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ADSORPTION KINETICS FOR THE REMOVAL OF METHYLENE BLUE AND METHYL ORANGE BY USING SUPER SAND

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ABSTRACT

This study investigated the preparation of super sand substance and used it as an effective adsorbent for the removal of two different dyes methylene blue (basic) and methyl orange (acidic). The initial concentration range of dyes that were used in the adsorption process was (50−200) ppm with a temperature range (20−35) °C, the surface characteristics of graphite, graphene oxide, and coated sand were investigated by AFM test. Three adsorption kinetics models were applied to the experimental data in this study, pseudo−first order, pseudo−second order, and interparticle diffusion model. The result was showed that the experimental data corresponded with pseudo−second order kinetic model with confidence level R^2= 0.99.

KEYWORDS: Super sand, composite material, graphene oxide, adsorption of dyes, methylene blue, methyl orange.

1. INTRODUCTION

The textile industries generate huge quantities of liquid waste. Such clothing wastewater supplies organic and inorganic compounds (Ado *et al.*, 2017), that leads to changes in the biological and chemical parameters of the receiving bodies of water. In recent years, regulation of water pollution has become more and more critical (Kaur and Sharma, 2015).

Color pollution is an escalating problem in aquatic environments (Pearce, Lloyd, and Guthrie, 2003), through the dyeing process, a portion of the dyes remains not fixed on the fabrics, and when washing, it is excreted with water and poses a great risk. High concentrations of dyes were found in the liquid flows raised. In addition to this, the increasing demand for the production of various textiles that consume various dyes has led to an increase in the dangers of dyes in industrial wastewater (Islam and Mostafa, 2018).

Dyes can be categorized in many respects, based on their trade names and chemical character. Coloring is a versatile, unsaturated aromatic compound that fulfills characteristics such as intense color, solubility, substantivizes, and speed. Most industrial use coloring is resistant to light and oxidation. Effluent use of colors and pigments causes collective toxicity that affects the aquatic environment (Markandeya, Shukla, and Mohan, 2017).

Various promising techniques have been used to remove dyes from wastewater. Such treatment systems, such as chemical, physical, and biological approaches, have their drawbacks like high expense, radioactive sludge production, etc. The most inexpensive and efficient adsorption process has been the most favored approach for dye removal (Seow and Lim, 2016).

There are also low-cost adsorbents used for the treatment of dyes. Some waste products from agricultural and industrial processes, bio sorbents, and natural materials often reflect alternate sorbents which are potentially economical. Some of these were checked and suggested for the elimination of dye. Adsorption waste treatment using low-cost adsorbent is a challenging field because it has double advantages, i.e. wastewater treatment and waste management (Yagub *et al.*, 2014).

Thanks to its broad theoretical surface area, strong water solubility and surface-containing oxygen functionalities, graphene oxide was used as an important adsorbent for color removal. For starters, it was used for the efficient removal from polluted aqueous media of potentially toxic materials. Groups of oxygen for linking metal ions and positively charged organic molecules via electrostatic interaction and coordination (Ali *et al.*, 2019).

The super sand Material has shown great interest among researchers. it was used as an essential filter media in wastewater treatment processes in developing countries all over the world. It showed excessive efficiency reaching five times the capacity of ordinary sand, this made it an attractive material in the field of wastewater treatment (Ajayan *et al.*, 2011).

Recently, Since synthetic dyes can not be efficiently decolorized by traditional methods in wastewater, attention has been focused on the use of adsorption technology on the surface of support solid material for removal of industrial dyes, due to the benefits of this treatment in comparison with the other methods, in terms of its cost and efficient (Oros, 2020).

The present study aims to prepare the super sand material and use it to remove dyes from wastewater. This material is receiving attention recently as it provides high efficiency in addition to low cost compared to other adsorbents. Kinetics models were studied in this work and showed the behavior of the rate of adsorption.

2. EXPERIMENTAL WORK

2.1. Materials

Materials that used in the experimental aspect included, graphite powder (granularity 150 µm, porosity 13%,), concentrated Sulfuric acid (H_2SO_4, 98%), phosphoric acid (H_3PO_4 ,70%), hydrogen peroxide (H_2O_2, 30%), potassium permanganate ($KMnO_4$), hydrochloric Acid (HCl, 35% wt) and sand which collected from Al- Najaf sand quarry, in addition, dyes that used, two different types of dyes used Methylene blue (Aldrich , USA) and Methyl orange (Aldrich, USA).

2.2. Preparation of graphene oxide

Preparation of graphene oxide was done by improved hummers method (Andrijanto et al., 2018), 360 ml of concentrated sulfuric acid (98% , Aldrich, Germany) was mixed with 40 ml phosphoric acid (70%, Aldrich, USA) in a Pyrex beaker and put into the 1000 ml conical flask which contains 3 gram of graphite powder (150 µm, Ultra-fine graphite, Germany). After that, the chiller was switched on and antifreeze was allowed to flow through the recycling condenser. the mixer was turned on and 18 gm of potassium permanganate (Alpha Chemika, Iso, India) was added slowly to the reaction mixture. This addition caused the temperature of the reaction mixture to gradually rise to 35 °C due to the occurrence of an oxidation reaction. then the mixture was heated further by the water bath until the temperature reaches 50 °C and the mixture still at these conditions for 12 hr. After that, the temperature of the solution was reduced to room temperature. Finally, 3 ml of hydrogen peroxide (30% H_2O_2, Panreac, Germany) was

added to the reaction mixture and graphene oxide (GO) resulted. the mixer was turned off and the mixture was left overnight to get the extreme precipitous of graphene oxide and the resulted (GO) was washed and filtered several times with tap water and ethanol (Aldrich, Germany) to remove the unreacted graphite or salts which produce after oxidation process.

2.2.1 Graphene oxide preparation apparatus

The reaction chamber was a three nick 1000 ml conical flask (Goel, Germany) equipped with a glass rod and Teflon stirring blades to prevent possible corrosion which could occur due to the use of a high concentration acid. The glass rod was connected via a heavy duty variable speed mixer (Ingco, China) to ensure vigorous mixing of reacting materials. The temperature of the reaction mixture was measured and recorded by inserting a mercury thermometer through the side nick of the conical flask onto the aqueous mixture. A recycle glass condenser was connected to the third arm of the conical flask to ensure recycling of any vapors from the reaction mixture. Fig. 1 shows the Photographic picture of the apparatus used for preparation.

The flask was put inside an antifreeze water bath (Hysc, CWB-20G; Korea) supplied with a copper coil of 3 m long. The coil as well as the recycling condenser was connected to an antifreeze chiller (Hysc, Korea) by a rubber tube and a set of valves that allows us to control the flow of antifreeze through the condenser and the coil. The chiller controls the temperature of the antifreeze down to about - 5 °C.

Furthermore, the temperature of the antifreeze inside the bath was digitally measured by inserting a thermocouple connected to an electrical recorder (Micro max, Germany) for further monitoring of the thermal stat of the apparatus.

Fig. 1 . Photographic picture of the apparatus used for preparation graphene oxide.

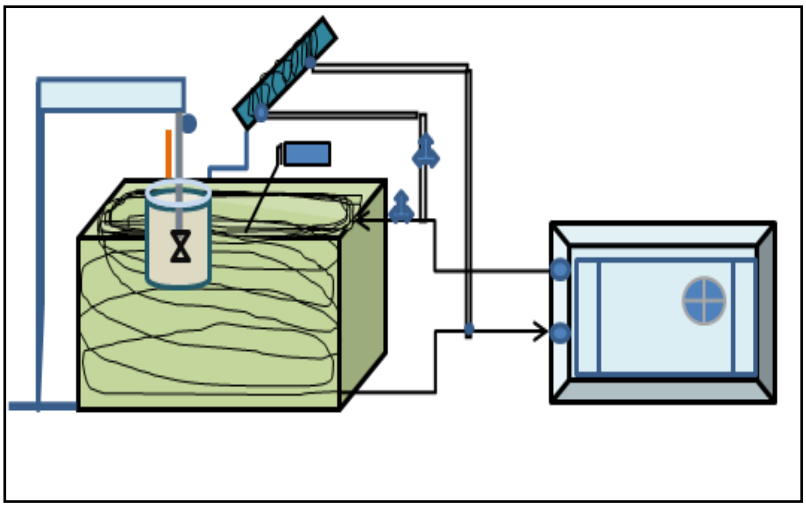

Fig. 2. Schematic figure of the apparatus used for preparation graphene oxide.

2.3 Sand coating

The sand was collected from the Al-Najaf sand quarry and sieved by using a laboratory sieving machine (Fritch, Germany). It consists of an electronic shaker and a set of sieves. The fraction (150−100) µm cut was chosen due to its quantity and quality with respect to surface area available for adsorption. Sand was washed several times with tap water and it was soaked with 10% HCl for 6 hours to remove all impurities and salts from sand then it was washed again several times until the PH becomes neutral. Finally, the clean sand was dried using drying oven for two hours to remove any excessive water.

2.4 Adsorption process

The stock solutions were prepared by weighing (0.5 g) from each type of dyes (methylene blue and methyl orange) and dissolved in 1 liter of distilled water . After that , solutions with desired concentrations were obtained by successive dilution with distilled water according to dilution law (Lacher, 2010).

Equilibrium experiments were done to determine the equilibrium time which was used for obtaining the dye concentration on the aqueous solution at different temperatures.

Firstly, equilibration times were determined by adding 3 grams of graphene oxide coated sand to a previously thermo stated 90 ml of each dye solution. The solution concentrations and temperature were chosen as the highest solution concentration (200 mg/l) and the lowest temperature (20 °C). These conditions represent the maximum adsorption amount that logically gives the maximum times for equilibrium attending under all our experimental work conditions. the mixture was vigorously mixed under reflux and 5 ml samples were withdrawn after each 30

min and filtrate in the filtration device to remove the particles of the adsorbent material (super sand). This process was repeated after every half an hour until the change in concentration after adsorption was almost constant, the concentration was approximately constant after (3 hr) and this time represent the equilibrium time (contact time), Fig. 3 shows the adsorption apparatus.

Fig. 3 . Photographic picture for the apparatus used for adsorption dyes by super sand.

The step followed by the equilibrium experiment was express the effect of temperature and initial concentration with constant contact time. This included take a range of concentration (50, 100, 150, 160, 180, 200) ppm (Andrijanto et al., 2018), from each type of dyes basic dye (methylene blue) and acidic dye (methyl orange) at different temperature degrees (20, 25, 30, 35)°C with constant contact time (3 hr), each experiment was done by taking (1 gram) from the adsorbent material (super sand) and it was putted in a Pyrex flask with (30 ml) from the dye stock solution then the adsorption process was done at the desired temperature with continuous stirring for three hours, this procedure repeated with each concentration from the two dyes at each temperature. When the time of experiment finished the solution filtrate in the filtration apparatus after that measured the absorbance of the dyes after adsorption. Finally, for computing the adsorption amount qe (mg/g) this done by applying equation (1) (Mutolib Bankole, 2019):

$$qe = \frac{(Ci - Ce) * V}{m} \qquad (1)$$

Where C_i and Ce are the initial and equilibrium concentration, v is the solution volume, and qe is the adsorption capacity (mg/g).

3. RESULTS

3.1 Morphology

Surface morphology of graphite, graphene oxide and coated sand was investigated by atomic force microscopy (AFM) analysis. Fig. 4 shows the three dimensional topography of graphite sample. The figure clearly shows the appearance of honeycomb stricture of the material. In addition, it could be recognized that the surface is rough and highly porous. This was concluded from the statistical data. Its shows the average value of thickness for the graphite equal to 44.9 nm and the surface coefficient roughness equals to Rms= 7.8 nm.

Fig. 5 shows the topography of the graphene oxide sample. The surface is more rougher than the surface of graphite due to the formation of functional groups (oxygen, hydroxyl and epoxy) that found on the surface and this causes an increase of the thickness of the surface layer. This result is in agreement with previously published work (Tefo *et al.*, 2013). This result was clearly shown by observing the statistical data of the pictures that determined the average thickness of graphene oxide as 59.4 nm and the roughness coefficient Rms as 8.3 nm. This foundation is in agreement with that previously observed by several authors. (Peng *et al.*, 2019) were used AFM spectra for studying the roughness of the graphene oxide surface and concluded that the surface is not smooth. The previous results and conclusions prove that the graphene oxide was fairly well.

Fig. 6 gives obvious details of the surface morphology of coated sand. It could be seen from this figure that the thickness of the surface layer was lower than that of of the graphene oxide. From the AFM analysis the average thickness and roughness coefficient were found to be equals to 17.26 nm and 3.56 nm, respectively. This decreasing of thickness and roughness of the coated sand indicates that the surface is more smooth after the coating process.

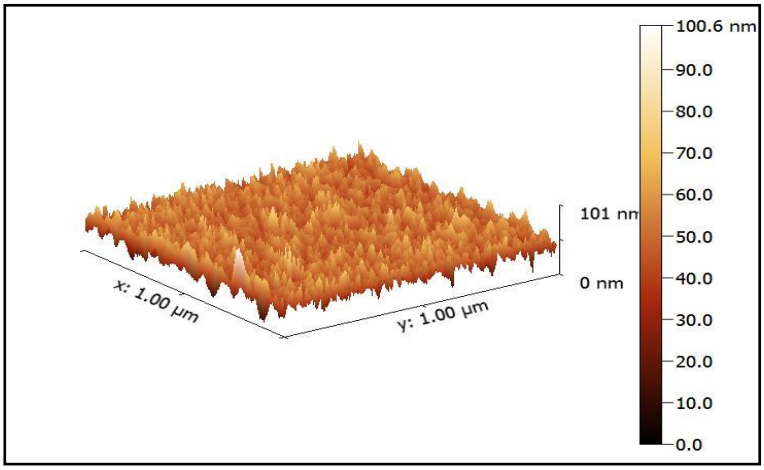

Fig. 4 . Atomic force microscopy (AFM) of graphite expressed as three-dimensional topgraphy.

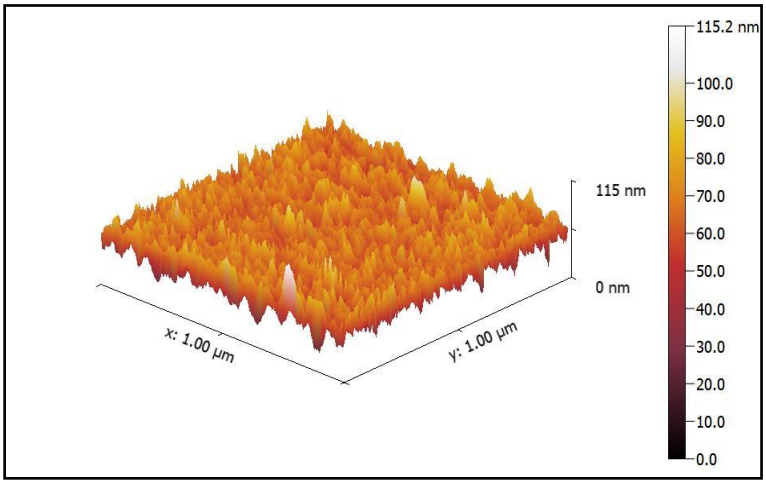

Fig. 5 . Atomic force microscopy (AFM) of graphene oxide expressed as three-dimensional topgraphy.

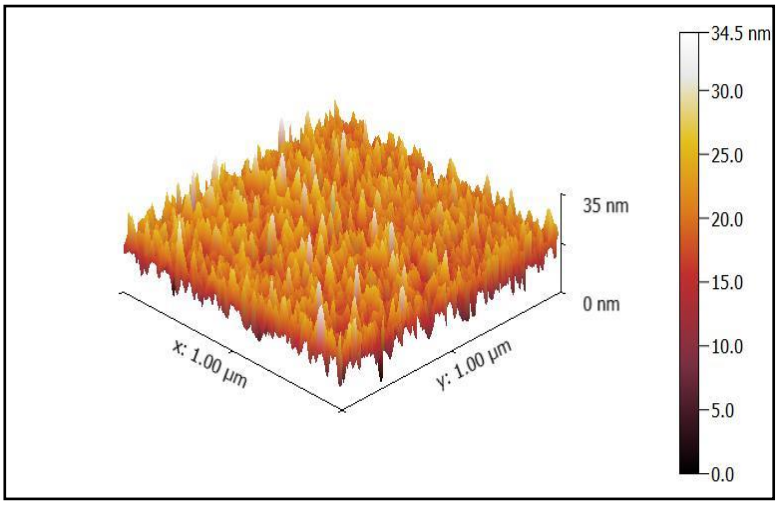

Fig. 6 . Atomic force microscopy (AFM) of coated sand expressed as the three-dimensional topgraphy.

3.2 Kinetics of adsorption

The experimental data was correlated by the most three wildly used models of kinetic, pseudo−first order, pseudo−second order and interpartical diffusion model. The mathematical equations were presented as (2), (3) and (4), respectively (Onal, 2007):

$$\frac{dqt}{dt} = \boldsymbol{k1} * (\boldsymbol{qe} - \boldsymbol{qt}) \quad (2)$$

$$\frac{dqt}{dt} = \boldsymbol{k2} * (\boldsymbol{qe} - \boldsymbol{qt})^2 \quad (3)$$

$$\boldsymbol{qt} = \boldsymbol{kint} * \boldsymbol{t}^{\frac{1}{2}} + \boldsymbol{C} \quad (4)$$

Where qt is the amount adsorbed of dye (mg/g) at time t (min), k1 is the pseudo−first order constant (1/min), k2 is the pseudo−second order constant (g/mg .min), kint is the interpartical diffusion constant (mg/g.min^-1/2), C is the constant.

Figs. 7 and 8 represent the rate of adsorption for methyl orange and methylene blue that are adsorbing on the super sand at the range of temperature (20–35) °C, these figures show that the rate of adsorption increasing rapidly at the first hour after that the change in the rate is not significant until reaching the equilibrium state. This is due to saturate the surface with particles of adsorbate after the first hour, so that the rate of adsorption is slow.

Figs. 9 and 10 show the pseudo−second order models for methyl orange and methylene blue dyes. It was clearly observed from these figures that the experimental data fitted well the second−order model with confidence level R^2=0.99 presented in Tables 1 and 2. Also, there is in an agreement between the experimental capacity values with the calculated values form plots.

Figs. 11 and 12 express the pseudo−first order models for methyl orange and methylene blue dyes. It was clearly showed from these figures that the first order model not corresponded with the experimental data.

Figs. 13 and 14 indicate the intraparticale diffusion models for methyl orange and methylene blue dyes. From these figures, it was appeared that the model not fitted the data because the lines not passé through the origin point and the values of the constant (C) will be not equal to zero. In comparison (Narayanan and Govindasamy, 2017) were applied three kinetic model pseudo first order, pseudo second order and interpartical diffusion models on the experimental data in their study for removal methylene blue from waste water. They concluded that the data fitted well the second order kinetic model with confidence level (R^2 =0.999).

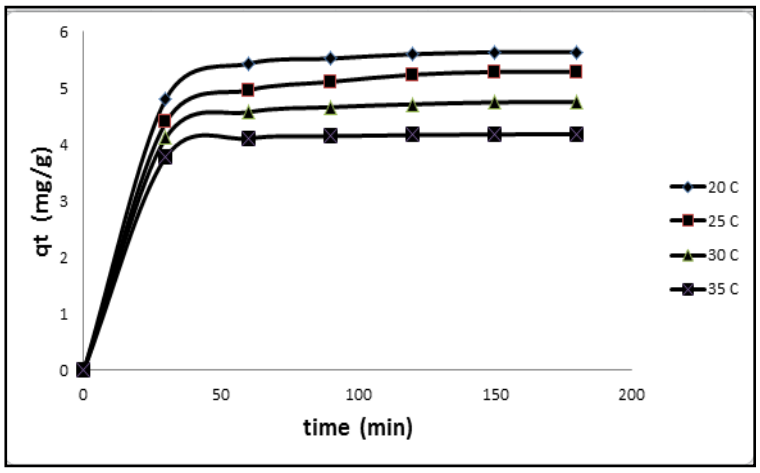

Fig. 7. rate of adsorption for methyl orange adsorbed on super sand at tmpreture range (20−35) °C.

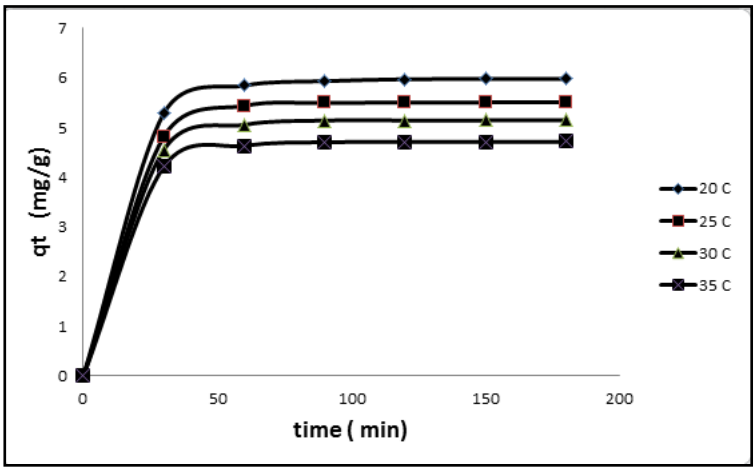

Fig. 8. rate of adsorption for methyLene blue adsorbed on super sand at tmpreture range (20−35) °C.

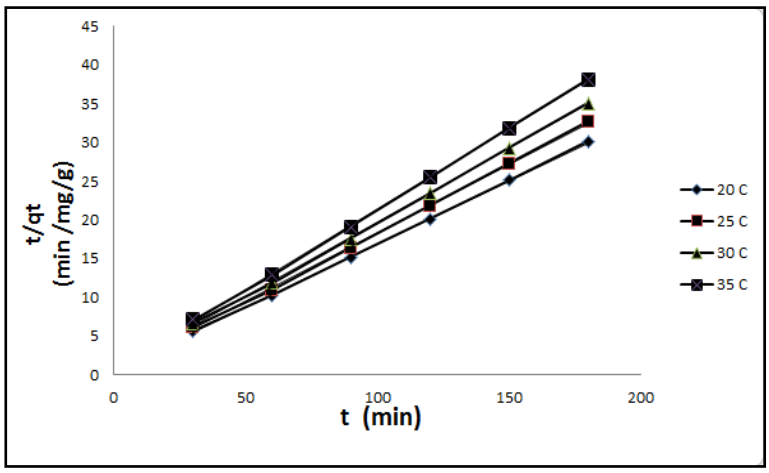

Fig. 9. second order kinatic model for methyl orange at tempreture range (20−35) °C.

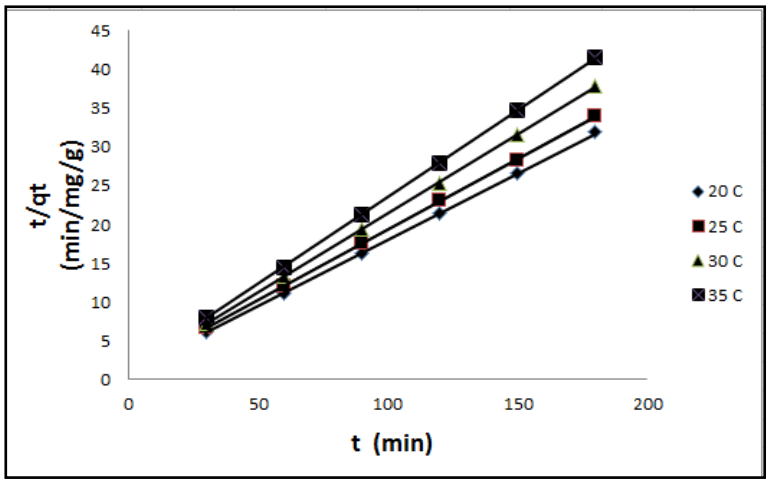

Fig. 10. second order kinatic model for methylene blue at tempreture range (20−35) °C.

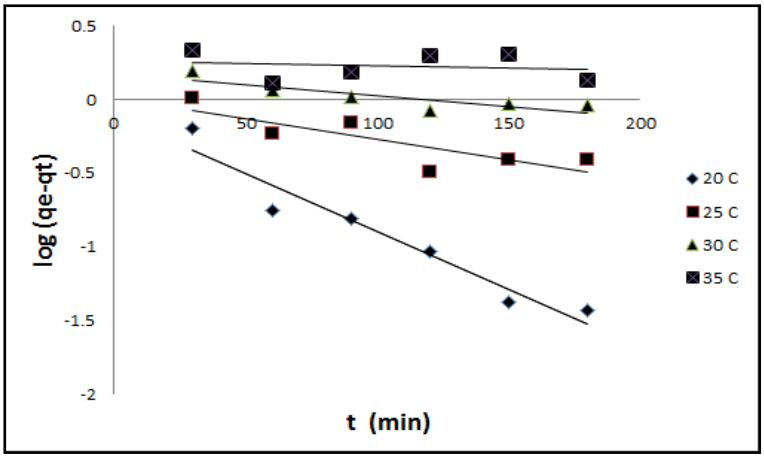

Fig. 11. first order kinatic model for methyl orange at tempreture range (20−35) °C.

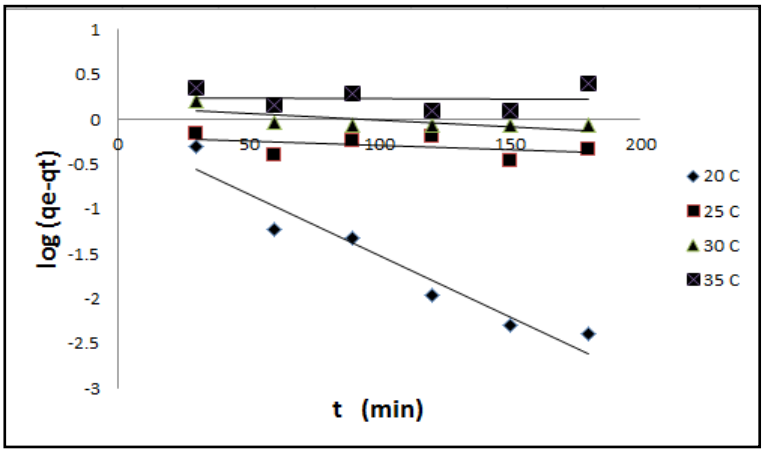

Fig. 12. first order kinatic model for methylene blue at tempreture range (20−35) °C.

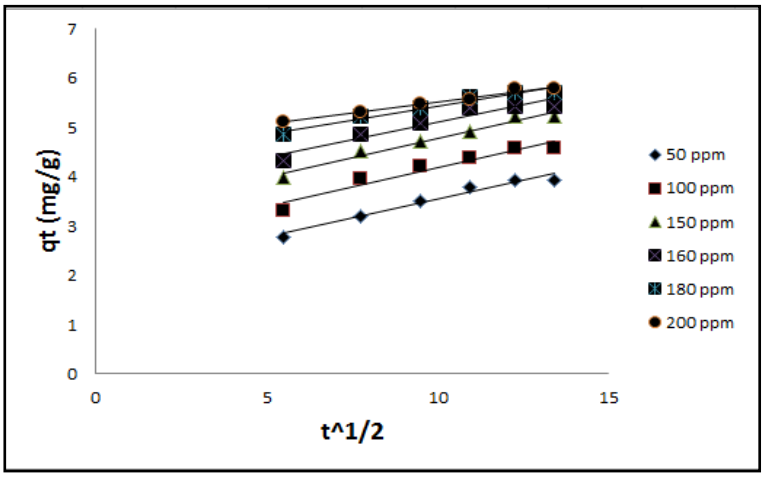

Fig. 13. intrapartical diffusion kinetic modal for methyl orange for concentration range (50−200 ppm) at 20 °C.

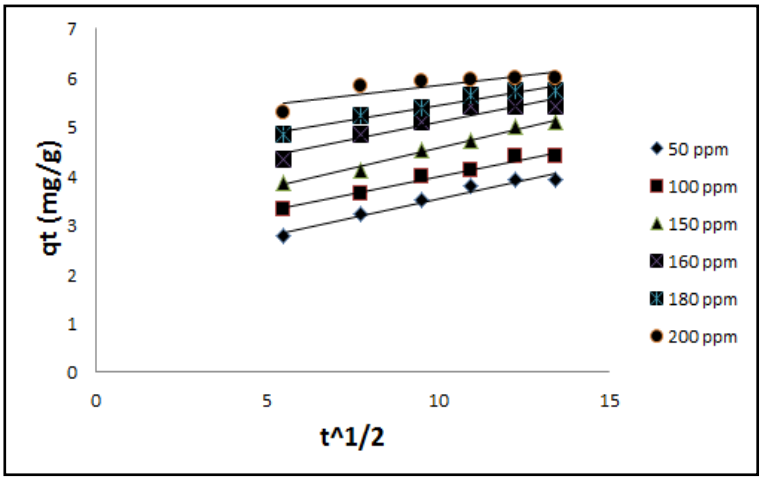

Fig. 14. intrapartical diffusion kinetic modal for methyl orange for concentration range (50−200 ppm) at 20 °C.

Table 1. Average value of kinetic parameter of the adsorption Process in methyl orange at temperatures (20, 25, 30, 35) °C.

Temp. °C	Second order model			First order model		
	qcal (mg/g)	k2 (g/mg. min)	R^2	qcal (mg/g)	k1 (1/min)	R^2
20	5.831	0.0266	0.9998	1.381	0.0193	0.9112
25	5.504	0.0403	0.9999	1.403	0.0064	0.8441
30	4.916	0.0456	0.9978	0.755	0.0035	0.8022
35	4.464	0.0575	0.9942	0.571	0.0021	0.7443

Table 2. Average value of kinetic parameter of the adsorption process in methylene blue at temperatures (20, 25, 30, 35) °C.

Temp. °C	Second order model			First order model		
	qcal (mg/g)	k2 (g/mg. min)	R^2	qcal (mg/g)	k1 (1/min)	R^2
20	6.119	0.0155	0.9995	1.542	0.2414	0.9022
25	5.631	0.0169	0.9941	1.057	0.0039	0.7601
30	5.241	0.0222	0.9982	0.867	0.0032	0.8292
35	4.81	0.0253	0.9955	0.617	0.0024	0.6142

4. CONCLUSION

- Graphene oxide which is prepared from graphite powder by the improved hummers method has good properties such as high dispersion in water.
- The coated process which done in two degrees of temperature 105 °C for three hours and 150 °C for two hours, it was gives super sand material with high stabilizing graphene oxide on the surface of sand grains.
- AFM (atomic force microscopy) analysis showed the difference in the morphological form of the surface of graphite, graphene oxide, and coated sand. It appeared that coated sand was more smoothness than graphite and GO.
- Kinetics of adsorption gives an idea about the rate of adsorption for methylene blue and methyl orange, and it was cleary observed that the pseudo−second order model corresponded with the experimental data.

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