Adsorption of Malachite Green (MG) on Low Cost – Adsorbent from Aqueous Solution

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Abstract:
The use of cheap adsorbent has been studied as an alternative substitution of activated carbon for the adsorption of MG from its aqueous solution .
The low cost adsorbent Egg Shell Powdered (ESP) was successfully used for the sorption dyes from its aqueous solution .This study investigates the potential of egg shell powder as a low cost adsorbent for malachite green removal from its solution The equilibrium time was 60 min.
The effect of initial concentration for MG , sorption time on dye removal ,and dose of adsorbent was studied . The equilibrium sorption isotherms have been analyzed by the linear , Freundlich and Langmuir models.
The kinetics studies were provided with Pseudo first order.

الخلاصة

تضمن هذا البحث استخدام مادة مازه رخيصة الثمن مقارنة بالفحم التجاري المنشط في دراسة امتزاز صبغة المليخايت الخضراء من محلولها المائي هذه المادة ألمازة الرخيصة هي قشور البيض حيث تم استخدامها بنجاح في امتزاز الصبغة من محلولها المائي.

كذلك تم دراسة تأثير التركيز الأولي للصبغة وزمن الامتزاز وكمية المادة ألمازة وكذلك منحنيات الامتزاز تم دراستها وفقا لمعادلات فريوندلج ولانكماير. علما أن زمن الاتزان كان 60 دقيقة.

كذلك تم دراسة حركيات هذا التفاعل وكان يخضع لتفاعلات الرتبة الأولى الكاذبة.

Introduction

Egg shell powder (ESP) has not being in use as stabilizing material and it could be a good replacement for industrial lime , since its chemical composition is similar to that of lime. Chicken egg shell is a waste material from domestic sources such as poultries ,homes and fast food joints (Fajobi *etal* 2005).Subsequent findings revealed that ESP was used for stabilization of a cohesion less soil in Japan (Carlson *etal* 1999).Various physicochemical and biological Techniques can be employed to remove dyes from waste water. they include the coagulation/flocculation (Bianchi *et al 1998)* ,adsorption (Hela *et al* 2000), ion exchange (Bilba *et al i1997)*, advanced oxidation (chlorination, ozonation) (Hawkyard *et al* 2003), chemical reduction and biological treatment(bacterial and fungal biosorption ,biodegradation in aerobic or anaerobic conditions.(Wafra *et al* 2003).Synthetic dyes have been increasingly used in the textile, paper, rubber ,plastic cosmetics pharmaceutical and food industries because of their ease of use inexpensive cost of synthesis, stability and variety of color compared with natural dyes (Durrant *et al* 2001).Today there are more than 10,000 dyes available commercially (Merchant *et al* 2000), most of which are difficult to biodegrade due to their complex aromatic molecular structure and synthetic origin.(Seshdari *et al* 1994) The extensive use of dyes often poses pollution problems in the form of coloured wastewater discharge into environmental water boodles, which interferes with transmission of sunlight into streams therefore reduces photosynthetic activity. (Suba *et al* 2001).

Some dyes can cause allergic dermatitis, skin irrigation, cancer and mutation in man. Recent estimates indicate that, approximately, 12% of synthetic textile dyes used each year are lost during manufacture and processing operation and 20% of these dyes enter the environment through effluents that result from the treatment of residual industrial waters (Weber *et al* 1993). Numerous approach have been made by various researchers to develop cheaper and effective adsorbents to remove dyes from a variety of starting materials from waste (Hameed *et al* 2007).Many investigators have studied the feasibility of using inexpensive alternative materials like pearl millet husk, and coconut shell as carbonaceous precursors for removal of dyes from water and wastewater.(Salvarani 2000 , Raghavan *et al* 1995)

ESP was used to study the removal of dyes from aqueous solution , and the data were analyzed using Langmuir and Freundlich isotherm models.(Ibrahim *et al* 2007) The purpose of this work is to study the potential of egg shell powder as a low cost adsorbent for dye removal. Methylene blue (MG) chosen for this study because of its known strong adsorption onto solids. The structure of the methylene blue is given as below.

Experimental part

A stock solution of MG (500 ppm) [BDH with 99.9%] was prepared and diluted accordingly to the required initial concentration. Adsorption experiments were carried out by agitating a suitable adsorbent dosage with 25 mL of MG solution of the desired concentration at 75 rpm in a bench shaker (E4 ELA SHAKER, Tokyo RiKAKIKAI Co .,LTD.) at room temperature

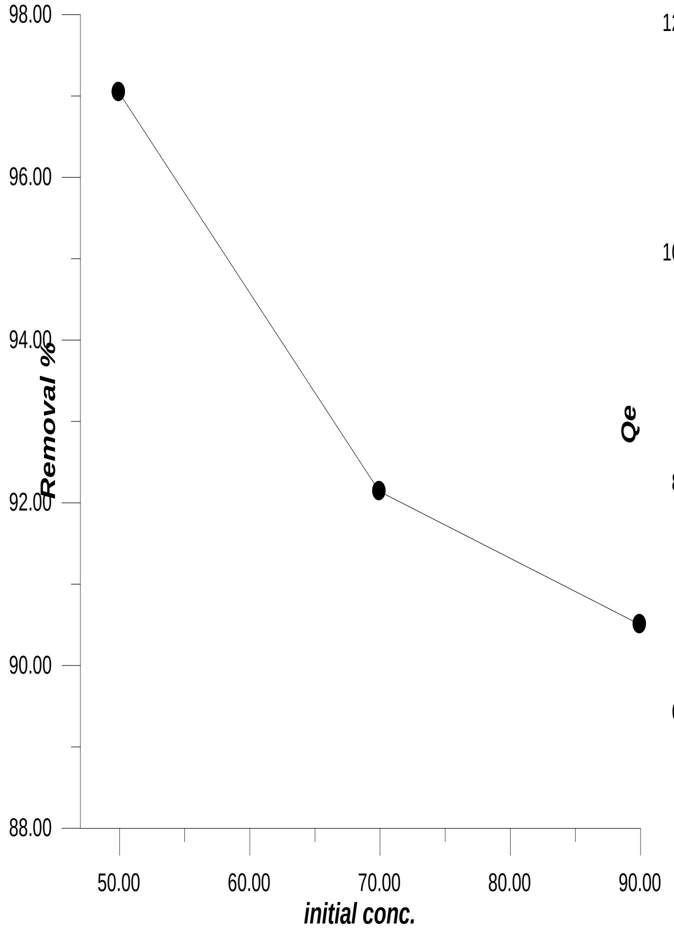
(20 ± 2C^0).After the equilibrium time is elapsed , the mixtures were centrifuged at a speed of 8000 rpm for 10 minutes, 2.5 ml of sample was withdrawn by syringe and analyzed by

Uv-Visible Spectrophotometer.

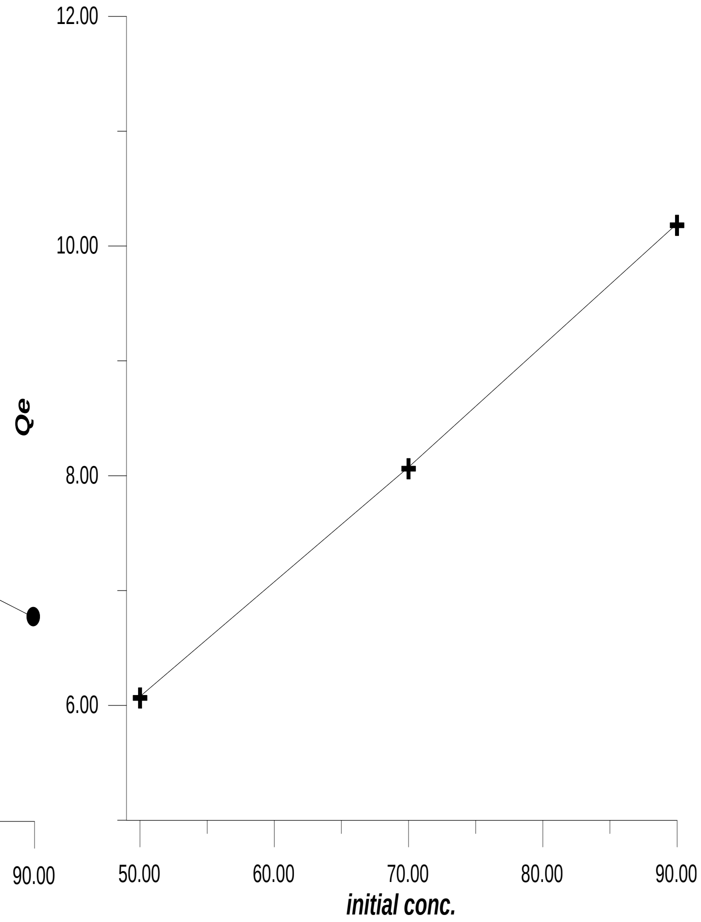
Result And Discussion

Effect of initial concentration :

The equilibrium was attained within 60 min.therefore a 60min.shaking time was found to be appropriate for maximum adsorption and was used in all subsequent experiments. The experimental results of adsorption MG on the (ESP) (200mg of adsorbent) at various initial concentrations of dye (50 , 70 , and 90 ppm) with contact time are shown in figures (1 and 2).The equilibrium data reveal that the percent adsorption decreases with the increase in initial dye concentration but the actual amount of dye adsorbed per unit mass of adsorbent increased with increases in dye concentration .It means that the adsorption is highly dependent on the initial concentration of dye .This is because at lower concentration the ratio of the initial number of dye molecules to the available surface area is low. However, at high concentration the available sites of adsorption becomes fewer , and hence the percentage removal of dye is dependent upon the initial concentration.



Figure(1) relation ship between Removal % and initial concentration(ppm).



Figure(2) relation ship between amount adsorbed and initial concentration(ppm).

Effect of adsorbent Dosage:

Figures (3 and 4) and table (1) show the adsorption of MG dye (10 ppm dye) as a function of dosage of Egg Shell powder (ESP). It is apparent that by increasing the adsorbent dose the percentage of dye removal increases , but adsorption density , the amount adsorbed per unit mass, decreases . it is readily understood that the number of available adsorption sites increases by increasing the adsorbent dose and it therefore results in an increase in the percentage of dye adsorbed .The decrease in adsorption density with an increase in the adsorbent dose is mainly because of un saturation of adsorption sites through the adsorption process (Dorris *et al* 2003).Another reason may be the inter-particle interaction, such as aggregation, resulting from high adsorbent dose, such as aggregation would lead to a decrease in the total surface area of the adsorbent and on an increase in diffusional path length (Shukla *et al* 2002).

Table (1) relation ship between dose of adsorbent ,equilibrium conc.(Ce) , Removal percentage , and amount adsorbed for 10 ppm of dye .

Dose of adsorbent (mg)	Ce of dye ppm	Removal %	Qe (mg/g)
50	2.083	79.2	3.956
100	1.736	82.6	2.066
150	1.319	86.8	1.447
200	1.111	88.9	1.111

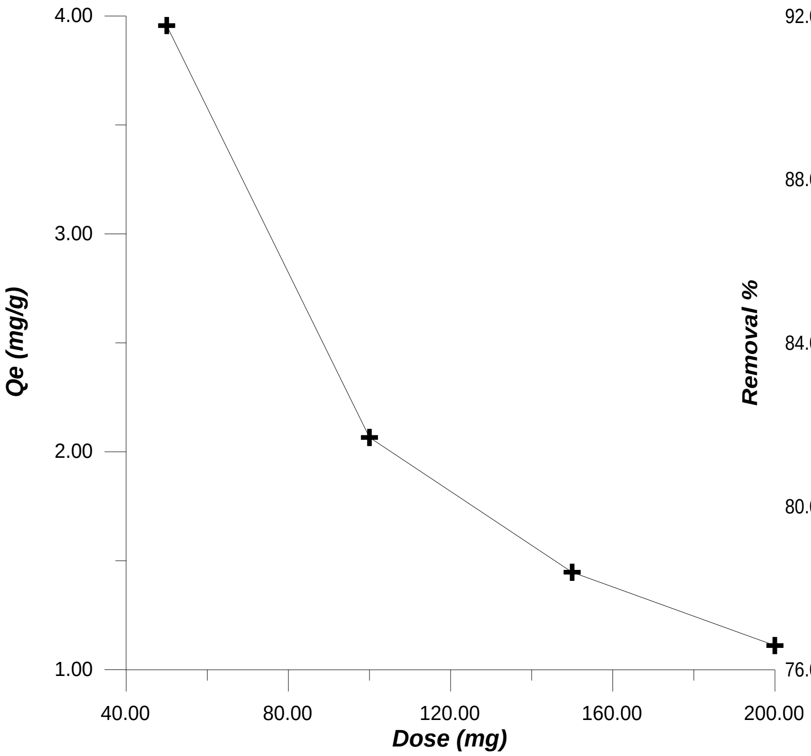


Figure (3) Effect of dose ESP on density of adsorption of dye.

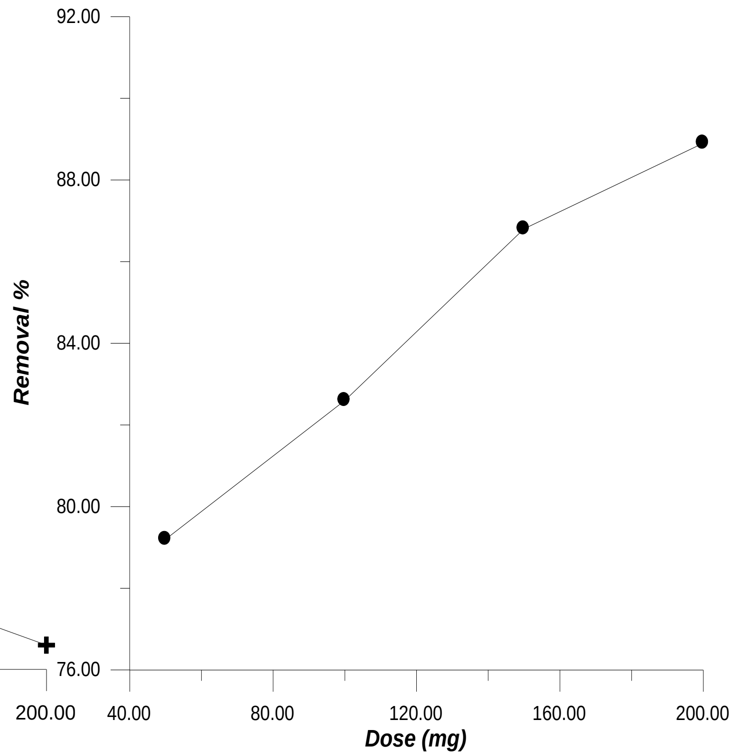


Figure (4) Effect of dose ESP on removal % of adsorption of dye.

Equilibrium studies:

The successful representation of the dynamic adsorptive separation of solute from solution on to an adsorbent depends upon a good description of the equilibrium separation between the 2 phases.

By plotting solid phase concentration against liquid phase concentration , graphically it is possible to depict the equilibrium adsorption isotherm.

The equilibrium studies conducted at different initial concentrations and fixed adsorbent dose were fitted into the linearized freundlich adsorption isotherm, which is of the form

$$\text{Log}(X/m) = \log k_f + 1/n \log C_e$$

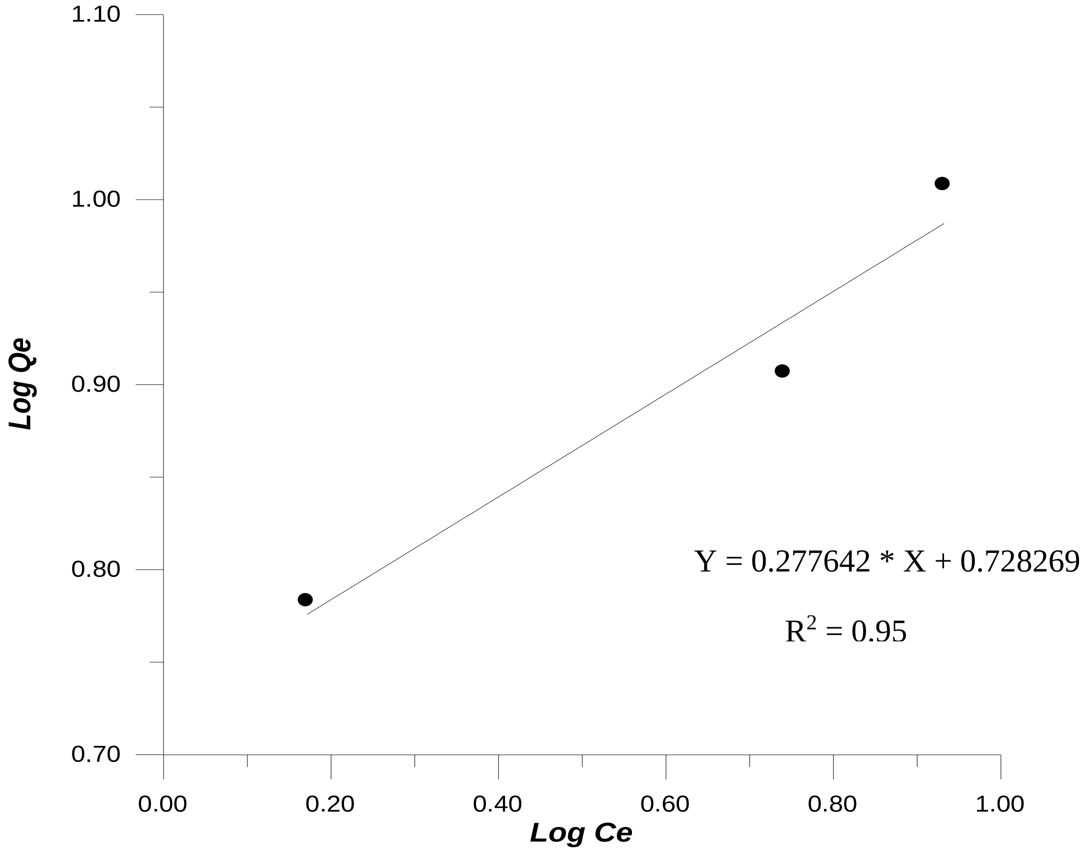
$$\text{Log}(Q_e) = \log k_f + 1/n \log C_e$$

Where X is the amount of dye removed (mg) , m is the weight of adsorbent used(g), Ce is the equilibrium concentration (ppm) , and K_f and n are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity , respectively. The linear plot of log(X/m) versus log Ce showed that the adsorption obeyed a Freundlich isotherm (figure 5) . Freundlich constants K_f and n were 5.34 mg/g and 3.61 respectively. It has been shown by Gardener (Gardener *et al* 1982)that
an **n** value between 2 and 10 indicates beneficial adsorption.
The Langmuir isotherm, which is in the form

$$C_e/Q_e = 1/Q_m b + Ce/Q_m$$

Was applied for adsorption equilibrium , where Ce is the equilibrium concentration (ppm) ,and Qe is the amount of dye adsorbed (mg) per gram at equilibrium (mg/g).Q_m and b are langmuir constants related to adsorption efficiency ,and energy of adsorption respectively. The linear plot of Ce/Qe versus Ce showed that the adsorption obeyed a Langmuir isotherm model (figure 6) .Q_m and b were determined from the slope and intercept of the plot and found to be 11.695 mg/g

and 0.584 L /mg ,respectively. The adsorption data obeyed both Freundlich and Langmuir models, exhibiting heterogeneous surface conditions and monolayer adsorption.(Lee *et al* 1999)



Figure(5)Freundlich isotherm for adsorption dye on ESP.

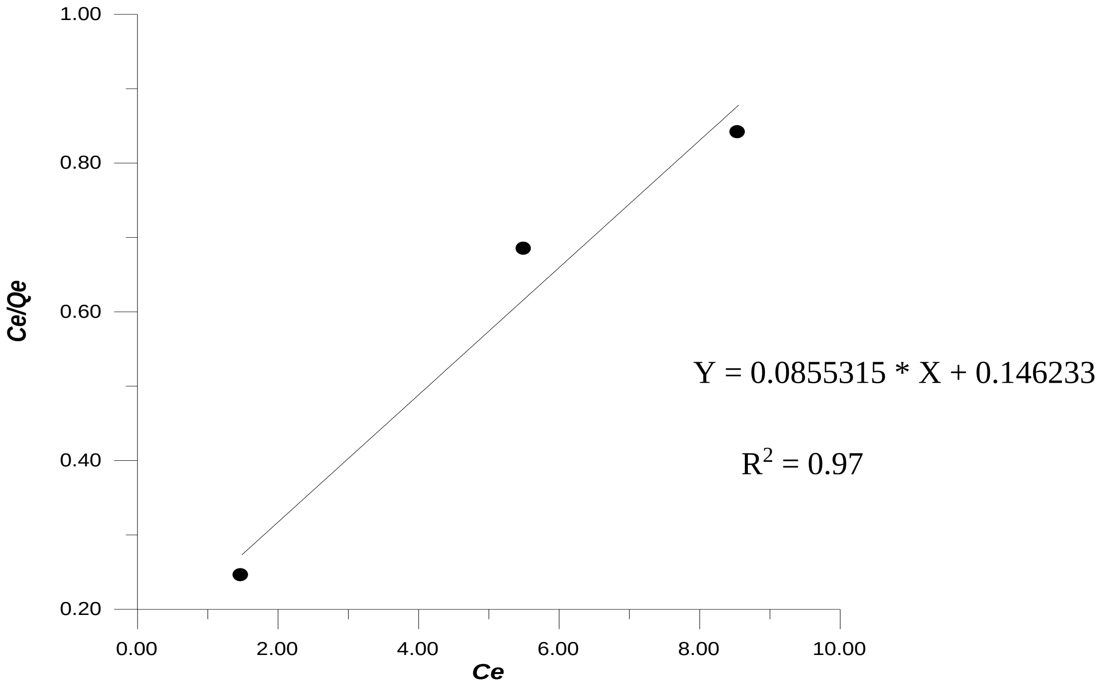


Figure (6)Langmiur isotherm for adsorption of dye on ESP.

Kinetics:

The kinetics of reactive dye sorption onto ESP was investigated using the pseudo – first order kinetics model.

The pseudo – first order equation of Lagergreen model, traditionally used for describing sorption kinetics , is generally expressed by equation (Kanchana *et al* 1992 , Szeto *et al* 2004) where k (mg/g.min)is the Lagergreen rate constant of the first order sorption, evaluated from the slope of the plot Ln (Qe – Qt) versus t (figure 7)

Ln (Qe – Qt) = Ln Qe - K1 . t

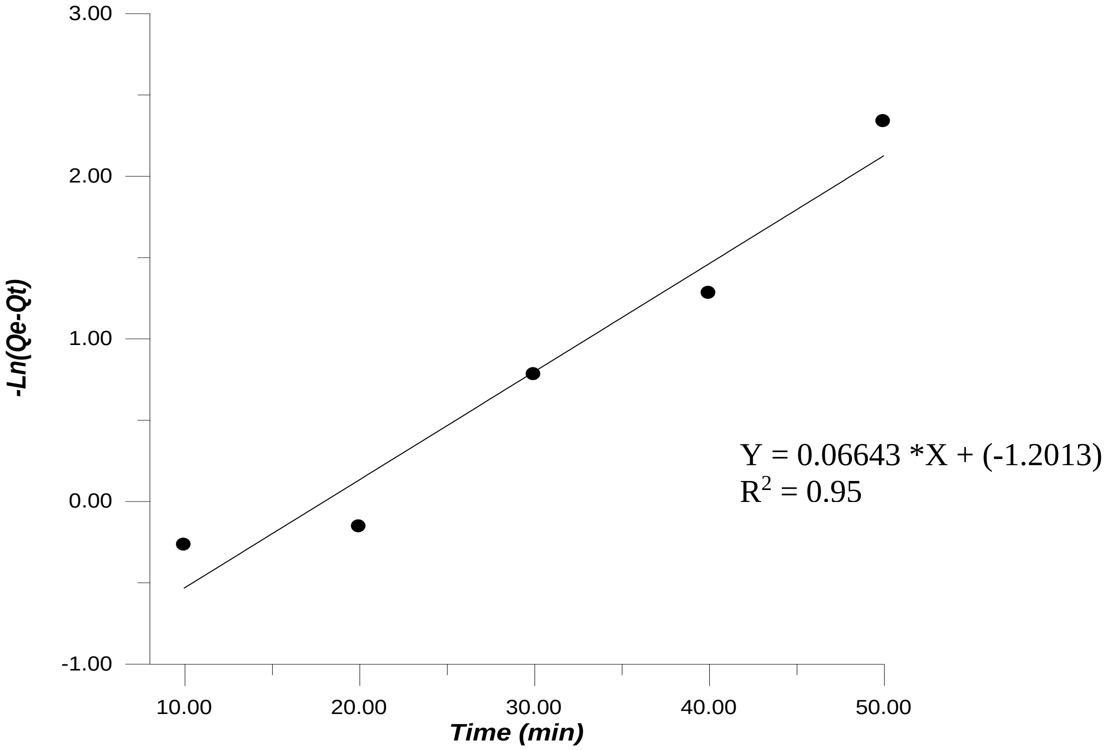


Figure (7) : Pseudo first order Kinetics models to MG sorption on ESP.

Conclusion

The present study, conclude that the egg shell powder could be employed as low cost adsorbent for removal dyes from its aqueous solution at low concentrations .The removal efficiency and adsorption capacity was found to be the highest for egg shell compared with commercial activated carbon that is found in papers.

The experimental data correlated reasonably well with the Langmuir and Freundlich adsorption isotherms and the respective isotherm parameters are calculated, the kinetics of this project was obeyed to Pseudo first order and the rate constant was 0.06643 min^{-1}.

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