Removal of malachite green by poly acrylic beads

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Abstract

This work investigates removing the Malachite Green (MG) dye, the poly acrylic hydrogel beads used as a surface to adsorb the dye, the isotherm of adsorption was examined and aspects that influence it, like increasing heat, adding salt, the influence of dry beads and effect of shaking. according to the results, the effect of the adsorption has been found that it is matched to the Friendlish equation much more than Langmuir and Temkin equations. A positive relationship between the adsorption process and the increase in temperature is found that adsorption increases when the temperature increase. Also, the adsorption increased when the salt was added at a temperature (of 20 C^0). As that the adsorption doesn't budge by adding either dry or wet beads of poly acrylic. The thermodynamic function was calculated **(ΔH, ΔS, ΔG)**. The kinetic parameters were examined by the Lagergren equation to first order, for second-order equations either, according to the results of experimental data showing us that the adsorption obeys the pseudo-second order more than the first-order.

Keywords

Malachite green, poly acrylic beads acid, Freundlich isotherms, Removal.

1.Introduction

Dyes with doubt are among an organic substrate which pollute water. The main causes for this is consequent to their large use in several industries, for instance, used in oil industry, the textile manufactures, dyeing, leather tanning, coloring of portrayal, many fields, and paper production that produce high colored waste effluents [1,2]. dyes low cost, advance a widely domain of colors, and are utilized for considerable applications such as paper, cosmetic manufactures, tanning, pharmaceutical, and photographic[3]. One of these dyes is Malachite Green [4]. (MG) is a synthetic organic component of tri phenyl methane, MG has been widely applied in accurate chemicals, pharmaceutical industries and food processing [5,6]. In spite of its many application, MG contain of poisonous properties which stay for too long in water and are hard to be lowest by microorganisms [7]. Malachite Green dye has a chemical structure is $C_{23}H_{25}N_2Cl$ that can be found in two prime forms after entering chemical reactions to other materials, the two forms of M.G are Malachite green hydrochloride and leucomalachite green. Leucomalachite are a miniature form of MG, while malachite green hydrochloride is a manufacturing stage [8, 9]. A lot of treatment methods are advanced for example developed oxidative processes [10], biological therapy [11], filtration in membranes [12], photodegradation [13,14], and adsorption [3]. the best effective method for treating or removing organic pollutants in a medium is the adsorption method [15]. The adsorption method is a dye elimination which has considerable properties. In fact, it can be utilized to nearly any kind of dye mixture of dyes, it hasn't demanded any private equipment or treatment, and the process can be reduplicated many times till the adsorbent has access its maximum adsorbing strength. The adsorption process as well economical as it has been take out in moderate conditions, decreasing the existing price to the adsorbent, that can be choosing accordingly [16,17]. A good adsorbent has the main specifications of high superficies area, a capacity of high adsorption, short adsorption times, economic and environmentally-friendly production processes. Poly acrylic acid (PAA) is used as a surface that is characterized is a flexible polymer, making the process easy to penetrate PAA [18]. PAA is colorless and used for removal [19].

2.Experimental

Materials: Malachite Green (MG) and (NaCl) are provided and deionized water had been used.

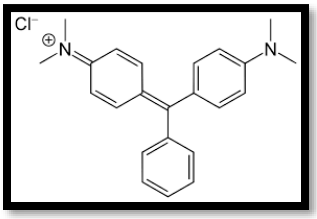

Figure (1) structure of (MG)

Poly acrylic beads used to adsorb the Malachite Green and the figure (2) shows the poly acrylic structure :

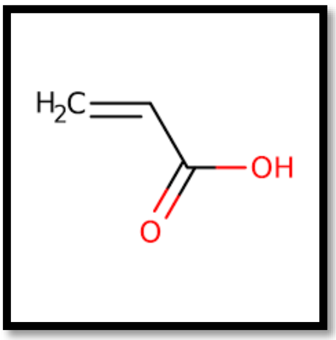

Figure (2) the poly acrylic acid beads

3.Methods

The instrument UV-Vis spectroscopy was applied to finding the absorption. The wavelength (λ max) of absorption of Malachite Green was (615 nm).
The contact time was measured to find the equilibrium between the adsorbent and adsorbate, there was mixing between concentrations and poly acrylic acid beads (0.025 g),

and then putting in the bath shaker at ($20C^0$), we measured the concentration in sequence at a different time to find the change of concentration through time.
Adsorption isotherm: Estimating the adsorption isotherm of a dye solution, putting (0.025 gm) of PAA in six round flasks with (50 ml) of the dye MG in each flask, then put six flasks in a bath shaker at a temperature of ($20\ C^0$), the quantity of adsorption was measured by the equation [20] :

Qe = (Co-Ce) Vs/m ………………(1)

Qe= quantity of adsorbed material (mg/g).
Co= initial concentration (mg/L).
Vs= the volume of solution (L).
m= the mass of surfaces (g)
Ce= the equilibrium concentration (mg/L).
The operation was repeated several times at different temperatures and apply the equation up at each temperature.

4.Results and discussion

The effect of contact time (equilibrium time) for Malachite Green is (160 min), as a function of time the adsorption is rise respectively and figure (3) shows the rise in adsorption

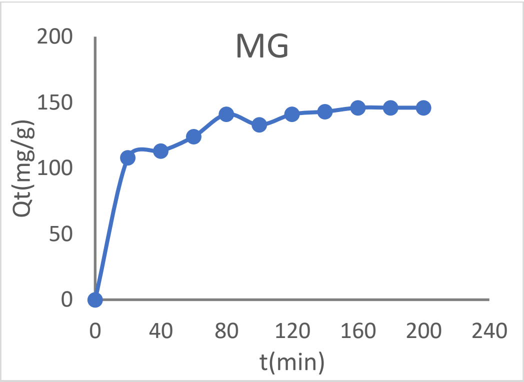

Figure (3) contact time for MG dye, condition (Temperature $20C^0$, Concentration 70 PPM, Rotation per minute 180 rpm, Equilibrium contact = 160 min).

Adsorption isotherms

For every concentration equilibrium, we calculated the adsorption quantity (Qe) vs Ce. Figure (4) below is plotted to explain the adsorption planner.

The general scheme of adsorption isotherm of MG on PAA refers to (S3) classify according to Giles classification, that the particles of adsorbate vertical [21]. the plotting format of (Langmuir, Temkin and Friendlish) equations proven that, the results found more identical with Freundlich equation and not applicable to Langmuir and Temkin, as shown in figures (5,6,7)

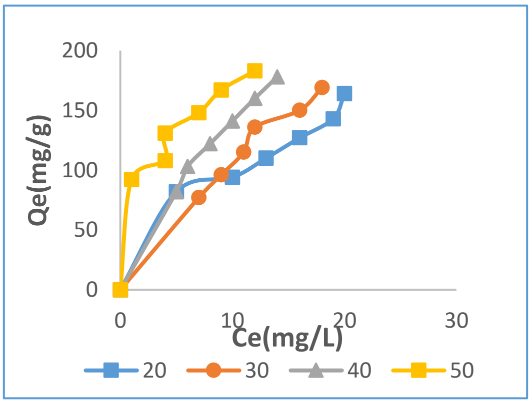

Figure (4) Adsorption isotherms samples of MG dyes on PPA at various temperature.

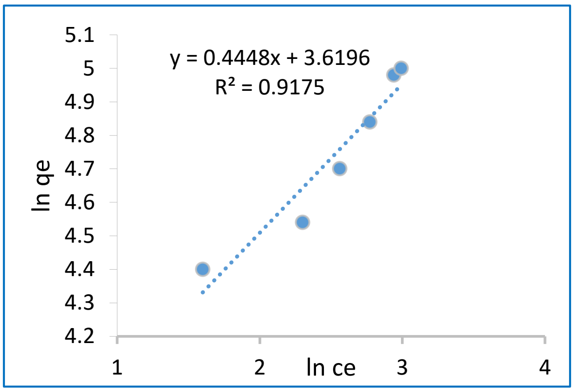

Figure (5) application of linear Freundlich equation.

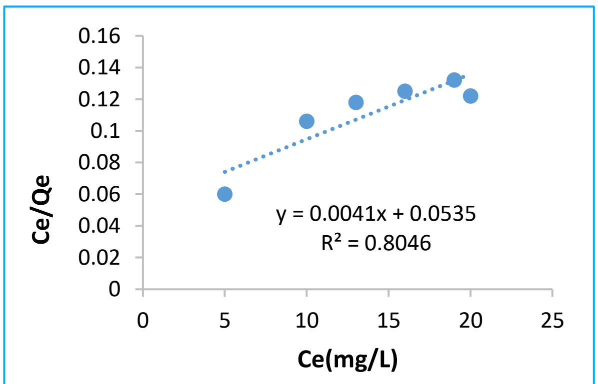

Figure (6) application of linear Langmuir equation.

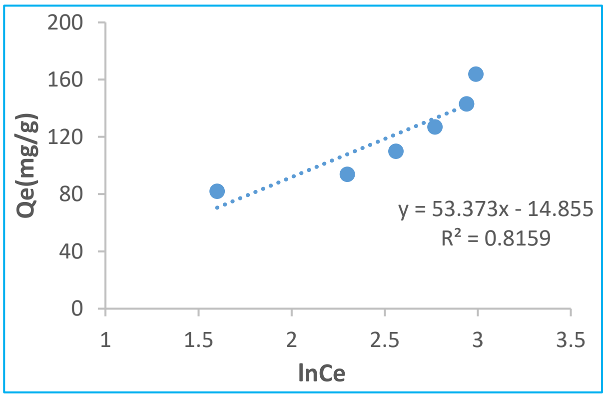

Figure (7) the linear equation of Temkin.

Thermodynamic studies

Thermodynamic Parameters including change in standard free energy (ΔG^0) , standard enthalpy (ΔH^0) and standard entropy (ΔS^0) for removal of malachite green by poly acrylic acid hydrogel beads are estimated according to the following Equation (2,3,4) at four temperature (293 , 303, 313, and 323 K)when temperature increase quantity of adsorption become higher, (ΔH) has been measured by Vant Hoff equations.

ln Qmax = $\frac{-\Delta H}{R\,T}$ + Constant …………….(2)

Qmax = The maximum quantity of adsorbed

R = constant of Gases (8.314 $j.mole^{-1}.k^{-1}$)

T = Temperature of process.

A Plot between Ln Qmax vs reverse temperature (1/T) as shown in Figure (8) below.

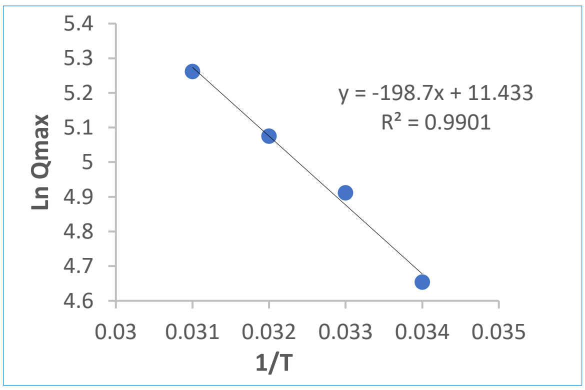

Figure (8) Application of Vant Hoff equation for MG dye and PAA .

According to Vant Hoff equation ΔG and ΔS is measured by

$\Delta G^0 = -nRTLnQmax$ ………………(3)

$\Delta G^0 = \Delta H^0 - T\Delta S^0$ …………………(4)

Table (1) Thermodynamic functions of MG at different temperature.

T(k)	ΔH^0(KJ/mole)	ΔG^0(KJ/mole)	ΔS^0(J/mole.K)
293		- 11.31	88.15
303	14.25	-12.31	88.84
313		-13.2	88.56
323		-13.98	86.62

The positive value of ΔH mean that the process are Endothermic, while the minus values of ΔG refer that the operation are spontaneous and the plus values of ΔS mean that the particles are arrangement in solution more than on surface [22].

Effect the ion strength

The adsorption has been measured when added (0.01 gm) Sodium Chloride salt, to check the efficiency of removal of adsorbed molecules, the process was in condition (temperature 20℃ , Rotation per minute 180 rpm, Equilibrium time = 160 min) at different concentrations. the effective of salt are shown that the removal is less compare with tab water under the same condition as shown in figure (9) below

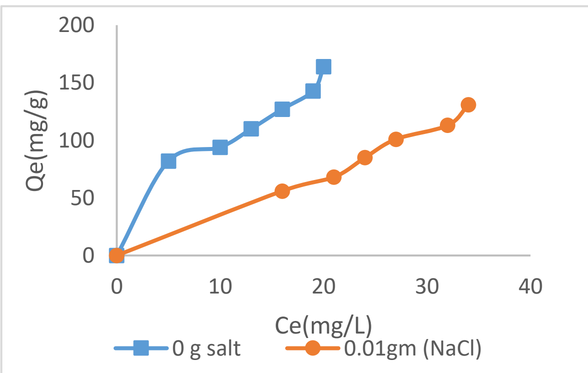

Figure (9) compare between Removal of prepared dye against tap water with 0.01gm (NaCl) at 293 K.

Shaking effect

The basic influential that changing of the adsorption procedure for dyes the reason that it is connecting with diffusion of dye particles to adsorbent PAA [23]. Shaking effect has been studied as shown in figure (10) below:

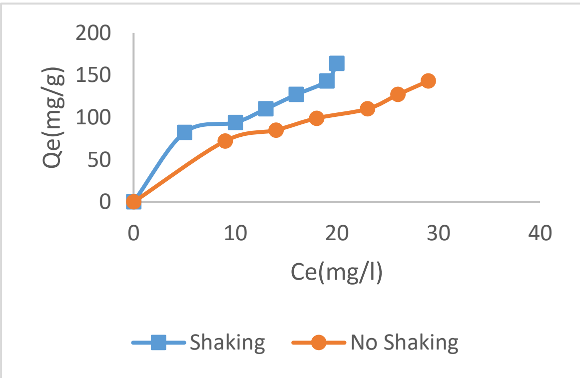

Figure (10) effect of shaking and no shaking at same conditions.

Effect of using wet PAA

The adsorbent molecules are putting in water for (24 hours) and the adsorption are making compare with dry molecules under same condition, figure (11) shown the difference:

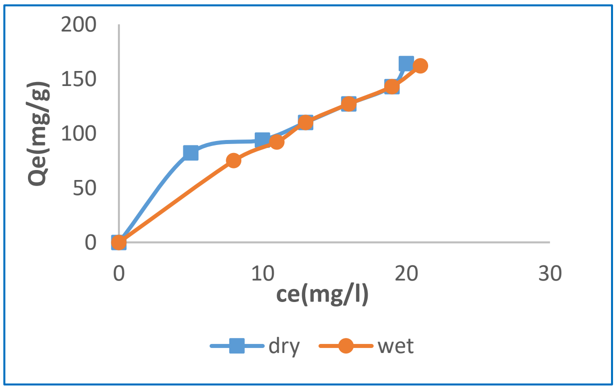

Figure (11) influencing of dry,wet PAA at 293 k

Removal percentage

The removal percentage was measured by putting a different concentration. 50ml for each concentration at 293K. the process arrive to equilibrium time then the remaining concentration has been measured as shown in figure (12)

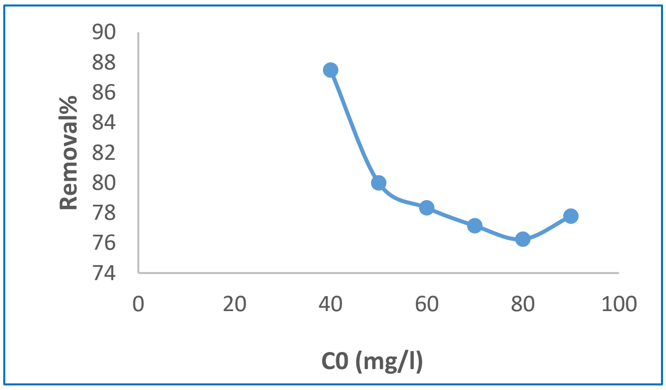

Figure (12) removal percentage at 293.

As shown in figure (13) of MG dye the removal percentage of dye is higher at low concentrations on the contrary at high concentrations. The capacity of dye doesn't reach the maximum, the reason that the ability to absorb much quantity of dye is low. Unlike at high concentration, it is reaching the maximum capacity. The removal percentage is measured by the equation:

$$\% \text{ Removal} = \frac{Initial\ conc. - Residual\ conc.}{Initial\ conc.} * 100\ \% \ \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Adsorption kinetic

The kinetic of removing the MG dye were studied by

1- **Lagergren equation**:

$$\text{Ln}\ (qe - qt) = \text{lnqe} - K_{ad}\ t \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

That the:

Qe, qt = susceptibility equilibrium in time (mg/l).

Kad = psedue the constant of first order (min^{-1}). [24]

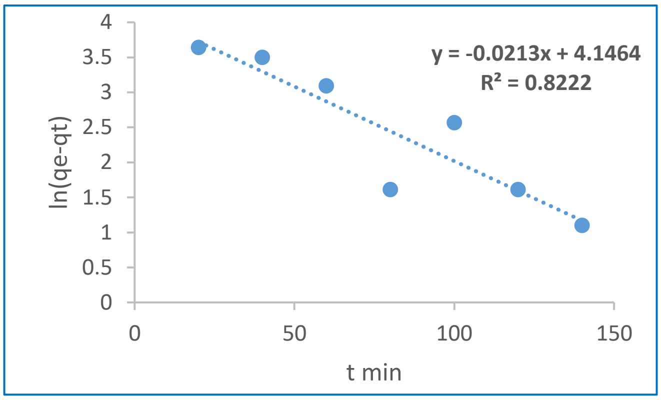

Figure (13) application of pseudo first-order from MG on PAA according to Lagergren equation.

2- The second-order

The second order measured throw the equation:

$$\frac{t}{qt} = \frac{1}{kqe} + \frac{t}{qe} \quad \ldots\ldots\ldots\ldots\ldots\ (7).$$

Where K = the constant of pseudo of second-order (min^{-1}). [25]

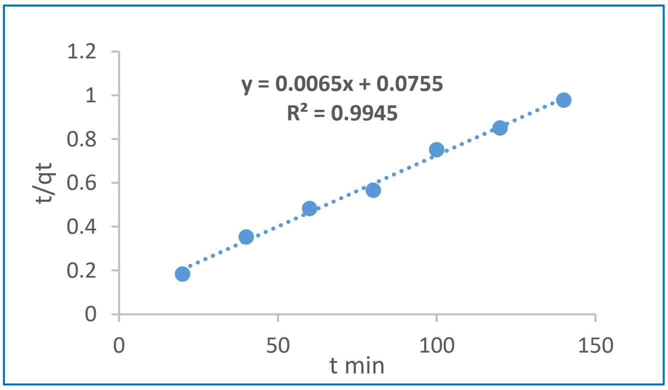

Figure (14) application of pseudo second-order from MG on PAA.

The results shown us that the process is obeys to second order.

Conclusion

In this study the poly acrylic acid hydrogel beads PAA is used to remove the Malachite Green dye, adsorption isotherm and factor that affect them such as (concentration, ionic strength, temperature, wet PAA and shaking effect) was calculated. Received results was shown as follow: the adsorption calculated at a temperature (323K,313K,303K,293K), The process of removal was increasing with increase of temperature. Malachite Green are obeyed with friendlish isotherm unlike the Temkin and Langmuir equations. the ionic strength (using sodium chloride) is affecting that the process of removal decreases when the salt are presence. The effect of wet PAA showed that the process doesn't affect when used dry PAA. the effect of shaking and the process of removal are increasing unlike when not shaking. the functions of thermodynamic were measured. the kinetic of adsorption of dye were studied on PAA. it found that the process are coordinated with second-order equation and not coordinate with Lagergren equation at first-order.

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