Study of removal Malachite Green dye from aqueous solution using snail shell powder as low-cost adsorbent

Raad k. Abbas and Muneer A. Al-Da'amy

College of Education for pure science, Department of Chemistry, University of Kerbala, Iraq.
raad.khudair@yahoo.com; dr.muneer76kb@yahoo.com

Abstract

This research using snail shell (Rostellaria) powder to remove (Malachite Green) dye from aqueous solution via adsorption. Experiments were conducted at 298 K to know the impact of initial concentration of Malachite Green, contact time, pH and effect of ionic strength. The optimum conditions for the adsorption of Malachite Green were realized at 0.0200 g of the adsorbent material. The maximum removal ratio was equal to 86.6585 % at 7.0000 mg/L, 10 min as adsorption time and 298 K. Equilibrium adsorption isotherms was investigated. The empirical data were analyzed by the Langmuir, Freundlich and Temkin models of adsorption at different temperature change from (298 to 338) K. The adsorption isotherm data were suitability well to Langmuir isotherm. The calculated thermodynamics information of the adsorption process \( \Delta G^\circ \), \( \Delta H^\circ \) and \( \Delta S^\circ \) refers that removal process occur via an adsorption process which features with spontaneous, exothermal and raise in the randomness of the molecules of the adsorbent dye. The obtained isotherms information from the experiments were conform For the type (S-curve) at Giles discretion.

Keywords: Malachite Green Dye, Study Adsorption system, Snail Shell, Isotherms, Freundlich, Langmuir and Temkin.

1- Introduction

The water is necessary for life and for all living things, and that the issue of water pollution is one of the topics that attracted the attention of scientists and specialists in all fields [1] Where water is exposed to pollution with the development of industry, where the human being uses the chemical generator in most affairs of life and participates in all industries such as pesticides, cosmetics, medicines, and others [2,3]. This is due to the exacerbation of this problem, as it has become important to find ways to address it [4]. There are also many of these methods: for example, chemical precipitation, ion exchange [5], precipitation, filtration[6], solvent extraction and adsorption, however, most of these methods are either expensive or of limited use [7,8]. Absorption method was used because it is simple and effective and also has a low cost and environmentally friendly as there are
many natural materials that can be used as adsorbent surface such as clay and waste of some plants as well as charcoal and others [9,10]. Malachite green consider is one of the base dyes that are distinguished by containing chromophore that are part of the positive ion (usually an amine salt or an amine ionized group), they are used to dye acrylic fibers, wool and silk these dyes are dissolved in water, alcohol or both [11,12]. This dye has been classified as having health risk of degree 2 however, it is still used in some countries due to its very low cost and high availability [13]. some studies have reported that it causes carcinogenicity, mutations, chromosome fractures and respiratory toxicity[14]. In the present study by using it varies with different treatment factors including initial dye concentration, contact time, pH, adsorbent weight and temperature, that we found the snail shell was an active material (adsorbent) to remove malachite green (adsorbate). Snails belong to the family (Rostellaria) and this type of snails is found commonly at the edges of beaches and lakes, where samples were taken from the southeastern coast of Lake Al-Razaa in Karbala Governorate [15]. In one study, snail shell powder was used to remove dye, polish and clean teeth [16]. And snail shell powder also used in removal some dyes like CBB-G250[17], Azure A[18]. and Azure B [19].

| Se.n | The Instrument name | company | Country |
|------|---------------------|---------|---------|
| 1    | UV – Visible Spectrophotometer | Shimadzu, Japan | Karbala University / College of Education for Pure Sciences |
|      | Double Beam -1800   |         |         |
| 2    | Atomic force microscopy – spam AA3000, USA 2008 | Shimadzu, Japan | Baghdad University / College of Science |
| 3    | Fourier Transform Infrared Spectrophotometer – 8900s | Shimadzu, Japan | Babylon University / College of Pharmacy |
| 4    | X-Ray Diffraction Spectroscopy – Lab XRD -6000 | Shimadzu, Japan | University of Baghdad / College of Education Ibn Al-Haytham |
| 5    | Scanning Electron Microscopy | Shimadzu, Japan | Kufa University / College of Science |
| 6    | Electronic Balance TP-214 | Germany Denver | Karbala University / College of Education for Pure Sciences |
| 7    | Oven Memort LOD – 080+N | Labtech, Korea | Karbala University / College of Education for Pure Sciences |
| 8    | Centerifuge – Hettich | Universal Germany | Karbala University / College of Education for Pure Sciences |
| 9    | PHEC-450 | Korea PHOENIK | Karbala University / College of Education for Pure Sciences |
| 10   | Thermo stated shaker GFL(D-300) | Germany | Karbala University / College of Education for Pure Sciences |
| 11   | Blender | Chine | Karbala University / College of Education for Pure Sciences |
2- Experiments

Instruments Used:

Materials:
All chemicals were extremely pure and commercially available. An organic green malachite dye was used. The adsorbent (snail shell powder as low-cost).

Preparation of the Malachite Green dye

Prepare Malachite Green dye solution with concentration 50mg/L where 0.0125g of the dye was dissolved in 250 ml by dissolving 0.0125 g of D.W. The characteristics of the selected dye are given in table (1) and their structures are shown in figure (1).

Table (1): Characteristics of Malachite Green [20]

| The Chemical name | \(4\)-\(\{4\)-(Dimethylamino)phenyl)\(\)phenyl)methylidene\(\)-N,N-dimethyl cyclohexa-2,5-dien-1-iminium chloride |
|-------------------|-------------------------------------------------------------------------------------------------|
| Formula | C23H25ClN2 |
| Class | Thiazine |
| Source | Aldrich |
| Solubility in water | Soluble |
| Molecular Weight | 364.911 g/mol |
| \(\lambda\) max | 617.50 nm |

Fig (1): Structural formula of Malachite Green dye [21]

Preparations of the adsorbent (snail shell powder)

The snail shell was collected from the dump site, then wash snail shell in depth with plain water from the tap first, then with deionized water to remove the particles from its surface. And after that, it is dried in the oven at 100 °C for 24 hours then it is crushed, ground, sifted by mechanical sieve Snail Shell properties are given in table (2). The
surface was also diagnosed using techniques (FT-IR, XRD, AFM and SEM) as shown in fig. (2,3 and 4) respectively.

Table (2): Specifications of Snail Shell [22]

| Initial formula | Snail Shell powder |
|-----------------|-------------------|
| CaO             | 52.70             |
| SiO2            | 2.40              |
| Al2O3           | 0.68              |
| Fe2O3           | 0.44              |
| MgO             | 1.50              |
| SO3             | 0.28              |

Figure (2): XRD spectrum of the tapered snail shell surface.

Figure (3): FT-IR infrared spectrum of tapered snail shell.
Batch adsorption experiments:-

Using 0.0100 g adsorbent with 25 ml of dye solutions 70,000 mg/L at 150 rpm in the mentioned thermal water shaker bath. The non-absorbing floating the remaining dye liquid in each solution was analyzed by a double digital beam (Shimadzu UV-Vis 1800) at a wavelength corresponding to λ max. Time to contact, effect of PH, the effect of ionic strength also, the effects of temperature were studied. The amount of adsorption is expressed by the x / m ratio, which is the quantity of adsorption in mg retained by the adsorption weight (g).

\[
\text{The percentage Removal} = \left( \frac{\text{C}_0 - \text{C}_e}{\text{C}_0} \right) \times 100 \quad \ldots \ldots (1)
\]

Where:
\( \text{C}_0 \), \( \text{C}_e \) the indicate the initial concentration and the equilibrium remaining concentration of solution in mg/L respectively. [23]

3-The results and discussion

Contact time effect

The Relationship between contact time and the percentage of green malachite dye is achieved through joint trials to realize balance as shown in figure (5). The results showed that the equilibrium time was attained within 10 minutes.
Fig.(5): Contact time effect on adsorption of Malachite Green dye by Snail Shell powder at Temp. 298 K, Conc. of MG dye 7.0000 mg/L and Weight of the adsorbent surface 0.0100 g.

Adsortent weight effect:-

Adsorption experiments were work by changeful the adsorbent weight from (0.0050-0.0800 g). The initial concentration of the MG dye was 7.0000 mg/L. At a temperature of 298 K. It is construe from the fig.6. That the ratio of the removal of the dye increases as the weight of the surface increases due to increased surface area of the surface and then reach a constant value representing the saturation of the surface (snail shell powder) of the material (Malachite Green). [24] So for this reason 0.0200 g was selected for further experiments.

Fig.(6): The effect of adsorbed weight on the absorption of Malachite Green dye via snail shell powder at Temp. 298 K.
PH effect:-

The effect of pH on the adsorption of dyes, one of the most important factors affecting the adsorption process is the pH, Because it can immediately affect the surface absorption charge and degree of ionization for functional adsorption groups, as well as the adsorption mechanism. [23]. With the aim of studying Hydrogen ion concentration (PH) on malachite green dye by adsorbed snail shell powder, dye solutions were prepared at 7.0000 mg/L and Adjusted for pH values in the range (2-12) using 0.1 N of HCl and 0.1 N of NaOH. The results are indicate in Fig. 7. Obviously, the amount of toxic dye removed is at a different pH. It is obvious that the quantity of dye removed at a different pH. Dye removal has a-high value at pH =8.

Fig.(7) : Effect pH on adsorption of Malachite Green dye via snail shell powder at Temp. 298 K.

3.4. The effect of ionic strength:-

Many experiences have been done to locate the effect of ionic strength designed to decrease the effect of ionic strength on the absorption capacity and rate of removal using various concentrations ranging from 0.0700 M to 0.0200 M of salts (NaCl, KCl, MgCl2, CaCl2). Fig.8 the obtained result is shown in the effect of ionic strength on dye removal.
Fig.(8): Effect of ionic straight on the adsorption of Malachite Green dye by Snail Shell powder at temp. 298 K.

**Impact of Temperature**

Malachite green dye was studied using Snail Shell powder at a range from 298 to 338 K. Determination of thermodynamic parameters such as free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) find them using equations 2 to 5, which are given in table 3 [25].

![Figure 9](image.png)

Figure (9): The effect Malachite Green dye adsorption temperature on snail Shell powder.

**Equations**

\[
\text{Keq} = \frac{(Qe m)}{(Ce V)} \quad \text{(2)}
\]

\[
\Delta G = -RT \ln \text{Keq} \quad \text{(3)}
\]

\[
\ln \text{Keq} = \left(\frac{-\Delta H^\circ}{RT}\right) + c_0 \quad \text{(4)}
\]

\[
\Delta S = \frac{(\Delta H - \Delta G)}{T} \quad \text{(5)}
\]
Table (3): Thermodynamic parameters $\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$ of Malachite Green dye on the adsorbent surface Snail Shell powder at temp. (298-338) K

| Adsorption system | Temp. K | $\Delta G^\circ$ (kJ/mol) | $\Delta H^\circ$ (kJ/mol) | $\Delta S^\circ$ (J/mol) |
|-------------------|---------|---------------------------|---------------------------|---------------------------|
| MG                | 298     | -4.6355                   | -2.6962                   | 15.5464                   |
|                   | 308     | -4.7053                   |                           | 15.2682                   |
|                   | 318     | -4.7713                   |                           | 14.9957                   |
|                   | 328     | -4.8932                   |                           | 14.7291                   |
|                   | 338     | -4.8932                   |                           | 14.4691                   |

Negative values of ($\Delta G^\circ$ and $\Delta H^\circ$) indicate the automatic nature of adsorption [26], the process is exothermic [27] and increased randomness at the solid–solution interface during the adsorption of MG dye on Snail Shell adsorbent [28].

**Adsorption Isotherm**

Where adsorbed isothermal, the distribution of adsorbed particles between the liquid phase and the solid phase explains when the adsorption process reaches equilibrium. Fig. 10 indicates the adsorption isotherms of Malachite Green dye onto snail shell powder at pH = 8.0, at temperature from 298 to 338 K, 0.0200 g of the adsorbent materials and the time of 10 min., where we note that the adsorption capacity for Malachite Green increases with the increasing equilibrium Malachite Green.

![Fig. (10): Shows adsorption isotherm of Malachite Green dye from aqueous solution using snail shell powder as low-cost adsorbent at various temperatures.](image-url)
Langmuir isotherm model:
Where assumes uniform adsorption capabilities on the surface without adsorption transfer from the surface. Therefore, the Langmuir isotherm model was chosen to estimate the maximum amplitude of absorption corresponding to the full monolayer coverage on the adsorbent surface. The Langmuir model of Langmuir absorption assumes that adsorption occurs at specific homogeneous sites within the adsorbent, and the Langmuir equation is expressed by the following relationship

\[
\frac{C_e}{Q_e} = \frac{1}{ab} + \frac{Ce}{a} \quad \ldots \ldots (6)
\]

whereas:

- \(Q_e\) is the quantity of Malachite Green dye adsorbed at equilibrium (mg/g).
- \(Ce\) is the concentration of equilibrium of Malachite Green dye in solution (mg/L).
- \(a\) and \(b\) are the Langmuir constants.

\[
RL = \frac{1}{(1 + b \cdot C_0)} \quad \ldots \ldots (7)
\]

Where:

- \(C_0\) It is the concentration of dye-initiation in solution mg/L.
- \(b\) It is the Langmuir constant L/mg.

Where RL values show the type of adsorption to be irreversible (RL = 0), favourable (0 < RL < 1), linear (RL = 1) or unfavourable (RL > 1) [29].

Freundlich isotherm model :
The Freundlich isotherm mode describes non-ideal and reverse adsorption, as well as which was not limited to the formation of any monolayer i.e. The Freundlich isotherm mode is applied to multi-layer adsorption on heterogeneous surface. The slope is between 0 and 1 and is a measure of adsorption intensity or a measure of surface heterogeneity, if the value is close to zero then the surface is more homogeneous. Where the value below the unit means the chemical absorption process, but if the value of \(n\) (adsorption density) is greater than 1, it is an indication of the cooperative process.
The Freundlich isotherm model studies the multi-layer adsorption (heterogeneous surface) [30]. The isotherm is given by the following equation:

$$\log Q_e = \ln K_f + \frac{1}{n} \log C_e$$  \hspace{1cm} (8)

where:
- $Q_e$ is the quantity of Malachite Green dye adsorbed at equilibrium (mg/g)
- $C_e$ is the concentration of equilibrium of Malachite Green dye in solution (mg/L)

The constants of the Freundlich isotherm model are $K_f$ and $n$.

![Figure 12](image12.png)

Figure (12): Shows adsorption Freundlich isotherms of Malachite Green dye from aqueous solution using snail shell powder as low-cost adsorbent at various temperatures.

**Temkin Isotherm model:**

It is very good for predicting gas phase equilibrium. This model takes into account the interaction between adsorbate and adsorbent. The Temkin Isotherm model assumed a uniform energy distribution of the link. Below is the Temkin Isotherm model equation:

$$Q_e = B \ln A_t + B \ln C_e$$ \hspace{1cm} (9)

Where:
- $A_t$ is the equilibrium binding constant
- $B$ is related to the heat of adsorption [31]

Where (Fig.13) shows the Temkin curves for MG dye adsorption.

![Figure 13](image13.png)

Fig.(13): Shows adsorption Temkin isotherms of Malachite Green dye from aqueous solution using snail shell powder as low-cost adsorbent at various temperatures.
Table (4): Langmuir, Freundlich and Temkin parameters of adsorption isotherms at (338-298) K.

| Temp. (K) | Langmuir isotherms | Freundlich isotherms | Temkin isotherms |
|----------|--------------------|----------------------|------------------|
|          | a (mg/g)          | b (mg/L)             | r² | RL  | Kf | n | r² | B | AT | r² |
| 298      | -9.7370           | -0.4726              | 0.9814 | -0.4346 | 11.259 | 0.5970 | 0.9556 | 14.0010 | 3.0578 | 0.6447 |
| 308      | -8.4817           | -0.4649              | 0.9608 | -0.4435 | 9.5499 | 0.5838 | 0.9521 | 14.308 | 2.7635 | 0.6296 |
| 318      | -6.3451           | -0.4928              | 0.9530 | -0.4082 | 8.2870 | 0.5307 | 0.9623 | 15.624 | 2.3579 | 0.6459 |
| 328      | -6.2034           | -0.4656              | 0.9444 | -0.4426 | 7.5110 | 0.5263 | 0.9581 | 15.5260 | 2.2535 | 0.6339 |
| 338      | -6.2266           | -0.4400              | 0.9336 | -0.4807 | 6.6742 | 0.5197 | 0.9574 | 15.6590 | 2.1049 | 0.6386 |

*The Langmuir model gives top r² so we conclude that adsorption was obeys Langmuir isotherms, this indicating that the adsorption of the MG dye toxin on the surface of snail shell powder was homogeneous sites within the adsorbent.

4-Conclusion

The current study demonstrated that snail shell can be used as an effective adsorbent to remove MG dye from aqueous solutions. In addition to reducing waste, the results also supply extra advantages for industrial wastewater handling, thermodynamic functions indicate that the adsorption of the MG dye on the surface of the snail shell is an isothermal process that occurs automatically.

Reference

1- Dojlido, Jan, and Gerald Arthur Best, (1993) "Chemistry of water and water pollution". Ellis Horwood Limited.
2- Pavko A., (2011). "Fungal decolourization and degradation of synthetic dyes". The fourth chapter. Waste Water—Treatment and Reutilization, University of Ljubljana, Faculty of Chemistry and Chemical Technology Slovenia, pp.65-88.
3- Ahmad MA, Ahmad N, Bello OS, (2014)" Adsorptive removal of malachite green dye using durian seed-based activated carbon". Water Air Soil Pollut 225:1–18. doi:10.1007/s11270-014-2057-z
4- Aksakal O, Ucun H, Kaya Y, (2009) "Application of Eriobotrya japonica (Thunb.) Lindley (Loquat) seed biomass as a new biosorbent for the removal of malachite green from aqueous solution". Water Sci Technol J Int Assoc Water Pollut Res 59:1631–1639. doi:10.2166/wst.5
5- Abd-El-Kareem MS, Taha HM, (2012)" Decolorization of malachite green and methylene blue by two microalgal species". Int J Chem. Environ Eng 3:297–302.
6- Ali H, (2010)" Biodegradation of synthetic dyes—a review". Water Air Soil Pollut 213:251–273. doi:10.1007/s11270-010-0382-4.
7- Adegoke KA, Bello OS, (2015) "Dye sequestration using agricultural wastes as adsorbents". Water Resour Ind 12:8–24. doi:10.1016/j.wri.2015.09.002.
8- Ali H, Ahmad W and Haq T, (2009) "Decolorization and degradation of malachite green by Aspergillus flavus and Alternaria solani". Afr J Biotechnol. doi:10.4314/ajb.v8i18.60239.
9- Anbia M, Ghaffari A., (2012) "Removal of malachite green from dye wastewater using mesoporous carbon adsorbent". J Iran Chem Soc 8:S67–S76. doi:10.1007/BF03254283.
10- Afkhami A, Moosavi R and Madrakian T, (2010) "Preconcentration and spectrophotometric determination of low concentrations of malachite green and leuco-malachite green in water samples by high performance solid phase extraction using maghemite nanoparticles". Talanta 82:785–789. doi:10.1016/j.talanta.2010.05.054.
11- Hameed B H and El-Khaiary M I, 2008"Kinetics and equilibrium studies of malachite green adsorption on rice straw-derived char". Journal of Hazardous Materials, 135(1-2) pp.701-708.
12- Natarajan S , Bajaj H C and Tayade R J, (2018)" Recent advances based on the synergistic effect of adsorption for removal of dyes from waste water using photocatalytic process". Journal of Environmental Sciences, 65, 201-222.
13- Gupta V K and Suhas , (2009)" Application of low-cost adsorbents for dye removal—a review". J Environ Manage 90:2313–2342. doi:10.1016/j.jenvman.2008.11.017.
14- Khan TA, Rahman R and Ali I et al ,(2014)" Removal of malachite green from aqueous solution using waste pea shells as low-cost adsorbent—adsorption isotherms and dynamics". Toxicol Environ Chem 96:569–578. doi:10.
15- Tewari K, Singhal G and Arya R K , (2018) "Adsorption removal of malachite green dye from aqueous solution". Reviews in Chemical Engineering, 34(3), 427-453.
16- Popoola L T, Aderibigbe T A , Yusuff A S and Munir M M , 2018"Brilliant green dye adsorption onto composite snail shell–rice husk Adsorption isotherm, kinetic, mechanician, and thermodynamics analysis". Environmental Quality Management.28 pp.63-78.

17- Hanadi K I , Munner A A and Eman T K ,2019 "Decolorization of Coomassie brilliant blue G-250 dye using snail shell powder by action of adsorption processes. Research J. Pharm. and Tech. 12(10)pp4921-4925.
18- Reham Q , Munner A A and Eman T K, 2018" Study on the Use of Snail Shell as Adsorbent for the Removal of Azure A Dye from Aqueous solution".Journal of International Pharmaceutical Research.45 pp.123-129.
19- Hanaki K I , Munner A A and Eman T K, 2018 " Effective Adsorption of Azure B Dye from Aqueous Solution Using Snail Shell Powder" .J Biochem Tech. 9(3) pp 39-44.
20- Vijayakumaran, V and Arivoli S , (2012) " Equilibrium and kinetic modeling on the removal of malachite green from aqueous solution using odina wodier bark carbon". J Mater Environ Sci, 3(3), 525-536.
21- AL-Da'amy, Muneer A , Noor A AL-Khazali, and Eman TK AL-Rubaey. "Removal of Malachite Green from Aqueous Solution by Iraqi Porcelanite Rocks." (2009).
22- Uma, Banerjee S and Sharma Y C,2013" Equilibrium and kinetic studies for removal of malachite green from aqueous solution by a low cost activated carbon". J Ind Eng Chem 19:1099–1105. doi:10.1016/j.jiec.2012.11.030
23- Eckenrode H M, Jen S H and Han J et al, 2005 "Adsorption of a cationic dye molecule on polystyrene microspheres in colloids effect of surface charge and composition probed by second harmonic generation". J Phys Chem B 109:4646–4653. doi:10.1021/jp045610q
24- Wang L, Zhang J, Zhao R, Li Y, Li C and Zhang, C, 2010 " Adsorption of Pb(II) on activated carbon prepared from Polygonum orientale Linn.: kinetics, isotherms,pH, and ionic strength studies. Bioresour". Technol. 101 (15), 5808e5814.
25- Sharma K K, and Sharma L K, 1986"A Text Book of Physical Chemistry". 8th ed. Vina Education, India.
26- Patil M R and Shrivastava V S, 2014 "Adsorption of malachite green by polyaniline–nickel ferrite magnetic nanocomposite an isothermand kinetic study" Appl Nanosci 5:809–816. doi:10.1007/s13204-014-0383-5.
27- Chowdhury S, Mishra R, Saha P and Kushwaha P, 2011" Adsorption thermodynamics, kinetics and isosteric heat of adsorption of malachite green onto chemically modified rice husk". Desalination 265:159–168. doi:10.1016/j.desal.2010.07.047.
28- Wang L, Zhang J and Zhao R et al, 2010" Adsorption of basic dyes on activated carbon prepared from Polygonum orientale Linn equilibrium, kinetic and thermodynamic studies". Desalination 254:68–74. doi:10.1016/j.desal.2009.12.012.
29- Langmuir I, 1918"The adsorption of gases on plane surfaces of glass mica and platinum". Journal of the American Chemical society, 40 pp.1361-1403.
30- Freundlich H, 1907"Uber die adsorption in losungen". Zeitschrift für physikalische Chemie, 57 pp.385-470.
31- Temkin M J and Pyzhev V., 1940"Recent modifications to Langmuir isotherms". Acta Physicochim. URSS. 12 pp217-225.