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Coated material (Graphene oxide coated sand) as a new approach in wastewater treatment field: Equilibrium and thermodynamic studies

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ABSTRACT

The present work describes a coating process that was carried out on the surface of graphene oxide powder. Coated material (GO−Sand composite) was prepared by soaking screened and washed sand particles (100 µm) with 3% graphene oxide aqueous solution. The coating process was done in two stages, first at a temperature of 105 ◦C for three hours then at 150 ◦C for two hours. FTIR spectroscopy was used to investigate the surface of graphite and graphene oxide. Adsorption of methylene blue and methyl orange dyes onto the prepared graphene oxide-coated sand was done experimentally using batch apparatus with controlled conditions of temperature and stirring. The effects of temperature and initial dye concentration for the adsorption process were examined. The analysis of adsorption equilibrium isotherms shows that the experimental data follows the Freundlich isotherm model with a coefficient of variance (R2) equal to (0.99). This indicates that the adsorption of both dyes onto the GO−sand was done on the heterogeneous surface with a multilayer of dye molecules. Furthermore, basic thermodynamic parameters for the adsorption of both dyes on GO−sand were calculated using the most well-known relationships. The results indicate that the process is spontaneous and exothermic as the values of Gibbs free energy changes lie between -37.078 and -24.231 kJ/mole and the values of enthalpy changes lie between -0.669 and -0.348 kJ/mole for methylene blue and methyl orange dyes. Finally, the activation energy for the adsorption process was determined using the Arrhenius equation and found to be equal to 28.643 kJ/mol and 20.224 kJ/mol for methylene blue and methyl orange adsorption, respectively. This proves the physical nature of dye adsorption on the surface of the adsorbent.

1. Introduction

Wastewater is one of the major environmental damages that seriously affect all aspects of life Albright et al. [1]. The effects of contaminants can differ depending on their form and source Inyinbor Adejumoke et al. [2]. Dyes in particular known as reactive basic acidic Lellis et al. [3]. Textile effluent treatment is necessary to protect the environment Yaseen et al. [4]. A wide variety of methods for the sorption of synthetic dyes from water and wastewater have been developed to reduce their environmental effects. Forgacs et al. [5]Various promising techniques have been used to remove dyes from wastewater. Such treatment systems, such as chemical, physical, and biological approaches, have their drawbacks.

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Nomenclature

Ea	Activation energy (Kj/mol)
qe	Adsorption capacity (mg/g)
Ce	Concentration of adsorbate solution
C2	Concentration of solution after dilution (mg/L)
C1	Concentration of solution before dilution (mg/L).
Kf	Constant of freundlich
Ke	Dimensionless equilibrium constant
ΔH°	Enthalpy energy change (Kj/mol)
ΔS°	Entropy energy change (J/mol.K)
A	Frequency factor
GO	Graphene oxide
ΔG°	Gipp's free energy (Kj/mol)
C0	Initial concentration
N	Intensity of adsorption
b	Langmuir isotherm constant (l/mg)
qm	Maximum adsorption capacity (mg/g)
MB	Methylene blue
MO	Methyl orange
Qm	Theoretical adsorption capacity (mg/g)
V1	The volume of solution before dilution (liter)
V2	The volume of the distilled water required for dilution in liter.

The most inexpensive and efficient adsorption process has been the most favored approach for dye removal Seow et al. [6]. Graphene oxide, especially as magnetic particles, has recently been used as a suitable adsorbent for wastewater treatment. It was successfully applied for heavy metals and organic materials (dyes, antibiotics, reactive black 5, etc.) treatments by Kyzas et al. [7]. The coating has been used in many applications such as wear resistance, corrosion protection, anti-fouling, thermal barrier, self-cleaning, etc. for a long time ago. However, its use in the field of coating adsorbents to remove industrial dyes from wastewater was still silent. It is a modern approach and advanced technology for treating industrial wastewater from organic pollutants such as dyes Azha et al. [8]. The adsorbent in the form of coated material has benefits over particulate adsorbents such as powders, pellets, or beads The objective is to easily separate after the adsorption process (e.g. filtration or centrifugation) as well as to increase the surface area by weight ratio of the adsorbent used and to reduce the amount of solid adsorbent needed Azha et al. [9].

The selection of the appropriate support material used for the coating process was one of the critical decisions to be taken when preparing for the coating process. To use the supporting materials for wastewater treatment, they must meet the following criteria: They are non-toxic, insoluble, non-biodegradable, lightweight, and non-polluting; High mechanical and chemically stable, flexible in general shape, high diffusivity, high proliferation, high biomass retention, low cost and minimal attachment to other organisms Martins et al. [10]. There are many types of support materials used in the field of wastewater treatment, but inorganic supported materials were the most important which included ceramic and sand polymer materials Singh et al. [11]. Sand is one of the important naturally supported materials that is widely used in wastewater treatment processes, studies focused on the use of sand as a support material more than other materials such as clay or clay minerals due to its distinctive characteristics and its meets effective adsorption requirements Jada et al. [12].

The study focuses on the use of sand as an inorganic support material in the field of wastewater treatment. Also, this work explains the stages of the coating process that was carried out on the surface of graphene oxide with specific conditions. studying the equilibrium and thermodynamic characteristics of the adsorption process was one of the important analyses applied in the present work.

2. Experimental work

2.1. Materials

The sand was collected from the AL-Najaf sand quarry. Also, chemicals that are used in the practical aspect have high purities with analytical grades including, H_2SO_4 (Aldrich, Germany), H_3PO_4 (Aldrich, USA), original graphite powder (>150 µm), potassium permanganate (Alpha Chemika, Iso Co., India), ethanol (Aldrich, Germany), hydrogen peroxide (Panreac, Germany).

2.2. Coated material preparation (graphene oxide−sand composite)

The preparation of coated adsorbent (GO−sand) included two main steps. Firstly, the preparation of graphene oxide powder. Secondly, coating the surface of the sand grains with prepared graphene oxide.

2.2.1. apparatus used for the coating process

The apparatus shown photographically and schematically in Fig. (1) and (2) was used for coating sand grains with graphene oxide. A coating container was used with a 1000 ml Pyrex glass beaker (Simax, Germany). The beaker was fitted with a glass stir bar for mixing the coating mixture manually. A digitally operated drying oven (Memmert, Germany) was used to dry any excessive quantity of solvent.

Figure 1. Photographic picture of the apparatus used for coating sand with graphene oxide.

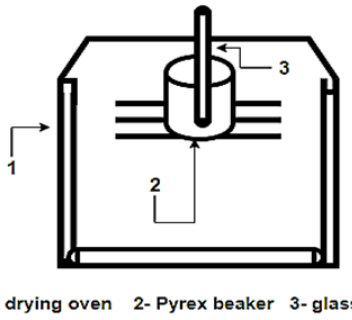

Figure 2. Schematic diagram of the apparatus used for the coating process.

2.2.2. Procedure

The modified Hummer method was used for the preparation of graphene oxide powder Andrijanto et al. [13]. A 9:1 mixture of two concentrated sulphuric acids (H_2SO_4, 98%) and phosphoric acid (H_3PO_4, 70%) was added to the conical flask, then (3 grams) from the original graphite powder (>150 μm) was put in the flask. After that, (18 grams) of permanganate potassium ($KMnO_4$) was slowly added to the mixture, after this addition, the temperature steadily rose to (35 ˚C) due to the occurrence of an oxidation reaction. Then the mixture is heated up until the temperature reaches 50 ˚C continuing to stir for 12 hours. After that, decrease the solution temperature to room temperature. Finally, hydrogen peroxide was added (3 ml) (30%, H_2O_2), Fig. (3) shows the schematic diagram for the apparatus used for preparing graphene oxide powder. The final product was washed and filtered by using filtration apparatus which show in Fig. (4). Finally. produced graphene oxide was dried in a drying oven at 60 ˚C for three hours.

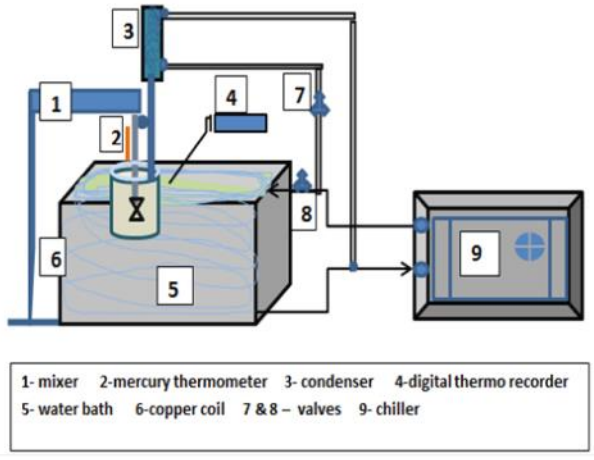

Figure 3. Schematic diagram of apparatus used for the preparation of graphene oxide.

After preparing graphene oxide powder the step followed was the coating process. The process was performed under certain conditions in the laboratory. Firstly, sand was prepared for coating, it was sieved by using a laboratory sieving device which shows in Fig. (5). The device consisted of six sections each section has its own mesh number and the size of diameter in (MIC). This test was important to select which section was appropriate in terms of quantity, mesh number and diameter, after sieving the second section was chosen (100 MIC).

Figure 4. Photographic picture for filtration apparatus.

Figure 5. Photographic picture of laboratory sieving machine.

Then sand was washed more than one time with tap water and soaked with 10 % HCl for 6 hours to remove impurities and salts, after that, a drying oven was used to dry the clean sand. The preparation of sand grains for the coating process shows in Fig. (6).

After washing and drying the sand, 30 grams of dried sand were taken and submerged in (50 ml) from a 3% suspended solution of distilled water and graphene oxide. then heated the mixture for three hours at 105 ˚C for water evaporation. After that, the mixture was heated at 150 ˚C for an additional 2 hours to stabilize the graphene oxide on the sand grain surface. The final product has resulted from the coating process was a black powder of sand coated by graphene oxide which represents the adsorbent material for the wastewater treatment process. Fig. (7) shows a photographic picture of prepared graphene oxide sand.

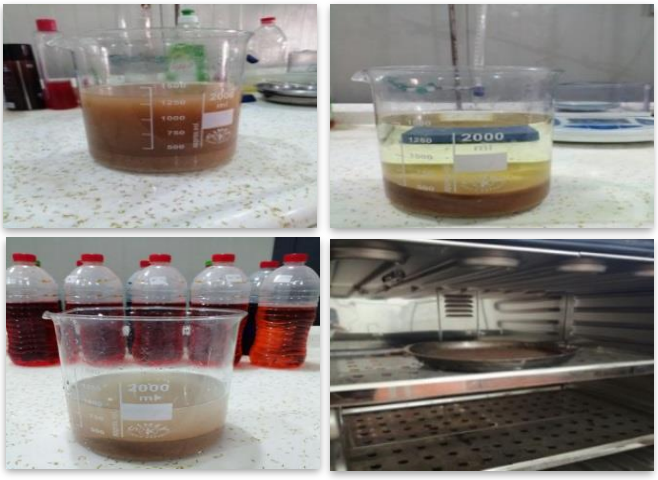

Figure 6. Photographic picture of the steps of the preparation and coating process.

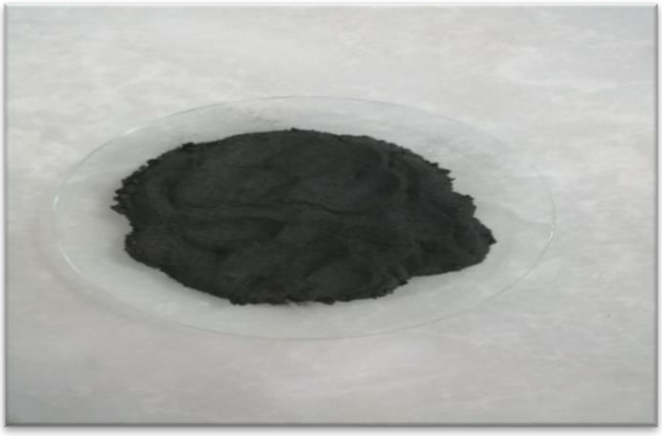

Figure 7. Photographic picture for GO-sand composite after the coating process.

2.3. Equilibrium experiment

Several methylene blue and methyl orange dyes solutions were prepared According to the dilution law [14]:

$$C1 * V1 = C2 * V2 \quad (1)$$

Adsorption equilibrium experiments were done in two steps. Firstly, the equilibrium time was determined at the highest dye concentration and the lowest temperature to ensure obtaining enough time for mass transfer. Secondly, dye concentration in aqueous solutions as a function of dye concentration in the solid phase was obtained at different temperatures. A 500 ml three-nick conical flask (Goel, Germany) was used as an adsorption chamber. A glass thermometer was immersed inside the flask for measuring and recording of adsorption temperature. The flask was equipped with a Pyrex glass recycling condenser to ensure retarding of any vapors from the adsorption mixture. An antifreeze chiller (HYSC, Korea) was used to supply condensing media at (-5 ◦C) for the recycling condenser.

Figure 8 . Photographic picture of the stock solution.

1000 ml Pyrex glass beaker (Simax, Germany) covered via a layer of glass wool insulation material was used as a water bath for the adsorption mixture. A thermos couple connected to a digital recorder (Micro Max, Germany) was put inside the beaker for continuous monitoring of the water bath temperature. The hole adsorption equipment was put over a hot plate magnetic stirrer (SH-2, Germany) for supplying the necessary heat required for the water bath as well as providing the vigorous mixing of the adsorption mixture. Fig. (9) and (10) show photographically and schematically batch adsorption devices.

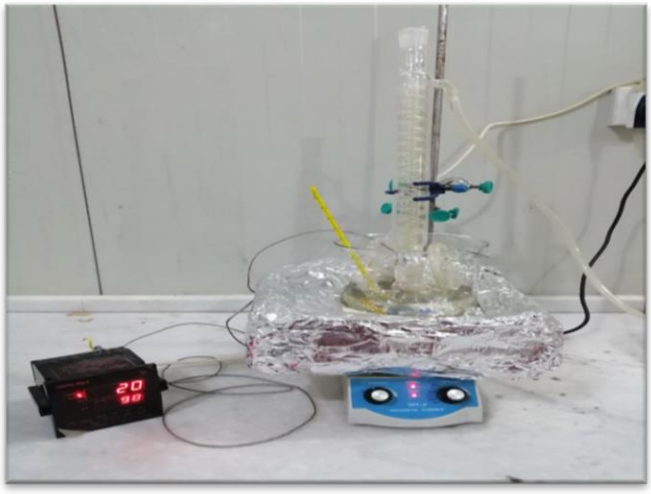

Figure 9 . Photographic picture for batch adsorption system.

Then, a set of experiments were conducted to examine the effect of temperature and initial concentration on the adsorption of methylene blue and methyl orange from the aqueous solution onto the prepared super sand. This was done by taking a range of concentrations (50, 100, 150, 160, 180, 200) ppm of basic dye (methylene blue) and acidic dye (methyl orange) at different temperatures (20, 25, 30, 35) ◦C with constant contact time 3 hours. Each experiment was done by putting 1 gram of the adsorbent material (super sand) in a Pyrex flask with (30 ml) of the dye solution. The color of solutions for the two dyes before and after the adsorption process were shown in Fig. (11).

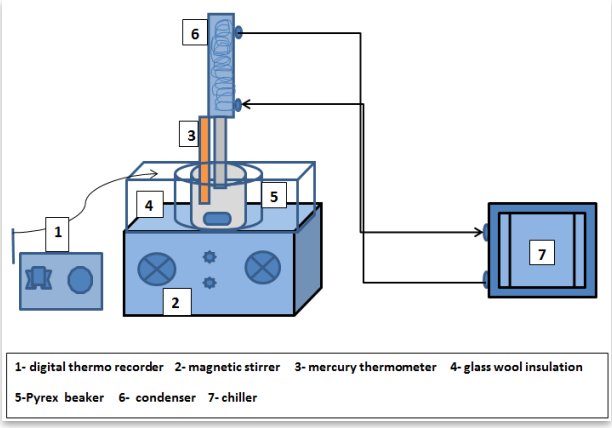

Figure 10. The schematic diagram for batch adsorption system.

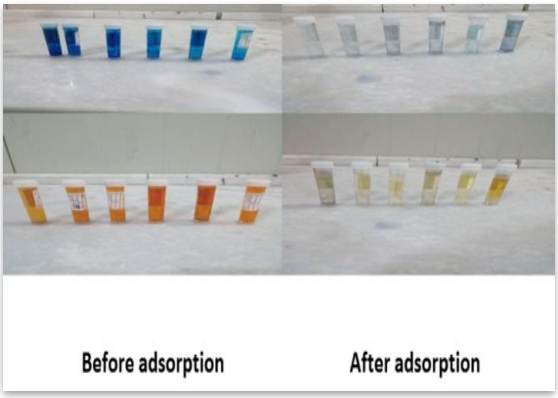

Figure 11. Photographic picture of methylene blue and methyl orange before and after adsorption

3. Result and discussion

3.1. Dyes concentration by Photometric method

Ultraviolet/Visible Absorption Spectrometer (UV−Vis) analyzes the light beam reflected from the surface of the sample or after passing through it. Where there is a linear relationship between the concentration of material and absorption. This makes UV spectroscopy very important in making quantitative measurements [15]. The wavelength of the methylene blue and methyl orange dyes was checked first. This was done by putting a sample from the two dye solutions in the sample cell of the machine. Distilled water was used as a comparative solution where it was put in the solvent cell. After that, a scan for the whole wavelength range was performed to analyze the peaks of the spectrum. **Fig. (12 and 13)** show the calibration curves of methylene blue and methyl orange dyes.

3.2. Characterization of prepared graphene oxide

Fourier Transform Infrared (FTIR) spectroscopy was used to investigate the presence of functional groups on the surface of graphene oxide. Fig. (14) & (15) show the spectra of graphite and graphene oxide. From Fig. (15), the characteristic peaks have appeared in different wavenumbers. The peak falls at (3332) cm^{-1} refers to the presence of hydroxyl stretching vibration (-OH). Several researchers suggested that the peaks at the range (3000−3500) cm^{-1} refer to (C-OH) groups on the surface of GO [16, 17]. In addition [18] study showed that the hydrophilic property of graphene oxide due to the presence of the hydroxyl functional group. The peak at (2973) cm^{-1} refers to the sp^3 (C-H) group which indicates that the prepared graphene oxide was produced in acidic media. This conclusion was based on the evidence recognized by Aziz et al. [19]. The peak at (1390) cm^{-1} indicates the presence of carboxyl stretching vibration (C=O) while the peaks at (1088) cm^{-1}, (1045) cm^{-1} and (879) cm^{-1} refer to (C-O) stretching vibration. The presence of all these functional groups (epoxy, hydroxyl, carboxyl) on the surface of prepared graphene oxide proves the successful preparation process that was used in our experimental work. These results were based on the observations that were done by several researchers[17, 20].

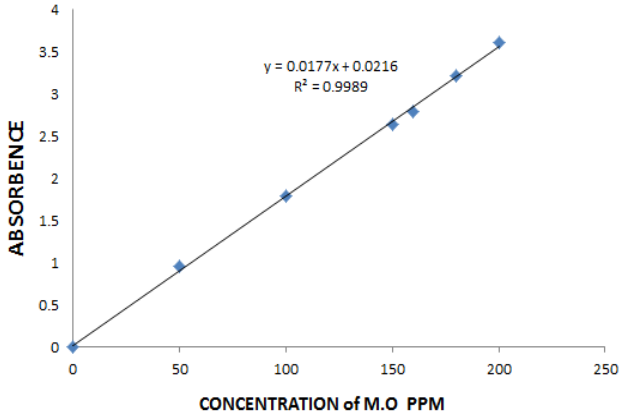

Figure 12. Calibration curve of methyl orange dye

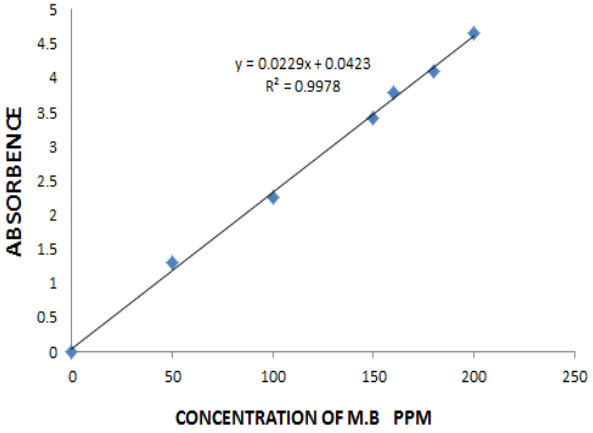

Figure 13. Calibration curve of methylene blue dye

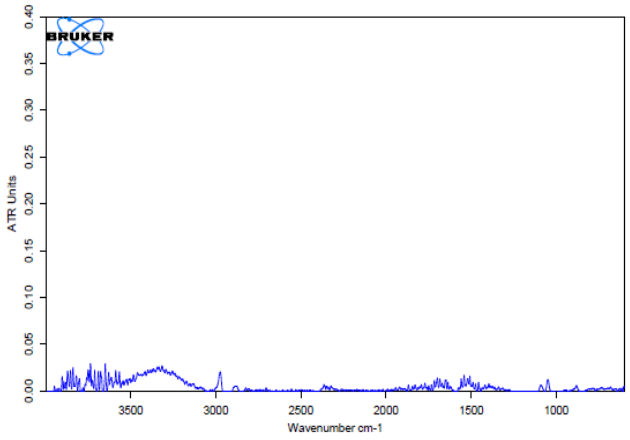

Figure 14. Fourier Transform Infrared (FTIR) for graphite.

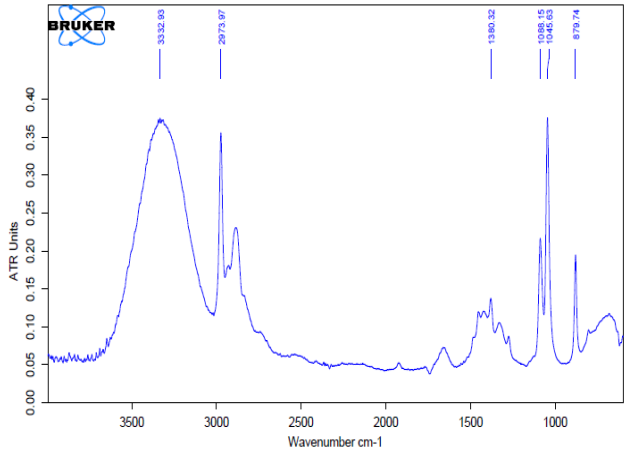

Figure 15. Fourier Transform Infrared (FTIR) for graphene oxide.

3.3. Equilibrium study of adsorption

Isothermal information analysis with the application of characteristic isothermal modeling is a major development in determining the appropriate model that can be used for design purposes. As a result, the relationship of equilibrium data that uses either a theoretical or experimental formula to understand and predict the degree of adsorption, in choosing the most extreme adsorption limit for a given adsorbent Foo et al. [21]. Fig. (16 and 17) represent the equilibrium adsorption isotherms curves for the acidic dye (methyl orange) and the basic dye (methylene blue) on the surface of the prepared graphene oxide-coated sand adsorbent. These curves were plotted for the range of concentration (50−200) ppm at different temperatures (20, 25, 30, 35 ◦C). It could be recognized from these figures that there is a proportional relationship between the concentration of dyes in the solution and its concentration in the adsorbed phase. This is clearly shown from the shape of isotherms curves that are of classical adsorption type. This means that an increasing concentration of dye in the solution increases the concentration of dye on the surface of the adsorbent. But this proportionality becomes less notable at high concentrations of dyes in the solution because the adsorbent reaches its maximum capacity. The values of maximum capacities for the prepared GO−sand are shown in Table 1.

Table 1. Maximum capacities of GO−sand for methylene blue and methyl orange dyes.

Temp.	Methylene blue		Methyl orange	
◦C	Ce	qe	Ce	qe
20	1.922	5.983	15.667	5.682
25	2.011	5.612	16.321	5.322
30	2.126	5.376	17.511	5.087
35	2.157	5.102	18.563	4.722

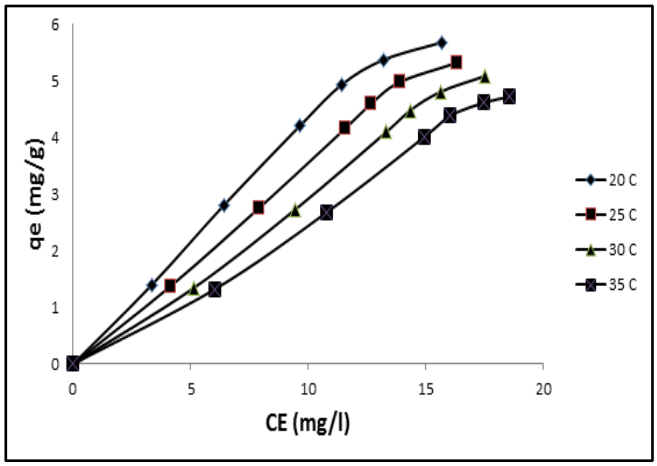

Figure 16. Adsorption equilibrium isotherms for methyl orange adsorbed on the GO−sand at different temperatures.

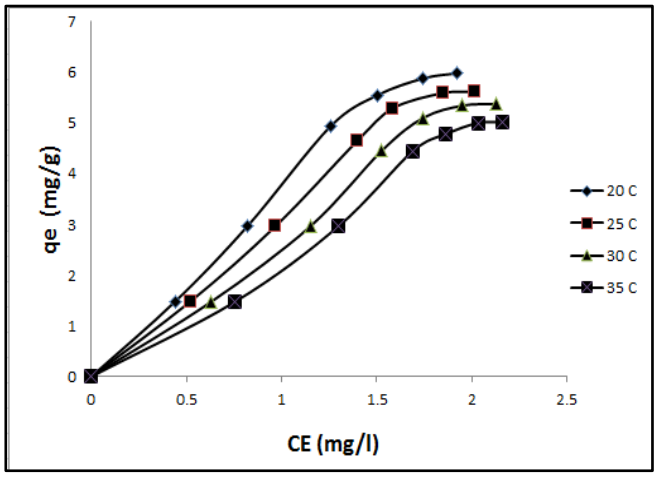

Figure 17. Adsorption equilibrium isotherms for methylene blue adsorbed on the GO−sand at different temperatures.

3.3.1. Langmuir and Freundlich Models

Langmuir and Freundlich adsorption isotherm models were used to correlate the experimental adsorption data of methylene blue and methyl orange onto the GO−sand composite. These models were used in the present study because they are the most well-known equations that could represent the adsorption of solute in an aqueous solution onto a solid

adsorbent [22]. Langmuir adsorption isotherm represents the adsorption of solute that limits to a single monolayer of solute molecules on the solid adsorbent. This is based on the Langmuir theory of adsorption which assume the surface of the solid adsorbent as a homogeneous surface. However, the Langmuir adsorption isotherm equation could be represented mathematically as [23]:

$$qe = Qm\ b\ Ce/(1 + b\ Ce) \quad (2)$$

Freundlich adsorption isotherm represents the adsorption of solute as a multilayer of molecules onto the heterogeneous surface of solid adsorbent. Freundlich adsorption isotherm equation could be represented mathematically as [22]:

$$qe = Kf\ Ce^{\frac{1}{n}} \quad (3)$$

Langmuir and Freundlich adsorption isotherm equations were expressed in linear forms respectively as follows:

$$Ce/qe = 1/(Qm\ b) + 1/Qm\ Ce \quad (4)$$

$$Log\ qe = Log\ Kf + 1/n\ \ Log\ Ce \quad (5)$$

The experimental data for the adsorption of methylene blue and methyl orange on prepared GO−sand composite were correlated with the linearized form of Langmuir and Freundlich adsorption equations and shown in Fig. (18 and 21). It was observed from these figures that the experimental data corresponded to the Freundlich isotherm very well. This result indicates that the adsorption of methylene blue and methyl orange onto the GO−sand was empirical and occurred on a heterogeneous surface and also due to the high concentrations used in the present work.

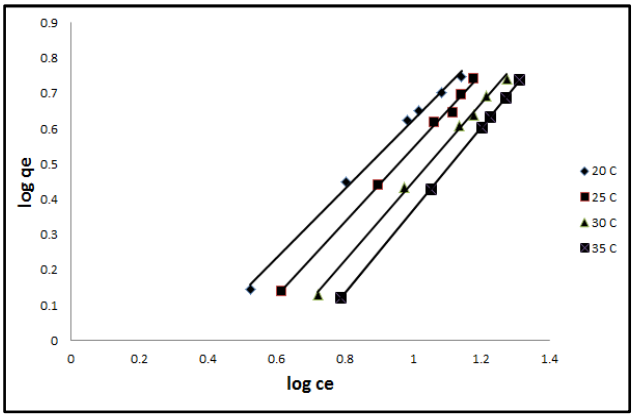

Figure 18. The linearized form of the friendlier isotherm model for methyl orange adsorbed at different temperatures.

This congruence with the Freundlich isotherm could be evident by recognizing the values of confidence level (R^2). Tables (2 and 3) show the comparison between the Langmuir and Freundlich isotherms for methylene blue and methyl orange dyes equilibrium adsorption data.

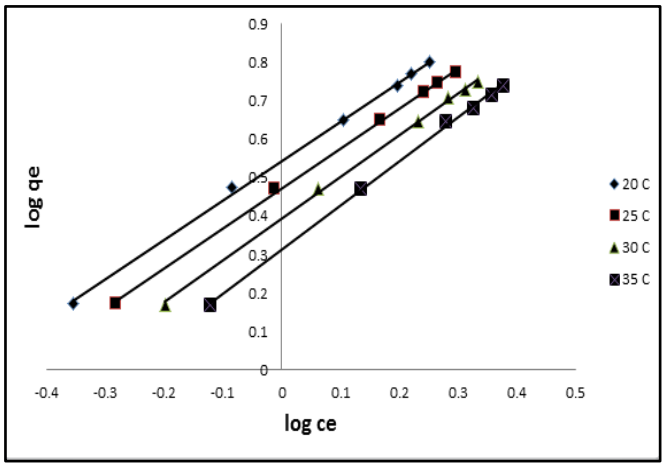

Figure 19. The linearized form of friendlier isotherm model for methylene blue. Adsorbed at different temperatures

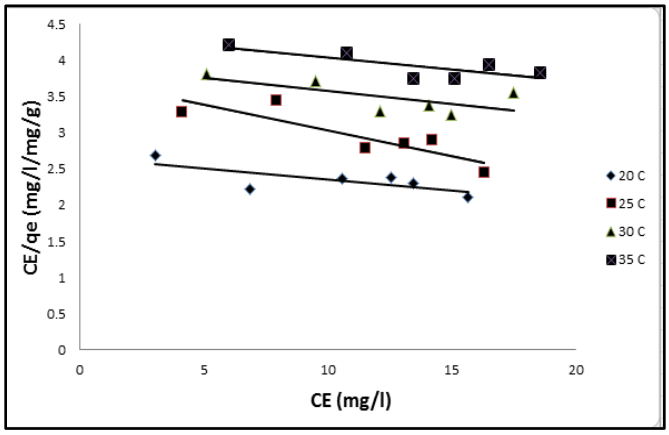

Figure 20. The linearized form of the Langmuir isotherm model for methyl orange adsorbed at different temperatures.

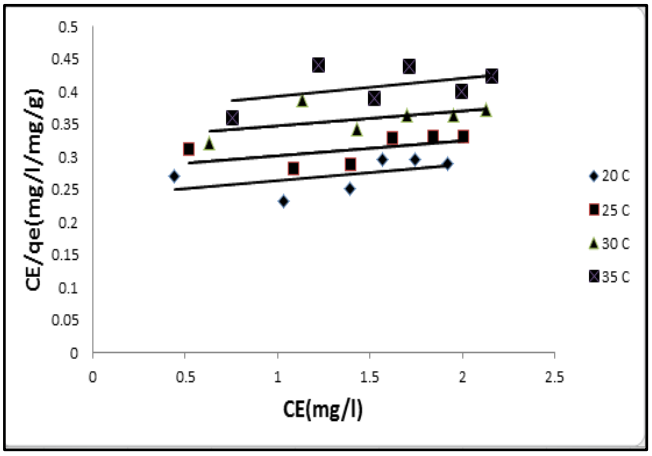

Figure 21. The linearized form of the Langmuir isotherm model for methylene blue adsorbed at different temperatures.

Table 2. Isotherm parameters for methyl orange at temperature range (20–35) ◦C.

Temp.	Langmuir model			Freundlich model		
◦C	Qm	b	R^2	Kf	n	R^2
20	5.682	0.066	0.5448	0.448	1.019	0.9961
25	5.322	0.05	0.75	0.293	0.949	0.9971
30	5.087	0.049	0.4601	0.176	1.115	0.9974
35	4.722	0.048	0.603	0.091	0.848	0.9999

Table 3. Isotherm parameters for methylene blue at temperature range (20 – 35) ◦C.

Temp.◦C	Langmuir model			Freundlich model		
	Qm	b	R^2	kf	n	R^2
20	5.983	0.702	0.2773	0.265	0.975	0.9985
25	5.612	0.638	0.3134	0.325	0.963	0.9988
30	5.376	0.574	0.2958	0.405	0.917	0.9988
35	5.102	0.537	0.2142	0.505	0.874	0.9986

3.3.2. Effect of initial concentration

The initial concentration of the dyes is an important tool in the study of the adsorption capacity. And the removal percentage of dye Zhang et al. [24], was calculated by the following equation Wang et al. [25]:

$$\%\, removel = \frac{c0-ce}{c0} * 100 \qquad (6)$$

Fig. (22 and 25) show the initial concentration of methyl orange and methylene blue dyes in the solution as a function of removal percentage of them due to adsorption on the surface of graphene oxide-coated sand.
It was clearly shown from these figures that an increase in the initial concentration of the two dyes in the solution was associated with a decrease in the removal percentage. However, the increase in initial concentration enhances the adsorption capacity but diminishes the removal percentage of dye. This is observed in Fig. (16 & 17) and (22−25), where the removal percentage at 20 ◦C decreased from 99.55% to 70.44% for methylene blue and decreased from 83.32% to 61.22% for methyl orange. This behavior is in agreement with the study by Foo et al. [21].

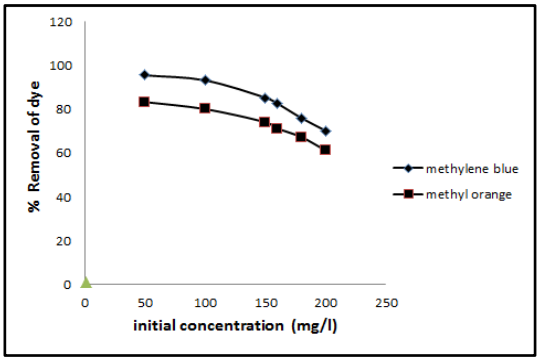

Figure 22. Removal percentage of methylene blue and methyl orange dyes for different initial concentrations at 20 ◦C.

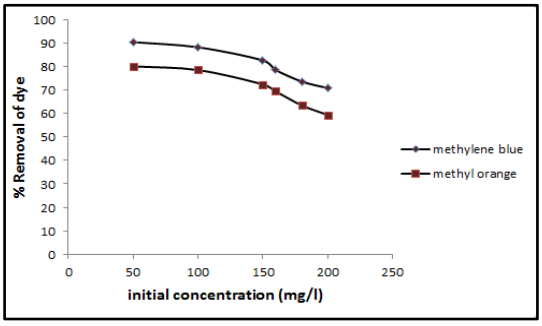

Figure 23. Removal percentage of methylene blue and methyl orange dyes for different initial concentrations at 25 ◦C.

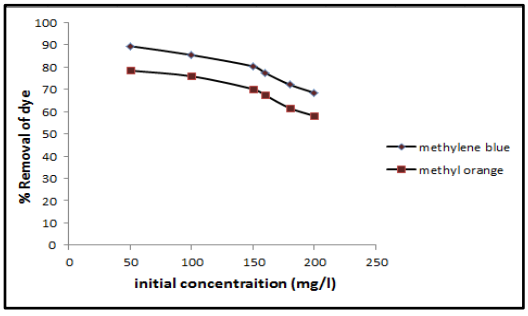

Figure 24. Removal percentage of methylene blue and methyl orange dyes for different initial concentrations at 30 ◦C.

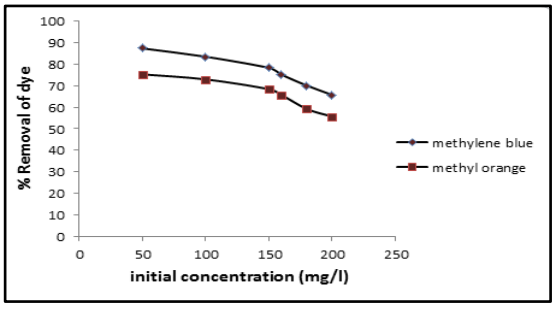

Figure 25. Removal percentage of methylene blue and methyl orange dyes for different initial concentrations at 35 ◦C.

This behavior may be explained as follows. In most cases of low concentrations of dyes in solution, the ratio of the initial number of dye molecules to the available Surface area is small Hence, the partial adsorption is independent of the initial concentrations. Although, in high concentrations of dyes in solution, the available adsorption sites become less as a result of reaching the adsorption sites saturation state. However, figures (22− 25) indicate that there is an optimal value for the initial concentration of both dyes in the solution. This optimal value is about 100 mg/l where the relationship between the removal percentage and the initial concentration up to this value is approximately a horizontal line.

3.3.3. Effect of temperature

In the adsorption process, it is very important to know the extent to which the temperature affects the efficiency of the adsorbents Corda et al. [26]. Fig. (16 and 17) show the effect of temperature on the adsorption capacity of GO−sand for methyl orange and methylene blue dyes. The temperature range used for the adsorption process is (20 – 35) ◦C, it was observed from these figures that an increase in the temperature causes a decrease in the adsorption capacity of the two dyes. This behavior refers that the adsorption phenomena is an exothermic process, this result is in agreement with the study by Yagub et al. [27]. They expressed that If the adsorption capacity increases with increasing temperature, this means adsorption is an endothermic process. This is due to the increased susceptibility of the dye molecules and the expansion in the active sites upon an increase in temperature. While the adsorption capacity decreases with increase in temperature, this means that the process is exothermic. This behavior may be due to the weakening of the attraction forces between the dye. molecules with active sites on the surface of the adsorbent upon increased temperature. Fig. (22 & 25) shows the effect of temperature on the removal percentage of dyes. The figures indicate that an increase in temperature leads to a decrease in the removal percentage of the two dyes. Where the removal of methylene blue decreased from 99.55% to 87.12% with increasing the temperature from 20 ◦C to 35 ◦C. Also, the removal of methyl orange decreased from 83.32 % to 75.33% with the same increase in temperature. This behavior is in agreement with the study by Gupta et al. [28]. They explained that the adsorption forces between the dye molecules and the active sites become weak when the temperature increases, which leads to a decrease in the removal percentage of dye.

3.3.4. Effect of adsorbate type

Fig. (22 & 25) show that the GO−sand composite is more effective in removing methylene blue than methyl orange. Where the maximum percentage of removal methylene blue reached to 99.55% at 20 ◦C. While the maximum percentage of removal methyl orange reached to 83.32% at the same temperature. This result is due to the extent of attraction and repulsion between the active sites on the surface of the GO sand and the different charges of the dye molecules. For this reason, the attraction is greater between the surface charges (acidic media) with methylene blue (basic dye) and less with methyl orange (acidic dye). This behavior is in agreement with the study by Santoso et al. [29]. The study showed that graphene oxide has a high efficiency in removing methylene blue from aqueous solutions due to the attraction between their different charges. In comparison this result with a study by Shahabuddin et al. [30], they used poly aniline-coated graphene oxide for the removal of methylene blue and methyl orange dyes from an aqueous solution. The results showed that the methylene blue removal percentage was 57% which it was higher than of methyl orange 36%. They concluded that the surface of the graphene oxide contains various functional groups such as (epoxy and hydroxyl), also the presence of sp^3 hybrid framework that makes it effective in removing basic dyes such as MB more than MO.

3.4. Kinetics and thermodynamic studies

The estimation of the thermodynamic parameters depends on the value of the thermodynamic equilibrium constant (Ke). The mathematical equations used in the thermodynamic calculations could be presented as [31]:

$$\Delta G^\circ = -RT\,ln(Ke) \tag{7}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{8}$$

$$ln\,(Ke) = -(\Delta H^\circ)/RT + (\Delta S^\circ)/R \tag{9}$$

$$Ke = qe/qm/(1 - qe/qm)(Ce/(C^\circ)) \tag{10}$$

Fig. (26 and 27) represent the plot of (lnKe) as a function of the inverse of the temperature (1/T) for the adsorption of methyl orange and methylene blue dyes onto the GO− sand. The values enthalpy change (ΔH°) and entropy change (ΔS°) were computed from the slops and intercepts of these lines.

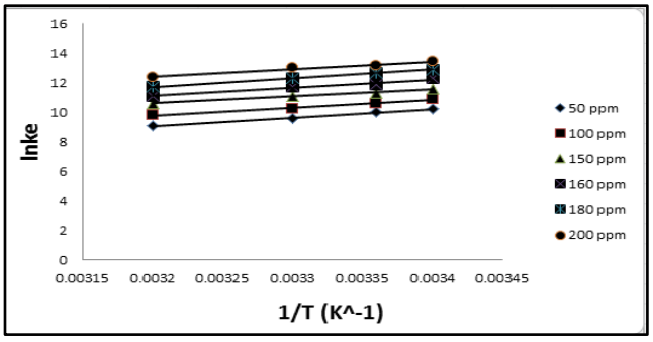

Figure 26. The thermodynamic plot of (lnKe) versus (1/T) for adsorption of methyl orange at different concentrations.

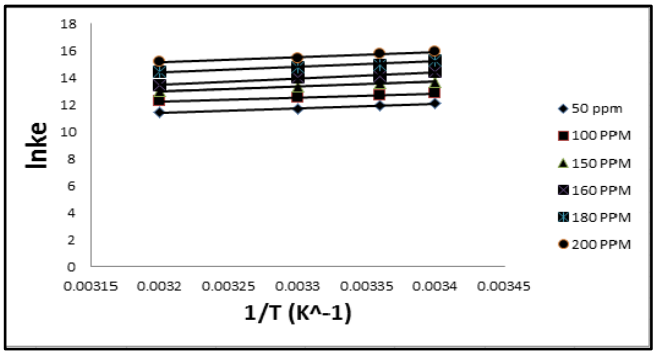

Figure 27. The thermodynamic plot of (lnKe) versus (1/T) for adsorption of methylene blue at different concentrations.

It was clearly observed from the figures that the slopes and intercepts of all lines are positive. Therefore, the adsorption of methyl orange and

methylene blue on the GO sand is an exothermic process since the enthalpy changes are always negative.

Table 4. Thermodynamic parameter for the adsorption of methyl orange on the super sand at temperature range (20−35) ◦C.

CONC. PPM	ΔH°	ΔS°	ΔG° (kJ/mol) 293 K	298 K	303 K	308 K	
50	-0.669	1.043	-25.358		-25.189	-24.231	-24.957
100		0.837	-60.33				
150	-0.629	0.569	-26.537		-26.277	-26.202	-26.242
160		0.756	-28.323				
180	-0.577	0.793	-29.902		-28.026	-28.023	-27.871
200		0.416	-31.405				
	-0.654		-31.962		-29.032	-28.764	-25.413
	-0.689				-30.253	-29.723	-29.165
	-0.597				-32.384	-30.686	-29.407

Furthermore, the process has happened spontaneously because the values of entropy changes are always positive. In addition, the positive values of the entropy changes (ΔS◦) refer to the randomness of the surface. This result is in agreement with a study done by Alghamdi et al.[32]. They used graphene oxide composite for the removal of azo dyes from aqueous solution. They computed the values of (ΔH◦, ΔS◦, and ΔG◦). Their results gave the same idea for the nature of the adsorption process. They concluded that the process was exothermic and spontaneous. The activation energy (Ea) for adsorption of methyl orange and methylene blue on the GO−sand was studied and computed by applying the Arrhenius equation Saha et al. [33]:

$$lnk = lnA - Ea/RT \quad (11)$$

Table 5. Thermodynamic parameter for the adsorption of methylene blue on the super sand at temperature range (20−35) ◦C.

CONC. PPM	ΔH°	ΔS°	ΔG° (kJ/mol) 293 K	298 K	303 K	308 K	
50	-0.402	0.085	-30.053		-30.236	-30.332	-30.337
100	-0.348	0.357	60.33		-31.225	-31.469	-31.602
150	-0.427	0.198	-31.225		-33.877	-33.376	-33.674
160	-0.559	0.171	-33.877		-35.098	-28.027	-34.259
180	-0.479	0.198	-35.098		-36.540	-33.827	-34.385
200	-0.459	0.351	-36.540		-35.765	-34.227	-34.901

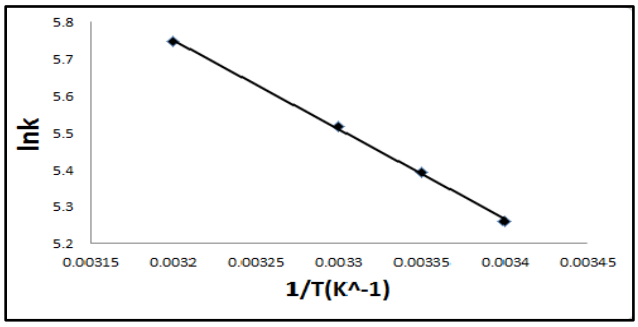

Figure 28. Arrhenius plot for methyl orange adsorption at temperature range (20 − 35) ◦C.

Figures (28 and 29) represent a plot of (link) versus (1/T) for methyl orange and methylene blue adsorption on GO−sand. The values of the activation energies were determined from the slopes of the figures for the two dyes. Tables (4) & (5) show the values of ΔG°, ΔS°, and ΔH energies for methylene blue and methyl orange dyes.

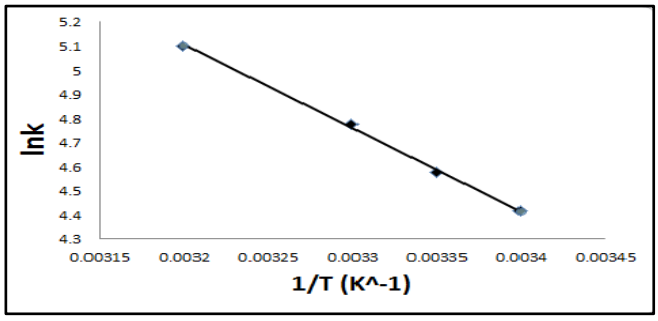

Figure 29. Arrhenius plot for methylene blue adsorption at temperature range (20 − 35) ◦C.

4. Conclusions

This research demonstrates the use of coated materials as a new approach to wastewater treatment. The coating process gave a good result of graphene oxide–sand composite with high dye removal efficiency from aqueous solution. This work will conclude on a variety of important points:

- The product of the coating process was a homogeneous compound of sand and graphene oxide. The process was completed successfully and gave graphene oxide fixed well on the surface of sand grains after five hours without the need for reheating.
- FTIR spectra showed the chemical structure of graphene oxide, the result expresses different functional groups (epoxy, hydroxyl, and carboxyl) distributed on the surface that indicate the success of the preparation process.
- The equilibrium adsorption isotherm was applied to the experimental data showing that the Freundlich isotherm fitted well with the experimental adsorption data with a confidence level of 0.99.
- GO−sand material has high efficiency in removing, where the maximum percentage removal of methylene blue and methyl orange equals 99.55% and 83.22%, respectively.

- Methylene blue has higher adsorption capacity than methyl orange, this may be due to the difference in the attracting forces between the surface of the adsorbent and the charges carried by the dyes.
- The thermodynamic study showed that the adsorption process was spontaneous and exothermic, due to the negative values of the Gibbs free energy change (ΔG°) and enthalpy energy change (ΔH°).
- The values of Gibbs free energy changes lie between -37.078 and -24.231 kJ/mole and the values of enthalpy changes lie between -0.669 and -0.348 kJ/mole. This result indicates that the adsorption process of the present study could be suggested as physical adsorption In addition, the activation energy was studied for the two dyes and the result showed that the activation energy was equal to Ea=28.643 KJ/mol and Ea=20.224 Kj/mol for methylene blue and methyl orange, respectively. It was concluded from these results that the energy needed for interacting the adsorbate and the adsorbent are not high and this refers to the physical nature of the process.

Authors' contribution

All authors contributed equally to the preparation of this article.

Declaration of competing interest

The authors declare no conflicts of interest.

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