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Removal of Methyl Orange from Aqueous Solutions by Adsorption Using Corn Leaves as Adsorbent Material

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ABTRACT

A comparative study was done on the adsorption of methyl orange dye (MO) using non-activated and activated corn leaves with hydrochloric acid as an adsorbent material. Scanning electron microscopy (SEM) and Fourier Transform Infrared spectroscopy (FTIR) were utilized to specify the properties of adsorbent material. The effect of several variables (pH, initial dye concentration, temperature, amount of adsorbent and contact time) on the removal efficiency was studied and the results indicated that the adsorption efficiency increases with the increase in the concentration of dye, adsorbent dosage and contact time, while inversely proportional to the increase in pH and temperature for both the treated and untreated corn leaves. The equilibrium data is best fitted to Freundlich isotherm for untreated adsorbent, while Langmuir isotherm show best agreement with the data when the treated adsorbent is used. The rate of adsorption was found to follow the pseudo first order kinetic model (PFO) when non-activated adsorbent is used, while the pseudo second order model (PSO) is fitted to the adsorption data using activated adsorbent.
Keywords: adsorption, methyl orange dye, corn leaves, adsorption isotherm, adsorption kinetics

إزالة صبغة الميثيل البرتقالية من المحاليل المائية عن طريق الامتزاز باستخدام أوراق الذرة كمادة مازة

الخلاصة

أجريت دراسة مقارنة على امتصاص صبغة الميثيل البرتقالية (MO) باستخدام أوراق الذرة غير المنشطة والمنشطة بحامض الهيدروكلوريك كمواد مازة. تم استخدام الماسح المجهري الإلكتروني (SEM) والتحليل الطيفي بالأشعة تحت الحمراء (FTIR) لتحديد خصائص المادة المازة. تمت دراسة تأثير العديد من المتغيرات (الأس الهيدروجيني، التركيز الابتدائي للصبغة، درجة الحرارة، كمية المادة المازة وزمن الامتزاز) على كفاءة الإزالة و بينت النتائج أن كفاءة الإمتزاز تزداد مع زيادة تركيز الصبغة و الجرعة الممتزة ووقت التلامس، بينما يتناسب عكسيا مع الزيادة في درجة الحموضة ودرجة الحرارة لكل من أوراق الذرة المنشطه وغير المنشطه. اظهرت نتائج بيانات التوازن توافقا مع Freundlich Isotherm عند استخدام المادة المازة غير المنشطه، في حين اظهر Langmuir Isotherm توافقا مع البينات عند استخدام المادة المازة المنشطه بالحامض. وجد بأن معدل الامتزاز يتبع معادلة حركيات الدرجة الأولى الزائفه (PFO) عندما يتم استخدام المادة المازة غير المنشطة، في حين يتبع معادلة حركيات الدرجة الثانية الزائفه (PSO) عند استخدام المادة المازة المنشطة.
الكلمات الرئيسية: امتزاز، المثيل البرتقالي، اوراق الذرة، نظام الامتزاز، حركيات الامتزاز.

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1. INTRUDCTION

Dyes are aromatic organic compounds that are used in dying and textile industries which cause severe problems to the humane health such as skin irritation or cancer **Geçgel, et al., 2016**. The wastewater from the final processing of textile industries reduces the quality of water resources and cause a major pollution problem since it contain complex aromatic molecular compounds. The issue in the polluted and colored wastewater is that it includes traces of the dyes which must be treated before discharge to their assigned sites. Adsorption is considered as the most suitable technique used to treat the polluted wastewater with the convenient adsorbent due to its high efficiency and simplicity **Chekwube and Dominic, 2017**.

Agricultural bio-waste are known to be the most common bio-sorbents due to their availability, cheapness and known as eco friendly to the environment used for the treatment of contaminated wastewater and solve environmental pollution problems. The adsorption of dyes by low cost bio-waste adsorbents had been studied by many researchers such as the adsorption of methylene blue by coconut leaves **Jawad, et al., 2015**, crystal violet by custard apple leaves **Rashmi, 2015** and rhodamine B by *Aleurites Moluccana* seeds **Postai, et al., 2016**.

Methyl Orange ($C_{14}H_{14}N_3NaO_3S$) is an azo dye which works as a pH indicator and frequently used in titrations because of its clear and distinct color change to yellow. It is also used for detecting microorganisms, treating dermatological diseases, dental materials, paints, pharmaceuticals, and textile industries. **Fig. 1** shows the chemical structure of methyl orange (MO) dye.

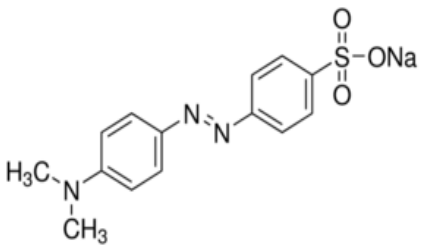


Figure 1. Chemical structure of MO dye

This study aims to characterize the adsorption of MO dye by using corn leaves as a low cost adsorbent and to make a comparison between activated and non-activated corn leaves for the adsorption process.Also, to study the effect of several factors (adsorbent dosage, concentration of dye, contact time, pH and temperature) on the adsorption process and to investigate the isothermal and kinetics studies.

2. MATERIALS AND METHODS

2.1. Preparation of the Dye

The stock solution of MO dye was prepared by dissolving 0.25 gm of powder MO in 250 ml distilled water then, by diluting the stock solution, different concentrations (10-50) mg/L of the dye were prepared.

2.2. Preparation of Adsorbent

At first, the corns were collected from the farms of Agriculture College, University of Baghdad. Then the leaves were separated and washed several times to get rid of dust and other impurities.The leaves were dried in the oven for 48 hr at 80^{o}C then grinded and sieved to get a particle size of <125 μm and dried again in the oven (Gemmy, Taiwan) at 70^{o}C overnight. The particles were divided into two parts; one of them was dried and used as adsorbent without treatment and the

other was mixed with 0.1% vol. HCl solution for 24 hr to activate it and then dried in the oven, both samples were stored in clean dried containers for further use.

2.3. Adsorption Study

A batch adsorption study was carried out using a full factorial design in which different amounts of the two samples (treated and untreated) dried corn leaves powder (0.5-0.25) gm were added to aqueous solutions of various concentrations of MO dye (10-50) ppm at an initial pH of 5.8 using 100 ml containers. The dye samples were shaken by using orbital shaker (JSR. Korea) at 150 rpm and room temperature with a contact time of 4 days. The effect of both of the pH and the temperature were investigated at the optimum conditions of the first set of experiments (30 ppm dye conc. and 0.2 gm adsorbent powder) in the ranges of 3-11 pH and 20-60℃ respectively. The dye equilibrium concentrations were calculated by measuring the absorbance using UV-spectrophotometer device (shmadzu, 1800) at a wave length of 484 nm. The plot of absorbance versus the concentrations is shown in **Fig. 2**.

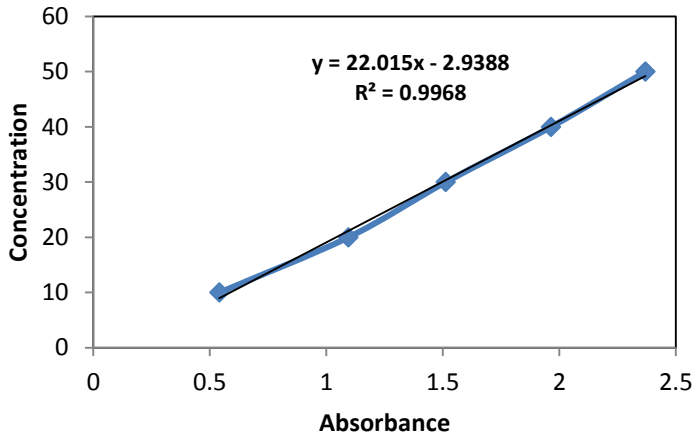


Figure 2. Absorbance versus concentration of MO dye at 484 nm wavelength

The dye removal efficiency and the amounts of adsorbate at equilibrium were calculated using the following equations:

$$\% \text{ removal} = \frac{Co - Ce}{Co} * 100 \qquad (1)$$

$$q_e = (C_o - C_e) * \frac{V}{M} \qquad (2)$$

where C_o and C_e are the initial and equilibrium concentrations of the dye (mg/L), respectively;
q_e is the equilibrium dye concentration on adsorbent (mg/g);
V is the volume of dye solution (L);
M is the mass of adsorbent (gm).

2.4. Isotherm Study

The results that obtained from the experimental work are examined by using Freundlich, Langmuir and Sips isotherms to describe the equilibrium relationship between the adsorbate dosage and the adsorbent uptake with time.

2.4.1. Langmuir isotherm

Langmuir assumes that a monolayer is formed at the maximum adsorption, which occurs on localised sites on the homogeneous surface **Cheung, et al., 2001**.
The Langmuir isotherm linear form can be represented by the following equation:

$$\frac{Ce}{q_e} = \frac{1}{K_l q_m} + \frac{Ce}{q_m} \quad \text{..... (3)}$$

where C_e is the equilibrium dye concentration (mg/L),
q_e (mg/gm) is the amount of dye adsorbed at equilibrium,
q_m (mg/gm) is the amount of dye adsorbed at saturation and K_l (g/l) is Langmuir constant.

2.4.2. Freundlich isotherm

Freundlich equation is used to describe distribution of solute between solid and aqueous phases at saturation **Baup, et al., 2000**. The Freundlich linear form can be expressed as:

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

where K_f $(g/l)^{1/n}$ and n are Freundlich constants, which give a measure of both intensity and capacity of adsorption respectively.

2.4.3. Sips isotherm

Sips isotherm is derived from the Freundlich and Langmuir isotherms. The model is used for localized adsorption without adsorbate interactions **Foo and Hameed, 2009**. At low equilibrium concentrations C_e, the Sips isotherm predicts the Freundlich adsorption characteristic, while, at high C_e, it effectively reduces to Langmuir monolayer isotherm .The Sips model is expressed as:

$$q_e = \frac{q_s k_s {C_e}^{1/n}}{1 + k_s {C_e}^{1/n}} \qquad (5)$$

where q_s (mg/gm), is the Sips maximum uptake of the adsorbate per unit mass of adsorbent;
K_s $(L/mg)^{1/n}$ is Sips constant related to energy of adsorption;
and n is the Sips parameter that characterizing the system heterogeneity.

2.5. Adsorption kinetic Study

Fitting the data that was obtained from the experimental work into different kinetic models such as Pseudo first order, Pseudo second order and Elovich equation can be used to study the adsorption rate, make a suitable model for the process and predict the required information about adsorbent/ adsorbate interaction **Martins, et al., 2013**.

2.5.1. Pseudo first order

The pseudo first order model can be expressed as:

$$\ln(q_e - q_t) = \ln q_e - (k_1)\, t \qquad (6)$$

where: q_e and q_t are the amounts of dye adsorbed (mg/gm) at equilibrium and time t (min) respectively;
k_1 is the rate constant of adsorption (min^{-1}).

2.5.2. Pseudo second order

Pseudo second order Kinetic is expressed by:

$$\frac{t}{q_t} = \frac{1}{(k_2\, q^2{}_e)} + \left(\frac{1}{q_e}\right) t \qquad (7)$$

Where k_2 (gm/mg.min) is pseudo second order constant.

2.5.3. Elovich's equation

The linear form of Elovich kinetic equation is expressed by:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \qquad (8)$$

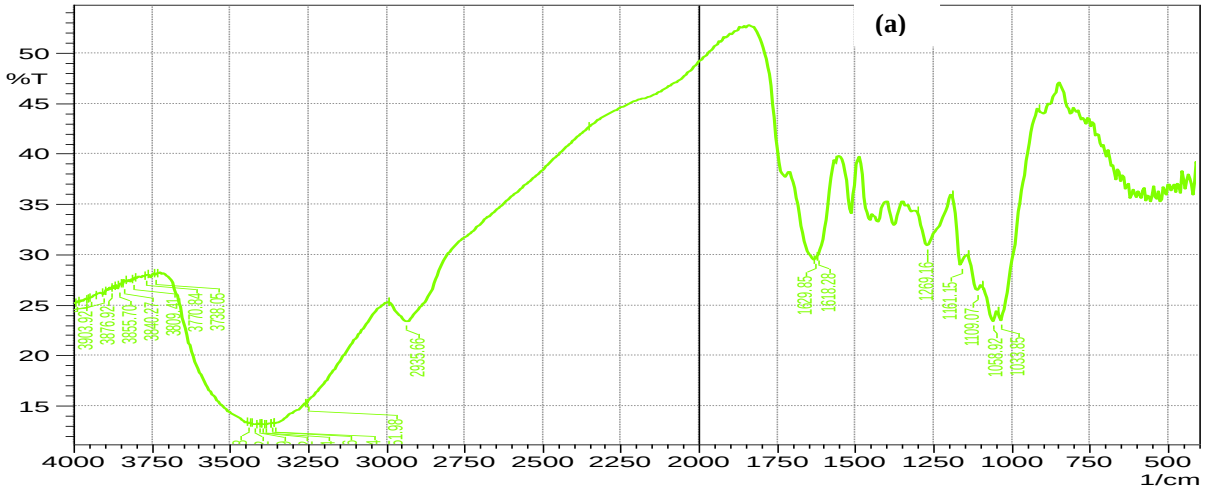
Where: q_t represents the amount of dye adsorbed at time t;
β I s the desorption constant and α the initial adsorption rate.

3. RESULTS AND DISCUSSION

3.1. Characterization of Corn Leaves

The chemical composition of the corn husk is 82.7% carbohydrates and 6.6% lignin **Barl, et al., 1991** which determines the existence of numerous hydroxyl groups and aromatic rings. FTIR spectrophotometer device was used to characterize the corn leaves and is presented in **Fig. 3a, a.1** and **3b, b.1**. Observing **Fig.3a** and **Fig.3b**, it can be seen that the functional OH group absorption at the region of (3250-3500) cm^{-1} stretching vibration in phenolic and aliphatic structures. The band at (2915-2930) cm^{-1} is assigned to C–H stretching vibration in aromatic methoxyl groups. The bands at 1629.85 cm^{-1} is characteristic for the aromatic skeleton vibrations. A prominent absorption peak of C=C stretch was observed at (1651-1658) cm^{-1} which refer to alkenyl group, also, C-O single bonds appear at around 1183 cm^{-1} **, Paşka, et al., 2014** . **Fig.3b** and **Fig.3b.1** shows obvious difference in the peak positions (1750-2000) cm^{-1} and (3000-3150) cm^{-1} and the intensity of the band is changed at some extent (1500-1650) cm^{-1} and (2250-2500) cm^{-1} due to the activation.

The Scanning Electron Microscopy (SEM) VEGA3 shows the morphological picture of the corn leaves particles which is luminous on the surface in **Fig. 4**.



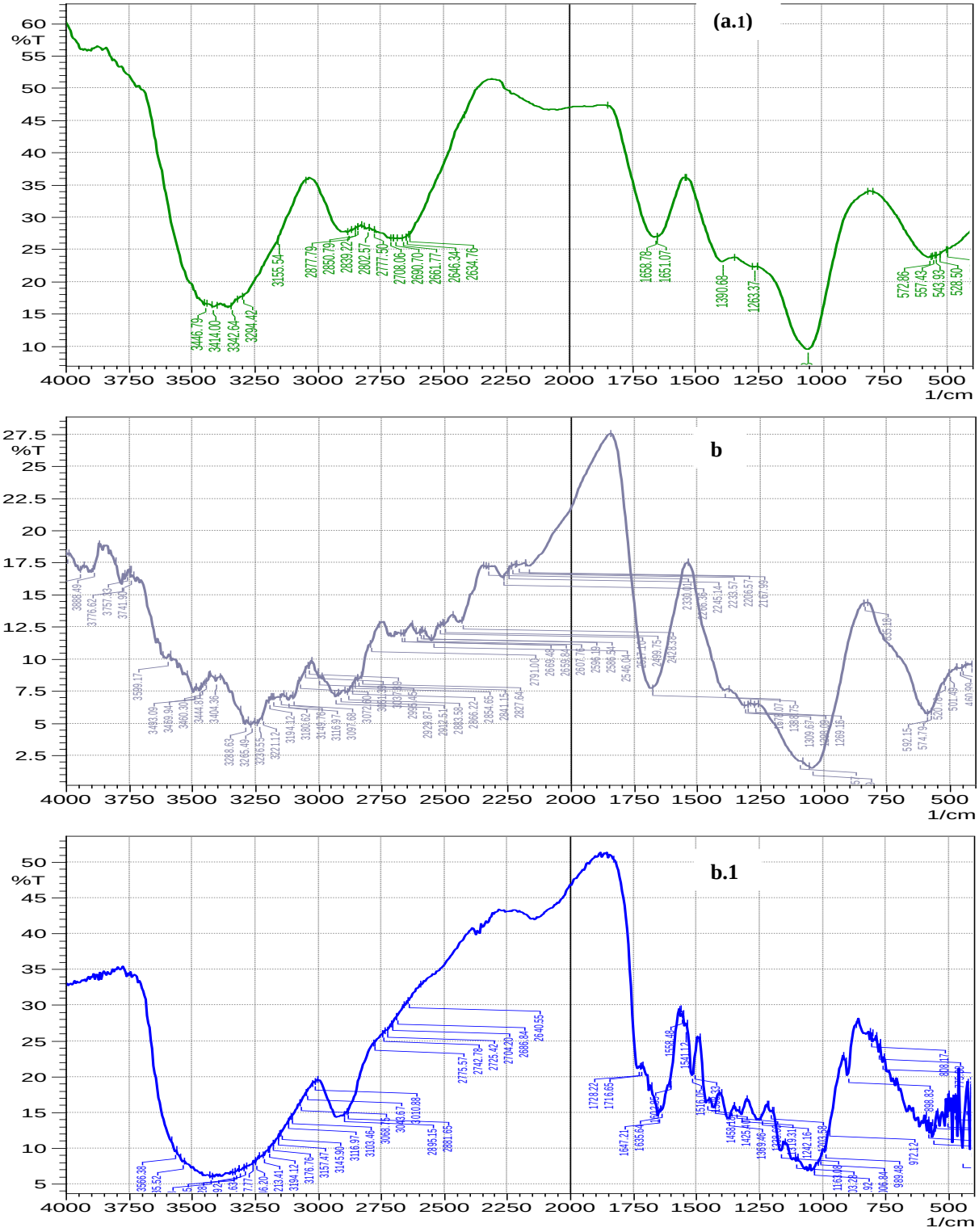


Figure 3. (a) FTIR spectrum of non-activated corn leaves adsorbent before and after adsorption and (b) FTIR spectrum of activated corn leaves adsorbent before and after adsorption

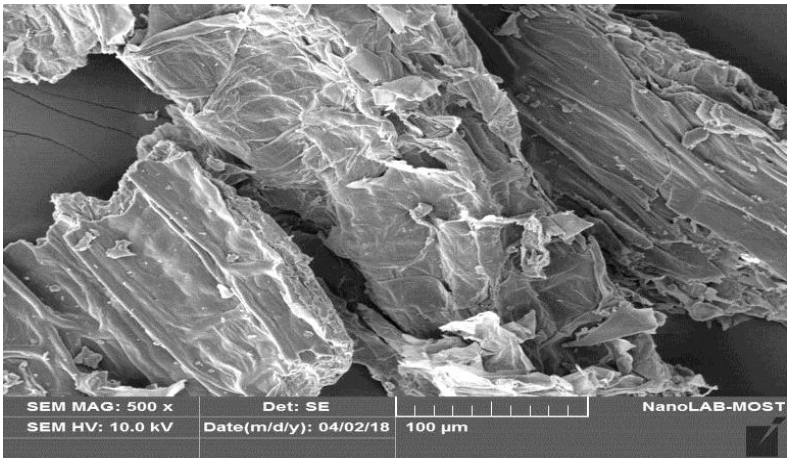


Figure 4. SEM image of corn leaves biosorbent.

3.2. Effect of MO concentration

The effect of MO concentration on sorption capacity is shown in **Fig. 5**. Increasing the concentration of the dye leads to increase the adsorption capacity and removal efficiency from 22% to 71% due to the increase in the ionic strength and mass transfer driving force which increases the adsorption of MO dye. After activation, the percentage removal increased to 93% which can be explained by the increase of the surface area and active sites at the adsorbent surface after activation. This result is in agreement with **Ghaedi, et al., 2012** and **Hazzaa and Hussein, 2015** and **Jawad, et al., 2015**.

3.3. Effect of adsorbent dosage

In the adsorption of MO using corn leaves, **Fig. 6** shows the effect of corn leaves dosage (with and without activation) on the adsorption of MO dye. For untreated corn leave, it was found that the percentage removal of the dye increases as the adsorbent dosage increase until it reaches the equilibrium point. After activation, the removal efficiency of the MO dye increases more rapidly due to the availability of the free active sites thus increases the surface area. The same conclusion was obtained by **Belay and Hayelom, 2014**.

3.4. Effect of contact time

Experiments were done to find out the effect of contact time on the adsorption of MO dye by activated and non-activated corn leaves. **Fig. 7** shows the effect of contact time on the adsorption of MO dye by activated and non-activated corn leaves adsorbent. The variation of contact time (1, 2, 3, 4 days) was investigated. As the time increases, the sorption capacity and the removal efficiency increase rabidly at the initial time then starts to be slower until it reaches the equilibrium point (day 4). This can be explained by the saturation of the active sites which do not allow for further adsorption to take place as proved by **Agarwal, 2013**.

3.5. Effect of pH

Fig. 8 shows the effect of pH on the adsorption of the dye by using activated and non-activated adsorbent. The effect of pH on the adsorption of MO dye was studied in the range of (3-11 step 2) by adjusting the samples using NaOH and HCl solutions. It is found that as the pH increases the adsorption capacity decrease and the removal efficiency decrease from (78.2% to 49.5%). This may be due to the surface functional groups and nature of the dye as **Kannan, et al., 2010** proved. For the activated corn leaves the removal efficiency also decreases (85% - 55%).

3.6. Effect of temperature

The effect of temperature was studied at the range of (20-60 step 10℃). The results in **Fig. 9** show that as the temperature increases, the removal efficiency decreases (49%-6%) and the adsorption capacity decreases for both activated and non-activated adsorbent. This can be explained by the weak bonds at high temperatures between the MO dye molecules and the active sites of the corn leaves adsorbent and because the adsorption is exothermic process. The results is in agreement with **Nwodika and Onukwuli, 2017**.

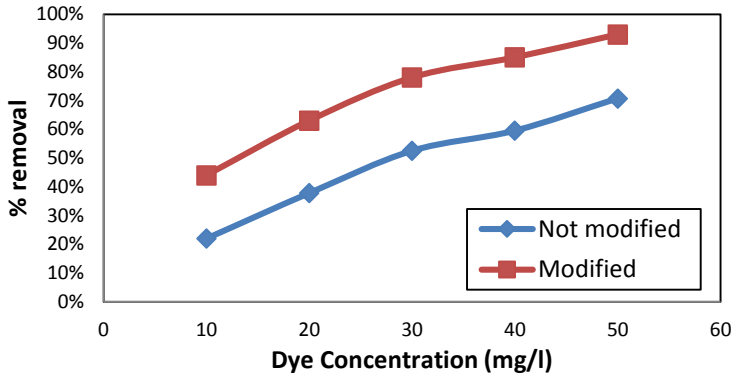


Figure 5. Effect of initial dye concentration on the percentage removal with and without activation pH 5.8, temp. 24℃, time 4 days and agitation speed 150 rpm

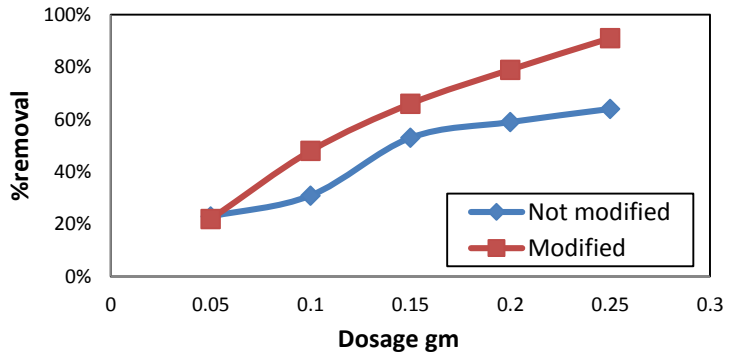


Figure 6. Effect of corn leaves dosage (with and without activation) on the percentage removal at pH 5.8, temp. 24℃, time 4 days, dye conc. 30ppm agitation speed 150 rpm

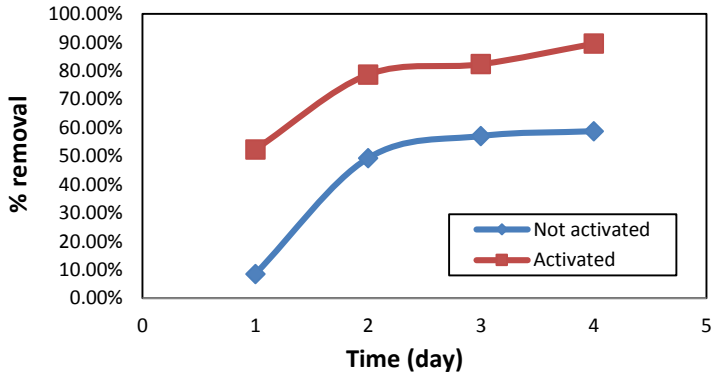


Figure 7. Effect of contact time on the percentage removal by activated and non-activated adsorbent at pH 5.8, dye conc. 30ppm, adsorbent dosage 0.2gm, agitation speed 150 rpm and temp. 24℃

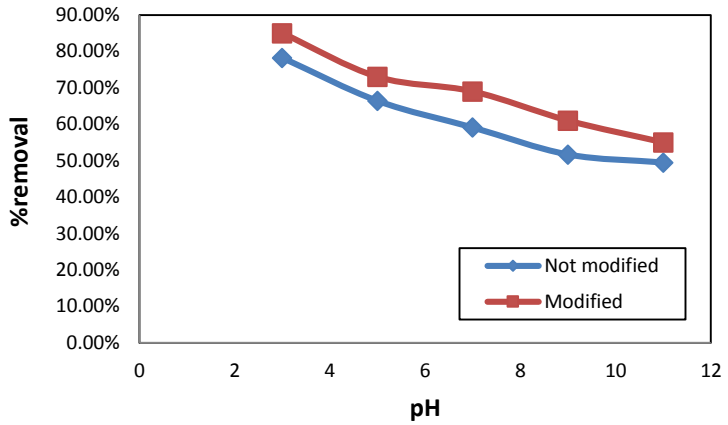


Figure 8. Effect of pH on the percentage removal by using both activated and non-activated corn leaves at temp. 24℃, time 4 days, dye conc. 30ppm, agitation speed 150 rpm and adsorbent dosage 0.2 gm

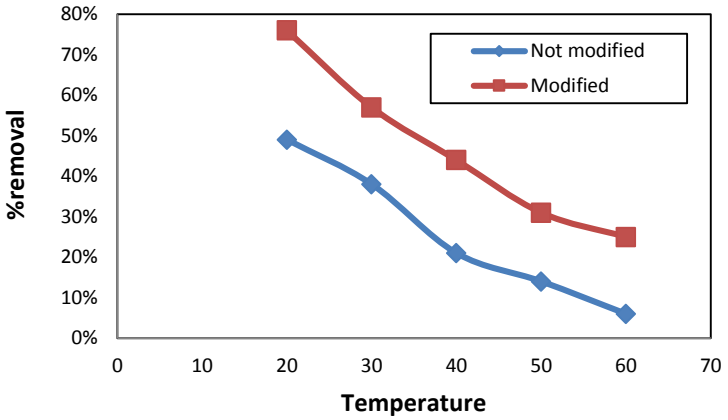


Figure 9. Effect of temperature on the percentage removal by using activated and non-activated corn leaves at pH 5.8, dye conc. 30ppm, adsorbent dosage 0.2 gm and Agitation speed 150 rpm,

4. ADSORPTION ISOTHERM

The equilibrium relations of the batch adsorption of methyl orange using corn leaves as adsorbent material were studied to specify the suitable isotherm. According to the relations in Eq. (3) through (5), regression analyses are conducted to calculate the model constants and the correlation coefficients.

Based on Langmuir isotherm the plot of C_e/q_e versus C_e gives the constant values k_l, q_m with the coefficient of determination R^2 as shown in **Fig. 10** and Table 1. The observed data did not agree with Langmuir isotherm according to R^2 value.

In the assumption of Freundlich and Sipes isotherms, regression analyses using Gauss-Newton's method was used to find the values of the constants which give the results fixed in Table 1 column 2 and assure that the adsorption fit with Freundlich adsorption isotherm with R^2 value of 0.9645.

Identical steps of the above analyses were implemented to specify the adsorption isotherm model that fit the observed data of the adsorption process using corn leaves activated with HCl. Results are shown in **Fig. 11** and Table 1 column 3 which confirmed that Langmuir isotherm is the most reliable model with the studied process. This means a change in the behavior of the adsorption process occurred after the activation of the adsorbent material (corn leaves) with hydrochloric acid from Freundlich to Langmuir isotherm.

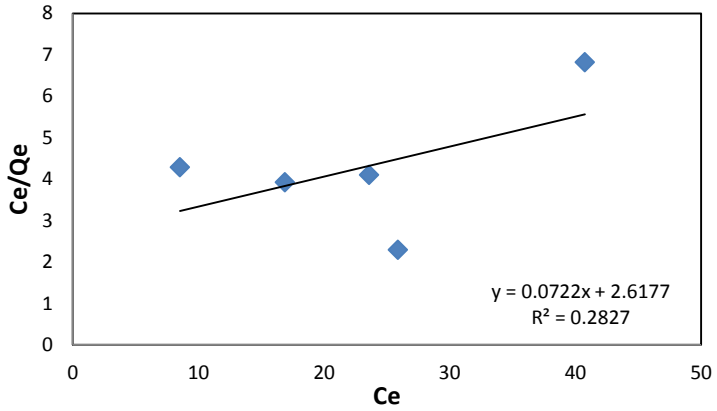


Figure 10. Fitting the adsorption data using non-activated adsorbent to Langmuir isotherm

Table 1. The adsorption isotherm parameters for MO removal using corn leaves at 30℃

Langmuir	$C_e/q_e = 1/k_L q_m + C_e/q_m$	
Parameter	Without Activation	With Activation
q_m	13.8504	4.9309
K_L	0.0276	-1.3938
R^2	0.2827	0.9157
Freundlich	$\ln q_e = \ln K_F + 1/n \ln C_e$	
n	0.9699	-3.3819
K_f	0.2426	9.8529
R^2	0.9645	0.3984
Sips	$q_e = (q_s K_s C_e^{1/m}) / (1+ K_s C_e^{1/m})$	
K_s	0.00009	318846.6
m	0.2814	23938.1
R^2	0.7128	--

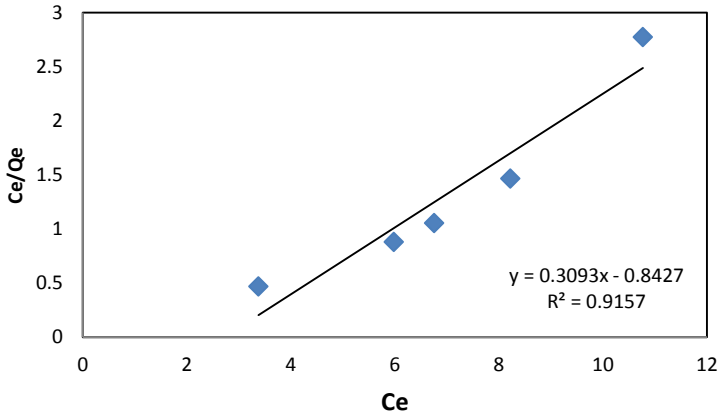


Figure 11. Fitting the adsorption data using activated adsorbent to Langmuir isotherm

5. ADSORPTION KINETICS

Three models, pseudo first order, pseudo second order and Elovich's equation were used to study the adsorption kinetics of MO dye on the corn leaves as adsorbent. Correlation coefficient (R^2) was used to express the conformity between the kinetic models and the experimental data.

Kinetic plots were represented in **Fig. 12**, **13** and **14** for non-activated corn leaves. The plot of ln (qe-qt) versus time gives a straight line for the (PFO), while (t/qt) versus time plot gives the (PSO) representation and its linear parameters. Elovich's kinetic equation can be shown in a plot of (qt) against ln(t).
From R^2 values of the three figures, it is clearly found that the adsorption process follow the PFO kinetics.

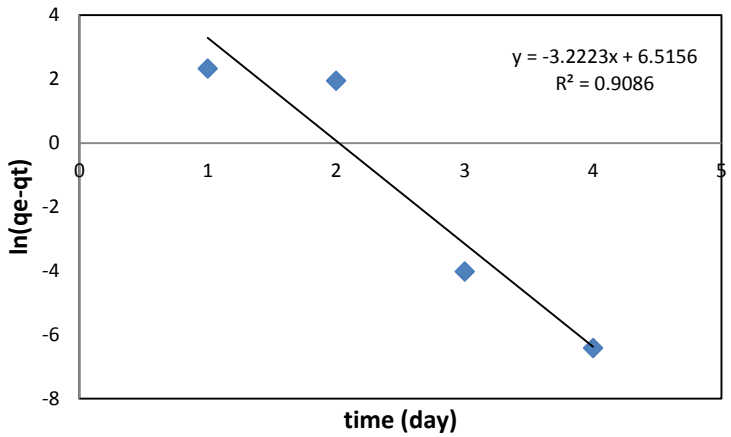


Figure 12. Pseudo first order plot of MO adsorption by non-activated corn leaf

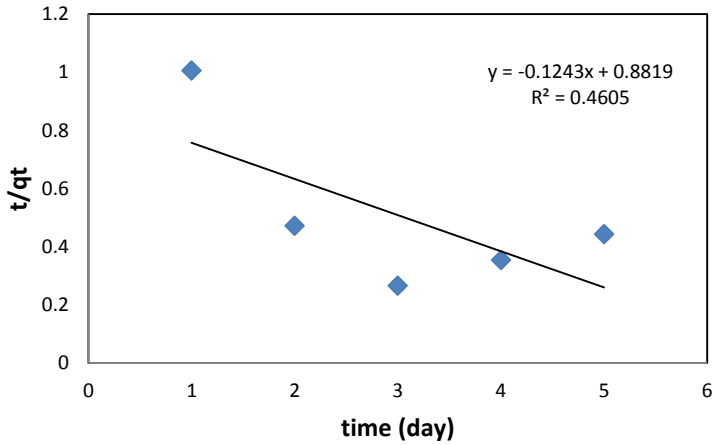


Figure 13. Pseudo second order plot of MO adsorption by non-activated corn leaf

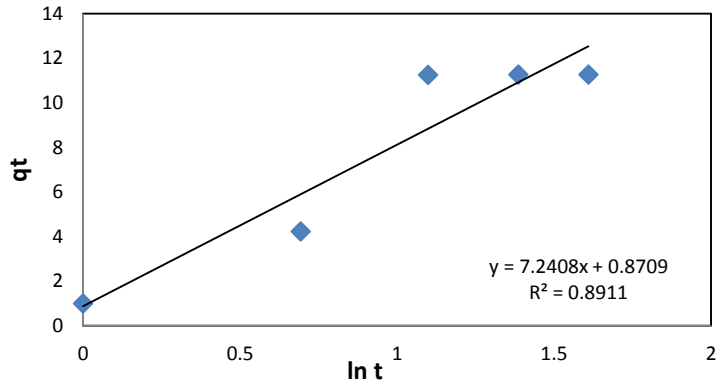


Figure 14. Elovich's plot of MO adsorption by non-activated corn leaf

In order to show the difference in the process behavior between the two cases (with and without activation), the same approach above are used to represent adsorption kinetics of MO using activated corn leaves with HCl as in **Fig. 15-17**.

Table 2 shows the models parameters and their correlation coefficients in the two cases using non-activated and activated adsorbent with HCl.

From the obtained results it is concluded that the adsorption kinetics behavior was changed from the PFO to the PSO when the adsorbent material was activated. This means that an increase in the process rate occurred with the activation using acidic medium due to the increase in the number of active sites and the surface area of contact between the adsorbent and adsorbate.

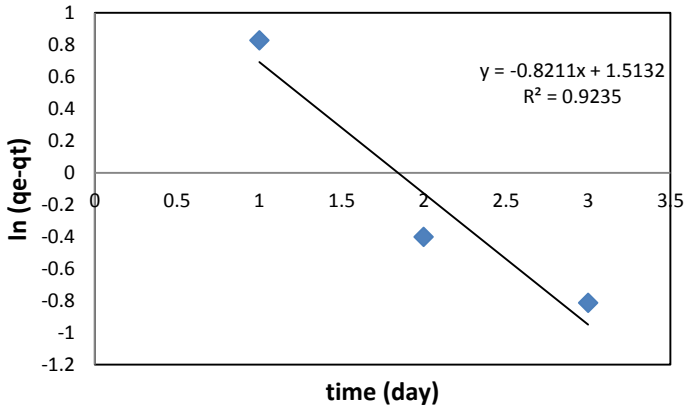


Figure 15. Pseudo first order plot of MO adsorption by activated corn leaf

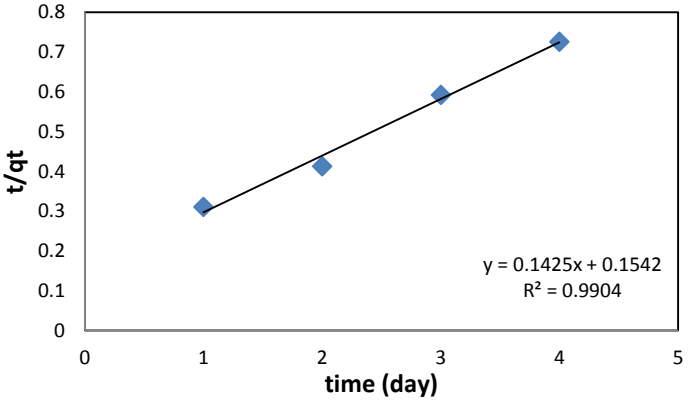


Figure 16. Pseudo second order plot of MO adsorption by activated corn leaf

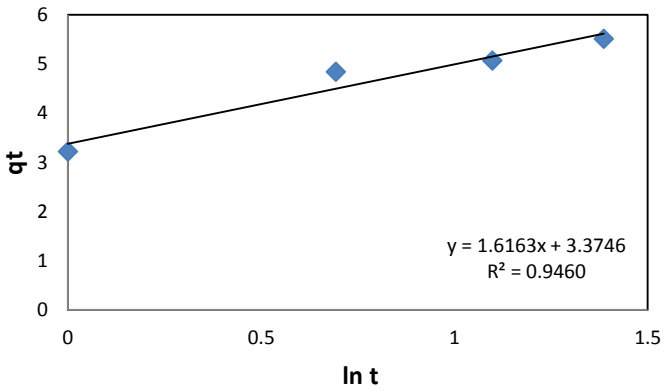


Figure 17. Elovich's plot of MO adsorption by activated corn leaf

Table 2. Kinetic parameters with R^2 for MO adsorption using non-activated and activated adsorbent

Pseudo first order $\ln(q_e-q) = \ln(q_e) - K_1 t$		
Parameter	Without Activation	With Activation
q_e	675.599	4.5412
k_1	3.2223	0.8211
R^2	0.9086	0.9235
Pseudo second order $t/q = (1/k_2 q_e) + (1/q_e) t$		
q_e	-8.0450	7.0175
k_2	-0.1409	0.9241
R^2	0.4605	0.9904
Elovich $q_t = (1/\beta) \ln (\alpha \beta) + (1/\beta) \ln (t)$		
α	8.1666	13.0396
β	0.1381	0.6187
R^2	0.8911	0.946

6. CONCLUSIONS

- Corn leaves can be used as cheap, available, ecofriendly and efficient bio-waste adsorbent for the removal of MO dye from aqueous solutions.
- The percentage removal of the dye increases as the concentration of the dye and the adsorbent dosage increases until it reaches the equilibrium point.
- As the adsorption time increased, the sorption capacity and the removal efficiency increases rapidly at the initial time then starts to be slower until it reaches the equilibrium point.
- After activation, the percentage removal increased in the three cases above as compared with the non-activated adsorbent.
- It is found that as the pH increase, the adsorption capacity and the removal efficiency decrease.
- The results show that, as the temperature increases, the removal efficiency decrease and the adsorption capacity decrease for both activated and non-activated adsorbent use.
- The equilibrium data is best fitted to Freundlich isotherm for the untreated adsorbent, while Langmuir isotherm show best agreement with the data when the treated adsorbent is used.
- The rate of adsorption was found to follow the pseudo first order kinetic model (PFO) when non-activated adsorbent is used, while the pseudo second order model (PSO) is fitted to the adsorption data using activated adsorbent i.e. a change in the adsorption behavior which increase the rate due to the adsorbent activation.

NOMENCLATURE

C_e = equilibrium concentration of adsorbate, mg/L

C_o = influent concentration, mg/L

FTIR = fourior Transform Infrared spectroscopy

k_1 = rate constant of adsorption of Pseudo First Order, min^{-1}

k_2 = rate constant of adsorption of pseudo second order, g/mg·min

k_f , n = freundlich constants, dimensionless

k_l = langmuir constant, L/mg

k_s = sips constant related to energy of adsorption, $(L/mg)^{1/m}$

m = sips parameter, dimensionless

M = mass of adsorbent, (gm)

MO = methyl Orange

PFO = pseudo First order

PSO = pseudo second order

q_e = the uptake of adsorbate at equilibrium, mg/g

q_m = amount of adsorbate required to form a monolyer, mg/g

q_s = sips maximum uptake of the adsorbate per unit mass of adsorbent, mg/g

q_t = amounts of the adsorbent at time t, mg/g

SEM = scanning Electron Microscopy

V = volume of solution, (L)

α = initial adsorption rate, dimensionless

β = desorption constant, dimensionless

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