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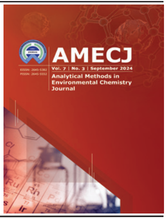

An efficient method for removing toluidine blue and malachite green from industrial wastewater using limestone as an adsorbent surface

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ABSTRACT

This study used an applied method to remove toluidine blue (TB) and malachite green dye (MG) via limestone residue as an adsorbent. The results showed that the TB and MG dyes were removed at a weight (4.0 g and 2.5 g) of limestone residue, pH (10 and 7), temperature (298 ^{o}K and 303 ^{o}K), and removal rate (98.07% and 99.65%) based on an equilibrium time 40 min with a granular size of 300 µm, respectively. The recovery, RSD (%), and absorption capacity (AC) for TB and MG were obtained at (98.8, 1.4, 1.98 mg g^{-1}) and (96.1, 0.89%, 0.55 mg g^{-1}), respectively, by UV-Vis spectrophotometers. The adsorption isotherms of the dyes and their applicability were studied using the Lankmeyer and Freundlich equations. The results also obtained showed that the application of the adsorption process to the Tamkin, Freundlich, and Lankmeyer equation through the values of the correlation coefficient (R^2), where the values for TB dye were (0.96, 0.81, 0.043) and for MG dye (0.9526, 0.7193, 0.819), respectively. Due to the thermodynamic studies, the positive ΔG^{o} values for toluidine blue dye (8.986, 9.293, 10.17, 10.12) and negative ΔH^{o} for malachite green dye (7.756, 8.015, 8.288, 8.614) were achieved at temperatures (293, 303, 313, 323^{o}K), respectively. So, ΔG^{o} values indicate that the adsorption processes were non-spontaneous and showed TB dye with positive ΔH^{o} values is endothermic, and MG with negative ΔH^{o} indicates exothermic. The positive entropy values indicate increased randomness when there is contact between the adsorbent surface and the dye solution.

1. Introduction

Throughout industry growth and development, water is susceptible to pollution, as humans employ chemicals in most aspects of their lives. Pollution directly impacts human health, and the types of pollutants include organic compounds and heavy metals [1]. Organic pollutants, commonly detected in water systems, can be considered dangerous [2-4]. Most of the dyes produced are used in several complementary industries, and their release into bodies of water seriously impacts the aquatic environment [5,6]. The presence of dyes in the aquatic environment calls for great concern because most of these dyes are harmful to human and aquatic life [7]. Many dyes are widely used in various industries, such as fabrics, leather, medicines, etc. The consumption of large quantities of dyes in textile industries has produced a large

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amount of waste in the environment [8]. Malachite green (MG) is one of the most widely used dyes for coloring cloth, wool, leather, cotton, etc., and is also used as an antimicrobial and antifungal agent [9]. The presence of malachite green pigment in water causes kidney and liver damage and heart failure, reduces the fertility rate, and is carcinogenic [10]. Another dye is toluidine blue, which is free from organic pollutants and is widely used to dye textiles such as cotton, cellulose, wood, and silk [8]. This dye causes harmful effects on humans and the environment due to its solubility in water. It causes carcinogenesis and chronic toxicity, mainly to the central nervous system [11]. Liquid waste from the textile industry is dangerously colored [12]. Many chemical and physical processes remove these dyes from water [13]. The most crucial method is adsorption, and it is considered one of the best techniques used not only in water treatment but can also be used to treat crude oil due to its ease of use, low cost, and high efficiency [14]. Adsorption is the process of adhesion or gathering of a liquid or gaseous adsorbent (Adsorbate) on the surface of a material. Solid substance: Adsorbent [15] is the process of physical or chemical bonding of several molecules with active sites on the surface of a solid material [16]. This process leads to forming a layer or several layers of molecules or atoms accumulated and densely concentrated on the surface of the solid [17]. The degree of adsorption depends on the relationship between the nature and size of the adsorbent and its surface area. Adsorption is also defined as the transfer of dissolved pollutants (adsorbent) from aqueous solutions to the surface of a solid material (adsorbent surface) [18]. In this research, limestone was used after grinding it to different sizes as an adsorbent surface to remove malachite green and toluidine blue dyes from water and purify them. The tests were conducted in the Hit laboratory, and the factors affecting adsorption efficiency, including adsorbent surface weight, contact time, adsorbent surface granular size, acidity function, and temperature, were studied.

2. Experimental

2.1. Preparation of the adsorbent

Limestone was collected from the waste of sculpture factories in Hit, Anbar, Iraq. It was dried at 105 ^{o}C, then ground with a grinder and sieved to obtain three particle sizes (150, 250, 300 mm) [14]. Limestone contains 80% or more calcium or magnesium carbonate, including marble, chalk, oolite, and marl. limestone composition has high Ca^{2+}, argillaceous (clayey), SiO_2, conglomerate, Mg^{2+}, dolomite, and other limestones. Limestone is extracted from mines. Due to its chemical composition and optical granulometry, it is calcinated at about 900 °C in lime kilns to produce quicklime and is hydrated to slaking. Then, the slaked lime slowly reacts with carbon dioxide to form calcium carbonate (limestone), as shown in Equation 1.

$$CaCO_3 \rightarrow \; CaO + CO_2$$
$$CaO + H_2O \rightarrow \; Ca(OH)_2$$
$$Ca(OH)_2 + CO_2 \rightarrow \; CaCO_3 + H_2O$$

(Eq.1)

2.2. Materials used

The standard solution of toluidine blue (CAS number: 92-31-9, BDH company) and malachite green (CAS number: 569-64-2, BDH Company) was prepared at a concentration of (100 mg L^{-1}) by dissolving (0.05 g) of each dye separately in (500 mL) of distilled water. A series of standard solutions for the two dyes were prepared from the leading solution at concentrations (0.1-10 mg L^{-1}) to conduct the standard calibration curve. Before mixing the adsorbent, the pH of each solution was adjusted to the required value using 0.1N sodium hydroxide or 0.1N hydrochloric acid.

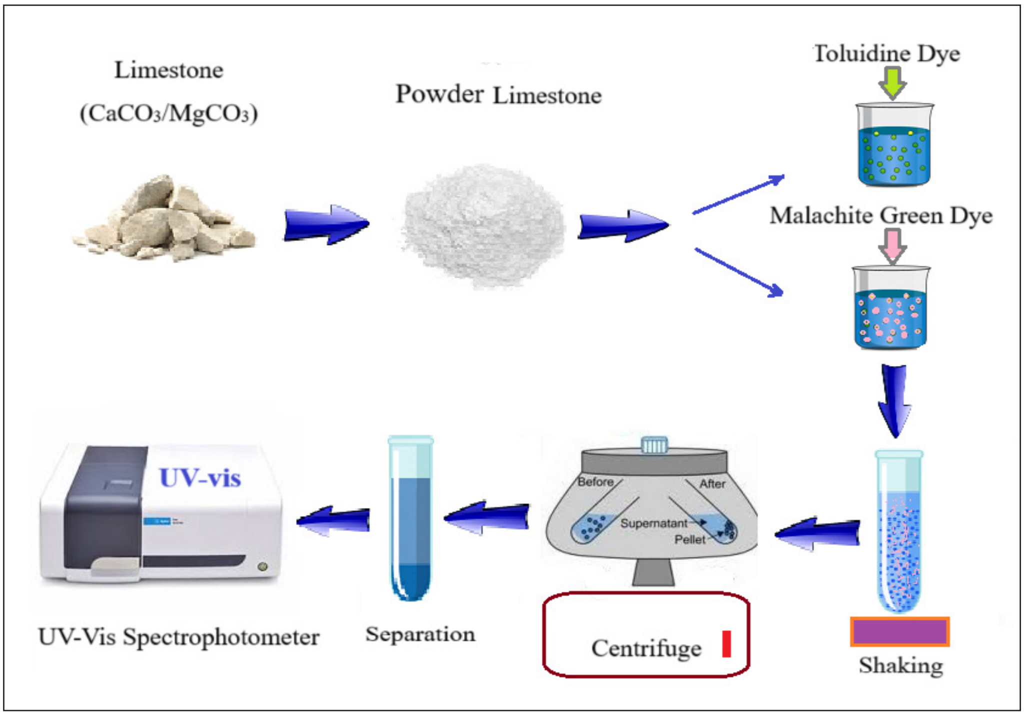
2.3. Adsorption Procedure

An adsorption experiment was conducted using toluidine blue dye, where the effect of contact time was studied by mixing a specific weight of limestone with (100 mL) at a concentration of (25 mg L^{-1}) of toluidine dye in a conical flask (Scheme 1). The flask was shaken for different periods (20, 40, 60, 80, 100, and 120 min). The filtrate was separated from the precipitate using a centrifuge, and the concentration of each solution was measured after adsorption using a UV-Vis spectrophotometer. The effect of the acid function was also studied at pH of 2, 4, 6, 8, 9, and 10 in different temperatures (298, 273, 313, 323 K). Adsorption experiments were also conducted using various concentrations of dye (5, 25, 45, 65, 85, and 95 mg L^{-1}). The effect of the adsorbent weight was studied using different limestone weights (0.5, 1, 1.5, 2.5, 3, 3.5, and 4 g). An adsorption experiment was also conducted using malachite green dye as an adsorbent; a specific weight of limestone was mixed with (100 mL) at a concentration of (50 mg L^{-1}) of malachite green dye in a conical flask. The flask was shaken for different periods (20, 40, 60, 80, 100, 120 min). The filtrate was separated from the precipitate using a centrifuge, and the concentration of each solution was measured after adsorption using an atomic absorption device. The adsorption experiment was also conducted at pH = (2, 4, 6, 8, 9, and 10) and different temperatures (298, 273, 313, and 323^{o}K). Adsorption experiments were also conducted using different concentrations of dye (5, 25, 45, 65, 85, and 95 mg L^{-1}). The influence of the size of the particle on the adsorbent surface was also studied using various sizes of the particle (150, 250, 300 µm), and the effect of the weight of the adsorbent was studied using different weights of limestone (0.5, 1, 1.5, 2.5, and 3.0 g). After the adsorption procedure, the concentration was measured using a UV-Vis spectrophotometer, and the adsorption capacity was calculated through Equation 2 and 1.

$$Q_e = \frac{(C_0 - C_e)V_L}{Wt}$$

(Eq.2)

Qe: The adsorption capacity (mg g^{-1})
VL: Total volume of dye solution (Liter)
C0: Initial concentration of dye solution (mg L^{-1})
Ce: The equilibrium concentration of the dye solution (mg L^{-1})
Wt: weight of the adsorbent surface (g)



Scheme 1. Adsorption procedure for removal of MG and TB in water sample by limestone

3. Results and Discussion

This study aims to use limestone as an adsorbent to remove toluidine blue and malachite green (MG) from aqueous solutions. The current study aimed to examine the factors affecting their adsorption efficiency, as well as to study the adsorption isotherms and their applicability to the Langmuir, Freundlich, and Tamkin equations.

3.1. Characterization of limestone

The FE-SEM image of the limestone in Figure 1 shows a rough and highly porous surface that explains the high adsorption of toluidine blue and malachite green from their aqueous solutions. The XRD image of limestone in Figure 2 shows that calcite is the dominant mineral in limestone [20]. Figure 3 shows the FTIR spectrum of the limestone sample. It shows the characteristic bands of calcite at 1,397, 875, and 712 cm $^{-1}$ [21].

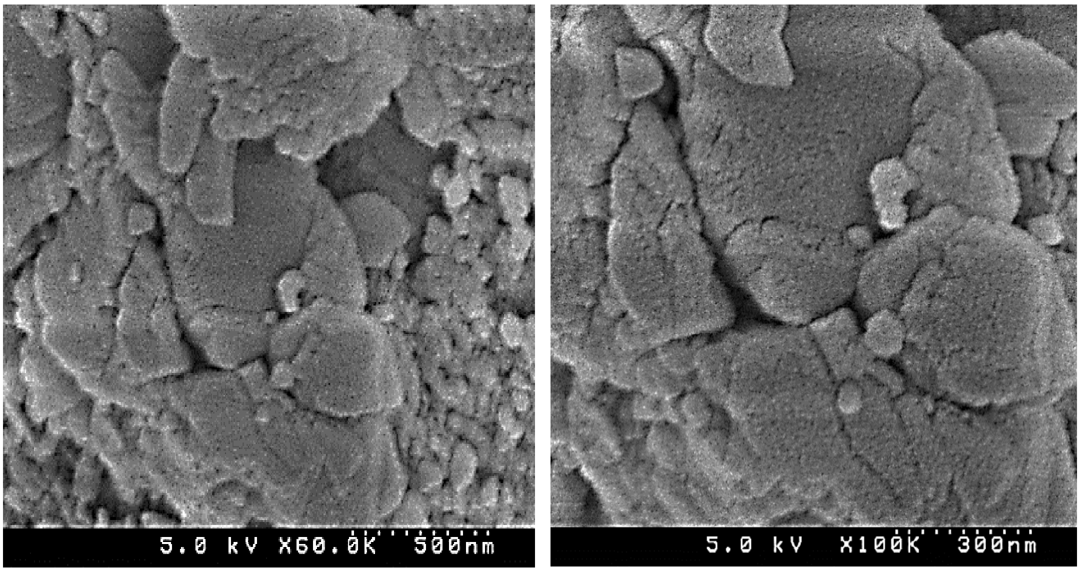


Fig. 1. SEM image of limestone

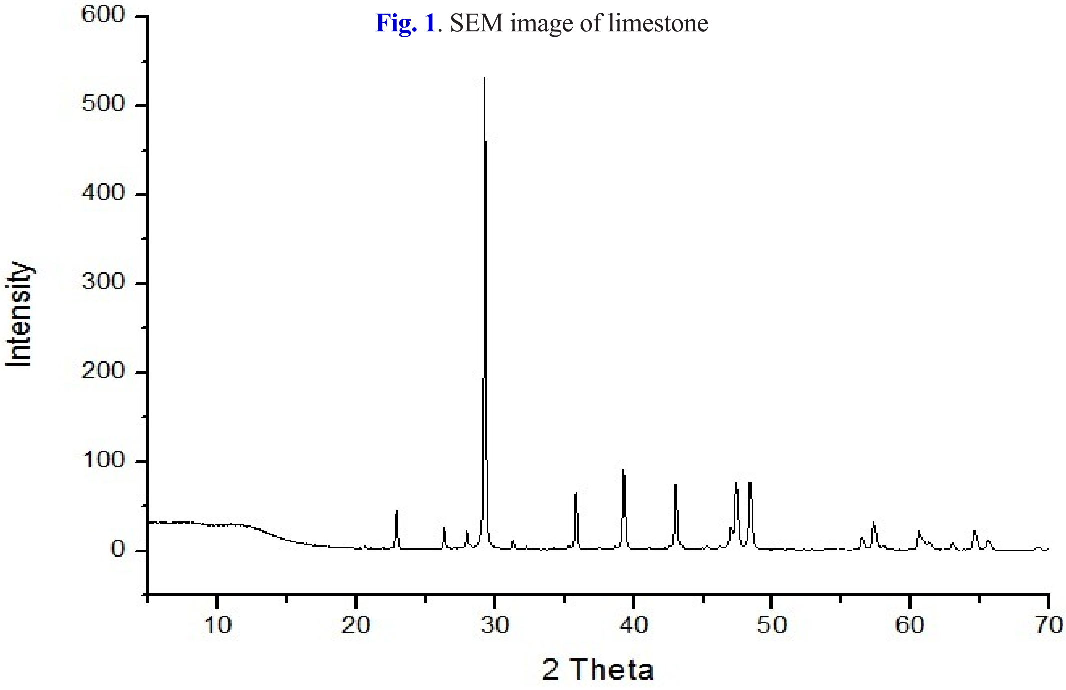


Fig. 2. XRD image of limestone

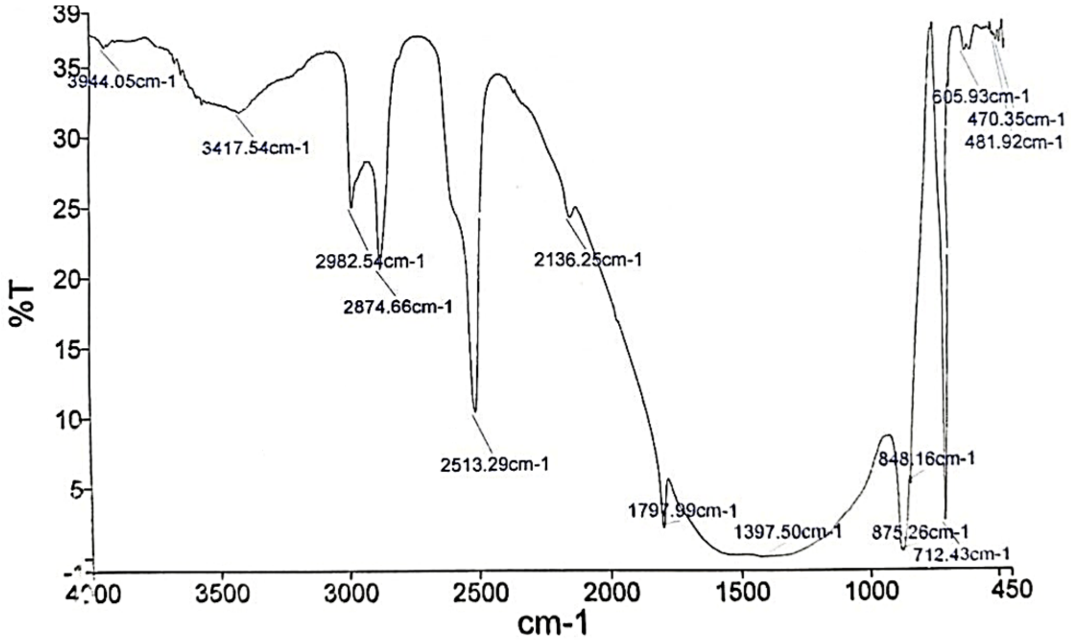


Fig. 3. FTIR spectrum of bulk limestone sample.

3.2. Effect of the adsorbent amount (limestone)

The effect of the adsorbent amount on removing toluidine blue dye was studied, and the results showed that the highest adsorption percentage was (89.08%) when using an amount of 4.0 g of limestone, as shown in Figure 4. As for the effect of the adsorbent surface on removing the malachite green dye, the results showed that the highest adsorption rate (99.30) was recorded when using an amount of 2.5 grams of limestone. This is ascribed to the availability of a larger surface area with increasing locations of active sites prepared for adsorption, and thus, the removal rate increases [22]. Stability is explained by the balance between the adsorbate (malachite green) and the adsorbent (limestone) [23], as shown in Figure 4.

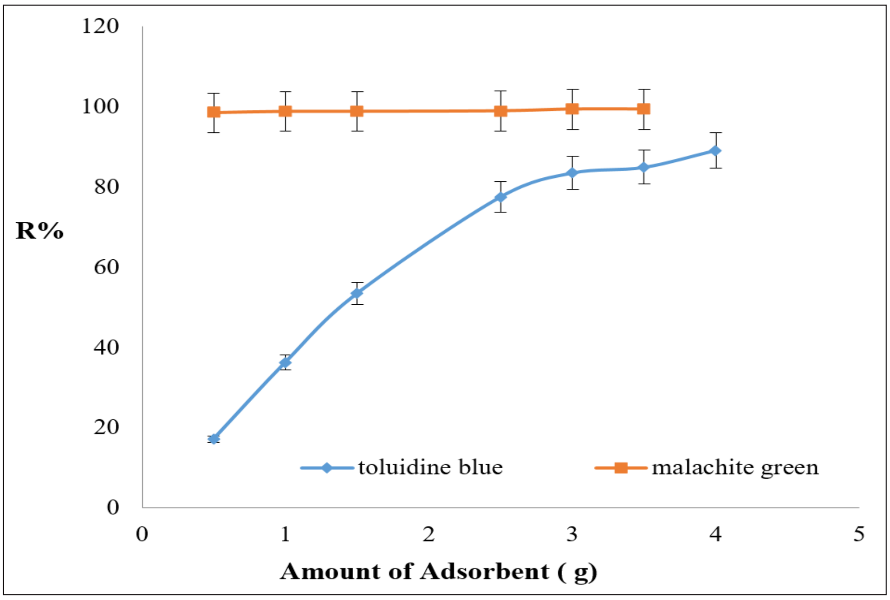


Fig. 4. The effect of limestone amounts on dye removal.

3.3. Effect of contact time

The effect of contact time between the adsorbent surface (limestone) and the adsorbent material (toluidine dye) was studied using a weight of (4.0 g) of the adsorbent surface and a fixed concentration (25 mg L^{-1}) of the dye at a temperature of (20^{o}C) and (pH = 7). Using different periods (20-40-60-80-100-120min), it was observed that the highest adsorption percentage (90.96%) was at 40min, as shown in Figure 5. The effect of the equilibrium time between the adsorbent surface (limestone) and the MG dye was also studied using a weight of 2.5 g of the adsorbent surface and a fixed concentration (50 mg L^{-1}) of the dye and at different times (20-40-60-80-100-120 min). The outcomes have shown that 40 minutes is the best equilibrium time for MG dye, giving the best removal rate (99.46%). It was also reported that there was an increase in time and a decreased removal rate. This is due to the saturation of the active sites of the adsorbent surface [24], as shown in Figure 5.

3.4. Adsorbent surface grain size effect

The effect of changing adsorbent surface grain size on the adsorption process of toluidine blue dye and malachite green dye was studied using different granule sizes (150-250-300 µm). Among the results obtained was that the highest removal percentage was reported at the grain size of 300 µm for the two dyes, (95.6%) of toluidine blue dye with a removal rate reaching (99.48%) when using malachite green dye as shown in Figure 6.

3.5. The effect of pH

The removal of toluidine blue dye from the surface of limestone was studied with different pH functions (2-4-6-8-9-10) using a fixed concentration of 25 mg L^{-1}, a weight of 4.0 g, and an equilibrium time of 40 minutes. Based on the results provided in Figure 7, it was shown that the function of pH = 10 gave the best dye removal percentage (99.9%). The removal of MG dye on the surface of limestone was also studied at different pH levels (2-4-6-7-8-9) using a fixed concentration (50 mg L^{-1}), a weight of 2.5 g, and an equilibrium time of 40 min. The results obtained are offered in Figure 7. It was found that the neutral pH = 7 gave the best removal percentage of MG dye (99.48%). pH = 9 was excluded to study its effect on removing the MG dye because the color of the dye disappears in this medium before the adsorption process starts.

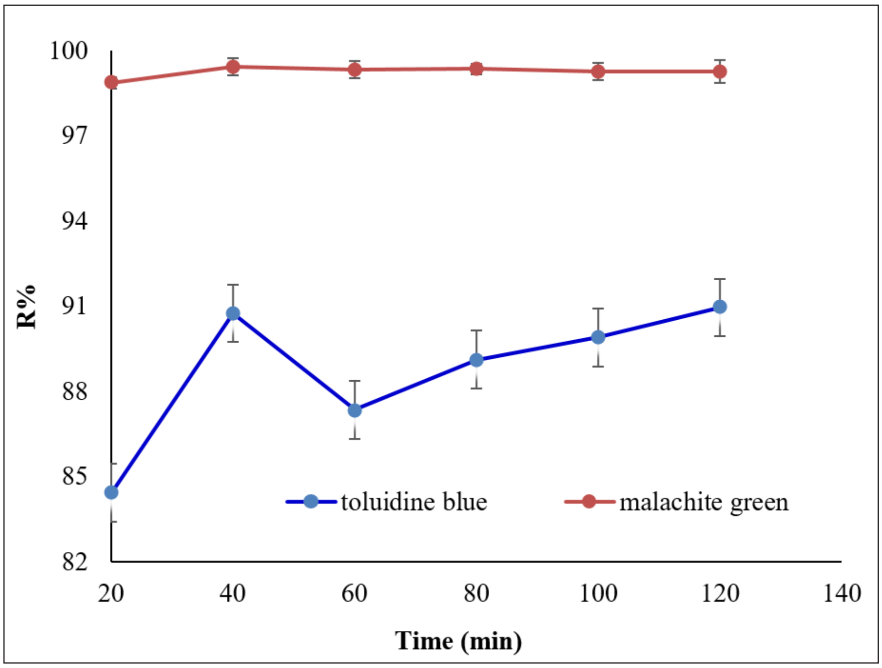


Fig. 5. The effect of time on the removal of dyes

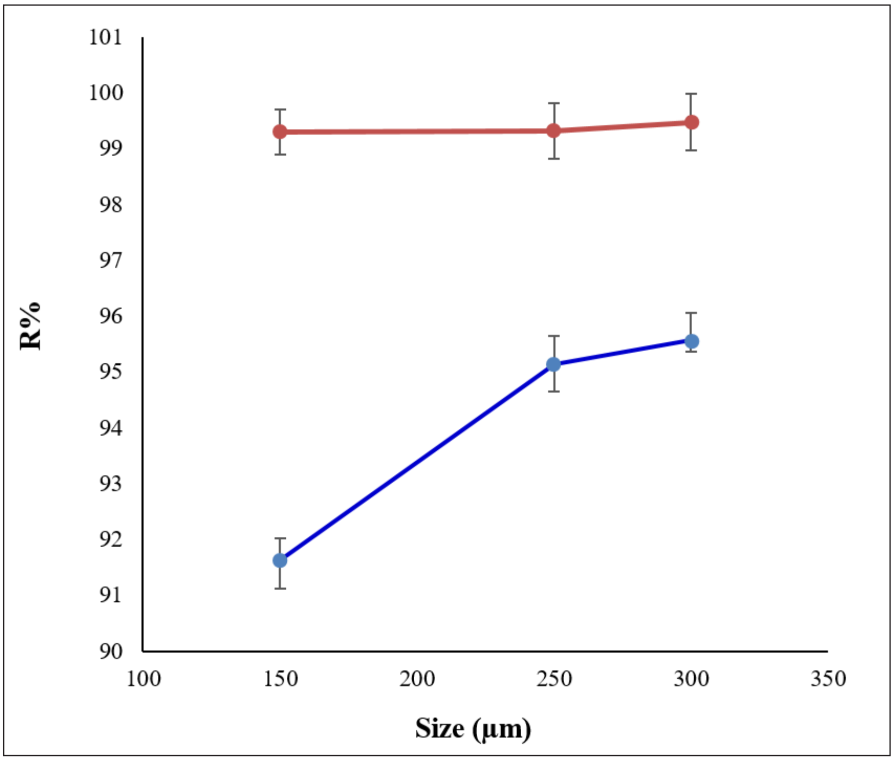


Fig. 6. The effect of the adsorbent particle size on the dye removal (TB blue and MG red)

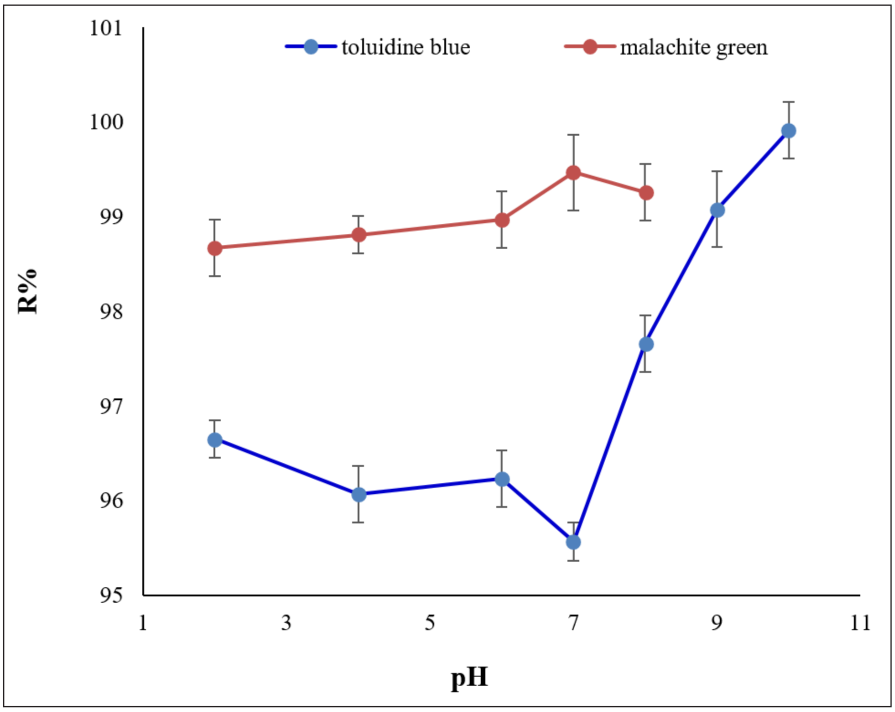


Fig. 7. The effect of pH on the removal of dyes

3.6. Effect of temperature

The effect of temperature on the removal of toluidine blue dye was studied, and the results show that the optimum temperature for adsorption was 293°K with a removal rate of 98.07%. Temperature decreased but started to increase at a temperature of 323°K. As shown in Figure 8, the effect of temperature on removing malachite green (MG) dye was also studied. The results showed that the optimum temperature for adsorption was 303°K, with a removal rate of (99.65%). The temperature then began to decrease. It was found that increasing the temperature led to a decrease in the adsorption rate because increasing temperature led to an increase in the kinetic energy of the molecules adsorbed on the surface, which in turn led to the possibility of their separation from the adsorbent surface and their return to the solution [25,26]. As shown in Figure 8.

3.7. Adsorbent (dye) concentration effect

The effect of the concentrations of the dyes (toluidine blue and malachite green) on the adsorption rate was studied, and the results showed that the adsorption rate increased due to the increase in the dye concentration, as shown in Figure 9.

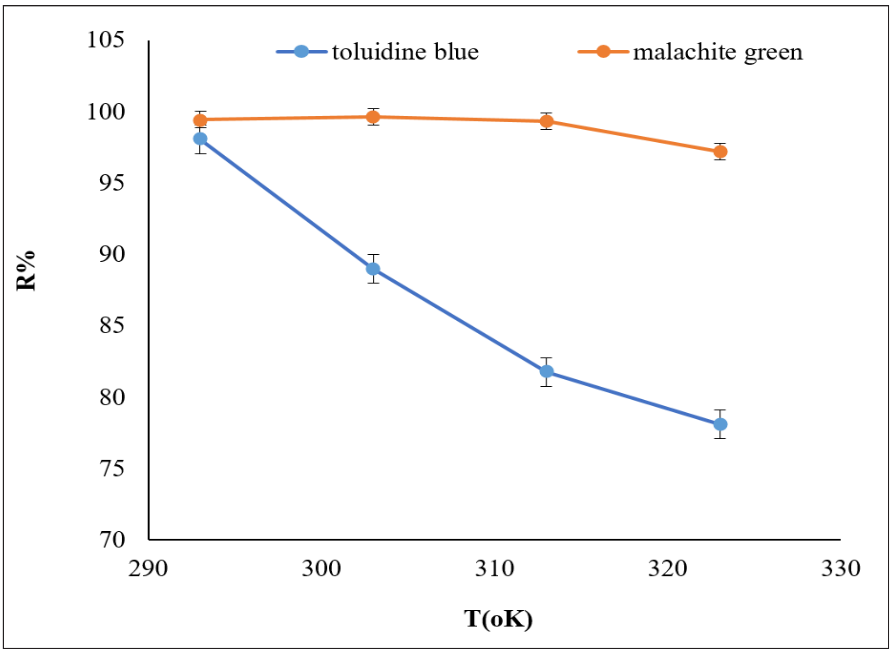


Fig. 8. The effect of temperature on the removal of dyes

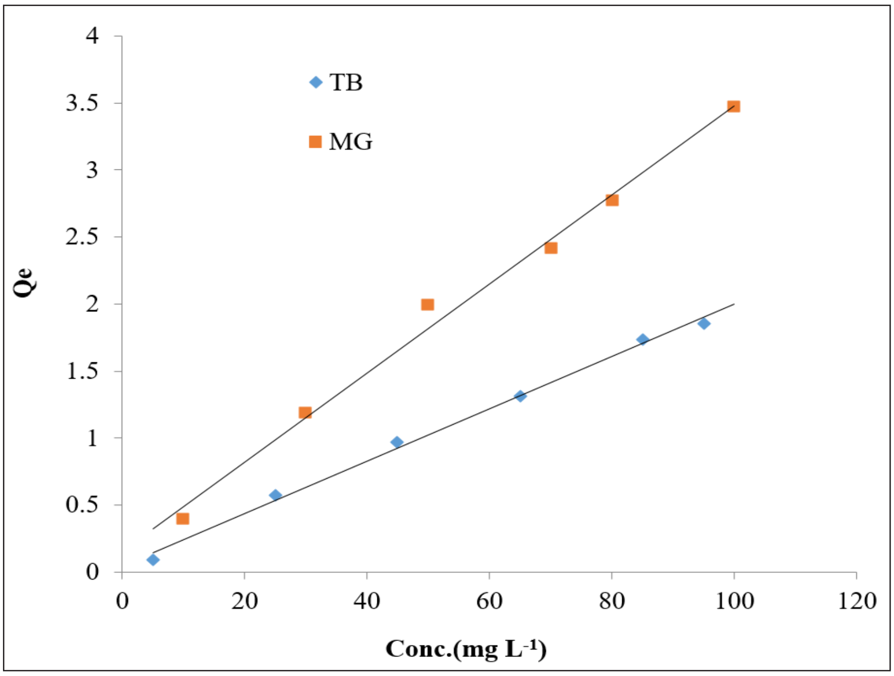


Fig. 9. The effect of initial concentration on the removal of dyes

3.8. Calculating thermodynamic functions

The thermodynamic functions (ΔH^o, ΔG^o, ΔS^o) for the adsorption processes of toluidine blue and malachite green dyes were calculated via van't Hoff equation by plotting the values of (LnK) versus (1/T), where the slope represents the value of ΔHo/R. As for the intersection, it means ($\Delta S^o/R$), and the values of (ΔG^o) were calculated. Below are the Equations (3-5) used for calculating thermodynamic functions (ΔG^o, K, Ln K) [27]. K is the adsorption equilibrium constant and is calculated through Equation 4.

$$\Delta G^{\circ} = RT\ LnK \qquad \text{(Eq.3)}$$

$$K_{eq} = \frac{X_{eq}}{a - X_{eq}} \qquad \text{(Eq.4)}$$

$$LnK = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \qquad \text{(Eq.5)}$$

R = General gas constant (8.314 J K^{-1} $mole^{-1}$)
T = Absolute temperature.
Keq = Equilibrium constant.
a = Initial concentration
Xeq = Amount of adsorbed substance at equilibrium
a-xeq = Concentration of the unadsorbed substance at equilibrium

Based on Table 1 for the adsorption process of toluidine blue dye, it is clear through the positive ΔG^o values that the reaction occurred non-spontaneously, that the reaction was endothermic through the positive ΔH^o value, and that the positive entropy value indicated an increase in randomness, at the contact between the adsorbent surface and the solution. Table 2 shows, through the positive ΔG^o values, that the reaction continued to be non-spontaneously for the process of adsorption of the malachite green dye (MG) and that the reaction produced heat through the negative ΔH^o value and the negative entropy value indicated a decrease in randomness when there is in contact between the adsorbent surface and the solution [28].

3.9. Adsorption isotherms

The adsorption isotherm was studied to determine the applicability of the adsorption process with the Langmuir and Freundlich equations. The study was conducted at a temperature of 293 K, an equilibrium time of 40 minutes, and a particle size of 300 µm in a neutral aqueous medium using different concentrations (5, 25, 45, 65, 85, 95 mg L^{-1}). When using toluidine blue dye, the concentrations (10, 30, 50, 70, 80, 100 mg L^{-1}) when using malachite green dye (MG). As shown in Tables 3 and 4. Also, the adsorption isotherm was shown in Figures 14-16, respectively. Table 5 shows a comparison of different adsorbents for the removal of MG and TB.

Table 1. The values of the thermodynamic functions for the adsorption process of TB dye on the limestone surface.

C_o (mg L^{-1})	T(°K)	K_{eq}	ΔH^o KJ $mole^{-1}$	ΔS^o KJ $(mol\ K)^{-1}$	ΔG^o KJ $mole^{-1}$
25	293	0.025	1.677	0.000079	8.986
	303	0.025			9.293
	313	0.020			10.17
	323	0.023			10.12

Table 2. The values of the thermodynamic functions for the adsorption process of MG dye on the limestone surface

C_o (mg L^{-1})	T(°K)	K_{eq}	ΔH^o KJ $mole^{-1}$	ΔS^o KJ $(mol\ K)^{-1}$	ΔG^o KJ $mole^{-1}$
50	293	0.041	-0.620	-0.028	7.756
	303	0.042			8.015
	313	0.041			8.288
	323	0.040			8.614

Table 3. Experimental constants for both the Freundlich and Langmuir model and their values when using toluidine blue dye

T(ºK)	Freundlich Constants			Langmuir Constants			Temkin Constants		
	R^2	n	K_f	R^2	Q_o	K_L	R^2	B	A
293	0.805	1.124	0.045	0.957	9.709	0.0017	0.043	0.587	4.528

Table 4. Experimental constants for both the Freundlich and Langmuir model and their values when using MG dye

T(ºK)	Freundlich Constants			Langmuir Constants			Temkin Constants		
	R^2	n	K_f	R^2	Q_o	K_L	R^2	B	A
293	0.7193	3.3647	73.62	0.9524	3.106	1.528	0.819	0.4437	67.20

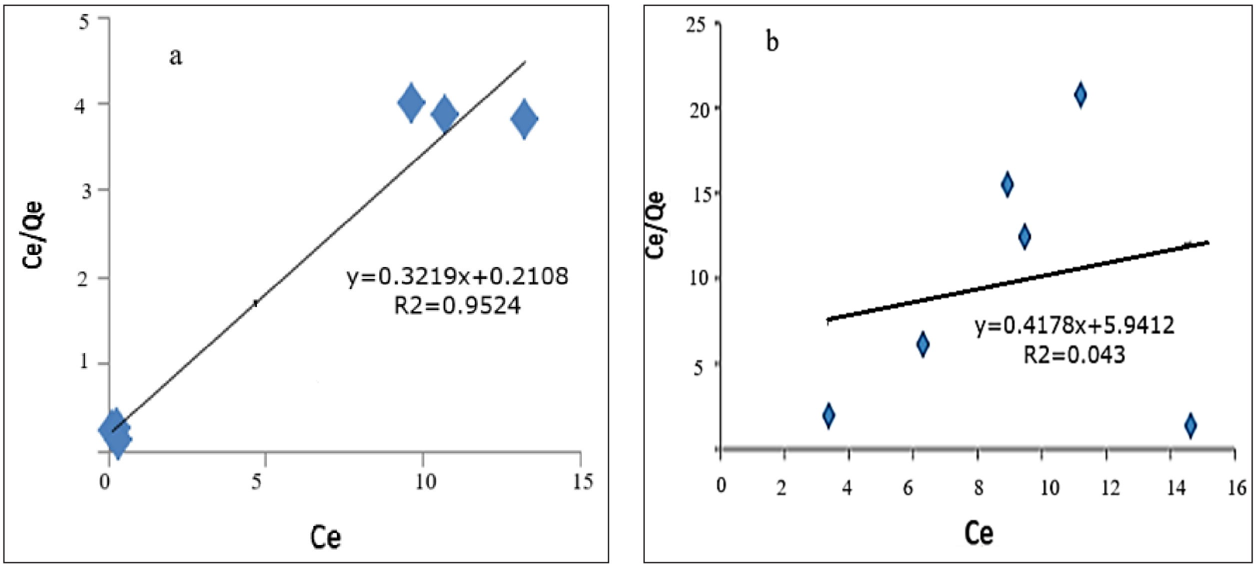


Fig. 14. The linear relationship of the Langmuir isotherm for adsorption a) MG b) TB

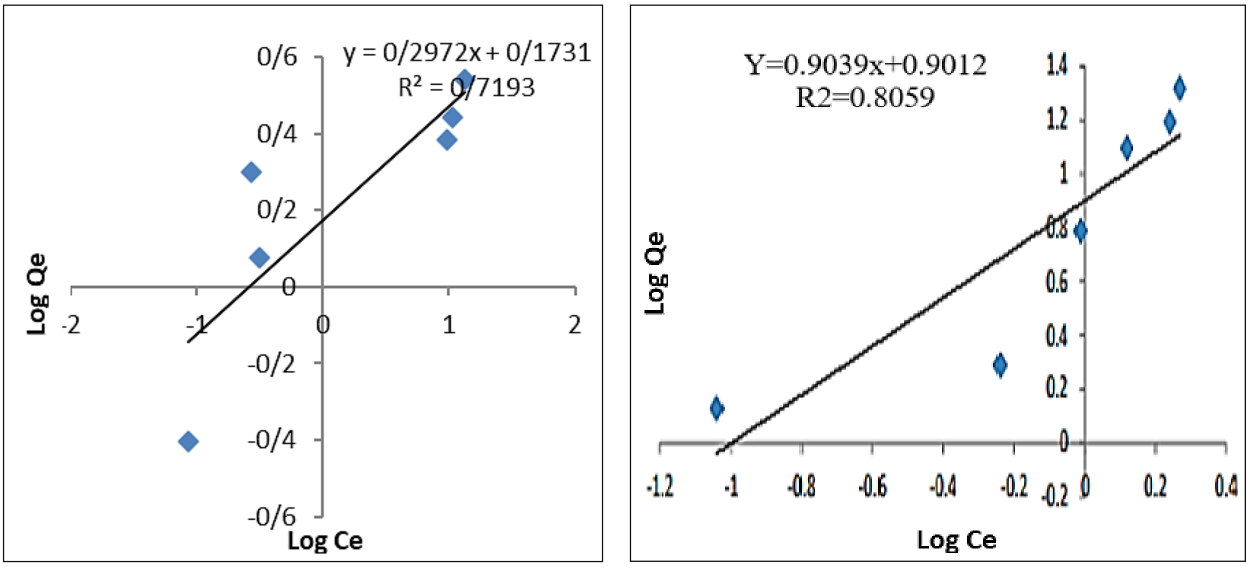


Fig. 15. The linear relationship of the Freundlich isotherm (MG, left) and (TB, right) dye adsorption

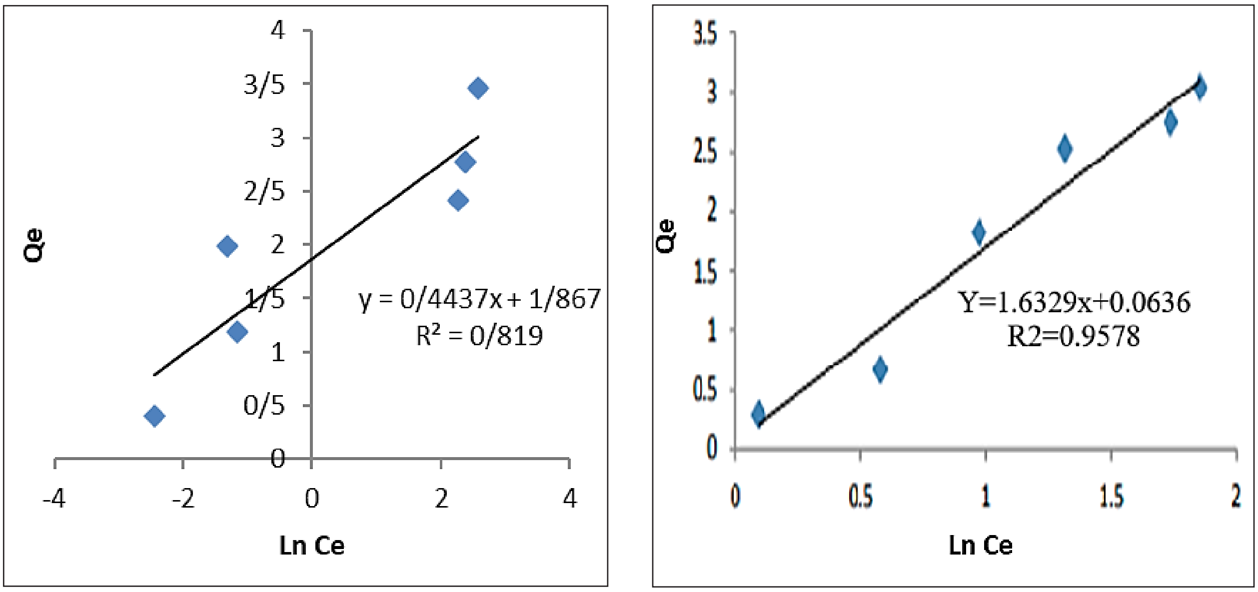


Fig. 16. The linear isotherm relationship enables adsorption for MG(Left) and TB (Right)

Table 5. The removal efficiency (RE%) of various adsorbents for the removal of MG and TB from aqueous solutions

Adsorbents	RE for MG	RE for TB	References
Remnants of tea leaf	---	96 %	29
Walnut shells	99.5 %	---	30
Chitosan-zinc oxide	98.5 %	---	31
Activated carbon (Rumex abyssinicus)	95.2 %	---	32
MgO nano-composite	92 %	---	33
TiO_2 nano-composite	---	99.6 %	34
Gum Arabic / acrylamide hydrogel	---	60 %	35
This work	99.65 %	98.07 %	---

4. Conclusion

The results showed limestone's high efficiency in removing malachite green dye and toluidine blue dye from aqueous solutions. This method is environmentally friendly and characterized by ease and low cost due to the availability of adsorbent surfaces in large quantities. The removal efficiency of malachite green dye was 99.65% at 2.5 g, pH=7, an equilibrium time of 40min, a particle size of 300 µm, and a temperature of 303°K. In addition, the removal effeciency for 4 g of toluidine blue dye was obtained at 98.07% (pH=10). Also, the equilibrium time of 40 minutes, a granular size of 300 µm, and a temperature of 298°k were obtained for TB dye. The recovery, RSD%, and absorption capacity of limestone for toluidine blue for malachite green were obtained at (98.8, 1.4%, and 1.98 mg g^{-1}) and (96.1, 0.89%, and 0.55 mg g^{-1}), respectively.

5. Acknowledgements

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