriate. The most often used models are the Langmuir and Freundlich models. The Langmuir isotherm model presupposes that there are a finite number of active sites that are evenly distributed over the adsorbent's surface.

All the sites of activation show identical connection to the adsorption of a mono-molecular layer, whereas adsorbed molecules exhibit no interact at all [15]. Fig.3, indicates the linear form of the Langmuir equation.

$1/q_e = 1/q_m + 1/qmbLC_e$

As q_e stands for the quantity of the adsorbed dye (mg/g) at equilibrium, C_e stands for the equilibrium concentration of the adsorbate (mgL^{-1}). *qm* and *bL* represent Langmuir constants linked with the maximum adsorption capacity (mg/g) and energy of adsorption (L/mg), respectively. A straight line with a slope of 1/qm and intercept 1/qmb should represent a plot of C_e/q_e versus C_e if the adsorption follows the Langmuir equation [16].

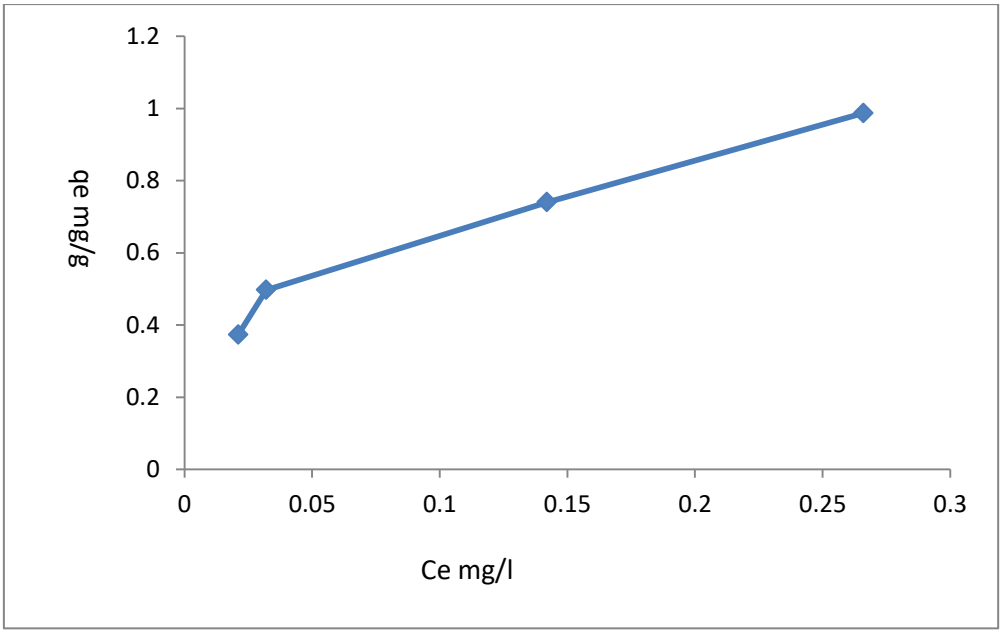

Figure 3- Langmuir isotherms for the adsorption of Methylene Blue onto sand

The Freundlich isotherm model is related to adsorption on different surfaces, as well as interactions between the adsorbed molecules. It's also possible to make a mono-layer with it. According to the model, when the adsorbate value increases, the concentration of adsorbate on the adsorbent surface increases as well. As a result, the sorption energy decreases in order to complete the adsorbent's sorption centers [17]. The Freundlich model is denoted by the following equation [17]:

$$lnqe = lnKf + \frac{1}{n} lnCe$$

Where q_e represents the quantity of dye which is adsorbed during equilibrium (mg/g), Kf represents the Freundlich constant, 1/n stands for the heterogeneity factor that is linked to the intensity and capacity of the adsorption, and, finally, C_e represents the concentration at equilibrium (mgL^{-1}). The amounts of Kf and 1/n can be formed from the slope and the snatch of the plot of ln q_e against ln C_e, is shown in Fig.4

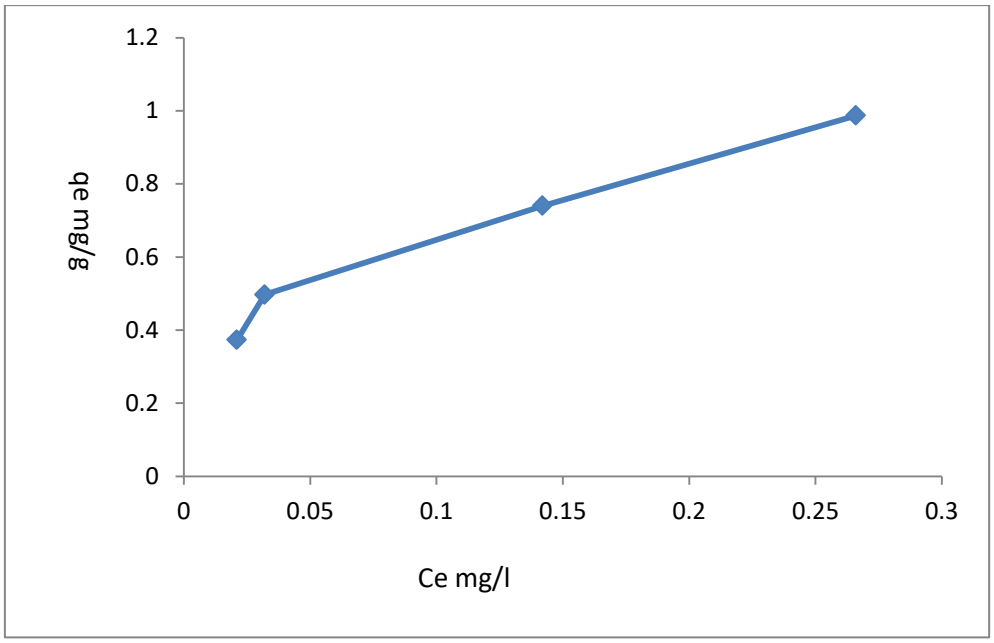

Figure 4-Freundlich isotherms for the adsorption of Methylene Blue on sand

The Temkin isotherm model, on the other hand, assumes that. Because of interactions between the adsorbent and the adsorbate, the temperature of adsorption of all molecules accessible on the layer decreases linearly, as does the coverage. Therefore, the adsorption has a specific feature of showing a uniform distribution of the binding energy [18]. The Temkin isotherm is given as [18]:

$$q_e = R_T/b_T \, In A_T + R_T/b_T \, In C_e$$

Whereas $1/b_T$ represents the adsorption potential of the adsorbent (J mol^{-1}) and A_T represents Temkin isotherm constant (dm^3g-1). A straight line of slope R_T/b_T and intercept of R_T/b_T In A_T is given by a plot of In C_e versus q_e. The Temkin isotherm plot for the adsorption of MB from aqueous solution onto the sand is shown in Fig 5[19].

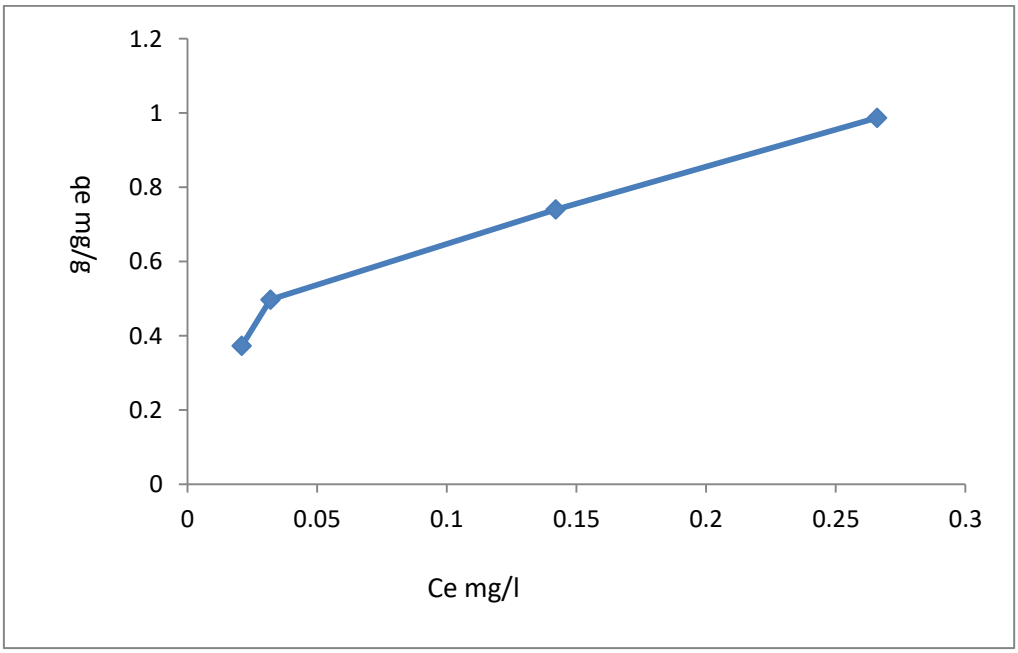

Figure 5-Temkin isotherms for the adsorption of Methylene Blue onto sand

According to Giles categorization, the findings of methyl blue dye adsorption on sand follow the L pattern, which indicates that the adsorbed particles on the adsorbing surface are horizontally oriented. That is, the adsorbent molecule's larger axis is parallel to the adsorbent surface.
The adsorption isotherm constant parameters for adsorption models are shown in Table 1:

Table 1-Adsorption isotherm constant parameters

Langmuir	
q mg/g	1
bL mg/g	28.5
R^2	0.9819
Freundlich	
Kf	1.5
1/n	0.35
R^2	0.9777
Temkin	
b_T. (J/mol)	37.34
A_T (dm^3/g)	260
R^2	0.9702

The methyl blue dye is in close accord with the Langmuir r equation, and the values of the Fernadlich, Temkin constants, and R^2 reveal that it is less than compatible with the Langmuir model, which refers to monolayer adsorption on the surface of the adsorbent material.

3.4 Kinetic Studies:

The determining procedure of dye adsorption from the aqueous solution has been examined by applying numerous kinetic models. In this study, the following models were applied: pseudo-first-order, pseudo-second–order, intra-particle diffusion and Elovich. The earliest well-known equation is Lagergren's first order rate equation, which is used to explain the adsorption rate built on adsorption capacity. Lagergren's first order rate equation has the following linear form [20].

$$\log(qe - qt) = logqe - \frac{K1}{2.303}t$$

As q_e stands for the quantity of dye which is adsorbed on the surface of the adsorbent at the stage of equilibrium (mg/g), q_t stands for the quantity of dye which is adsorbed on the surface of the adsorbent at any time t during the experiment (mg/g), and, finally, K_1 (min^{-1}) stands for the speed constant of the pseudo-first-order adsorption. The linear-plot-of-log slope (q_e - q_t) vs. t can be used to calculate K_1 (min^{-1}) (slope= K1/2.303, log q_e = exp intercept.
The rate-limiting step determines a pseudo-second-order model for adsorption. Because the removal of a solution is the consequence of physicochemical interactions between both phases, this will result in surface adsorption. The following is the pseudo-second-order model:
$t/q_t = 1/K_2q_{e2} + t/q_e$

As K_2 ($gmg^{-1}min^{-1}$) represents the rate constant of the pseudo-second-order adsorption, q_e (mg/g) represents the quantity of dye which is adsorbed on the surface of the adsorbent at the equilibrium stage, and q_t (mg/g) is the quantity of dye which is adsorbed on the surface of the adsorbent at any time of the experiment [21]. The slope and intercept of the plot of t/q_t against t can be used in calculating K_2 ($gmg^{-1}min^{-1}$).
The following form may express a simple Elovich kinetic model:
$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t$
For qt represents the quantity of dye which is adsorbed on the adsorbent at any time t during the experiment (mg/g), α represents an adsorption initial rate (μg g-1mint-1), and β represents the desorption constant (μg g-1min-1) [22]. A linear relationship for the applicability of the

simple Elovich kinetic model should be given by a plot of qt versus ln t. The experimental results of the adsorption Methylene Blue on sand were analyzed using the Elovich model. All the values of qt, α, β, and R2 are given in Table2.

Intra Particle diffusion kinetic model is as follows:

$$q_t = K_d t^{1/2} + C$$

Where K_d represents the initial rate of intra-particular diffusion (mg g^{-1} $min^{-1/2}$), and C represents the constant which gives information regarding the thickness of the boundary layer (mg g^{-1}) (y-intercept) [23]. All the values of intra-particular diffusion constants (Kd) at all concentrations are summarized in Table 2.

In the table 2, the kinetic constants and R2 for both models were determined. The second-order model's R2 values are relatively high, and the amount of adsorbed material estimated by this model is close to the value found by tests. While the R2 of the Pseudo first order model is dubious, the adsorption system is not. As a result, the pseudo-second-order model is better suited for describing adsorption kinetics for Methylene Blue adsorption on sand at various concentrations. It is noted that the alpha (adsorption initial rate) values increase with increasing concentration of the solution, Beta (desorption constant (μg g-1min-1) values decrease with increasing concentration of the solution indication of the difficulty of desorption at high concentration. To reveal the mechanics of diffusion during the adsorption process kd (diffusion constant)has been calculated as its value increases with concentration, so the adsorption process is mechanically good, and with different C (thickness of the boundary layer)values , as a higher value indicates a greater effect for this layer.

Table 2-Kinetic parameter Pseudo first order, Pseudo second order, Elovich kinetic and Intra Particle diffusion kinetic for the adsorption Methylene Blue on sand at different concentrations

	Pseudo 1st order			Pseudo 2nd order			Elovich kinetic			Intra particle diffusion		
con	k_1	q_e	R^2	k_2	q_e	R^2	α	ß	R^2	Kd	C	R^2
3	0.04	0.92	0.7789	1.78	0.376	1	1586	41	0.8048	0.0076	0.3	0.6367
4	0.05	4.61	0.9002	0.381	0.516	0.9997	0.85	14	0.9223	0.0232	0.2	0.7861
6	0.029	5.21	0.9426	0.43	0.751	0.9999	5.65	13	0.9339	0.0239	0.5	0.8186
8	0.023	3.51	0.9735	0.273	0.992	0.9997	27	10	0.9773	0.032	0.6	0.9153

Conclusion

The viability of employing a low-cost native sand sample as a material for extracting Methylene Blue dye from a liquid solution as a waste water pollutant was investigated in this work. Experiments were carried out at 25 ˚C. At a reaction duration of 120 minutes and an adsorbent dosage of 0.08g, the best removal efficiencies were achieved. The Langmuir adsorption model fits the MB adsorption data better than other isotherm models, with the MB capacity at 8 mg/l equal to 966.75 mg/g. The pseudo-second-order model and the adsorption kinetic data are satisfactorily related. It's been discovered that dye may be taken from a solution and deposited over the sand's surface under ideal conditions.

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