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Kinetic and thermodynamic studies of the adsorption of Malachite Green dye onto Elaeagnus Kernel powder

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ABSTRACT

Supplies pollution by numerous pollutants is a global issue. Among numerous water pollutants, taxonom is an important pollutant. This research used buckthorn to adsorb Malachite Green as a cation taxonom from aqueous .This research shows the effect of several operative parameters such as contact duration time , primary taxonom concentration (5-30 g/l) adsorbent dose (0.025-1 g/l) and PH(5-11) in a discontinuous system. Concentration of solution measured before and after adsorption by spectrophotometer. The adsorption data evaluated successfully according to ASAMI. Adsorption kinetics data analyzed by two kinetics model; quasi second order and intra molecular infiltration in order to figure out the adsorption operation of Green Malachite with buckthorn seed powder. According to research results by increasing in tangency time , PH and adsorbent dose ;there is an increasing in taxonom elimination efficiency also by ESM several models in Malachite Green taxonomy elimination process with buckthorn seed powder showed that obeys quasi second order kinetics model .ESM model explains the results of adsorption well. Thermodynamics parameter showed adsorption is automatic and pyrogenic. This research showed that buckthorn seed powder could be used as an effective and inexpensive adsorbent.

Key words: Malachite Green, Thermodynamics parameter, kinetics model, Adsorption , water pollutants.

INTRODUCTION

Most industries such as wood crafts, weaver, paper industry and paste release most of taxonom sullage to rivers without refinement; because of expensive usual refinement ways. Few amount of color in water (1 mg/l) is visible an unfavorable. [1-2] the discharge of colored effluents without treatment, causes several problems, because dyes are toxic, recalcitrant, mutagenic and carcinogenic [3].

Conventional techniques including chemical precipitation, solvents extraction, ion exchange, membrane separation and adsorption can be used to remove dyes or metal ions from wastewaters [4]. Malachite Green is indissoluble and harmful also toxic for aquatics and other existents. Several studies showed Malachite Green has pernicious effects on freshwater fish, these cause dangers to general health and hygienic also possible environmental problems. [5-6-7]

Generally there are several techniques in order to eliminate taxnom from precious water supplies such as Physical techniques (purification , sedimentation) chemical techniques (oxidation process , including free radicals and coagulation electrodes), Physical – chemical techniques (adsorption , ion exchange , stripping , chemical oxidation , coat separation) Biological techniques (aerobic an anaerobic) , sonic techniques and radiation .The adsorption processes are more efficient in order to eliminate contaminants from sullage . Adsorption could be described as substance aggregation in joint of liquid and solid. [8-9]

Adsorbent, adsorbate and other materials adsorbed on the surface called adsorbate that includes a solid phase (adsorbent, or bio-adsorbents, biological materials) and a liquid phase (water and solvent). Adsorption is a efficient way to separate and eliminate contaminant from water. [19-20-21]

Adsorption in comparison with other water purification ways because of financial issues, simplicity, design easy to operate and being non sensitive about toxic pollutants is superior; also adsorption has not shown any toxic formation in process. Adsorption by inexpensive materials is affordable and effective in order to eliminate color. [22]

Nowadays because of expensive adsorbents, mostly inexpensive adsorbents to sullage purification are noticed [12]. According to some studies; agricultural crops including coffee beans[13], almonds crust[14] , lemon peel [15], mango seeds [16], rice crust's ash[17] , grain crust and rice crust are potential adsorbents to eliminate color and taxonom from industrial sullage .[18]

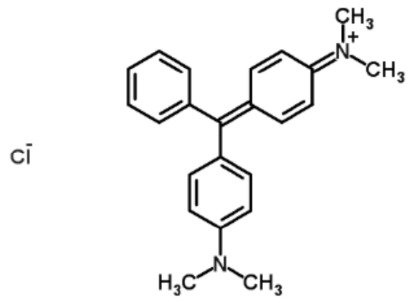
This research notices buckthorn seed powder as an inexpensive absorbent to eliminate taxonom Green Malachite .As there is not any study used Buckthorn seed powder for adsorption formerly , so this study focuses on buckthorn seed powder as adsorbate to Green Malachite purification from aqueous .This research shows process and the effect of several operative parameters like tangency duration , adsorbents dose , primary taxonom concentration and PH of Malachite Green. Adsorption Kinetics to find out kinetics equation and equation isotherm used to figure out appropriate isotherm are being used.

MATERIALS AND METHODS

Chemicals

NaOH (0.1 N) and HCl (0.1 N) solutions, MG dye were supplied from merk company. General characteristics and chemical structures of malachite green dye are indicated in Table 1.

Table1: Characteristics of MG dye.

C.I. Name	Empirical Formula	Molecular weight	Maximum Adsorption Wavelength	Chemical Structure
Basic Green 4	$C_{23}H_{25}ClN_2$	364.91 g/mol	615 nm	

Instruments

The concentration of remaining in the solution after shaking with shaker model (Heidolph 1010) for 120 min was analyzed using spectrophotometer, UV- Vis (model: Lamda 25). A pH meter (model: Metrohm) was applied for pH measurements of the MG dye solutions. The sea shell was characterized by FT-IR (model: Bruker).

METHODS

Preparation of adsorbent

Core Elaeagnus Angustifolia that the mill was now pressed powder, washed with distilled water were to remove impurities, and then was used dried at room temperature.

Preparation of dye stock solution

A stock solution of 100 mg/l was prepared by dissolving 0.1 g of MG dye in 1000 ml distilled water.

Adsorption process

The dye of malachite green at 100 mg/l was using distilled water. The experiments were performed at batch system. In each experiments For dye adsorption kinetics studies, 0.025 g of adsorbent added to 10 ml of MG dye solutions at of pH= 9 (opt), initial concentration of MG dye was ranged (5- 10 – 15- 20-25- 30) ppm and contact time (5-120) min. The dye removal percentage (%R), equilibrium adsorption capacity (q_e) and adsorption capacity at any time (qt) were determined by Eqs. 1–3, respectively [17].

$$\%R = \frac{(C_0 - C_e)}{C_0} 100 \quad (1)$$

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (2)$$

$$q_t = \frac{V(C_0 - C_t)}{m} \quad (3)$$

Where q_e is the equilibrium capacity of dye on the adsorbent (mg. g−1), C_0 is the initial concentration of dye solution (mg L^{-1}), C_e is the equilibrium concentration of dye solution (mg L^{-1}), V is the volume of dye solution used (L), Ct is the MG concentration in liquid at any time (mg L^{-1}) and m is the weight of adsorbent (g) used [18].

RESULTS AND DISCUSSION

Characterization of adsorbent

The FTIR spectrum of Elaeagnus Kernel powder is illustrated in figure 1. The broadband at around 3412.99 cm^{-1} is typically attributed to hydroxyl groups. because, the FT-IR spectrum of Elaeagnus Kernel powder exhibit a band at 1789 cm^{-1} assigned to carbonyl of the hydroxyl groups.

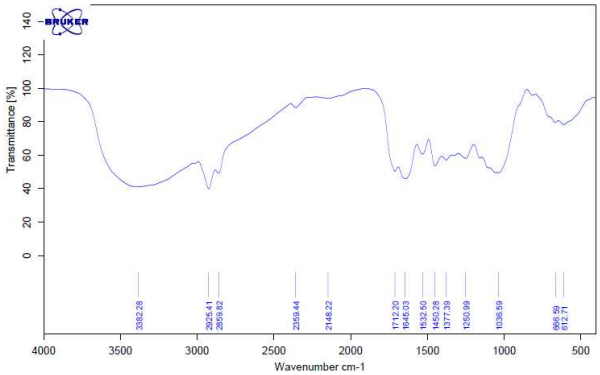


Figure 1: FT-IR spectrum of Elaeagnus Kernel powder

Effect of pH

Solution pH plays an important role in controlling the surface charge of the adsorbent, the degree of ionization of the adsorbate in the solution as well as dissociation of various functional groups on the active sites of the adsorbent [19] . The influence of initial solution pH on the adsorption of MG dye onto Elaeagnus Kernel is illustrated in Fig.2. Adsorption experiments were carried out at pH 5, 6, 7, 8, 9, 10 and 11, for the initial dye concentration 10 ppm, the agitation speed (3 rpm), contact time (120 min) and o.025 g of adsorbent. According to results illustrated in figure3, maximum adsorption of the dye was achieved at pH 9 . With increasing pH the number of positively charged sites decreased and the number of negatively charged sites increased. This phenomenon favors the sorption of positively charged dye due to electrostatic attraction [20].

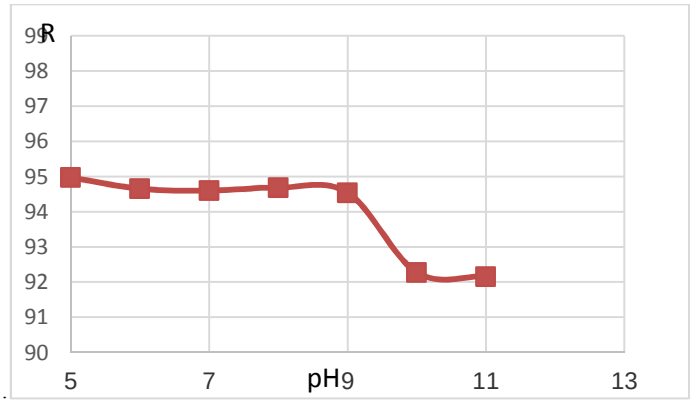


Figure2: Effect of pH on the adsorption of Malachite green dye by Elaeagnus Kernel.
(U: 3rpm, V: 25 ml; C_0: 10ppm; M: 0.025 g; pH: 5 -11; Time: 120 min)

Effect of dosage

The Elaeagnus Kernel powder dosages were in the range from (o.o25- 1 g), Contact time (120 min), agitation speed (3 rpm),pH=9 and initial dye concentration 10 mg/L. Figure 3 shows the effect of dosage on removal percentage of MG dye onto Elaeagnus Kernel powder. According to results indicated from figure 3, when the adsorbent dosage increases, the removal percentage of MG dye increases. There was 83.27% removal of MG dye with 0.025 g amount Elaeagnus Kernel was observed. Hence, optimum dosage were accept to be 0.025 g for the removal of MG dye using Elaeagnus Kernel powder. It is readily understood that the number of available adsorption sites and the surface area increase by increasing the adsorbent dose, it therefore, results in the increase of amount of adsorbed dye [21].

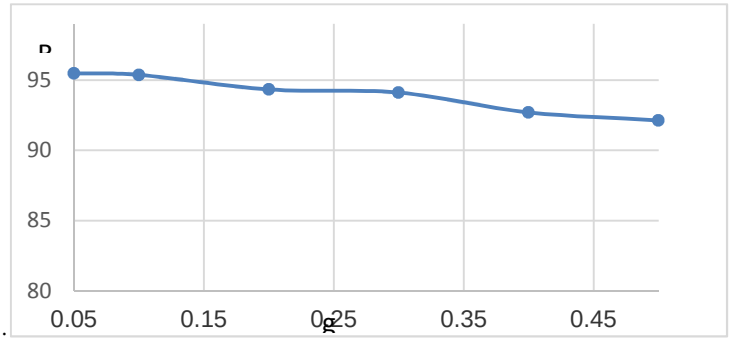


Figure 3: Effect of dosage on the adsorption of malachite green dye by Elaeagnus Kernel. (U: 3 rpm, V: 25 ml; C_0: 10ppm; M:0.025- 1 g; pH:9; Time: 120 min)

Effect of contact time and initial concentration

The effect of contact time and initial concentration on MG adsorption is shown in Fig.4. The effect of contact time and initial concentration on the removal of MG adsorbed o.025 g of Elaeagnus Kernel powder, pH=9, different contact time (5-120) min and initial concentration (5-30) mg/l was investigated at room temperature. The percentage removal increased from 79.42 to 94.84% by increasing the initial concentration of MG from 5 to 30 mg/l. Adsorption of MG dye was rapid in first 90 min and after 90 min the removal percentage of MG dye was constant. The curves are single, smooth and continuous indicating the formation of monolayer coverage on the outer surface of the adsorbent. The increase in the rate of colour removal with agitation time may be attributed to a decrease in the diffusion layer thickness surrounding the adsorbent particles [22].

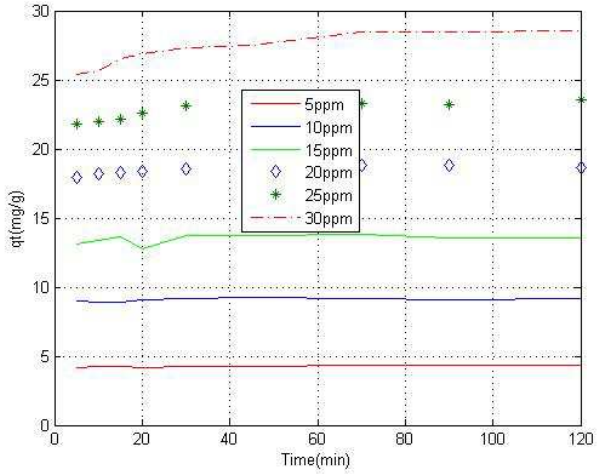


Figure4: Effect of contact time and initial concentration on the removal percentage of malachite green dye by Elaeagnus Kernel. (U: 3 rpm, V: 25 ml; C_0: 5-30ppm; M: 0.025 g; pH:9; Time: 120) min)

Adsorption kinetics

Pseudo second order

If the rate of adsorption is a second-order mechanism, the pseudo-second-order chemisorptions kinetic rate equation is expressed as (4)

$$d_q/d_t = k\,(q_{eq} - q_t)^2 \qquad (4)$$

Where k is the rate constant of pseudo-second-order sorption (g/ (mg min)) [23].The pseudo second- order equation after transformation into linear from can be written as eq5:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \qquad (5)$$

q_t— The amount of adsorbate adsorbed at time t (mg/g)
q_e— The amount of adsorbate adsorbed at equilibrium (mg/g)
k_2— the pseudo-second-order rate constant of adsorption (g/mg h) or (g/mg min) [24]

Pseudo second- order model of kinetics curves were presented in figure5. The correlation Coefficients (R^2) for the second order rate kinetic model indicated in table.2. The correlation coefficients (R^2) for the second order rate kinetic model are rather than Elovich and Intra-particle diffusion (> 0.99). Thereby, the second- order kinetic is best model.

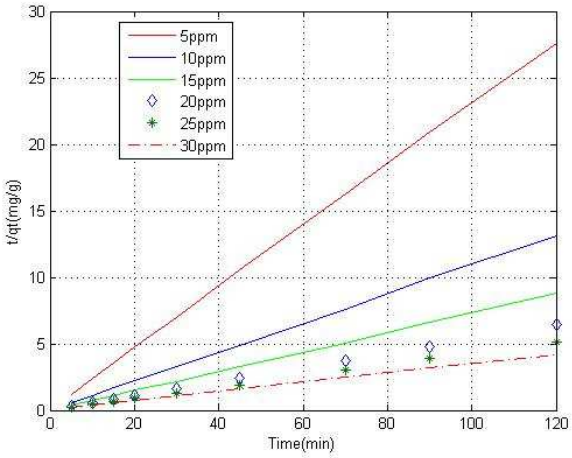


Figure. 5: Pseudo second- order model of kinetics curves

Intra- particle diffusion model

Intra- particle diffusion model based on the theory proposed by Weber and Morris was tested to identify the diffusion mechanism [25]. According this theory (6):

$$q_t = k_{id}\, t^{0.5} \qquad (6)$$

Where k_{id} ($mg.g^{-1}.min^{-0.5}$) is intra-particle diffusion rate constant. In table 2 illustrated the values R^2 determined the slop and intercept of the plot of against $t^{0.5}$.

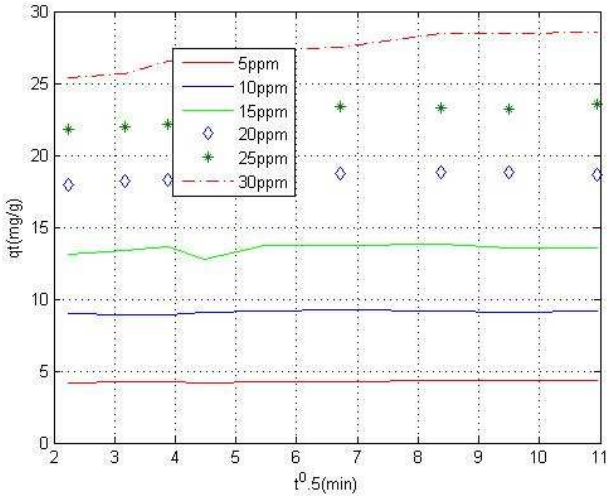


Figure 6: Intra-particle kinetics for MG dye by Elaeagnus Kernel
Table 2: The correlation coefficients (R^2) for the (Pseudo –second-order)

C_0	5 ppm	10 ppm	15 ppm	20 ppm	25ppm	30 ppm
Pseudo –second-order model	0.9999	0.9999	0.9997	0.9999	0.9999	0.9999

CONCLUSION

These results showed the best potential of using Elaeagnus Kernel as low-cost MG dye adsorbent. The kinetics of MG dye adsorption using sea shell followed a pseudo-second-order model. It was indicated that percentage removal of MG dye was achieved maximum of 0.025 g of adsorbent. The results of contact time and initial concentration dye shows, that the percentage removal increased, by increasing the initial concentration of MG. Then, maximum adsorption of the dye was achieved at pH 9.

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