Technique of Batch Adsorption for the Elimination of (Malachite Green) Dye from Industrial Waste Water by Exploitation Walnut Shells as Sorbent

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ABSTRACT

This study proposes an easy and cheap technique to get rid of dangerous Malachite Green (MG) dye from waste material by victimization carbon from walnut shells. The simple treatment was carried out by heating at temperature in which was set to the best carbonization degree to arrange carbon from these shells; thus, the temperature was set to 200 °C. Optimum conditions for sorption like the quantity of adsorbent, contact time, particle size of adsorbent, pH scale and initial MG concentration were conjointly examined. The results showed that the simplest removal was obtained once victimization 1 g of carbon with particle size 150 μM and time contact 150 min. However, the sorption of the dye was not affected by the pH except the sorption was very low at pH = 2. The removal potency was high approximating 99.53%. The results conjointly showed that the sorption equilibrium of MG onto carbon that was ready from the walnut shell has been evaluated via Langmuir and Freundlich models.

Keywords: Malachite Green; walnut shells; batch adsorption

INTRODUCTION

The annual rate for the assembly of dyes within the world could reach 7 million tons. These dyes are utilized in several industries like paper, plastics, leather, pharmaceutical, food, cosmetics, dyestuffs, and textiles industries [1]. An quantity of 10-15% of the dyes utilized in coloring is discharged as effluent [2]. Moreover, concerning 20% of commercial effluent is truly developed as dyes, wherever it discharged to the closest bodies of water like rivers, lacks, and seas [3]. These industrial effluents are the supply of the many pollutants like bases, acids, organics, inorganics, dissolved solids, and color [4].

These effluents cause several environmental issues as a result of being unhealthful and non-biodegradable with a potentiality to be of a cancer nature [5], moreover, the negative influence of those effluents isn't restricted to the unhealthful result of dyes on aquatic life, however it may cause skin irritation, dermatitis, allergies, and cancer of the human person and a few agent [6-8]. Color pollution is undesirable as a result of its prominence. It additionally works on intense the dissolved O₂ and prevents the re-oxygen within the receiving water [9]. Additionally, color pollution is tough to be treated owing to its high resistance to aerobic digestion and its stability in heat, light, and oxidant, and also the bio-recalcitrant elements [10]. This resistance takes place, because of the complicated molecular structure of pigments, that makes treatment ways used deficient and cost [9].
There are several techniques that are wont to take away dyes from the waste like flocculation-coagulation, membrane separation, chemical oxidization, aerobic or an aerobic digestion and chemistry techniques [11]. The bulk of those techniques are of high price and cause the formation of by-products or generation of sludge [12]. The sorption technique is taken in to account the most effective among those ways owing to affordable value, high sensitivity to pollutants, simple style and operation. Besides, it doesn't turn out any harmful substances [13].

Carbon is wide accustomed take away dyes from the effluent owing to its high sorption capability, giant extent and microporous structure. However, it's some disadvantages like low property, exhausting regeneration, and high value [14].

The physical and chemical properties of carbon depend upon the kind of raw materials used and also the activation method conditions [15]. On the premise of form and size, there are 3 styles of activation carbon fibrous, powder, and granular in line with form and size [16].

There is variety of natural adsorbents such clay [17], granular kohlrabi peel [18], peel [19], rice husk [20], raw barley straw [21], peanut husk [22], crab shell [23], and walnut shell [24]. Walnut shells are considered agricultural wastes with sensible chemical stability, high mechanical strength, simple regeneration and huge specific area. Walnut shells are utilized in the treatment of significant metals in industrial effluents like Chromium, mercury, zinc, Cesium and copper [25]. Mineral inexperienced MG may be a dyestuff that is employed for coloring several products like paper and animal skin product and for coloring wool, silk and cotton. Discharging this dye into the stream can lead to harmful effects with in the liver, the gall, the kidney, the internal organ, and therefore the gonads for the aquatic life [26], it's doable that this dye can enter into the organic phenomenon and cause cancer and agent effects on humans [27].

There are several adsorbents that are won't to take away MG from waste matter like, lotus seed [28], durian seed based [29], weed [30], wood [31], marine protects [32] sugar canemud [33], dead leaves [34], and rice husk [35].

The present study focuses attention on the adsorption of malachite green dye on walnut shells. The walnut plant it is one of the most plant found in north of Iraq. In this study, two widely used adsorption isotherm, and kinetic study were estimated to find maximum dye removal ability and certain constants correlated to the adsorption phenomena, correspondingly. In totaling, a commercial adsorbate was used for further comparison.

Fig 1. Walnut shells before and after burn and different sizes of adsorbent

EXPERIMENTAL SECTION

Adsorbent Preparation

The adsorbent surface was ready via taking a quantity of walnut shells and laundry it by traditional water to get rid of dirt, then the quantity was washed with diluted HCL 0.1 M for the aim of removing soluble substances. Finally, it had been washed with H2O to get rid of the acid used. Thus, the shells became prepared for thermal activation, wherever they were placed within the melting pot and burned at 200 °C for 1 h. After this, the activated charcoal was washed by little amounts of H2O to get rid of the ash mud ensuing from the thermal treatment method exploitation filtration funnel so it had been dried at 100 °C. Walnut shell is content: 51.2% carbon; 5.8% hydrogen; 0.51% potassium; 0.34% phosphorus; 0.14% sulphur; 0.22% magnesium; 0.12% calcium and 0.1% nitrogen and a low quantity of mineral compounds, which are considered as ash content in the walnut shell 0.9%. On the walnut shell cell surface there is a huge amount of several functional groups that are capable to deception and bond more dye and metals from solutions. The subsequent photos show the stages of the preparation of the adsorbent. The photographs show the walnut shells before and when burning at a temperature of 200 °C for 1 h. Totally different sizes of the adsorbent 75 to 850 μM were ready as shown in Fig. 1.
Table 1. Physiochemical properties of malachite green (MG)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C_{23}H_{25}ClN_{2}</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>364.9 g/mol</td>
</tr>
<tr>
<td>Color Index</td>
<td>42000</td>
</tr>
<tr>
<td>CAS</td>
<td>2437-29-8</td>
</tr>
<tr>
<td>Nature</td>
<td>Cationic dye</td>
</tr>
</tbody>
</table>

Adsorbent dye preparation

Malachite Green (MG) (4-[(4-(dimethylamino) phenyl) (phenyl)methylidene] -N,N-dimethylcyclohexa-2,5-dien-1-iminium chloride). The structure of (MG) is show in Fig. 2. The physiochemical properties show in Table 1.

Stock solution was prepared by dissolving exactly 0.05 g of the dye in 500 mL of distilled water to give the concentration of 100 mg/L. The Stock solution was used to prepare another concentration, and specific density 1.18 to be diluted in 250 mL of distilled water.

Preparation of HCl solution 0.1 M

The HCl was prepared by taking 2.1 mL from concentrated HCl with 35%.

Preparation of NaOH solution 0.1 M

One gram of NaOH is prepared in a beaker to be later transferred to a volumetric flask of 250 mL which should be filled up with distilled water up to the level indicated by the mark.

Batch adsorption studies

The adsorption capacity and removal efficiency of activation carbon were calculated by the following equation:

\[ q_e = \frac{V}{W} (C_o - C_e) \]  \hspace{1cm} (1)

Removal efficiency(%) = \( \frac{C_o - C_e}{C_o} \times 100 \) \hspace{1cm} (2)

where \( q_e \) is that the quantity of MG that adsorbate per unit weight of activated carbon (mg/g); \( C_o \) the initial concentration of MG dye at equilibrium time (mg/L); \( V \) the solution volume (L); \( W \) is that the activation carbon dose (g).

Sorption isotherm model

Adsorption isotherms are thought of one in every of the essential necessities to spot the link between adsorbate and adsorbent. They are additionally of nice importance to attain the most effective style for dye removal [36]. Moreover, they are very necessary to explain variety of particles distributed between the 2 phases at the equilibrium state. Several models are utilized in the literature like Langmuir, Freundlich, Dubinin–Radushkevich, Temkin, Sips, Brouers–Sotolongo, Radke–Prausnitz and Vieth–Sladek [29]. During this study, the Langmuir and Freundlich models were chosen, as follows:

The Langmuir isotherm equation [37]

\[ q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \] \hspace{1cm} (3)

where \( q_e \) is that the quantity adsorbable per unit mass of sorbent material at equilibrium (mg/g), \( q_m \) is that the most sorption capability (mg/g), \( C_e \) is that the equilibrium activation carbon concentration of the solution (mg/L) and \( K_a \) is that the sorption constant.

The plot of \( C_e/q_e \) versus \( C_e \) in equation (4) is linear this means the sorption of MG onto activation carbon follows Irving Langmuir line.

\[ C_e = \frac{1}{K_a q_m} \times C_e + \frac{C_e}{q_m} \] \hspace{1cm} (4)

The vital features of Langmuir model can be definite by a dimensional constant called equilibrium parameter, \( R_L \) [38] that is definite by:

\[ R_L = \frac{1}{1 + b C_0} \] \hspace{1cm} (5)

where \( b \) is that the Irving Langmuir constant and \( C_0 \) is that the initial concentration. The worth of \( R_L \) indicates the form of the line to be either un auspicious (\( R_L > 1 \)), linear (\( R_L = 1 \)), auspicious (\( 0 < R_L < 1 \)) or permanent (\( R_L = 0 \)).

The Freundlich isotherm equation [39]

\[ \log q_e = \left( \frac{1}{n} \right) \log C_e + \log K_f \] \hspace{1cm} (6)

where \( q_e \) is that the quantity adsorbat per unit mass of adsorbent at equilibrium (mg/g), \( C_e \) is that the equilibrium MG of the solution (mg/L), \( K_f \) and \( n \) are the Freundlich constants, \( n \) provides a sign of the favorability and \( K_f \) (mg/g (L/mg) \( 1/n \)), The values of \( K_f \) and \( n \) is obtained from the plate of \( \log q_e \) versus \( \log C_e \) and that they capable the intercept and slope of the plate severally. The worth of \( n \) lies between two and ten, which suggests smart sorption.

RESULT AND DISCUSSION

Calibration Curve of MG

Various solutions of the dye are ready with concentrations starting from 0.01–9 mg/L. Spectroscopically scanning of the dye in each the ultraviolet region and also the visible region uncease that the $\lambda_{\text{max}} = 618$ nm (UV/Vis PG LTd). Then the absorbance of the ready concentrations at this wavelength was taken as shown in Fig.3.

Effect of Amount of Adsorbent

The result of C weight on the proportion of decolorization of MG dye was investigated via taking 100 mL of 50 mg/L from dye solution in conical flasks with varied weights of C addition such as 0.5, 1, 1.5, 2, 2.5 and 3 g. The solutions were later place within the shaker (Barnstead International) for 1 h. One gram of C gave the most effective removal quantitative relation and at all-time low price, and therefore the proportion of removal ranged from 67.27% to 99.53% with the rise in weight respectively 3, as shown in Fig.4.

Effect of Contact Time

Contact time impact was examined by put 1 g of carbon in 8 conical flasks, then 100 mL of 50 mg/L was supplementary in every flask. These flasks were place within the shaker for varied durations such as 20, 30, 45, 60, 80, 120, 150 and 180 min. The Fig. 5 shows that the simplest time for equilibrium was recorded at 150 min. Later times witnessed a continuing removal proportion as a result of active sites for sorption are already saturated [19].

Effect of Particle Size of Adsorbent

The result of bit size of activated carbon on the sorption of MG dye has been examined during this study by taking completely different sizes of WSC that are of 0.075, 0.15, 0.3, 0.42, 0.6 and 0.85 mm. The experiments were applied by exploitation 6 conical flasks, a weight 1 g of six completely different sizes of the WSC were place in these six flasks and 100 mL from 50 mg/L of dye were further to those conical flasks. The flasks were place within the shaker for 150 min. It had been found that the removal magnitude relation will increase with the decrease within the size of the WSC and therefore the removal quantitative
Fig 6. Effect of particle size on adsorption capacity of MG onto WSC

Fig 7. Effect of pH (a) adsorption percentage and (b) amount of dye adsorbed

Fig 8. Result of initial concentration on sorption capacity of MG against WSC 150 μM bit size and 1 g sorbent dose

Fig 9. Linearized Langmuir model sorption line model of MG onto walnut shells carbon

Fig 10. Linearized Freundlich model sorption isotherm model of MG onto WSC

The effect of pH scale on the sorption of dye via WSC was applied by taking 6 conical flasks to be full of 100 mL of the dye with an initial concentration of 50 mg/L. The pH scale was adjusted by 0.1 N HCl or 0.1 N NaOH exploiting the pH scale meter (WTW). One gram of WSC that contains a particle size of 150 μM with varied pH scale 2, 3, 4, 5, 6, and 8 was more to every flask. The flasks were then placed in an exceedingly shaker for 150 min. The Fig. 7 shows that there was no important result of pH scale on the adsorption process [30].

Effect of Initial MG Concentration

To identify the result of initial dye concentration on the sorption ability, totally different concentrations of MG dye 10, 30, 50, 70, 90 and 100 mg/L were taken and else to 6 conical flasks that contain 1 g of WSC with 150 μM particle size. These flasks were later place during a shaker for 150 min. The results obtained indicated that the sorption capability raised from 0.99 to 9.78 mg/g with the rise of the concentration of the dye from 10 to 100 mg/L, Fig.8.

Isothermal Analysis

By Irving Langmuir isotherm, the most sorption capability $Q_m$ was 11.36 mg dye per gram of the Walnut shells carbon. The pertinence of Irving Langmuir isotherm prompts a monolayer treatment of dye on the
Table 2. Sorption isotherm factors for MG dye elimination

<table>
<thead>
<tr>
<th></th>
<th>Langmuir</th>
<th>Freundlich</th>
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<tbody>
<tr>
<td>$q_m$ (mg/g)</td>
<td>11.3636</td>
<td></td>
</tr>
<tr>
<td>$K_L$ (L/mg)</td>
<td>2.9239</td>
<td>$(1/mg)^{1/n}$</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9714</td>
<td>0.4372</td>
</tr>
<tr>
<td>$R_L$ (0.0330 – 0.0034)</td>
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</table>

The separation issue RL values are often revealed by Fig. 11, that they're within the vary of 0–1, demonstrating that the sorption was satisfactory method [32,41-42].

From Freundlich isotherm, the worth of $1/n$, the Freundlich limit, that was between 0–1 additionally confirmed that the sorption was favorable and useful as low price sorbent [24,41-43].

The larger worth of KF, the upper the sorption, because, this worth indicates to additional heterogeneous the surface once it'll nearer the zero 10. The Walnut shells carbon, studied as adsorbent for removal of MG, well-trying that its mechanisms well. The sorption submitted each Freundlich and Langmuir isotherms exhibiting heterogeneous surface circumstances and monolayer sorption 2. Fig 12 explains the aberration of those models from the investigational information. It seems that the sorption of MG on Walnut shells carbon may be well fitted by the tow isotherms.

CONCLUSION

The definitions of this work expose that the Walnut shells carbon (WSC) that merely and plentifully accessible agro north in our country could also be simply rehabilitated into wise adsorbent by exploitation simple ways in which an applicable quantity 1 g/L of the Walnut shells carbon adsorbent would possibly removal the most amount as 99 exploit the dye from an solution 50 ppm if stressed for 150 min incontestable enough probable of Walnut shells carbon as an sorbent for the deletion of the MG dye, from water solutions. The sorption of the MG was most round the natural pH of the solution of metal. This displays that sorption of the dye could be disbursed on WSC with applying every Langmuir and Freundlich isotherm.

REFERENCES

[34] Hamdououi, O., Saoudi, F., Chiha, M., and Naffrechoux, E., 2008, Sorption of malachite green by a novel sorbent, dead leaves of plane tree.


