

The Behavior of Adsorption and Thermodynamic For Removing Methylene Blue Dye from Aqueous Solutions Using Silicon Powder

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سلوك الامتزاز والديناميكا الحرارية لإزالة صبغة الميثيلين الأزرق من المحاليل المائية باستخدام مسحوق السليكون

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Abstract:

The widespread use of dyes has led to an increase in their presence in the environment through industrial wastewater discharges, causing water pollution. Getting rid of them at the lowest possible cost has become a focus of research, leading to the use of silicon powder to treat water contaminated with industrial dyes by adsorption. This study focused on removing methylene blue dye from aqueous solutions at different initial concentrations (5-25 ppm) using varying weights of (0.2-1.5 g) at different pH values and temperatures (25-60°C). The results showed that the silicon powder achieved the maximum level of methylene blue (MB) dye removal at an initial concentration of 10 ppm°C, using 0.4 grams of silicon powder at a temperature of 25 °C. The highest removal rate using silicon powder was also observed at a pH of 6. Applying the Langmuir, Freundlich, and Temkin model confirmed that the R² value agrees with the Temkin model. The positive value of ΔH indicates that the process is endothermic and is classified as physical. The ΔS and ΔG values indicate that the reaction is random and that adsorption occurs non-spontaneously. The study also showed that silicon powder is highly efficient at removing this dye from aqueous solutions. Furthermore, it possesses a large surface area for adsorption, making it an effective material for dye removal.

Keywords: Silicon, Methylene Blue, Adsorption, Pollution, Dye.

المخلص:

إنّ التوسع الكبير في استخدام الأصباغ زاد من تواجدها مع مخلفاتها الصناعية المائية المطروحة في البيئة والتي تسبب في مشكلة تلوث المياه، وأصبحت عملية إزالتها بأقل تكلفة محط اهتمام الكثير من الباحثين، مما دفع إلى استخدام مسحوق السليكون لغرض معالجة المياه الملوثة بالأصباغ الناتجة من مختلف الصناعات بواسطة عملية الامتزاز حيث اعتمدت هذه الدراسة على إزالة صبغة الميثيلين الأزرق من المحاليل المائية وذلك عند تراكيز ابتدائية مختلفة لهذه الصبغة وتتراوح قيمتها بين (5-25 ppm) وذلك باستخدام أوزان مختلفة من مسحوق السليكون (0.2-1.5 g) عند قيم PH مختلفة ودرجات حرارة مختلفة (25-60°C) وقد بينت النتائج المتحصل عليها من هذه الدراسة أن أعلى نسبة إزالة لصبغة الميثيلين الأزرق كانت عند تركيز ابتدائي 10 ppm عند استخدام وزن 0.4 جرام ودرجة حرارة 25 °C لمسحوق السليكون كذلك كانت أعلى نسبة إزالة للصبغة باستخدام مسحوق السليكون عند قيمة PH=6 وقد تبين من خلال تطبيق

نموذج لانغموير وفرندليش وتيتمكين لوحظ ان قيمة R2 تتوافق مع معادلة تيمكين. ومن نتائج قيمة ΔH الموجبة تعتبر العملية ماصة للحرارة وتصنف على اساس انها فيزيائية. وأن قيم ΔS و ΔG تدل على ان التفاعل عشوائي وان الامتزاز يحدث بشكل غير تلقائي. أظهرت الدراسة أيضاً أن مسحوق السيليكون يتمتع بكفاءة عالية في إزالة هذه الصبغة من المحاليل المائية. بالإضافة إلى ذلك، يتميز بمساحة سطح كبيرة للامتزاز، مما يجعله مادة فعالة للاستخدام في إزالة الأصباغ.

الكلمات المفتاحية: السيليكون، الميثيلين الأزرق، الامتصاص، التلوث، الصبغة.

Introduction:

Environmental pollution is a serious problem resulting from the waste products of various industries and the rapid development of technology. In general, liquid waste from various industries includes papermaking, electroplating, textiles, cosmetics, as well as a variety of dyes such as azo dyes, acid dyes, and dispersants [1], discharged into the nearest water source, such as lakes, seas, and rivers, negatively affecting aquatic life and those who depend on these water sources [2]. Research indicates that over 100,000 types of dyes are used annually in various fields worldwide. It is also estimated that between 10-15% of liquid dyes are released into wastewater annually during the treatment process [3]. Researchers have found it difficult to analyze the numerous dyes that enter water bodies, which in turn cause many problems for the ecosystem [4]. The most significant of these problems is that even small amounts of these dyes can be toxic to living organisms [5]. Other problems caused by dyes include various diseases, such as cancer [6], anemia, eye burns, a decrease in red blood cells, delayed blood clotting, and damage to the heart, kidneys, lungs, and liver [7]. These dyes are also problematic because they cause allergies and resist biodegradation [8]. Recently, many different methods have been developed to remove dyes and reduce their negative effects on the environment. One of the most prominent of these methods is catalytic photolysis [9], photo-oxidation [10], solvent extraction [11], ozonation, flocculation, coagulation [12], electrochemistry, biodegradation, catalytic degradation, ion exchange, precipitation, microbial degradation, filtration, wet air oxidation, and adsorption [13, 14].

Studies have shown that wastewater treatment using adsorption technology has yielded satisfactory results using various types of adsorbents such as natural zeolite, fly ash [15], silica [16], natural polymers, alumina, and inorganic nanocomposites [17]. Several studies have pointed to the role of the various functional groups present on the surface of diatomite in the adsorption process. [15]. The most common material used for dye removal by adsorption is activated carbon, which is considered an inexpensive adsorbent [20]. Activated carbon is used in the removal of industrial pollutants, in catalytic processes, and in biomedicine [19]. Adsorption is one of the most prominent methods used for removing dyes, due to its high efficiency, economic viability, and ability to handle harmful substances [20].

Studies in thermodynamics have contributed to improving our understanding of the nature of adsorption as they have provided important thermodynamic information relating to the adsorption of dyes, such as the change in free energy (ΔG), changes in enthalpy (ΔH), and changes in entropy (ΔS). The aim of this study was to evaluate the potential use of silicone powder as an adsorbent for removing methylene blue dye from contaminated water. Factors affecting the adsorption efficiency of methylene blue were analyzed, including the effects of time, temperature, concentration, and pH. Additionally, adsorption curves were applied to interpret experimental data at various temperatures, and the dynamic and kinetic aspects of the adsorption process were studied.

Material and methods:

The following chemicals and equipment were used in this research: sodium hydroxide (NaOH), methylene blue ($C_{16}H_{18}N_3ClS$), Oxalic acid ($C_2H_2O_4$), Spectrophotometer - pH meter - sensitive balance and a stirring device.

In this study, solutions were prepared by dissolving 0.1 g of methylene blue dye in a 1000 mL volumetric flask to obtain a solution with a concentration of 100 ppm. From this solution, diluted standard solutions were prepared at different concentrations (5-25 ppm) and diluted with distilled water to the mark in 100 ml volumetric flasks. Measurements were taken using a wavelength of 630 nm.

Concentration determination:

To achieve the optimal concentration for adsorption of MB dye on the surface of 0.4 g of silicon powder, 20 ml of the various concentrations were drawn off and then placed on a shaking apparatus for 30 minutes. After that, the samples were filtered and measurements were taken by a spectrophotometer before and after the addition of silicon powder for each concentration.

Weight determination:

A concentration of 10 ppm was prepared, and 20 ml of it was taken with different weights of silicon powder (0.2 g -1.5 g). The samples were placed on a shaker for 30 minutes, then filtered, and their absorbance was measured.

Time determination:

To determine the required time, 20 mL of a 10ppm solution containing 0.4 g of silicon was taken at varying time intervals of 10, 20, 30, 40, 50, 60, and 90 minutes, with the samples placed on a shaker. After each time interval, the solutions were filtered and their absorbance measured.

Determining the pH value:

A solution with a concentration of 10 ppm was prepared to determine the optimal pH level for the adsorption of methylene blue dye onto the silicon surface, and 20 ml of this solution was taken. The pH value was measured across a range of (2-3-4-5-6-7-8-9-10-11) using diluted solutions of sodium hydroxide and oxalic acid. 0.4 grams of silicone were added to each solution, and the mixture was shaken for 20 minutes. The solutions were then filtered, and the absorbance of each solution was measured.

Temperature determination:

To establish the ideal temperature for the adsorption of (MB) dye onto a silicon surface, 20 ml of a 10ppm solution at pH=6 and 0.4 g of silicon were placed in a water bath for 20 minutes at various temperatures (20, 30, 40, 50, and 60°C). The solutions were then filtered, and their absorbance was measured.

Adsorption equations:

The quantity of material adsorbed (Q_e) on the silicon surface was determined using the following equation:

$$Q = \frac{c_i - c_e}{w} \times V \quad (1)$$

The removal efficiency (removal ratio) was determined as follows:

$$\text{Removal \%} = \frac{c_i - c_e}{c_e} \times 100 \quad (2)$$

Isotherms of Langmuir:

The Langmuir model is represented by the equation:

$$\frac{C_e}{Q_e} = \frac{1}{q_{max}} C_e + \frac{1}{q_{max}b} \quad (3)$$

C_e: Final concentration, **Q_e**: Amount of substance adsorbed at equilibrium, **q_{max}**: Maximum amount of substance adsorbed, **b**: Langmuir constant.

Isotherms of Freundlich:

Freundlich's assumption is represented by the following equation:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (4)$$

q_e= amount of adsorbed substance, **k_f**, **n**= the fixed standards of proportionality that express the adsorption capacity and strength, **C_e**= final concentration.

Isotherms of Temkin:

Temkin's postulate is represented by the equation shown below:

$$Q_e = \frac{RT}{b} \ln(A) + \frac{RT}{b} \ln(C_e) \quad (5) \quad \text{where } B = \frac{RT}{b} \quad (6)$$

Results and discussion:

Effect of Concentration:

The effect of the initial concentration of (MB) dye on adsorption rates was investigated by using different concentrations of the dye (5, 10, 15, 20, and 25 ppm). The results indicated that the highest amount of dye adsorbed onto the silicon surface was at a concentration of 10 ppm, reaching 93.45% (Figure 1). A study using an attapulgitte clay surface for MB adsorption revealed that the optimal value was at a concentration of 10 ppm [21].

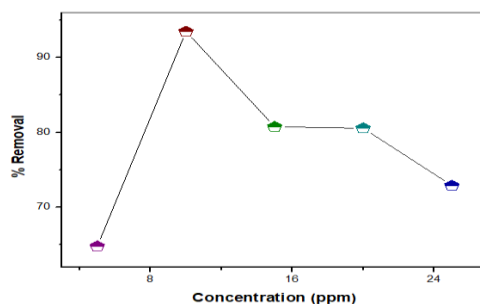


Figure (1): Effect of concentration (ppm).

Effect of Weight:

The impact of weight on the uptake of MB dye was investigated by using different quantities of silicon, namely 0.2, 0.4, 0.6, 0.8, 1, and 1.5 g. The findings indicated that the maximum uptake of the

dye occurred with the application of 0.4 g of silicon, reaching 99.28% (Figure 2). These results are somewhat consistent with studies on the adsorption of MB on pine-derived carbon [21].

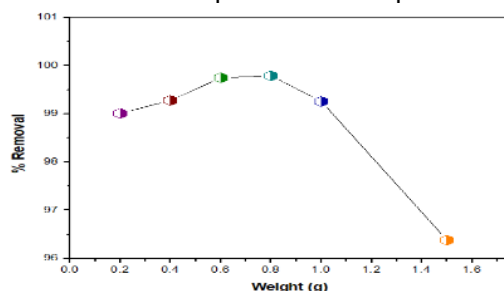


Figure (2): Effect of weight (g) Values.

Effect of Time:

The effect of the contact process on the absorption of MB dye was evaluated using a 10 ppm silicon solution, shaken for multiple time periods (90, 60, 50, 40, 30, 20, and 10 minutes). The results showed that the dye reached a stable state after 20 minutes, with a result of 96.83% (Figure 3). Research [22] showed that the best absorption efficiency of MB dye was achieved by using sawdust after 25 minutes, and this is consistent with our results.

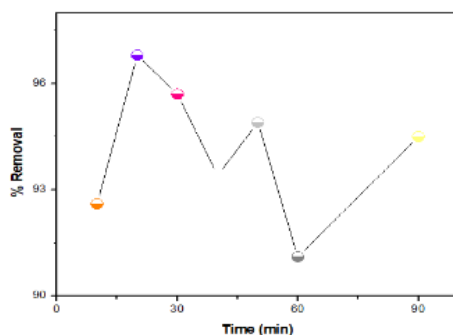


Figure (3): Effect of time (min) Values.

Effect of Ph:

The effect of pH on the adsorption capacity of methylene blue (MB) was studied by conducting a series of tests that included different pH values (2-3-4-5-6-7-8-9-10-11). The pH level of the solution was adjusted by using a dilute solution of sodium hydroxide and oxalic acid. The optimal absorption level of MB was found at pH 6, reaching 96.41% (Figure 4). This was consistent with previous studies [23, 24], which demonstrated that the ideal pH range for MB methylene blue absorption is between 6 and 8.

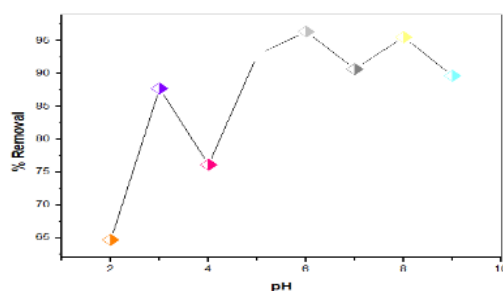


Figure (4): Effect of pH Values.

Effect of Temperature:

How temperature affects the absorption of MB dye was analyzed within the temperature range (25, 30, 40, 50, 60 °C). The maximum dye absorption rate was observed at a temperature of 25 degrees Celsius, reaching 98.31% (Figure 5). This result was consistent with the previous study on the removal of MB using Balanites Aegyptiaca powder at 25°C [24].

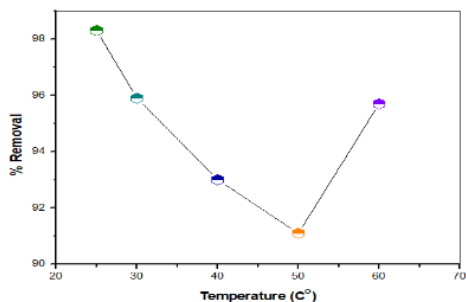


Figure (5): Effect of temperature.

Isotherm Adsorption:

Using the Langmuir, Freundlich and Temkin equations, the absorption of the MB dye on the surface of the silicon powder at a temperature of 25°C was studied, as shown in Figures (6, 7 and 8). The Langmuir, Freundlich, and Temkin constants, as shown in Table (1), were used, and the R² coefficient was evaluated. It was observed that the MB dye did not conform to the Langmuir, Freundlich isotherm but matched the Temkin isotherm.

Table (1): The Isotherm of Silicon powder.

Isotherm of Silicon powder						
Isotherm Models	Correlation Parameter					
Langmuir	Intercept 28.89884	Slope 55.40223	qmax(mg/g) 0.034603	KL 0.521638	RL 0.160865	R ² 0.66906
Freundlich	Intercept .725770	Slope 1.25467	1/n 1.25467	Kf 44.24967	R ² 725770.	
Temkin	Intercept 44.01779	Slope 231.4868	Pt (j mol-1) 231.4868	CT (jmg-1) 0.826833	R ² 0.8407	

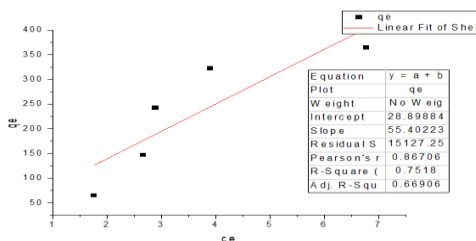


Figure (6): The Langmuir model.

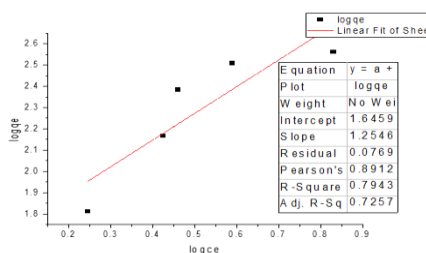


Figure (7): The Freundlich model.

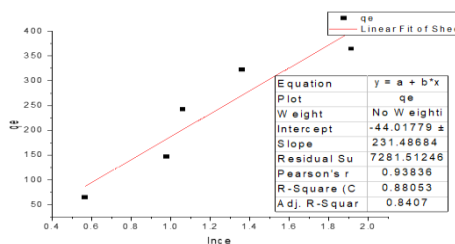


Figure (8): The Temkin model.

Thermodynamic functions of silicon powder:

The information in Table (2) indicates that the absorption of methylene blue dye on the silicon surface increases with increasing temperature. From the positive value of ΔH , we conclude that the process absorbs heat, and therefore this process is classified as physical [23]. In addition, the simple positive value of ΔS indicates a level of disorder within the reaction, and considering the value of ΔG , we find that it decreases with increasing temperature, indicating that the adsorption process occurs non-spontaneously.

Table (2): The thermodynamic functions of Silicon powder.

Temperature (K)	ΔG (KJ/mol)	ΔS (J/mol. K)	ΔH (KJ/mol)
298	17,489	3,0662	18,40
303	15,539		
313	14,535		
323	14,297		
333	14,130		

Conclusion:

The increasing need for economical methods to purify water contaminated with dyes, a major industrial waste product in the field of chemistry, has led to the use of silicon powder as one of the most effective and widely used materials for treating contaminated water. The data showed that the absorption efficiency of methylene blue dye is affected by a number of factors, such as contact time and temperature. The Langmuir, Freundlich, and Temkin models were applied, and Timken's model showed the highest value for the coefficient of determination R^2 , confirming that it is the most effective in representing adsorption data. Based on these results, we emphasize the importance of investigating the effectiveness of silicon powder in removing other organic pollutants from wastewater produced by chemical plants. In addition, factories that use dyes in their processes must adopt effective water treatment systems to reduce the health and environmental damage associated with pollution.

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