# Adsorption of basic dyes by Low Cost Agricultural (Olive Solid Wastes)

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**Abstract:**

Dyes are usually present in trace quantities in the treated effluents of many industries. The effectiveness of adsorption for dye removal from wastewaters has made it an ideal alternative to other expensive treatment methods. The removal of color from aquatic systems caused by presence of synthetic dyes is extremely important from the environmental viewpoint. The effectiveness of dye adsorption from wastewater has made to get alternative different low cost adsorbent to other expensive treatment methods. The ability of an unconventional bio-adsorbent, Olive Solid Wastes (OSW) for the adsorption of methylene blue (MB) from aqueous solution was studied. The effects of different system variables, adsorbent dosage, initial dye concentration, agitation speed, solution pH and contact time were studied. The results showed that as the amount of the (OSW) was increased with decreasing pH solution, (OSW) dose, contact time, and agitation speed whereas, the amount of MB removed increases with increasing initial MB concentration. Equilibrium data fitted very well with the Freundlich isotherm model, confirming the monolayer adsorption capacity of methylene blue onto (OSW) with a monolayer adsorption capacity of 56.65 mg/g. The results also showed that the process follows by pseudo second-order kinetics model.

**Key-words:** Methylene blue, Adsorption, Olive Solid Wastes.

**الملخص:**

وجود ملوثات الأصباغ في مجاري المياه العادمة اصبح من المشاكل الكبيرة على الإنسان والبيئة. لذلك تعتبر إزالة الأصباغ من مياه المخلفات الصناعية مسألة ذات أهمية كبيرة في مجال تلوث المياه. النفايات الزراعية متجددة ومتوفرة بكثرة بدون تكلفة أو بتكلفة منخفضة. تم استخدام العديد من أنواع المنتجات الزراعية الثانوية لإزالة الميثيلين الأزرق من محلولها. تمت في هذه الدراسة قدرة نفايات الزيتون الصلبة لامتصاص الميثيلين الأزرق تحت عدة تأثيرات مختلفة مثل جرعة الممتز، و تركيز الصبغة المبدئي، و سرعة التفاعل، والأس الهيدروجيني. و أظهرت النتائج أنه تزداد كمية المتزاز مع تناقص تأثير كل من والأس الهيدروجيني و جرعة الممتز، وسرعة التفاعل، بينما تزداد الكمية مع تزايد تركيز الصبغة المبدئي. تتوافق بيانات التوازن جيدا مع نموذج العالم فرندلش الحراري بسعة امتصاص أحادية تبلغ 56.65 مجم / جم. كما أظهرت النتائج أيضا أن هذه العملية تتبع نموذج حركي من الدرجة الثانية.

**Introduction**:

Water is a source of life and energy, although millions of people worldwide are suffering with the shortage of fresh and clean drinking water. The main sources of freshwater pollution can be attributed to discharge of untreated sanitary and toxic industrial wastes, dumping of industrial effluent, and run off from agricultural fields[1] . Wastewater effluents from many industries, including paper, leather, textiles, rubber, plastics, printing, cosmetics, pharmaceuticals and food contain several kinds of synthetic dyestuffs [2]. Dye The presence of even very low concentrations in discharge effluents to the environment is worrying for both toxicological and esthetic reasons [2]. To reduce the negative effects of dye contaminated wastewater on humans and the environment, the wastewater must be treated carefully before discharge into main streams [2].

Many types of day are discharging from the industry; methylene blue (MB) is the one of these dyes. Methylene blue is the most general water-soluble dye, generally used for dyeing leather, cotton, printing, calico, and tannin [3]. Although this dye is not greatly toxic to human, it can cause eye and skin irritation, systemic effects including cyanosis and blood changes[3] . It may because nausea, vomiting, profuse sweating, diarrhea, gastritis and mental confusion[3] . With the ever increasing use of water for municipal and industrial purposes, it has become more important to appraise water quality on a continuous basis. Water treatment process selection is a complex task involving the consideration of many factors which include, available space for the construction of treatment facilities, reliability of process equipment, waste disposal constraints, desired finished water quality and capital and operating costs[4] . The treatment of wastewaters to make them suitable for subsequent use requires physical, chemical and biological processes[1] .

A number of technologies are available with varying degree of success to control water pollution. Some of them are coagulation, foam flotation, filtration, ion exchange, aerobic and anaerobic treatment, advanced oxidation processes, solvent extraction, adsorption, electrolysis, microbial reduction, and activated sludge [3]. However, most of them require substantial financial input and their use is restricted because of cost factors overriding the importance of pollution control. Among various available water treatment technologies adsorption processes considered better because of convenience, ease of operation and simplicity of design. Furthermore, this process can remove and minimize different type of pollutants and thus it has a wider applicability in water pollution control[1] . Adsorption refers to the accumulation of a substance at the interface between two phases such as solid and liquid or solid and gas. The substance that accumulates at the interface is called adsorbate and the solid on which adsorption occurs is adsorbent[1]. The adsorption process has been widely used for the removal of solutes from solutions and gases from air atmosphere[6]. Many numbers of materials have been extensively investigated as adsorbents in water pollution control. Activated carbon has undoubtedly been the most popular and widely used adsorbent in wastewater treatment throughout the world. Charcoal, the forerunner of modern activated carbon has been recognized as the oldest adsorbent known in waste water treatment. The product obtained is known as activated carbon and generally has a very porous structure with a large surface area [7]. Activated carbon has been found to be a versatile adsorbent, which can remove diverse types of pollutants such as metal ions anions dyes, phenols, detergents, and many other chemicals and organisms. In spite of abundant uses of activated carbon, its applications are sometime restricted due to its higher cost. Therefore, researchers are looking for low-cost adsorbents for water pollution control, where cost factors play a major role. As such, for quite some time, efforts have been directed towards developing low-cost alternative adsorbents. Low-cost alternative adsorbents can be prepared from a wide variety of raw materials, which are abundant and cheap. The preparation of low-cost adsorbents from waste materials has several advantages, mainly of economic and environmental nature[8]. A wide variety of low-cost adsorbents have been prepared from different waste materials utilizing agricultural as well industrial and municipal wastes[1].

The main objective of this study is use the treated Olive Stone Waste (OSW) as low cost alternative to remove methylene blue dye from its solutions.

**Material and Methods :**

**Adsorbent :**

Libya is one of the Mediterranean see countries producing high amounts of olive oil. This production generates a significant amount of olive solid wastes (OSW), which consists of skin, pieces of pit, and pulp of the olives and a small amount of olive oil. The utilization of OSW as a low-cost sorbent is therefore beneficial for in removal of basic dyes from aqueous solutions by adsorption process. The OSW was obtained from a traditional olive oil extraction plant in Sabratha, Libya. It was dried in oven after washed by deionized water, then crushed into powder, and sieved.

**Adsorbate and other chemicals :**

The basic cationic dye, Methylene Blue (MB), was tested as the adsorbate in this study. The formula of methylene blue is $C_{16}H_{18}N_3SCL.3H_2O$, and molecular weight is (319.85 g). It was used without further purification. The stock dye solution was prepared by dissolving (1 g) of methylene blue in (1000 ml) distilled water. The experiment solutions were obtained by diluting the stock dye solution with deionized water to give the appropriate concentration of the experiment solutions. The pH measurements were done using orient pH meter. The SP-2800 UV/VIS spectrophotometer was used to determine the concentration of MB in solution. A calibration curve was also plotted between absorbance and concentration of dye solution to obtain absorbance concentration profile. Unknown MB concentration was measured using calibration curve.

**Set Up Process** :

Adsorption measurement was determined by batch experiments of known amount of the adsorbent with 50 ml of aqueous methylene blue solutions of known concentration in a series of 250 ml conical flasks. The mixture was shaken at a constant temperature Orbital Shaker Incubator at 100 rpm at for 120 min. At predestined time, the bottles were withdrawn from the shaker, and the residual dye concentration then measuring the absorbance of the supernatant at the wave length that correspond to the maximum absorbance of the sample. Dye concentration in the reaction mixture was calculated from the calibration curve.

**The Theory of Basic:**

The amount of dye adsorbed (OSW) powder at time t is $q_t$ (mg/g) which was calculated by the following mass balance equation[10]

$$q_t = \frac{(C_0 - C_t)}{m} \qquad \text{(Eq.1)}$$

And the dye removal efficiency, i.e. % of Adsorption was calculated as:

$$\%Adsorption = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad \text{(Eq.2)}$$

Where: $C_0$ is the initial dye concentration (mg $L^{-1}$), $C_t$ is the concentration of dye at any time t, V is the volume of solution (liters), and m is the mass of OSW powder in grams.

**Dye Adsorption Kinetic Mechanism:**

The controlling mechanisms of adsorption process such as chemical reaction, diffusion control or mass transfer coefficient are used to determine by kinetic models. The kinetics of dyes adsorption onto adsorbent materials is prerequisite for choosing the best operating conditions for the full-scale batch process. The study of adsorption kinetics illustrates how the solute uptake rate and obviously this rate controls the residence time of the adsorbate at the solution interface. The kinetics of anionic and cationic dye onto various adsorbent materials was analyzed using different kinetic models which are presented below[11].

**Application of Lagergren pseudo-first-order model:**

The linearized integral form of the Pseudo-first-order Model generally expressed as:

$$Log(q_e - q_t) = Log q_e - \frac{K_1}{2.303} t \qquad \text{(Eq.3)}$$

Where: qt and $q_e$ are the adsorption capacity at time t and at equilibrium, respectively (mg $g^{-1}$), $k_1$ is the rate constant of pseudo-first-order adsorption ($min^{-1}$) and t is the contact time (min) .

To plot $\log(q_e - q_t)$ versus t give a linear relationship from which $k_1$ and predicted $q_e$ can be determined from the slope and intercept of the plot.

**Application of Lagergren Pseudo-second-order:**

The linearized integral form of the Pseudo-second-order Model generally expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{1}{q_e} t \qquad \text{(Eq.4)}$$

The plot of t/qt versus t shows a linear relationship. Values of $k_2$ and equilibrium adsorption capacity $q_e$ were calculated from the intercept and slope of the plot of t/qt versus t according to equation (Eq.4).

**Application of Adsorption Isotherm Models on dye adsorption:**
The adsorption isotherm is significant for the explanation of how the adsorbent will interact with the adsorbate and give an idea of adsorption capacity. They play an important role to understanding the mechanism of adsorption [12].

**Langmuir Adsorption Isotherm Model:**
The linearized form of Langmuir isotherm that can be written as;

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_a q_m} \qquad \text{(Eq.5)}$$

Where: $q_e$ is the amount of dye adsorbed at equilibrium time (mg/g), $C_e$ is equilibrium concentration of dye in solution (mg $L^{-1}$ ), $q_m$ is maximum adsorption capacity (mg/g) and $K_a$ is isotherm constants for Langmuir (L $mg^{-1}$ ). The slop and intercept of plot between $C_e$ / $q_e$ vs. $C_e$ will give $q_m$ and $K_a$ respectively.

**Freundlich Adsorption Isotherm Model:**
The linearized form of Freundlich can be expressed as;

$$Lnq_e = LnK_f + \frac{1}{n}(LnC_e) \qquad \text{( Eq.6)}$$

Where: $q_e$ is the amount of metal ion adsorbed at equilibrium time (mg/g), $C_e$ is equilibrium concentration of dye in solution (mg $L^{-1}$ ). $K_f$ is the capacity of the adsorbent and n is the intensity of adsorption constant for Freundlich. The plot of $Lnq_e$ versus $LnC_e$ is employed to determine the $K_f$ and n from intercept and slope respectively.

**Result and Discussion:**
**Concentration calibration curve:**
The spectrophotometer SP-2800 UV/VIS was used to measure the concentration of MB dye in solution. The calibration curve was plotted between the absorbance and concentration of MB dye solution to obtain the linear calibration equation as shown in

Figure 1. The concentration of the MB dye at any time will be measured from the calibration curve.

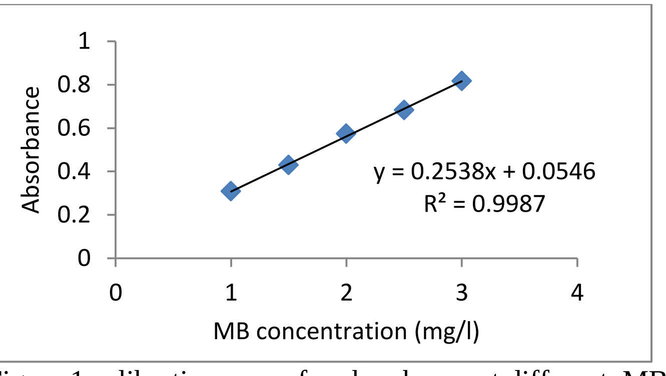


Figure 1 calibration curve for absorbance at different MB

## Factors Affecting Adsorption of Dye

### Effect of solution pH

The effect of solution pH on the MB dye adsorption solution was studied in the pH of 5,7,9 and 11 as shown in Figures (2 and 3) It was found that the amount of dye adsorbed $q_t$ (mg/g) and percentage dye removal were increased with the decrease of solution pH. At acidic pH, the electrostatic repulsion gives poor adsorption between MB dye and positively charged adsorbent surface. In addition, higher adsorption of methylene blue at acidic pH might be due to the presence of excess $H^+$ ions.

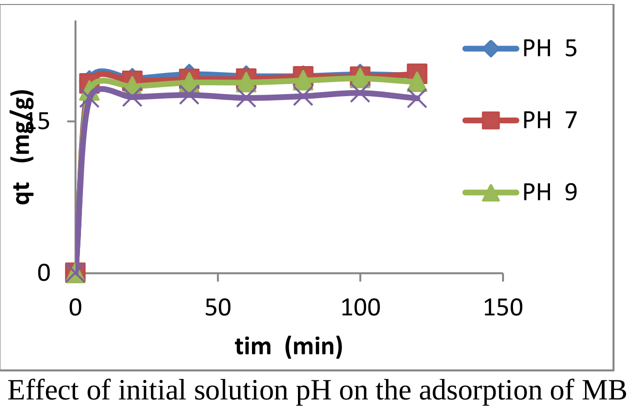


Figure 2 Effect of initial solution pH on the adsorption of MB dye on OSW.

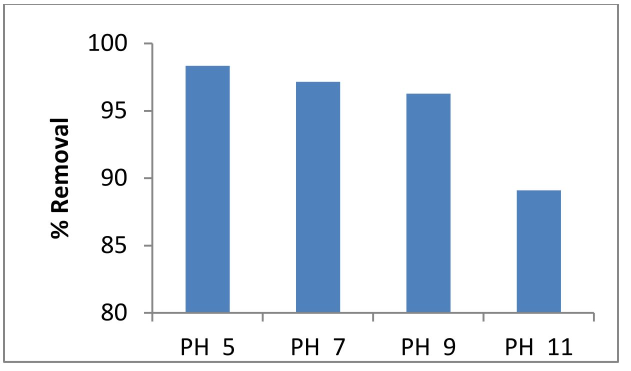


Figure 3 percentage dye removal for initial solution pH on the adsorption of MB dye on OSW.

## Effect of Initial Dye Concentration

The initial dye concentration has a significant effect of dye removal from its aqueous solutions. MB dye concentration was 10,15,20, and 25 mg/L The effects of various initial MB dye concentration on the amount of dye adsorbed qt (mg/g) and percentage dye removal were studied and results are presented in Figures 4 and 5 respectively. It was observed that the amount of adsorption capacity qt (mg/g) and percentage dye removal were increased rapidly with increasing initial dye concentrations. The increase in initial concentration enhances the interaction between adsorbent and dye.

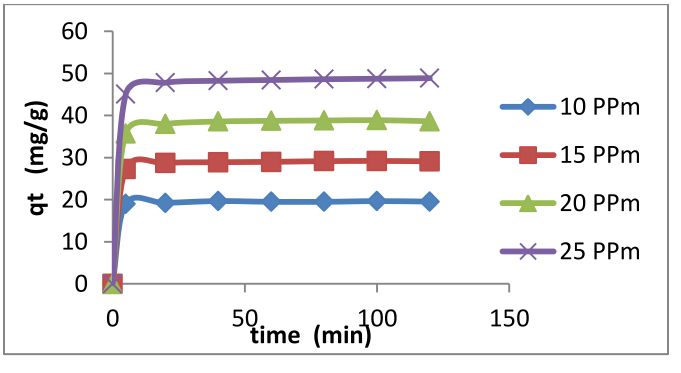


Figure 4Effect of Initial Dye Concentration on adsorption of MB dye on OSW

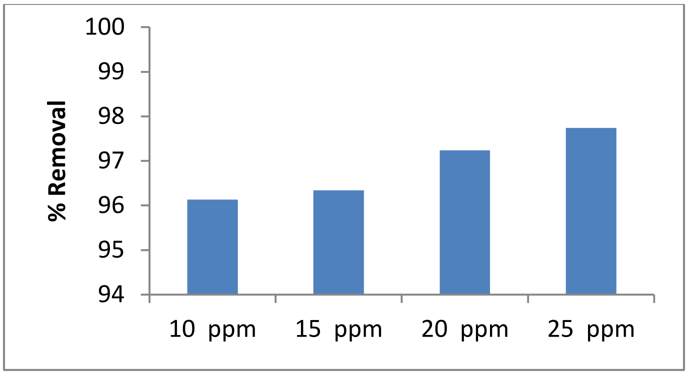


Figure 5 Percentage dye removal for Initial Dye Concentration on adsorption of MB dye on OSW

## Effect of adsorbent dose on adsorption

The effectiveness of OSW doses on MB dye adsorption were studied. Effect of various OSW doses of 20, 25, and 30 mg in the removal of MB dye from its solution were studied. Results are presented in Figure 6 and 7 respectively. The decreases in amount of dye adsorbed $q_t$ (mg/g) with increasing the adsorbent mass as shown in Figure 6 is due to the split in the flux or the concentration gradient between solute concentration in the solution and the solute concentration in the surface of the adsorbent. Doses lead to a very fast adsorption of MB dye on the adsorbent surface which gives a lower adsorbate concentration in bulk solution compared to low adsorbent dose situation. Thus, with increasing adsorbent dose, the amount of MB dye adsorbed per unit mass of adsorbent qt (mg/g) decreased. At lower adsorbent dose, the adsorbate dye molecules are more easily accessible hence the dye removal per unit mass of adsorbent is high.

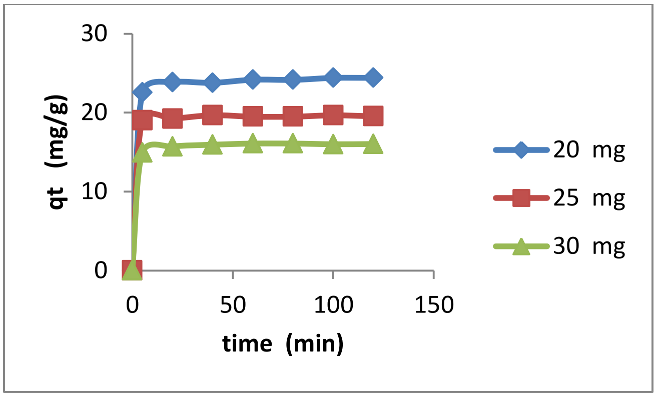


Figure 6 Effect of adsorbent dose on adsorption of MB dye on OSW.

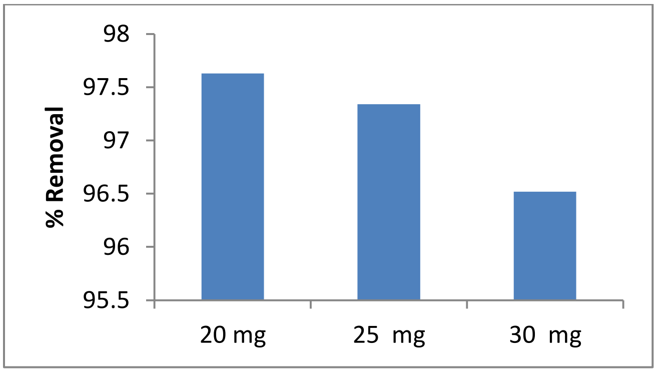


Figure 7 percentage dye removal of effect of adsorbent dose on adsorption of MB dye on OSW

## Effect of agitation speed

To determine the effect of agitation speed on the equilibrium adsorption, batch runs were conducted at different speeds ranging from 100 to 200 rpm. Figures 8 and 9 shows that the amount of adsorption and the percentage of dye adsorption increased as the agitation speed increased. This fact can be attributed to the decrease in turbulence and the decrease in boundary layer thickness around the adsorbent particles.

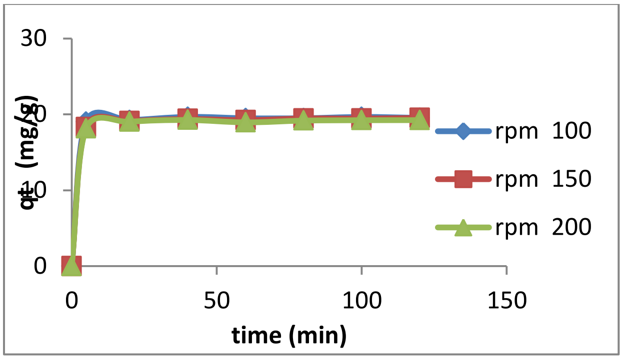


Figure 8Effect of agitation speed on adsorption of MB dye on OSW.

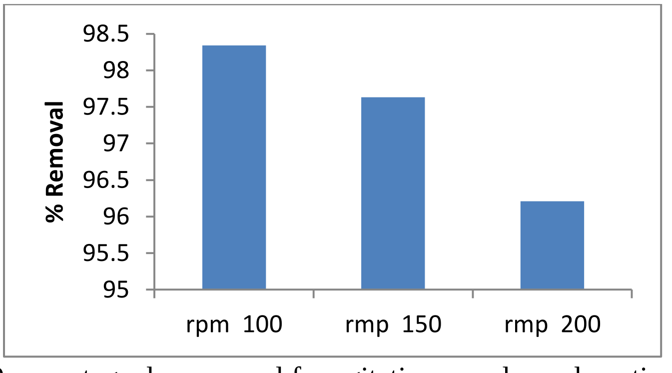


Figure 9percentage dye removal for agitation speed on adsorption of MB dye on OSW.

**Pseudo first order adsorption kinetics model**

The applicability of pseudo-first-order model was tested to investigate the adsorption nature of MB dye onto OSW as per equation (Eq.3). Experimental data at various physico-chemical process parameters were not fitted into Pseudo-first-order kinetic model. The calculated amount of MB dye adsorbed qe (mg/g) values were obtained from the intercept of the linearized form of the plot log (qe-qt) verses time (t) as shown in Figure 10 and 11.

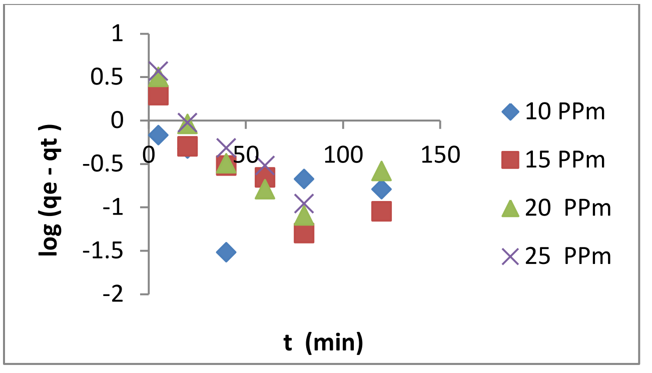


Figure 10 Pseudo-first-order kinetic model fitting for MB dye adsorption by OSW initial MB concentration.

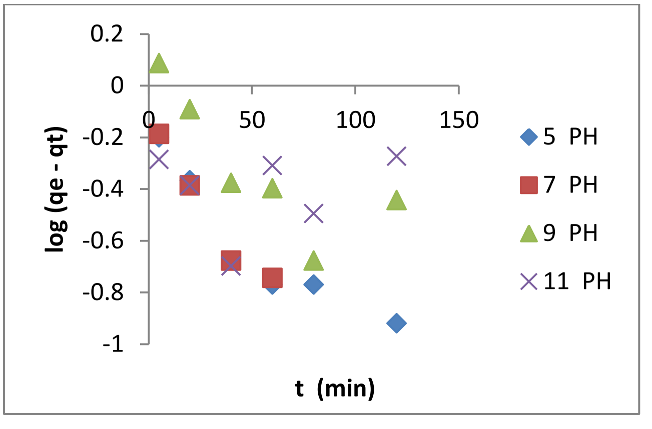


Figure 11 Pseudo-first-order kinetic models fitting for MB dye adsorption by OSW solution pH

## Application of pseudo-second order kinetic model

Pseudo-second-order kinetics model was applied to investigate the applicability of MB dye adsorption nature onto OSW as per equation (Eq.4). Experimental data were fitted into pseudo-second order kinetic model and the calculated amount of MB dye adsorbed qe (mg/g) values were obtained from the intercept of the linearized form where (t/qt) verses time (t) as shown in Figures 12 and 13.

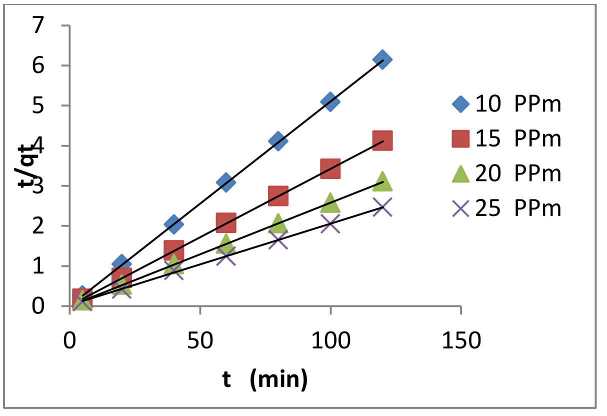


Figure 12 Pseudo- second t-order kinetic model fitting for MB dye adsorption by OSW initial MB concentration

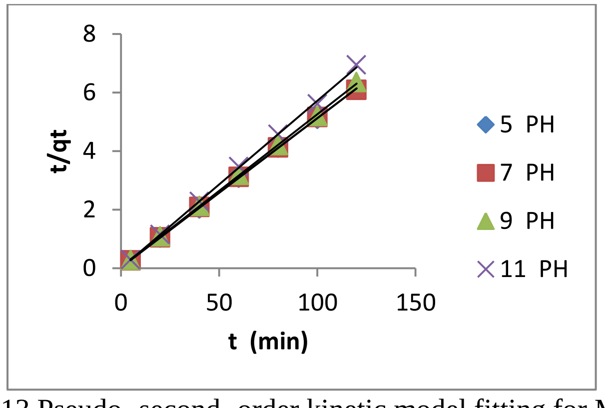


Figure 13 Pseudo- second -order kinetic model fitting for MB dye adsorption by OSW solution Ph

## Adsorption Equilibrium Isotherm Models

Equilibrium isotherm studies are important to describe how MB dye molecules interact with the OSW surface and determine the max adsorption capacity of adsorbent. The applicability of the isotherm equation is compared by judging the correlation coefficients, $R^2$. Figure 14 showed that the Langmuir isotherm model was not fitting for OSW adsorbent with low linear regression. The maximum monolayer adsorption capacity of OSW, $q_m$, and constant related to the binding energy of the sorption system, Ka, is calculated from the slop and intercept of this plot. The maximum monolayer adsorption capacity $q_m$ of OSW was 111 mg/g and the constant related to the binding energy of the sorption system Ka was 1.0 L/g .

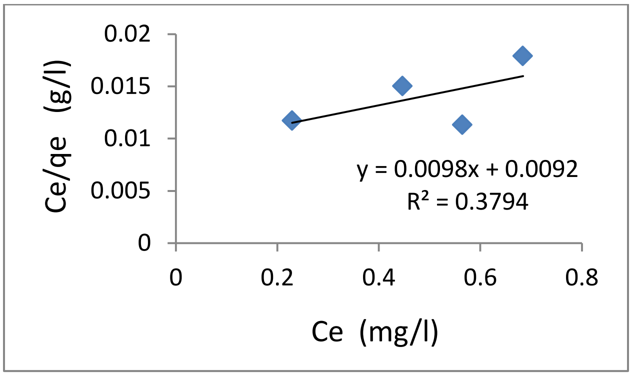


Figure 14 Langmuir plot: amount of adsorbent (OSW)

On the other hand, Freundlich isotherm fittings for OSW adsorbent are shown in Figure 15. The linear correlation coefficients $R^2$ was high. This mean the Freundlich model was the best comparing to Langmuir model, rate of adsorption, n and adsorption capacity $K_f$, are calculated from these plots, which is 1.656 and 56.65 mg/g, respectively.

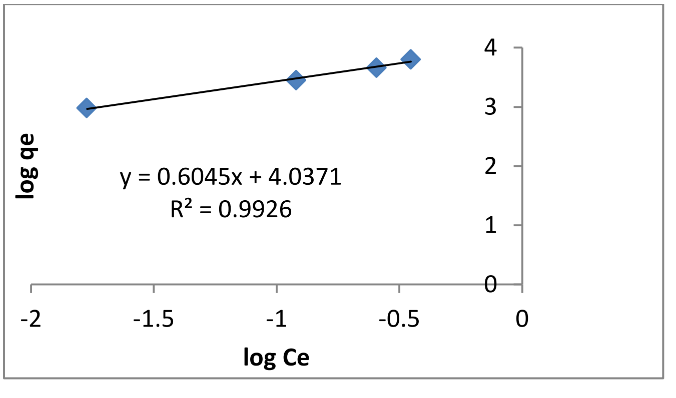


Figure 15 Freundlich plot: amount of adsorbent (OSW)

## Conclusion

The summary of the study that showed, the ability of Olive Solid Wastes (OSW) to remove Methylene blue from aqueous solution was investigated. We can conclude that the amount of MB removed by (OSW) increases with decreasing pH solution, (OSW) dose, contact time, and agitation speed but the amount of MB removed increases with increasing initial MB concentration. Equilibrium data fitted very well with the Freundlich isotherm model, confirming the monolayer adsorption capacity of methylene blue onto Olive Solid Wastes ~~(OSW)~~ with a monolayer adsorption capacity of 56.65 mg/g. The results also showed that the process follows by pseudo second-order kinetics model.

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