ISSN: 0067-2904
GIF: 0.851

Potential Application of Natural and Modified Orange Peel as an Eco–friendly Adsorbent for Methylene Blue Dye

Taghried A. Salman, Mayasa I. Ali*
Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq

Abstract

In this paper, the adsorption behavior of Methylene blue dye by orange peels, which was chemically modified with sodium hydroxide, has been investigated. Physical and chemical properties of both sorbents under study were determined using Fourier Transform Infrared Spectrophotometer (FTIR), Scanning Electron Microscope (SEM), Atomic Force Microscope (AFM) and Brunauer, Emmett and Teller (BET) specific surface-area measurement techniques. Effect of the solution–pH, adsorbent dose, adsorption time, temperature and initial methylene blue concentration were studied in batch experiments. The experimental data were fitted into the following kinetic models: pseudo-first order, pseudo-second order, and the intraparticle diffusion model. It was observed that pseudo-second order kinetic model described the adsorption process with high coefficients correlation (R^2) better than any other kinetic models. The kinetic investigations also reveal that intraparticle diffusion mechanism was operative equilibrium isotherms, for the adsorption of MB on OP and Sodium orange peels were analyzed considering the Langmuir, Freundlich and Temkin isotherms models. The Freundlich isotherm provided the best fit for MB dye adsorption onto OP and SOP, and the maximum adsorption capacity was found to be 14.164 mg.g^{-1}for OP and 18.282 mg.g^{-1}for SOP, respectively. Different thermodynamic parameters, namely Gibb's free energy, enthalpy and entropy of the adsorption process have also been evaluated, and the data obtained indicated that the adsorption process of dye onto OP and SOP surfaces was exothermic in nature. The results show additional chemical modification of the adsorbent by NaOH leads to increased adsorption capacity.

Keywords: orange peel, sodium hydroxide modified orange peel, methylene blue, adsorption, kinetic, thermodynamic studies

الفعالية التطبيقية لقشور البرتقال الطبيعية و المطورة باعتبارها من السطوح الصديقة للبيئة لامتزاز صبغة المثيلين الأزرق

تغريد علي سلمان، مياسة عصام علي*
قسم الكيمياء، كلية العلوم، جامعة النهرين، بغداد، العراق

الخلاصة

تم في هذا البحث دراسة سلوك امتزاز صبغة الميثيلين الزر قاء بواسطة قشور البرتقال، التي تم تعديلها كيميائيا باستخدام هيدروكسيد الصوديوم. درست الخواص الفيزيائية والكيميائية للمواد المازة باستخدام تقنيات طيف الأشعة تحت الحمراء (FTIR)، مجهر المسح الإلكتروني ..(SEM)، مجهر القوة الذري (AFM) وقياس المساحة السطحية (BET) . تم دراسة تأثير درجة حموضة المحاليل، وكمية المادة المازة، وزمن الامتزاز ودرجة الحرارة والتركيز ألاولي لصبغة الميثيلين الأزرق باستخدام طريقة الوجبة. و بعدها تم استخدام ثلاث معادلات حركية وهي: معادلة الدرجة الاولى، معادلة الدرجة الثانية وintraparticle diffusion و اشارت

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*Email:miar201262@yahoo.com

النتائج الى ان عملية الامتزاز تخضع لمعادلة الدرجة الثانية وفقا لمعامل الارتباط (R^2) الذي اعطى أفضل قيمة مقارنة مع النماذج الحركية الأخرى. بينت النتائج الحركية أيضا امكانية تطبيق diffusion intraparticle للنظام قيد الدراسة. و بعدها تم تحليل نتائج امتزاز صبغة المثيلين الزرقاء على سطوح قشور البرتقال الطبيعية و المطورة باستخدام ايزوثيرمات لانكماير و فريندلج و تيمكان . اظهرت النتائج ان ايزوثيرم فريندلج هو الانسب لتمثيل عملية الامتزاز و تم الحصول على اقصى كمية امتزاز لتكون 14.164 ملي غرام/ عرام بالنسبة ل OP و 18.282 ملي غرام/ غرام لSOP، على التوالي. تم حساب الدوال الثرموديناميكية لعملية الامتزاز ، وهي طاقة جبس الحرة، وتغير الانثالبي و الانتروبي وأشارت النتائج التي تم الحصول عليها أن عملية امتزاز الصبغة على سطوح OP وSOP كانت باعثة للحرارة و مصحوبة بنقصان في العشوائية. بينت النتائج على ان التعديل الكيميائي لقشور البرتقال باستخدام هيدروكسيد الصوديوم ادى إلى زيادة قدرتها على الامتزاز .

1- Introduction:

Water pollution is a plague in our modern society. Increased industrial and agricultural activities resulted in the generation of various types of toxic pollutants. Polluted wastewater must be depurated and returned to water receptors or to land. Dyes are an important class of pollutants which came in large amounts from textile, dyeing, paper and pulp, tannery and paint industries [1]. The main use of dyes is to modify the color characteristics of different substrates as paper, fabric, leather and others [2, 3]. It is already demonstrated that dyes largely affect the photosynthetic activity [4]. Moreover, many dyes are toxic and even carcinogenic thus affecting the aquatic biota and human health [5–6]. Methylene blue (MB) is a cationic dye having various applications in chemistry, biology, medical science and dyeing industries. Its long term exposure can cause vomiting, nausea, anemia and hypertension [7].Various methods such as adsorption, coagulation, advanced oxidation, and membrane separation are used in the removal of dyes from wastewater. However, adsorption is one of the most effective processes of advanced wastewater treatment. Therefore, many industries use adsorption techniques (mainly in the tertiary stage of biological treatment) for reducing hazardous inorganic/organic pollutants present in industrial, agricultural and other wastes can contribute to the pollution of these valuable resources, and water pollutants can damage human and animal health. Chemical water pollutants can be classified into three important classes: heavy metals, inorganic pollutants and organic pollutants [8].

Agricultural byproducts such as fruit peel are relatively cheap and show high adsorption capacities for organic and inorganic pollutants [9-10]. The application of orange peel as a biosorbent material presents strong potential due to its main component of cellulose, pectin, hemicellulose and lignin acid bear various polar functional groups, including carboxylic and phenolic acid groups [11-12].

The aim of this study was to modify orange peel (OP) by sodium hydroxide to enhance the adsorption capacity of the by -product and investigate the adsorption of methylene blue dye on it. The study includes a characterization of the adsorbent and the determination of the factors affecting the sorption, including contact time, dose of the adsorbent, temperature, and pH. The adsorption data were analyzed using Langmuir, Freundlich, and Temkin isotherms. The kinetics characteristic of adsorption was studied with pseudo first-and second –order equations.

2. Materials and Methods

2.1. Adsorbent preparation

2.1.1. Raw OP

The OP was obtained from a local fruit field. It was cut into small pieces, washed several times with distilled water and dried under sunlight and in an oven at 70 C^0 for a period of 5 hours and kept in airtight containers. The product was then ground and sieved by using a 75 µm sieve.

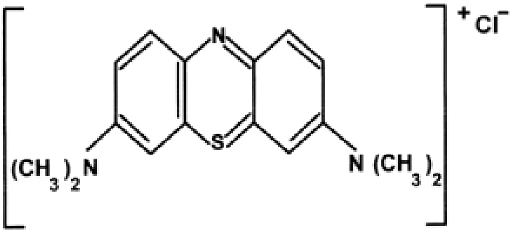
2.1.2. Chemical modification with sodium hydroxide

Sixty grams of dried OP was immersed in 250 ml of (0.1M) NaOH for 24 h under occasional shaking. After decantation and filtration, this saponified product (NaOH-treated OP.(SOP) was washed with distilled water until the pH of the filtrate reached 7.

2.1.3. Preparation of methylene blue dye solutions

Methylene blue (BDH,85% dye content) was without further purification in this study. The stock solution (35mg/L) was prepared by dissolving 0.035 g methylene blue in 1000 ml distilled water. Experimental solution was obtained by dilution.

Dye concentration was determined by using absorbance values measured before and after the treatment, at **λ Max** 655nm by using UV-VIS Spectrophotometer (UV-Visible spectrophotometer, Double beam, Shimadze. PC 1650, Japan).



Molecular formula: $C_{16}H_{18}N_3SC$
Molecular weight: 319.85g/mol
λ $_{max}$ = 655 nm

Figure1-Structure of methylene blue

2.3. Characterization of OP and SOP

FT-IR spectra were observed using FT-IR System Shimadzu.8400, spectrophotometer/ Japan within 400–4000 cm^{-1}. Scanning electron microscope, SEM, from (FEI) company, 2 channel,BSD Amplifier; was used to observe the morphology of OP and SOP surfaces. Atomic force microscope, AFM (AA 3000, Advanced Angestrum Inc., USA), was used to obtain Comprehensive characterization of surface structures. The specific surface area of OP and SOP was measured by BET N_2 adsorption using Quantasorb surface area analyzer (Micromeritics ASAP2020 V3.04G analyzer (micromeritics, Inc,USA)) .

2.2. Batch Adsorption Experiment

In each adsorption experiment, 25 ml of dye solution known concentration was added to 0.05 g of adsorbent s in 100 ml conical flask at room temperature and mixture stirred on electronically shaker at 160 rpm. The adsorbed amount of methylene blue was calculated from the concentration of solutions before and after adsorption according to the equation:

$$Qe = V_{sol.}(C_0 - Ce)/m \quad \textbf{(1)}$$

$$\%R = Co - Ce/Co \quad \textbf{(2)}$$

Where C_0 and Ce are the initial and equilibrium liquid phase concentration of dye solution (mg/L), respectively; Qe is equilibrium dye concentration on adsorbent (mg/g).V is the volume of dye solution (L), and m is the mass of the adsorbent used (g).

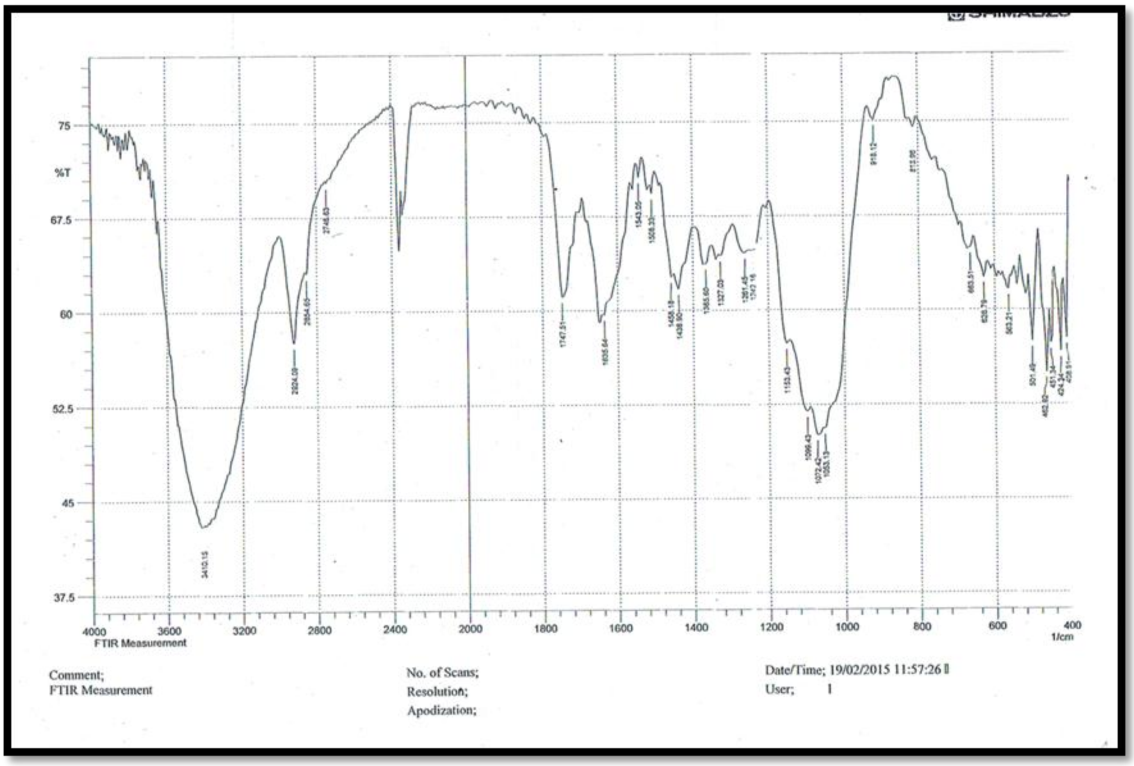
3. Results and Discussion

3.1. The chemistry of the surfaces of OP and SOP

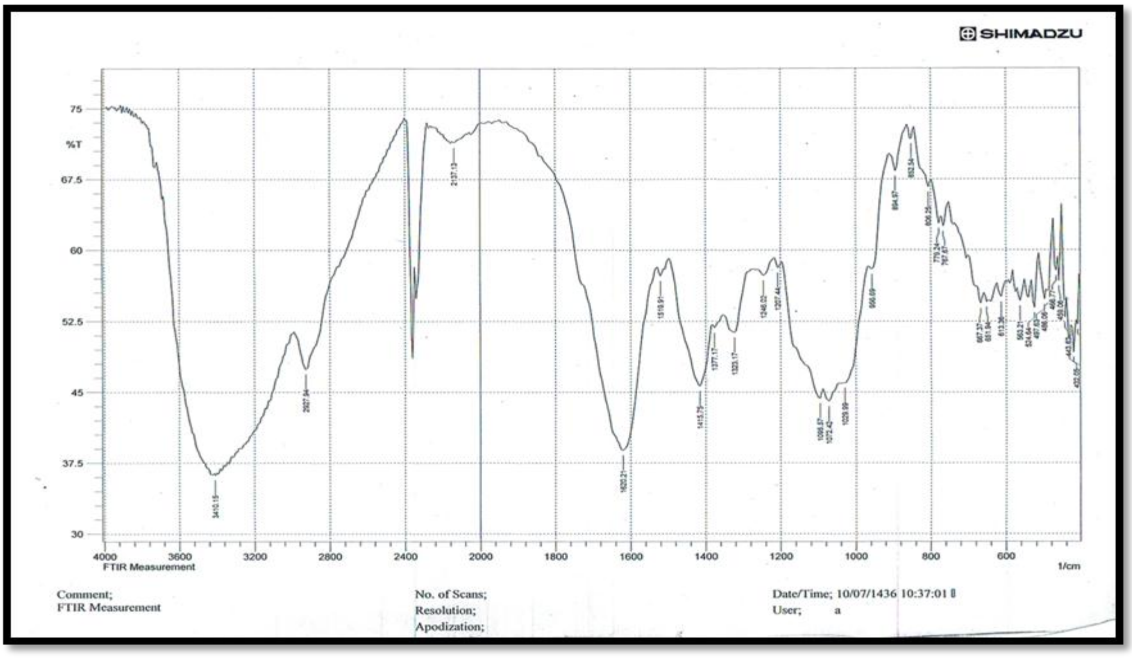
3.1.1. FTIR of OP and SOP

Infrared techniques have been used for the identification of adsorbents and determine the main functional groups present. Usually, the band at 3410 $cm\text{-}^{1}$ denotes the OH stretching of polymeric compounds. Band at 2924 $cm\text{-}^{1}$ is the stretching vibration of C-H.The band at 1747 cm^{-1} is the stretching vibration of COO and C=O. the bands between 1130-1000 is the vibration of C-O-C,C-O-P and O-H of the polysaccharides[13].

The FTIR curve of SOP is shown in Figure-2b. It indicates the weakening intensity of the peak at 1747 $cm\text{-}^{1}$ after the NaOH pretreatment, which can enhance the binding ability of the biomass [14].



a) OP

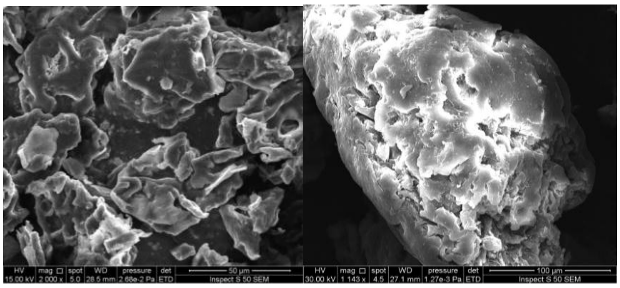


b) SOP

Figure 2-FTIR spectra of a) OP and b) SOP

3.1.2. SEM of OP and SOP

The scanning electron microscope (SEM) micrographs showed the highly heterogeneous porous structure of the orange peel (OP) [15].But after treated with NaOH sodium orange peel (SOP) has a more irregular and more porous structure than OP [16].



a) OP **b) SOP**

Figure 3- SEM Images of OP and SOP

3.1.3. AFM of OP and SOP

The orange peels and sodium orange peels are characterized by AFM to determine their average particle size and its distribution. The AFM image in three – dimensional and granularity distribution charts for both orange peels (OP) and sodium orange peels (SOP) were represented in Figures 4, 5, 6, and 7 respectively. Figures (4-7) show that the size of the particles were (25.54 and 2.00 nm) for orange peels (OP) and sodium orange peels (SOP) respectively and the average particle size was (109.40 and 94.45 nm) for orange peels (OP) and sodium orange peels (SOP) respectively. These results indicate that the lower average particle size for modified orange peels forms than orange peels.

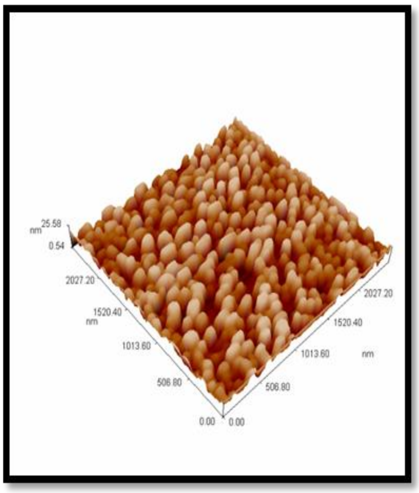


Figure 4- AFM surface images of orange peel

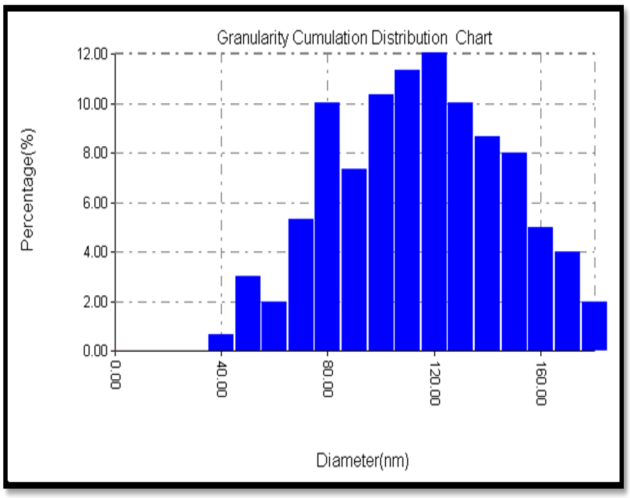


Figure 5- Granularity cumulating distribution chart of orange peel (OP)

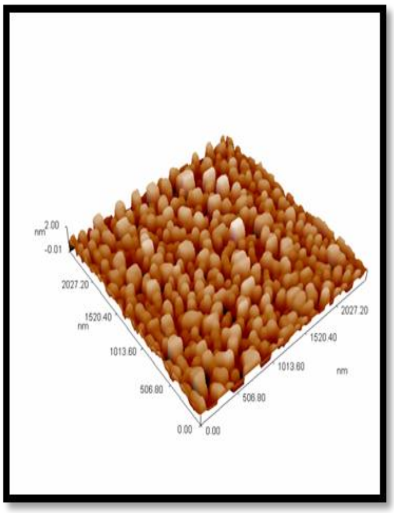


Figure 6- AFM surface images modified orange peel (SOP)

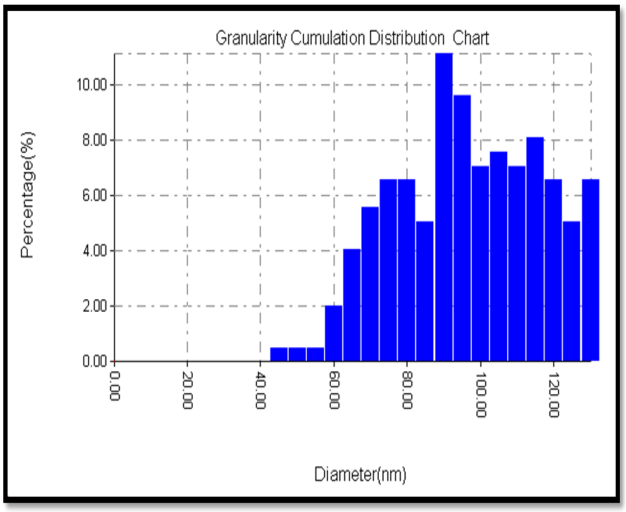


Figure7-Granularity cumulating distribution chart of modified orange peels (SOP)

3.1.4. BET Analysis

The surface area values were obtained by BET method are 0.7069 m^2/g for orange peel (OP) and 1.1705 m²/g for sodium orange peels (SOP), respectively. The N_2 adsorption gave the surface area value which is close to the values as recorded in literature for orange peels.

3.2. Effect of contact time

Adsorption methylene blue dye (25mg/L) solution onto natural orange peel and sodium orange peels were examined at different time as shown in Figure-8.The result showed that the rate of adsorbed MB dye onto both OP and SOP were rapid and then become slower near the equilibrium. Most of the maximum quantity adsorption of methylene blue dye was attained after 30 min for each natural orange peel and sodium orange peel [17].

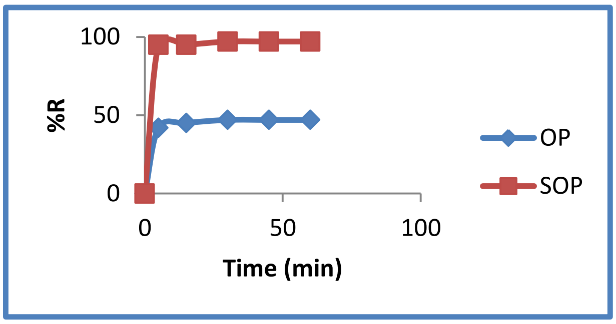


Figure 8- Effect of contact time on the uptake of methylene blue (OP: orange peel, SOP: sodium orange peel)

3.3. Effect of adsorbents dose

The percentage removal of methylene blue dye (25 mg/L) on to OP and SOP increases with adsorbent dose loading up to (0.01g-0.09g); Figure-9.Increase in adsorbent dose increased the percentage removal of dye. These results can be explained by the fact that the adsorption sites remain unsaturated during the adsorption reaction where as the number of a site available for adsorption site increases by increasing the adsorbent dose [18].

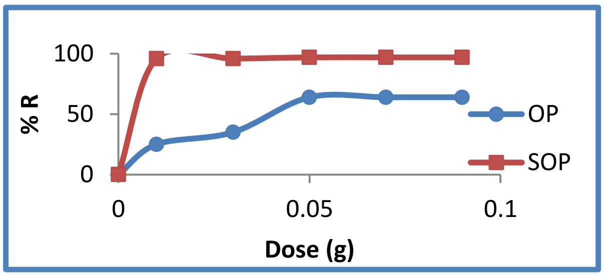


Figure 9- Effect of adsorbents dose on the uptake of methylene blue

3.4. Effect of pH

In this experiment, 25 ml of (15-30mg/L) of dye solution in the pH range 3-12 have been studied. The pH of the solutions was adjusted by using 0.1 M hydrochloric acid (HCl) and 0.1 M of sodium hydroxide (NaOH) solution using a pH meter. The results are shown the maximum percentage removal at pH= 4 for orange peels. The higher adsorption at very acidic media could be due to the interactions between the positively charged dyes cations with surface functional groups present in orange peels . But the maximum percentage removal reaches at pH=9, because increases the concentration of hydroxide ions in solutions [19].

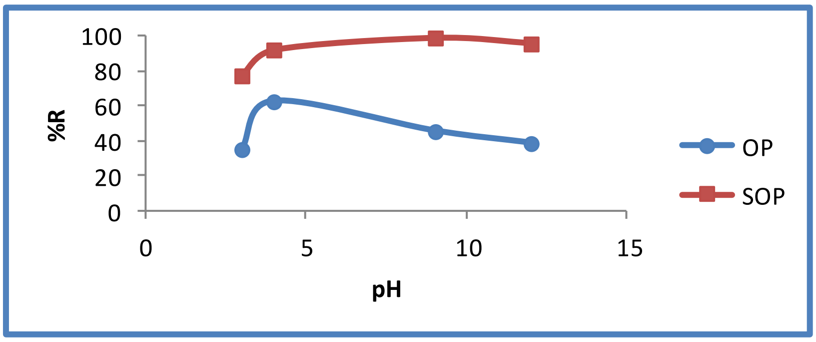


Figure 10- Effect of solution –pH on the uptake of methylene blue

3.5. Adsorption isotherms

The adsorption mechanism and relationship between the concentrations of the adsorbate and adsorption capacity of both, adsorbents was studied using different adsorption isotherms.

3.5.1. Langmuir Adsorption Isotherm

The Langmuir isotherm was applied for adsorption equilibrium

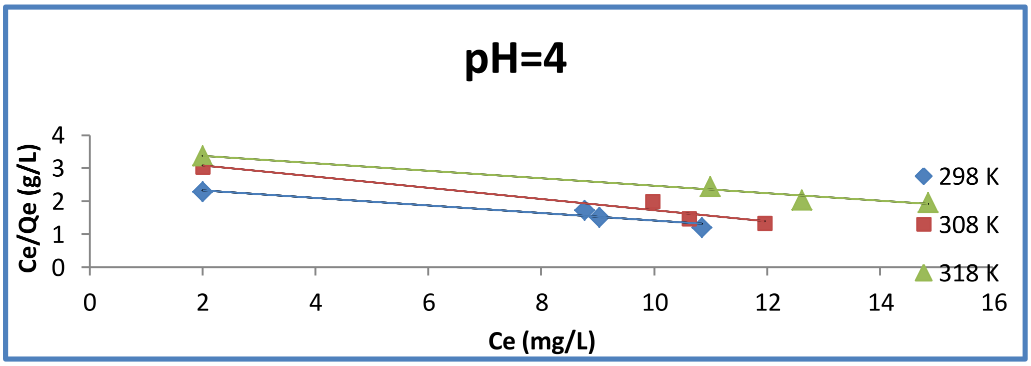
$$Ce/Qe = 1/k_L\, q_{max} + (1/q_{max})Ce \qquad \textbf{(3)}$$

Where Ce is the equilibrium concentration (mg/L), Qe is the amount of dye adsorbed at equilibrium concentration (mg/g), $q_{max,}$ k_L Co, are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The linear plot of Ce/Qe vs Ce shows that the adsorption obeys Langmuir isotherm model in Figure-11. Qmax (mg/g) and k_L (L/mg) were determined from the slope and intercept of the plot. The essential characteristics of Langmuir isotherm can be expressed in term of dimensionless constant separation factor for equilibrium parameter, R_L [20] which is defined by

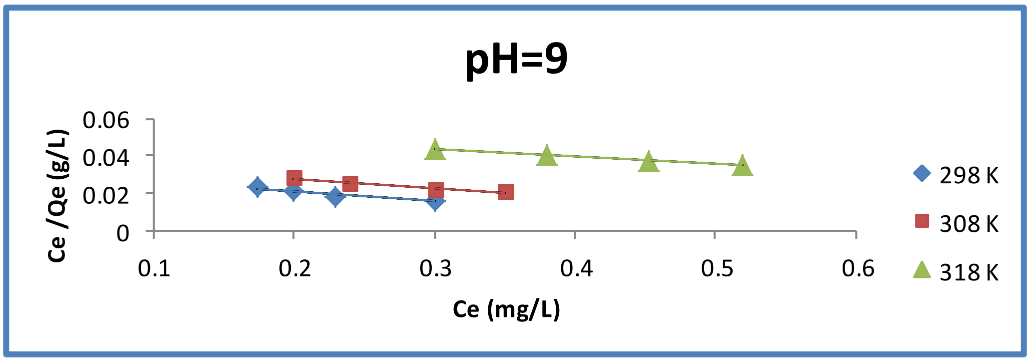
$$R_L = (1+k_L\, Co) \qquad \textbf{(4)}$$

The dimensionless factor (R_L), indicates the shape of isotherm as follows:

RL < 1	Favorable
RL > 1	Unfavorable
RL = 1	Linear



a) OP



b) SOP

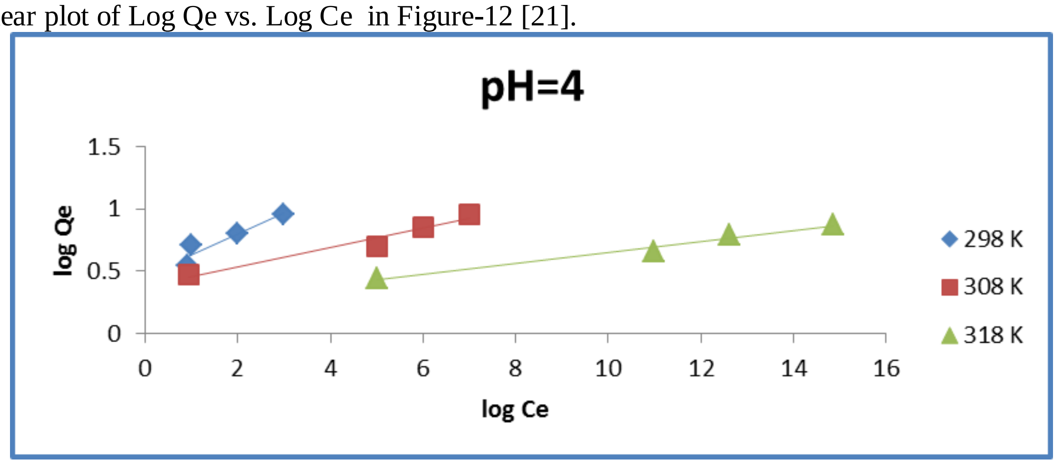
Figure 11- Langmuir isotherm for a) orange peels (OP) and b) sodium orange peels (SOP) at three different temperatures.

3.5.2. Freundlich Adsorption Isotherms

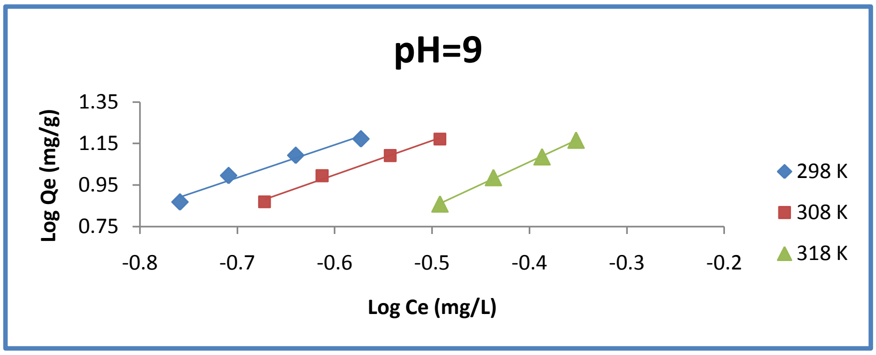
The Freundlich isotherm described as:

$\text{Log } Qe = \text{Log } k_F + 1/n \text{ Log } Ce$ **(5)**

Where k_F is the Freundlich constant indicative of the relative adsorption capacity of the adsorbent (mg/g), 1/n is the adsorption intensity. k_F and 1/n can be determined from the slope and intercept of the linear plot of Log Qe vs. Log Ce in Figure-12 [21].



a) OP



b) SOP

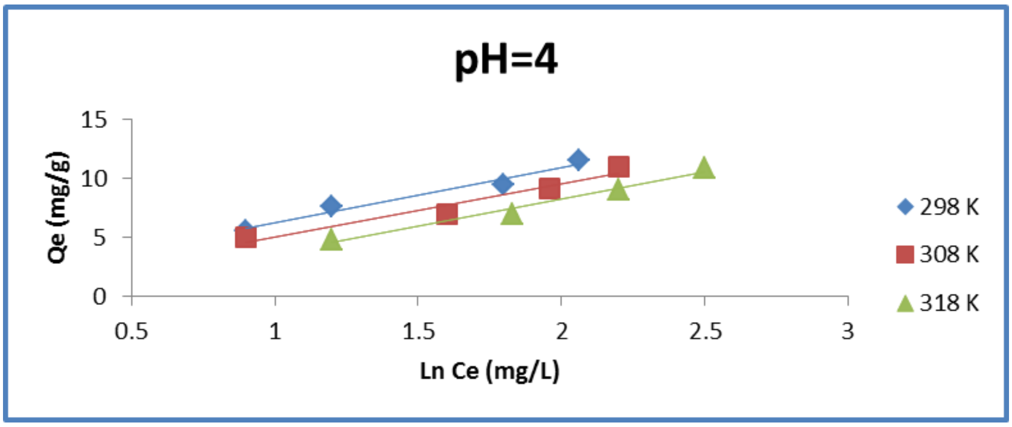
Figure 12- Freundlich isotherm for a) orange peels (OP) and b) sodium orange Peels (SOP) at three different temperatures.

3.5.3. Temkin Adsorption Isotherm

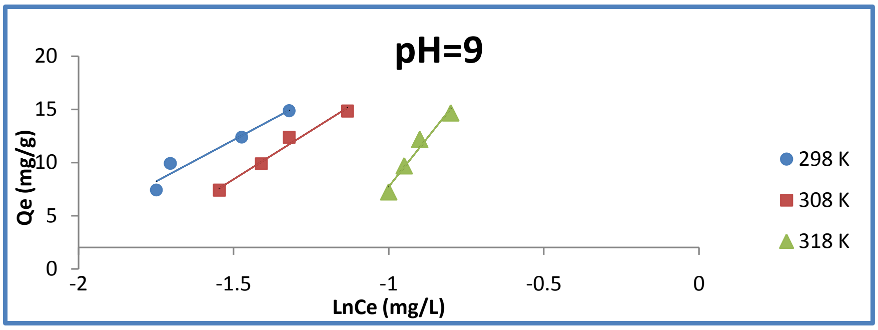
The Temkin isotherm describes the behavior of adsorption systems on a Heterogeneous surface, and is represented as follows:

$Qe = B_T \text{ Ln } A_T + B_T \text{ Ln } Ce$ **(6)**

Where B_T is a constant related to adsorption heat, and at is the equilibrium binding constant (L/mol), corresponding to maximum binding energy. A plot of *Qe* vs. ln *(Ce)*, is used to determine isotherm constants from the slope and intercept in Figure-13 [22].



a) OP



b) SOP

Figure 13- Temkin isotherm for a) orange peels (OP) and b) sodium orange peels (SOP) at three different temperatures.

Table 1- Langmuir, Fruendlich and Temkin constants for orange peels (OP) and sodium orange peels (SOP) at three different temperatures.

	Tem. (K)	Langmuir constants				Freundlich constants			Temkin constants		
		q_{max}	K_L	R_L	R^2	n	K_F	R^2	A_T	b_T	R^2
OP	298	14.164	0.0143	0.737	0.807	0.797	0.130	0.992	1.003	541.469	0.984
	308	8.625	0.0278	0.589	0.769	0.734	0.109	0.991	1.001	559.052	0.948
	318	7.924	0.0193	0.675	0.852	0.710	0.072	0.981	1.000	569.337	0.935
SOP	298	18.282	1.720	0.023	0.913	0.631	0.008	0.970	1.249	159.461	0.947
	308	19.157	1.356	0.029	0.919	0.609	0.010	0.991	1.293	139.817	0.981
	318	24.331	0.734	0.052	0.988	0.460	0.012	0.999	1.862	71.714	0.967

From the results all the isotherms were found to be fit well to the experimental data the Freundlich isotherm is slightly better than Langmuir and Temkin isotherm as indicated by higher R^2 value.

3.6. Adsorption Kinetic study

For evaluating the adsorption kinetics of methylene blue, the pseudo-first order equation of lagergren first – order and second order models were used to fit the experimental data. The first order equation:

$$\log(qe-qt) = \log qe - k_1t/2.303 \qquad (7)$$

where qe is the amount of adsorbed dye at equilibrium concentration (mg/g), qt is the amount of adsorbed dye at any time t and k_1 is the pseudo first – order rate constant (1/min) [23].The plot of Log (qe –qt) vs. t gave straight line of slope k_1 and intercept qe (mg/g) as shown in Figure-14.

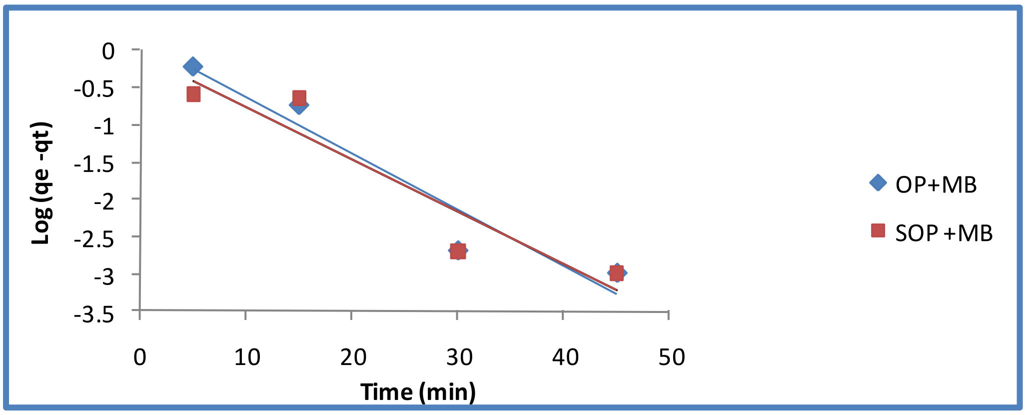


Figure 14- The pseudo first – order kinetic model to methylene blue (25mg/L) on orange peels (OP)

A pseudo-second order model may also be applicable to kinetic adsorption and the equation is [24]:

$t/qe = 1/ k_2. qe^2 + t/qe$ **(8)**

Where k_2 is the rate constant of second order model, the plot of t/qe vs. t gave a straight line in Figure-15 Which k_2 and qe determine from the slope and intercept.

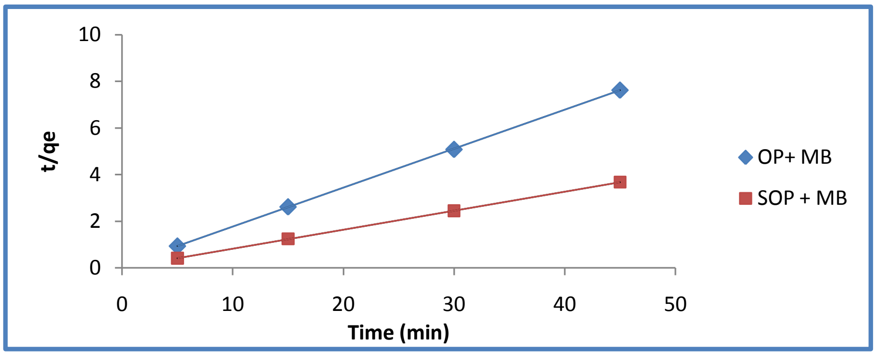


Figure 15- The pseudo-second order kinetic model to methylene blue (25mg/L) on orange peels (OP) and sodium orange peels (SOP).

Adsorption process also incorporates the transport of adsorbate species from the bulk of the solution into the pores of the adsorbent through an intraparticle diffusion process [25]. Intraparticle diffusion could be the rate-limiting step in this case. This was tested by using the intraparticle diffusion model [26]:

$qt = k_D t^{1/2} + C$ **(9)**

Where k_D is the rate of diffusion and C is the intercept Figure-16. Show the linear plots of the above equation. Kinetic parameters obtained after subjecting experimental data to the three kinetic models are shown in Table-2.

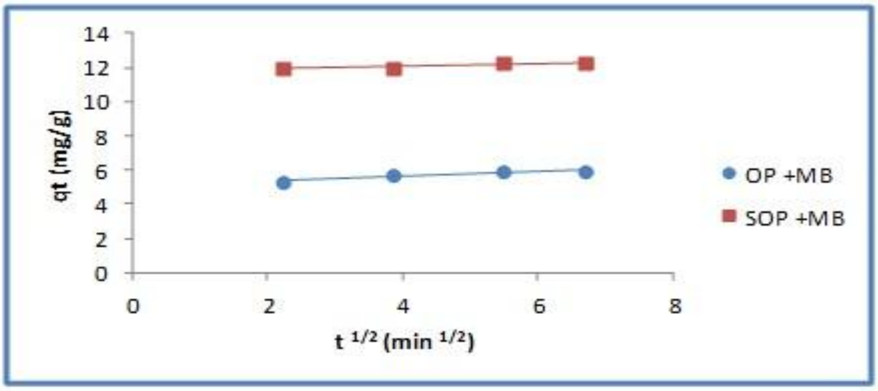


Figure 16-The Intraparticle diffusion plots of adsorption of methylene blue (25mg/L) on orange peels (OP) and sodium orange peels (SOP).

Table 2- Adsorption Kinetics Parameters of Pseudo-First ,Second Order and Intra particle diffusion constant of Methylene Blue on Orange Peels (OP) and Sodium Orange Peels (SOP).

	Pseudo-first order			Pseudo-second order			Intrapartical diffusion		
	k_1 (1/min)	qe (mg/g)	R^2	k_2 (g/mg. min)	qe (mg/g)	R^2	k_D (mg/g. min$^{1/2}$)	R^2	
OP	0.175	1.369	0.921	0.261	5.995	0.999	0.086	0.861	
SOP	0.030	1.174	0.883	0.361	12.300	0.998	0.069	0.862	

From the results of the Table-2, it can be concluded that pseudo-second order equation provides the best correlation coefficients R^2 with good agreement between the calculated equilibrium sorption capacities (qe) values. The results suggest that the pseudo-second order sorption mechanism is predominant. Although the regression of intraparticle diffusion was linear, the plot didn't pass through the origin, suggesting that adsorption involved intraparticle but wasn't the only rate-controlling step [27]. Value of the intercept is an idea of the thickness of the boundary layer; the larger the intercept, the greater the boundary layer effect [28]. The values of k_D , which are less than k_2, have also been confirmed that the intraparticle diffusion was rate-controlling step [29].

3.7. Thermodynamics Study of Adsorption

The parameters for thermodynamic study, particularly Gibb's free energy, enthalpy and entropy have a significant role to know the spontaneousness and heat change involved in the adsorption process. Equilibrium constant can be used to calculate the thermodynamic parameters mentioned above, enthalpy change (ΔH^o) and entropy (ΔS^o) of adsorption were calculated, equation (10):-

$$\ln k_{eq} = -\Delta H^o / RT + \Delta S^o / R \qquad \textbf{(10)}$$

Where k_{eq} is the equilibrium constant, T is the solution temperature and R, the gas constant (8.315 J.K-^{1}.mol^{-1}) [17]. ΔH^o and ΔS^o were obtained from the slope and intercept of a plot of ln keq against 1/T, Figure-17 [30].The free energy change can be obtained from the following equation:-

$$\Delta G^o = -RT \ln K_{eq} \qquad \textbf{(11)}$$

The results obtained of the three thermodynamics parameter are listed in Table-3.

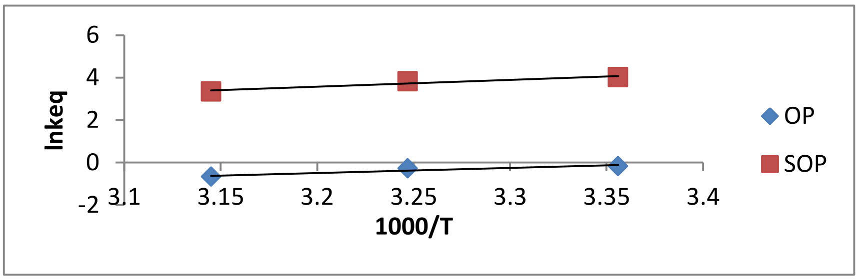


Figure 17- Plot of Ln K against Reciprocal Absolute Temperature for Adsorption of methylene blue (MB) Dye on Orange Peel (OP) and sodium orange peels (SOP) Surfaces at Different Temperature

Table 3- Thermodynamics parameters of adsorption of methylene blue dye on orange peels (OP) and sodium orange peels (SOP) surfaces

	T (K)	$-\Delta H$ (kJ mol^{-1})	$-\Delta S$ (J K^{-1} .mol $^{-1}$)	ΔG (kJ mol^{-1})
OP	298	19.693	67.108	+0.421
	308			+0.722
	318			+1.779
SOP	298	26.461	54.957	-9.959
	308			-9.809
	318			-8.842

The value of ΔH was negative, indicating that the adsorption process was exothermic in nature. The negative value of ΔS for methylene blue indicates decrease in randomness at the solid/solution interface with some structural changes in the adsorbate and the adsorbent and an affinity of the OP and SOP toward dye [31]. Gibb's free energy of the process at all temperatures was positive for OP and this indicates for non-spontaneous process but it has negative value for SOP at all temperature and this indicates for spontaneous process.

Conclusions

1- The SOP proceeds via the modification of OP have been successfully utilized for the removal of MB dye from an aqueous solution via the surface adsorption process involving the electrostatic attraction mechanism (physical adsorption). The MB dye-adsorption on the surfaces of OP and SOP at equilibrium is strongly governed by the contact time, initial MB dye concentration, and initial pH –solution, respectively.

2- Effects of the experimental conditions on the both adsorbents (OP and SOP) were investigated. According to results, it was shown, that the maximum adsorption capacity of MB dye was found to be 14.164mg.g^{-1}for OP and 18.282 mg.g^{-1}for SOP, respectively. The effect of pH investigated for values ranging from 2 to 11, showed maximum adsorption of MB on the OP was at pH 4 and for SOP was at pH 9.

3- The Freundlich adsorption isotherms were demonstrated to give the best fit for the adsorption of MB dye onto both OP and SOP surfaces. On the other hand, The kinetics results conforms the best correlation of the experimental data of adsorption of dye on OP and SOP by pseudo second–order equation.

4- Thermodynamic functions of the adsorption reveal the exothermic nature of process as did the negative sign of enthalpy change ΔH, accompanied by negative sign of entropy change ΔS and for adsorption process was negative, indicating feasible and spontaneous adsorption of MB dye onto SOP surfaces.

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