

Ultrasonically assisted improved sorption of cationic dye by a cheaper sorbent

H. Ghodbane*

Univ Souk Ahras, Fac. Sci& T Dept. Process Engineering. Souk Ahras, Algeria
Laboratory of physics for matter and radiation, Mohamed Cherif Messadia-Souk Ahras
University, P.O.Box 1553 Souk ahras, 41000, Algeria.

*Corresponding author: ghodbane.houria08@gmail.com

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ABSTRACT/RESUME

Abstract: The goal of this investigation was to evaluate the sorption of malachite green (MG) from aqueous solutions using pumpkin seed peels in the absence of mixing and under low frequency ultrasound. Batch experiments were performed to examine the effect of operating parameters such as sorbent dose (0.05- 0.6 g), initial dye concentration (5– 20 mg/L), initial solution pH (2–8), temperature (25°C–45°C) and ionic strength (0–1 g/L). The following data reveal the quantum of sorption of MG was greatly enhanced under ultrasound conditions. Dye stuff sorption when ultrasound is used was significantly increased by increasing the initial sorbent concentration and by reducing the sorbent quantity. The ionic force hinders the sorption of the pollutant. The basic pH was found to be the most advantageous for the sorption of MG. At pH 2, sorption is low due to competition between H^+ ions and VM molecules to occupy the sorption sites. At this pH, the pumpkin seed surface is positively charged ($pH < pH_{PZC} = 4.92$). The sorption kinetic data were found to be well-represented by the pseudo-second-order rate equation, both in the absence and presence of ultrasound ($r \geq 0.996$). Analysis of the sorption kinetics results reveals that film and particle diffusion are successful sorption mechanisms. Additionally, the sorption isotherm data were analyzed by two isotherm models Langmuir and Freundlich models. Equilibrium data can be well described by the Langmuir model for both methods, showing maximum monolayer sorption capacity (q_m) of 8,9445 and 15,0375 mg/g at 21°C, respectively.

I. Introduction

Dye containing wastewater poses serious environmental problems due to its color and potential toxicity. The elimination of dyes from the wastewater has attracted a lot of attention in the latest years in the related industries. In recent years, a great deal of attention has been focused on the removal of dyes from the effluents of textiles industry. The projected reports are distressing: 10-20% of the dyes used in manufacturing textiles are lost in waste liquor by incomplete depletion and cleaning operations [1].

Weighing in on the weak concentration of dyes in the wastewater is very noticeable and is not wanted, and it decreases the incidence of light penetration, which causes inhibition of photosynthesis and strict limitations on the organic content of industrial effluents.

In this report, the dye chosen is Malachite green (MG), a basic dye. It is the largest dye used for colouring, compared to those of its category [2]. This substance has been recognized as being a serious killer of people and could lead to the creation of liver tumors.

The usage of such tincture was forbidden in numerous countries. Nevertheless, because of its simple production and cheaper price, it is used in some countries with fewer restrictive legislation for non-aquaculture applications. The removal of the dye is therefore of considerable significance. Hence, The elimination of dyes is of primary interest.

There are many ways to remove dyes from manufacturing effluents. Compared to the previous techniques, Sorption was deemed superior due to its straight forward design, cost, usability and insensitivity to hazardous compounds. Basically, the sorption process is a mass transfer concept.

To improve the sorptibility of the contaminants, it is necessary to introduce ultrasound technology.

Indeed, ultrasonic propagation within the medium results the oscillation of micrometer gas bubbles which, under appropriate factors, undergo a high variation in volume and collapse in an almost adiabatic manner.

This type of pattern is usually designated as acoustic cavitation, and the concentration of energy at the instant of collapsing leads to extreme localized states, especially high temperatures (~5000 K) as well as pressures (~1000 atm) at the interior of the cavity [3, 4]. A variety of chemical and physical processes can occur within and in the liquid surrounding the cavitation bubbles.

Homolysis and pyrolysis reactions of the gas are taking place, while the heating of the cavity is in operation, leading to the generation of radicals. Water vapor in an aquatic medium is decomposed to the following radicals: H and OH, and in the presence of other species, several other radicals can be produced. The bubbles' movement through oscillation and collapse induces important effects on the fluent circulation, similar to micro-jets as well as powerful forces of shearing. In addition, when the bubbles collapse, strong shaking waves are created and spread in fluid at higher frequencies than natural sound rate [5].

Throughout the globe, pumpkins are planted primarily for food and, more importantly, for medicinal purposes [6-8]. When pumpkin is treated in seeds and peelings a lot of waste is produced. There are approximately 51.0% of oil as well as 36.5% of protein in the powdered pumpkin seeds [9].

Pumpkin peels are extremely rich in pectin and the skins have been applied successfully to extract the alcohol-insoluble polysaccharide [10]. Given the challenges of the agri-food industry, in an attempt to reduce unnecessary waste, extensive attention is being paid to optimising food manufacturing systems. Residues generated by the food manufacturing companies can either be reused as a side product, or as feedstock for other manufacturing companies [11].

In this study we were interested in using pumpkin seed peels as a sorbent material for wastewater treatment.

The primary focus of this research is to evaluate the sorption of MG into an agricultural residue from an aqueous medium under and without ultrasound, as well as to understand and interpret the ultrasonic impact upon kinetics of sorption. In this way, the following impacts of a number of operational factors including sorbent dose, initial dye concentration, pH, ionic strength and temperature of solution on MG removal have been investigated.

II. Materials and methods

II.1. Method of preparing the sorbent

In the laboratory, pumpkin seeds purchased from a commercial market were peeled from their skins individually. After collection, the shells were repeatedly cleaned with water and subsequently with distilled water to dislodge any adhesive contaminants. Afterwards, it was kiln dried to a constant mass. The dry product was ground, graded to a granulometry of 0.5 to 1 mm, and preserved in a plastic flask for subsequent usage.

II.2. Sorbate

The dye, malachite green oxalate, C.I. Basic Green 4, C.I. Classification Number 42,000, chemical $C_{25}H_{56}N_4O_{12}$, MW = 927.00, $\lambda_{max} = 617$ nm (measured value) was supplied by Merck. This dye was chosen as a model compound of triarylmethane dyes. Figure 1 is an illustration of the chemical structure of this dye.

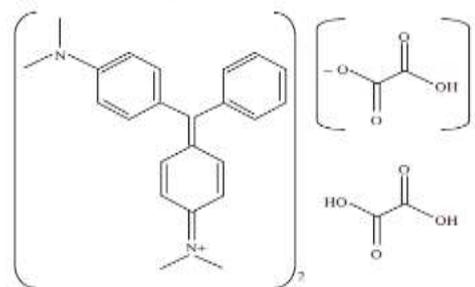


Figure 1. A chemistry structure of MG (oxalate salt) (oxalate salt) [12].

II.3. Experimental apparatus and procedures

A pattern of the experiments device was depicted in Figure. 2. Experiments were performed in a 400 mL cylindrical jacketed glass vessel that was attached to an overhead mechanical stirrer. The recipient was entered into an ultrasonic cleaner working within a frequency of 30 kHz with a current rating of 30 W. Acoustical power dissipation throughout the medium has been calculated according to the standard calorimetric approach [13].

For dye elimination kinetics experiments, a predefined mass of pumpkin seed peel was brought into contact with 100 ml of MG solutions. The mixture was agitated at a fixed mixing speed of 100 rpm and concurrently agitated (100 rpm) and sonication over a period of 120 min that is more than necessary for the establishment of equilibrium with both methods examined.

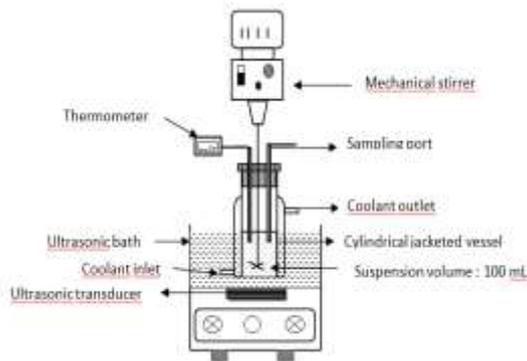


Figure 2. Experimental setup.

The dye elimination efficiency, R (%), was determined by the following formula:

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

The amount of dye sorbed at time t , q_t (mg/g), and the sorption capacity at equilibrium, q_e (mg/g), were determined by the following expressions:

$$q_t = \left(\frac{C_0 - C_t}{m} \right) \times V \quad (2)$$

$$q_e = \left(\frac{C_0 - C_e}{m} \right) \times V \quad (3)$$

Where C_0 , C_e and C_t (mg/L) are the dye concentrations initially, at equilibrium and at time t , respectively, V (L) is the volume of the dye solution and m (g) is the weight of the material being sorbed.

Experiments were conducted to investigate the effects of sorbent dose, initial dye concentration, pH, ionic strength and temperature of solution on MG sorption.

In order to examine the impact of the initial dye concentration varying over the range of 5 to 20 mgL^{-1} , contact was made between a fixed mass of sorbent (0.2 g) and 100 mL of aqueous solutions of MG at 21°C.

In an aim to establish how sorbent dosage affects MG sorption, various quantities of biomaterial in a range of 0.05 to 0.6 g was introduced to 100 mL of MG solution at 21°C.

A study on the role of temperature on MG sorption was performed by contacting 0.2 g of sorbent with 100 ml of dye solution under a choice of temperatures (25-45 °C).

To determine the equilibrium isotherms, a constant weight of material (0.2 g) was brought into contact with 100 ml of MG solution in both the absence and presence of ultrasound. A UV-Vis spectrophotometer was used to analyse the solutions for residual MG concentration once equilibrium was reached.

III. Results and discussion

III.1. Identification of sorbent characteristics

FTIR spectrum of pumpkin seed peels is plotted in Figure 3. FTIR spectral data of pumpkin seedpeels was obtained in the range of 4000–500 cm^{-1} . It is clear from Figure.3 that pumpkin seedpeels showed different bands around 3436.91, 2920.03–2345.28, and 667.32–11620.09 cm^{-1} . These bands might be assigned to the stretching vibrations of hydroxyl and disulfide groups, O–H, C–H symmetric and asymmetric stretching of aromatic and amine group and C–O–C group, respectively.

The point of zero charge (pHPZC) of the pumpkin seedpeels was determined using the pH drift method as reported in the literature [14]. The pH at the point of zero charge obtained in this work is 4.92.

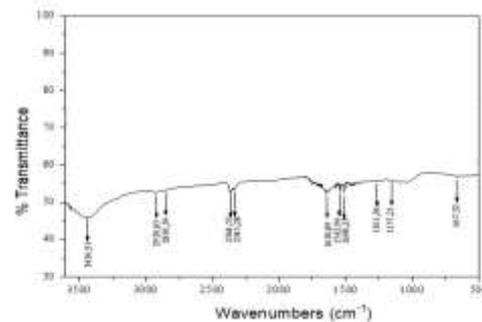


Figure 3. FTIR spectra of pumpkin seeds before sorption

The effect of biosorbent dose in the range of 0.5 to 5 g L^{-1} was used for the adsorption experiments and the results are given in Figure 1. We note that, the removal rate of Cr(VI) ions increases gradually with increasing biosorbent dose.

III.2. Sorbent dose impact

Sorbent dosage applied for removal of 10 mg L^{-1} MG by Pumpkin seed peels varied from 0.05 to 0.6 g (Figure 4). The sorption rates as well as the

equilibrium sorbed quantities in the presence of the ultrasonic field are higher than those obtained by the conventional method, at any mass of biosorbent. This finding can be associated with their ultrasonic and cavitation physical impacts, leading to a powerful convection in the environment through several physical mechanisms. In addition, Diffusion convection in the system restricts the sorptive process. The global mass transfer restriction is decreased through an increase in convection within the media or in other terms through a more turbid system. If a bubble collapses close to the solid surface, it impedes symmetrical cavitation and collapses asymmetrically. The non-symmetrical implosion of bubbles in an inhomogeneous system generates very fast micro-jets. In addition, the symmetric and asymmetric collapses produce shock waves, which provoke a very high flow turbulence across the liquid-solid interface, resulting in an elevated ratio of mass transfer close to the solid surface.

The quantity of dye sorbed per unit mass of material diminishes as the sorbent dose rises, as indicated in Fig. 4. A similar study was found by Guechi et al in the investigation of elimination of MG from liquid media upon adsorption using a new sorbent (Cattail leaves) [15]. It is important to note that in the case of greater proportions of sorbent to sorbate concentration, a very quick superficial sorption is taking place on its surface, leading to a weaker solute concentration in the liquid compared to a lesser sorbent to sorbate concentration proportion.

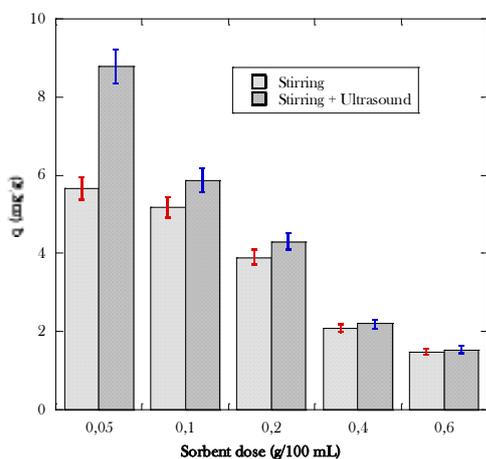


Figure 4. Effect of dosage sorbent on the removal of malachite green in presence and in absence of ultrasound ($T = 21^{\circ}\text{C}$, sorbent dose = 0.05–0.6 g/100 mL, initial concentration = 10 mg L⁻¹, sonication power = 11 W).

III.3. Impact of initial dye concentration

Graph 5 depicts MG sorption upon pumpkin seed peels under ultrasonic (sonication + mechanical

agitation) and non-ultrasonic conditions for several initial dye concentrations with a sorption amount of 0.2 g/100 ml depending on the contact time. According to the findings, the elimination of the dye depends on the initial concentration of MG. Dye sorption has been found to rapidly produce. With a higher initial dye concentration, the sorption ability of the MG will rise. It is important to note that the higher the initial dye concentration, the higher the sorption ability of the MG on the pumpkin seed peels, particularly by means of ultrasound.

Equilibrium uptake increases as the initial dye concentration rises. By increasing the initial dye concentration over 5 to 20 mg L⁻¹, an elevated equilibrium sorption ability was achieved between 2.14 and 6.58 mg g⁻¹ via classical method and between 2.34 and 8.15 mg g⁻¹ through the combination of ultrasonics and mechanical agitation. The coupling of ultrasonication and mechanic mixing enhances sorption, which is attributed to the intensification of mass transfer and thermal ultrasonic impacts, but also upon the perfect mixing that produced in the vessel. This may be due to attribute to the induced turbulence and additional convective mass transport within the pores and at the surface induced by high velocity micro-jets and high pressure shock waves as well as by microstreaming.

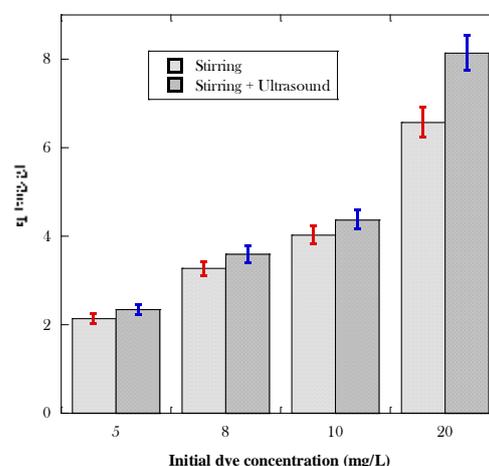


Figure 5. Effect of initial dye concentration on the removal of malachite green in presence and in absence of ultrasound ($T = 21^{\circ}\text{C}$, sorbent dose = 0.2 g/100 mL, initial concentration = 5–20 mg L⁻¹, sonication power = 11 W).

III.4. Effect of solution pH

The pH of the medium represents a parameter with a significant influence on the sorbent binding capacity on the biomaterial. The tests have been undertaken with varying degrees of pH within the interval of 2 to 8 and the pH of the solution has been regulated with either 0.1 N HCl or 0.1 N

NaOH aqueous solutions. However, it is important to note that the influence of the pH solution on the quantity of MG sorbed at equilibrium for the conventional technique and for the ultrasound assistance has been depicted in Figure. 6. A lowering of sorption with a declining pH is apparent for the combined method. The quantity of MG sorbed at equilibrium for the conventional method is nearly equal between pH 4 and 8 for conventional method. A similar approach has been reported for sorption of MG by treated ginger waste [16]. The lowest dye sorption was recorded at pH 2 in the absence and the presence of ultrasound. It is possible to explain, the role of the pH of the solution on the adsorption of the dye from the zero point charge pH_{pzc} , of the sorbent. At $pH > pH_{pzc}$ favourable sorption of cations on any sorbent will happen. This makes the surface of the sorbent appear with a negative charge and promotes the sorption of cationic dyes owing to the stronger electrostatic attraction strength. At $pH < pH_{pzc}$ favourable sorption of cations on any sorbent will happen. This makes the surface of the sorbent appear with a negative charge and promotes the sorption of cationic dyes owing to the stronger electrostatic attraction strength. Consequently, MG sorption via pumpkin seeds becomes more prominent at the highest pH (values above pH_{pzc} , 4.92). However, the positively charged surface of the sorbent at weaker pH ($pH < pH_{pzc}$) leads to high H^+ concentrations that interact with the positively charged MG cations for available sorption spots, resulting in reduction of dye sorption.

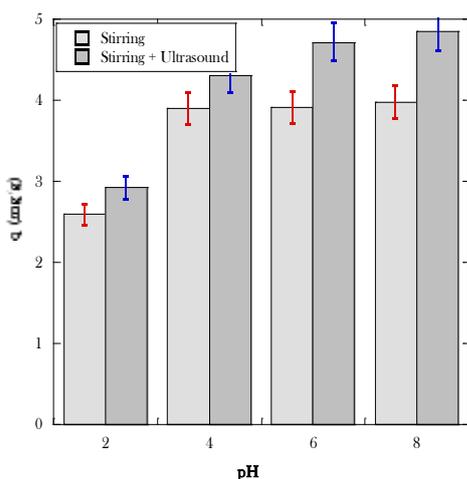


Figure 6. Effect of initial pH on the removal of malachite green dye in presence and in absence of ultrasound ($T = 21^\circ C$, sorbent dose = 0.2 g/100 mL, initial concentration = 10 mg L^{-1} , sonication power = 11 W).

III.5. Temperature influence

In the current research, at an initial dye concentration of 10 mg L^{-1} and a sorbent mass of 0.2 g, the impact of temperature on the equilibrium adsorption of pumpkin seeds in both the absence and presence of ultrasound was investigated. Figure.7 shows that the sorption of MG rose as the temperature increased in the absence and presence of ultrasound. Upgrading of sorption by raising the temperature reveals that the sorption of MG by pumpkin seeds occurs as an endothermic phenomenon. It is possible that this is related to the rise in the dyestuff's mobility as the temperature of the solution rises. In the investigated temperature interval, the quantity of sorbed MG was clearly raised and augmented by ultrasound. The use of sonication facilitated the sorption of the MG ion by means of the extremely high conditions generated by collapsing bubble. Due to the decay of the tension and viscosity of the liquid, cavitation bubbles are more frequently occurring under elevated temperatures [17]. Besides, the endothermic sorption of MG by the sorbent particles is assisted if this bubble collapse is taking place in the proximity of the sorbent surface. These results indicate also that the influence of ultrasound on the increase of the sorption process consists of their thermal and non-thermal effects. The non-thermal phenomenon is induced by the acoustic vortex microcurrent and by the high-velocity microjets and high-pressure shock waves caused by the acoustic cavitation [18]. The thermal impact is mainly given by localised hot spots formed during bubble cavitation as well as by the heating of the piezoelectric transducers [18].

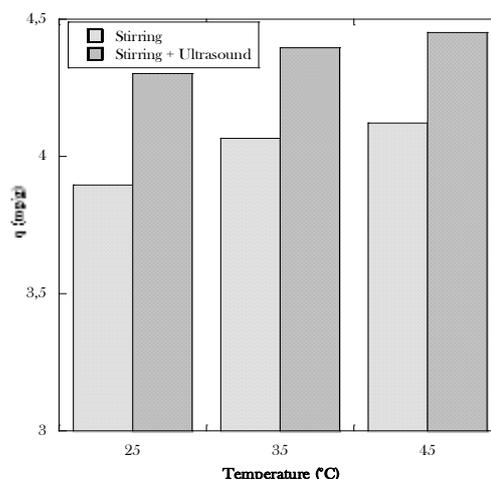


Figure 7. Effect of temperature on the removal of malachite green dye in presence and in absence of ultrasound ($T = 25 - 45^\circ C$, initial dye concentration = 10 mg L^{-1} , sorbent dose = 0.2 g/100 mL, sonication power = 11 W)

III.6. Effect of ionic strength

In water, salt is found in a large concentration range, according to the origin and state of water available. Availability of salts in liquid form may have an impact upon the sorption of dye. In the case of pumpkin seeds, Ionic strength impact on MG sorption was evaluated in the absence and presence of ultrasound. The ionicity of the dye solution was varied using different dosages of NaCl (0.1-1 g L⁻¹). In accordance with this, the impact of NaCl concentration on the release of MG from an aqueous solution by pumpkin seeds is depicted in Figure 8. The Sorption Potential was found to diminish with rising salt (NaCl) concentration in the environment in the absence and in the presence of ultrasound. As the ionic strength increases, the electrical double layer encircling the sorbent surface is compressed, resulting in a diminution in electrostatic potential. This indirectly led to a decline in the coulomb free energy and a diminution of the sorption of basic dye ions. [19]. The same findings as in the published research have been noted for the sorption of the dyes [15, 19-21].

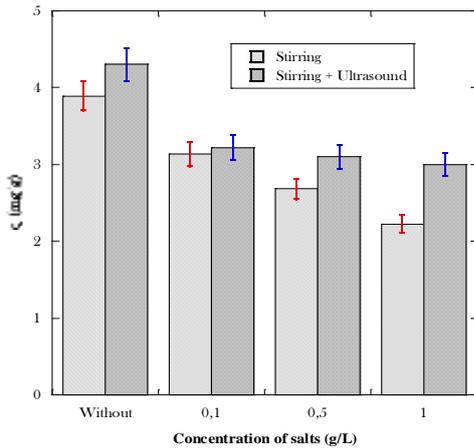


Figure 8. Effect of salt concentration on the removal of malachite green dye in presence and in absence of ultrasound ($T = 21^{\circ}\text{C}$, initial dye concentration = 10 mg L^{-1} , sorbent dose = $0.2\text{ g}/100\text{ mL}$, sonication power = 11 W).

III.7. Sorption kinetics studies

For a more performing compression of the sorption kinetics, several models like the pseudo first order Lagergren, pseudo second order and other kinetic models were employed. Although, currently, just the Lagergren pseudo-first-order and pseudo-second-order kinetic models have been applied to the sorption of MG by pumpkin seeds at several initial concentrations (5-20 mg L⁻¹).

The most appropriate model has been taken on the basis of both the linear regression correlation coefficient (r) and the sorbed dye quantity data

(q_e). For investigating the adequacy of the pseudo-first order kinetic model and obtaining the rate constants, the Lagergren equation was adopted. This formula is expressed like this [22]:

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (4)$$

The quantity of MG sorbed at equilibrium and at each point in time t , are $q_e(\text{mg g}^{-1})$ and $q(\text{mg g}^{-1})$, with $k_1 (\text{min}^{-1})$ being the sorption velocity constant. Lagergren's model parameters and correlation coefficients in the absence and presence of ultrasound are resumed in Table 1.

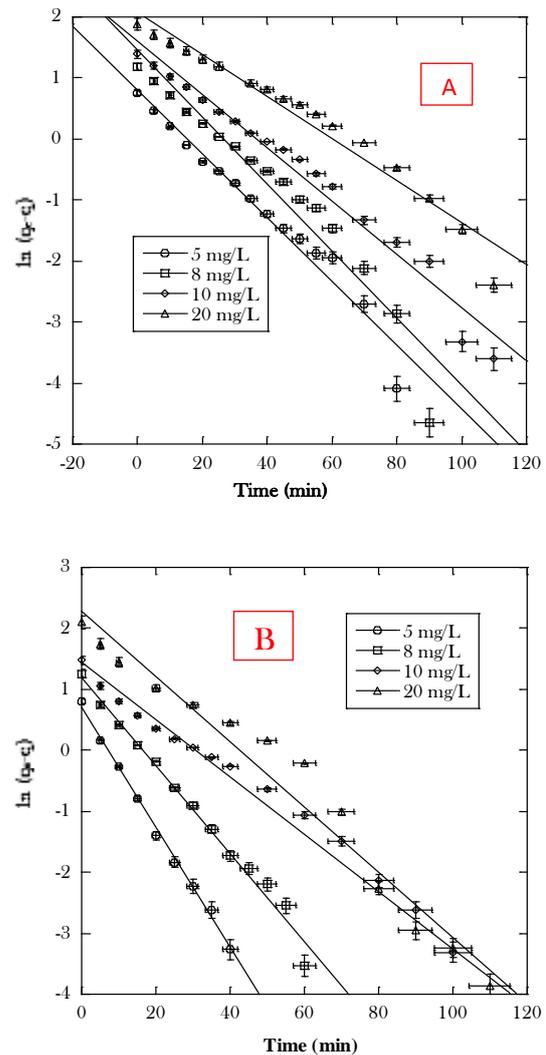


Figure 9. The kinetics of pseudo-first-order sorption of MG by pumpkin seeds: (A) Classical method and (B) Ultrasound with stirring. (conditions: 100 mL of MG solution, initial concentration $5\text{--}20\text{ mg L}^{-1}$, sorbent mass 0.2 g , acoustic power 11 W , stirring speed 100 rpm , temperature $21\text{ }^{\circ}\text{C}$).

Table 1. Modelling kinetic settings for MG sorption through pumpkin seeds peels upon several concentrations., k_1 (min^{-1}), k_2 ($\text{g mg}^{-1} \text{min}^{-1}$), h ($\text{mg g}^{-1} \text{min}^{-1}$), $q_{e(\text{calc})}$ (mg g^{-1}), $q_{e(\text{exp})}$ (mg g^{-1}).

C_0 (mg/L)	$q_{e(\text{exp})}$ (mg g^{-1})	Pseudo-first-order model			Pseudo-second-order model		
		k_1 (min^{-1})	$q_{e(\text{calc})}$ (mg g^{-1})	R^2	k_2 ($\text{gmg}^{-1} \text{min}^{-1}$)	$q_{e(\text{calc})}$ (mg g^{-1})	R^2
Conventional method							
5	2.1256	0.0521	2.2159	0.9644	0.0233	2.5557	0.9986
8	3.2664	0.0548	4.2558	0.9356	0.0114	4.0665	0.9974
10	4.0301	0.0436	4.9303	0.9731	0.0069	5.1182	0.9957
20	6,5878	0.0345	7.9581	0.9604	0.0027	8.9158	0.9982
Ultrasound-Stirring							
5	2.2256	0.1006	2.0200	0.9964	0.0543	2.5953	0.9984
8	3.5220	0.0894	3.3260	0.9878	0.0262	4.0471	0.9990
10	4.375	0.0490	4.9303	0.9767	0.0156	4.8878	0.9994
20	8.1510	0.0534	9.7561	0.9652	0.0051	8.9976	0.9960

The kinetic data were further analyzed using a pseudo-second-order relation [23, 24]:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

Where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the pseudo-second-order rate constant, and q_e and q represent quantity of sorbed dye (mg g^{-1}) at equilibrium and at each time t .

For the measurement of the initial sorption rate h ($\text{mg g}^{-1} \text{min}^{-1}$), the constant k_2 is applied according to the following formula

$$h = k_2 q_e^2 \quad (6)$$

Figure 10. illustrates the pseudo-second order patterns for MG via pumpkin seed peels under a range of concentrations (from 5 to 20 mg L^{-1}). Table 1 includes the pseudo-second order rate constants and the associated linear regression correlation coefficients (r). It was revealed that for every initial dye concentration and over the entire sorption time with and without ultrasound, there were greater values for the linear regression correlation coefficient, reaching from 0.9957 to 0.9994. It was demonstrated that there was excellent consistency in the experimental and measured data. In a second step, it is also demonstrated that this kinetic equation and the pseudo-secondary nature of the MG sorption process by pumpkin seed husks are feasible.

The k_2 values achieved were also plotted as a function of the initial dye concentration (figure not shown). It was noticed that there was no linear relationship between the rate constants and the concentration. The resulting k_2 values on the basis of the initial dye concentration have been graphically depicted (figure not illustrated). No linear connection has been noted with velocity constants and concentration. It is impossible to

identify a significant relationship based on the values of k_2 and the presence of ultrasonic waves.

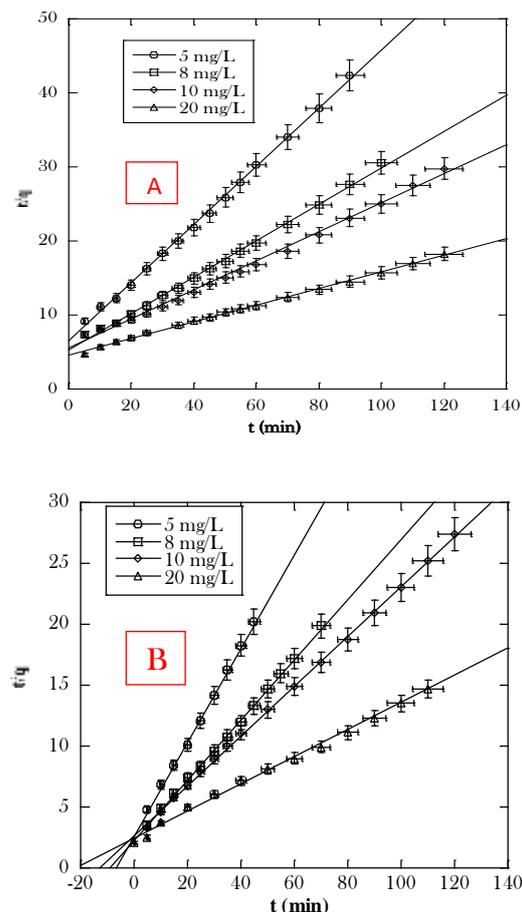


Figure 10. The kinetics of pseudo-second-order for the sorption of MG by Pumpkin seeds: (A) Classical method and (B) Ultrasound with stirring (conditions: 100 mL of MG solution, initial concentration 5–20 mg L^{-1} , sorbent mass 0.2 g, acoustic power 11 W, stirring speed 100 rpm, temperature 21 °C).

In order to understand the diffusion mechanism, the kinetic data has been analysed via the intraparticle diffusion model, which is formulated as follows [25]:

$$q = k_i t^{1/2} + C_i \quad (7)$$

Where q is the quantum of MG sorbed (mg g⁻¹) with time t, k_i is the intraparticle diffusion constant (mg g⁻¹ min^{-1/2}), and C_i is the intercept. Figure 11.B illustrates the sorbed quantity of MG according to t^{1/2} at varied initial dye concentrations within the intraparticle diffusion for the ultrasound with stirring system. The findings indicated that there are three steps occurred in the process. The first is the instantaneous sorption or the sorption onto the outer solid surface. The second step is the gradual sorption stage involving limitative intraparticle diffusion.

In addition, a final stage prior to equilibrium, referred to as the third area, is where intraparticle diffusion commences to decelerate due to the weak concentration of solute in solution. The plots are not linear for the entire time interval, indicating that sorption is affected by several processes.

Based on the coefficients of determination of this diffusion model, it is expected that the sorption of MG by pumpkin seed peels may be monitored via an intraparticle diffusion model.

Another finding is that the graphs do not traverse the point of origin, reflecting a certain level of controlling the boundary layer and illustrating that intraparticle diffusion is not the only velocity-limiting stage, rather other processes are able to act as controllers of the sorption velocity.

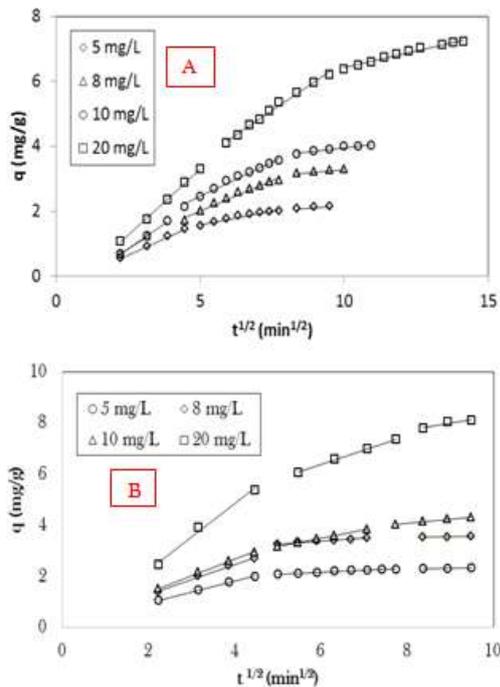


Figure 11. Intraparticle diffusion plot for the sorption of MG by Pumpkin seeds: (A) conventional method and (B) ultrasound with stirring

(conditions: 100 ml of MG solution, initial concentration 5–20 mg L⁻¹, sorbent mass 0.2 g, acoustic power 11W, stirring speed 100 rpm, temperature 21 °C).

III.8. Modelling of sorption isotherms of MG

Sorption isotherms are intended to explain the relationship between the quantity of sorbates absorbed upon the sorbent and the concentration of sorbates dissolved within the liquid at steady state. A number of isotherm formulations were applied to describe the equilibrium information. Langmuir, Freundlich, Elovich, Flory-Huggins, Harkins-Jura, Dubinin-Radushkevich, Redlich-Peterson and further isothermal models are cited through the literature.

In the current investigation, the equilibrium sorption data of MG by pumpkin seed peels were modelled by Langmuir and Freundlich models.

On the basis of the Langmuir sorption model [26] it is assumed that the maximum sorption is equivalent to the saturation of a monolayer of solute on the sorbent surface.

The linearity of the Langmuir formula is defined as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{b q_m} \quad (8)$$

The specific sorption (C_e/q_e) versus equilibrium concentration (C_e) is plotted linearly (Fig. 12), revealing that the sorption follows the Langmuir model.

From the slope and intercept of the graph, the Langmuir constants q_m and b have been established and reported in Table 2.

Table 2. Isotherm parameters for the sorption of MG by Pumpkin seed peels.

	Stirring	Stirring+Ultrasound
Langmuir		
b (L mg ⁻¹)	0.4099	0.3212
q _m (mg g ⁻¹)	8.9445	15.0375
R ²	0.9992	0.9990
Freundlich		
n	1.9923	1.4945
K _F (mg ¹⁻ⁿ L ^{1/n} g ⁻¹)	2.6334	3.5261
R ²	0.9756	0.9884

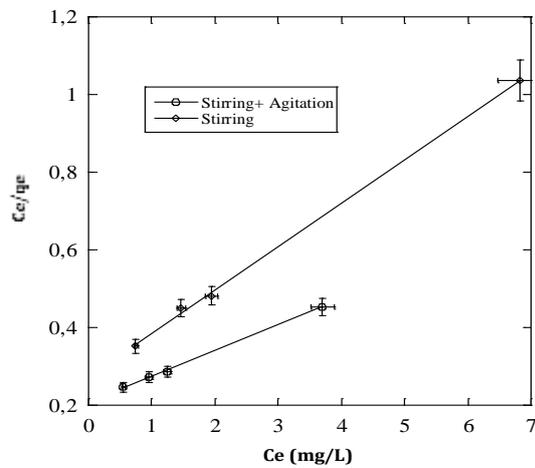


Figure 12. Sorption isotherm of Langmuir for MG by Pumpkin seed peels (conditions: 100 ml of MG solution, initial concentration 5–20 mg L⁻¹, sorbent mass 0.2 g, acoustic power 11W, stirring speed 100 rpm, temperature 21 °C).

The determination coefficient values appear to be indicative of the fact that the Langmuir isotherm is expected to be a satisfactory fitting to the isothermal dataset for both systems examined. A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L also known as the separation factor, given by [27]:

$$R_L = \frac{1}{1 + b \times C_0} \quad (9)$$

whereas b was set as Langmuir's fixed value and C_0 corresponded to the initial concentration of the sorbate. If the R_L factor is situated within the interval 0-1, this means a favoured adsorption, whereas $R_L > 1$ signifies an unfavoured adsorption, and $R_L = 1$ is indicative of a linear adsorption, although the adsorption occurs irreversibly when $R_L = 0$.

The calculated R_L values were 0.1087 in the case of the classic method and 0.1346 when assisted by ultrasound with agitation. R_L values in the ranges of 0.1087 and 0.1346 for both methods studied indicate that MG adsorption is a favoured technique.

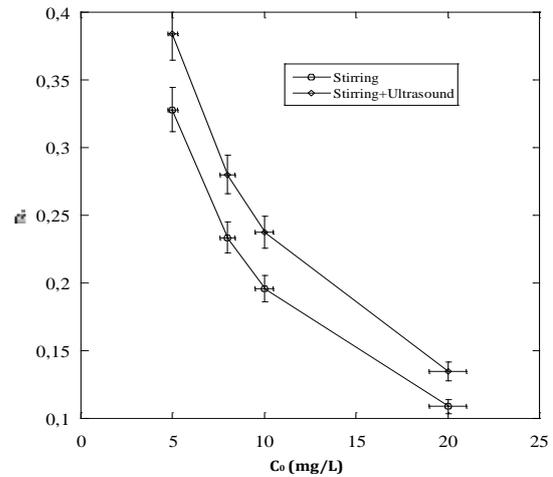


Figure 13. Separation ratio (R_L) for the sorption of MG by Pumpkin seed peels.

The first relationship designed to define the sorption formula is the Freundlich isothermal model [28]. A satisfactory empirical isotherm is available for non-ideal sorption implying heterogeneous surfacing energetic systems. The linear form of the Freundlich model is defined by the formula below:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (10)$$

Where K_F ($\text{mg}^{1-(1/n)} \text{L}^{1/n} \text{g}^{-1}$) is broadly index of the sorption capacity and n is the sorption level. Typically, the greater the K_F value, the greater the sorption capacity of the sorbent for any desired sorbate.

n denotes the level of non linearities of solution concentration with adsorption according to the following: When $n = 1$, it means that the adsorption is linear; in the case where $n < 1$, it is chemical Adsorption; but if $n > 1$, it is physically beneficial adsorption. In Table 2, the Freundlich factors (K_F , n) and the correlation coefficients (r) are mentioned. The finding reveals that the values of n are greater than 1 indicating that adsorption for MG onto Pumpkin seed peels is a favorable physical process.

It is important to note that correlation coefficients, measured via Freundlich's model ($r \geq 0.9757$), were found to be comparable to those calculated via the Langmuir model (Table 2). This outcome provides an indication that the experimental information is in accordance with the Freundlich model.

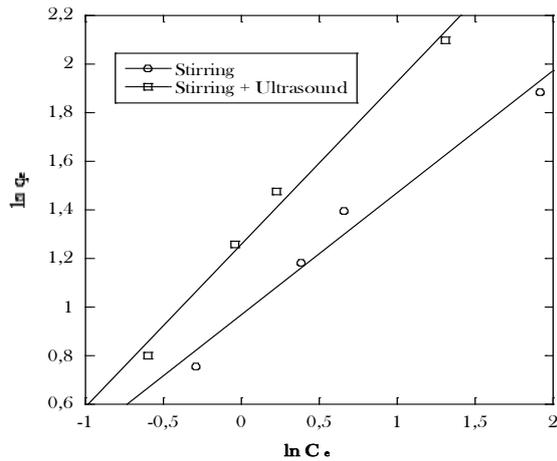


Figure 14. Sorption isotherm of Freundlich for MG by Pumpkin seed peels (conditions: 100 ml of MG solution, initial concentration 5–20 mg L⁻¹, sorbent mass 0.2 g, acoustic power 11W, stirring speed 100 rpm, temperature 21 °C).

III.9. Evaluation of Pumpkin seed peels absorbent

A further comparative value of the maximum sorption amount (q_m) of MG by a number of cheap sorbents is enumerated in Table 3. The highest sorption capacity in this report is reasonably high (15.0375 mg g⁻¹) at natural pH and environmental temperature (21±1°C). Using this foundation, we may consider that Pumpkin seed peels an environmentally friendly sorbent.

Table 3. Comparison of sorption capacity of the Pumpkin seed peels with that of various sorbents

sorbent	q_m (mgg ⁻¹)	References
Bentonite clay	7.716	[29]
Arundodonax root	8.490	[30]
Neem sawdust	4.35	[31]
Rice husk	7.40	[32]
Tamarind fruit shell	1.95	[33]
chitosan ionic liquid beads A-B	8.07-0.24	[34]
modified chitosan composite	4.8	[35]
Raw <i>Lupinus albus</i> peel waste	6.6	[36]
AC was prepared from oak wood	4.4	[37]
Pumpkin seed peels (Conventional method)	8.9445	This work
Pumpkin seed peels (Stirring + Ultrasound)	15.0375	This work

IV. Conclusion

The current investigation reveals that pumpkin seed peels may be useful as a sorbent material for eliminating MG from aqueous medium. It appears from the research that the velocity and extent of MG sorption was markedly augmented under ultrasonic conditions. Dye elimination has been noted to be related to the initial concentration and dosage of the sorbent. By raising the initial dye concentration up from 5 to 20 mg L⁻¹, an increase in equilibrium sorption ability from 2.14 to 6.58 mg g⁻¹ was achieved using the classic method while a combination of ultrasonics and mechanical mixing resulted in an increase from 2.34 to 8.15 mg g⁻¹. The sorption of MG is favored by high temperatures for both methods.

The ionic force is disadvantageous for dye sorption in both the presence and absence of ultrasound. Basic pH values are more advantageous for MG sorption.

The kinetic data are analysed by means of pseudo-first-order and pseudo-second-order models. The result obtained demonstrate that the sorption kinetic data are well described by the pseudo-second order equation. Analysis of the sorption kinetics results indicates that film and particle diffusion are performing sorption mechanisms. The findings of this research may be useful for applying this waste material as economical sorbent to eliminate basic dyes in wastewater treatment systems, especially as this material is abundantly supplied in large quantities.

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Symbols

- C_0 Liquid phase initial concentrations of dye , mg/L
- C_e Liquid phase concentrations of dye at equilibrium time, mg/L
- k_1 Rate constant of Lagergren pseudo-first-order model, min⁻¹
- k_2 Rate constant of pseudo-second-order model, g/mg min
- k_d Intraparticle diffusion rate constant, mg/g min^{1/2}
- K_F Freundlich biosorbent capacity, mg^{1-1/n}L^{1/n}/g
- n_F Freundlich model constant
- pH_{pzc} Point of zero charge
- q_e Amount of biosorption at equilibrium, mg/g
- q_m Maximum monolayer biosorption capacity, mg/g
- r Correlation coefficient
- R_L Dimensionless constant separation factor of Hall
- t Time, min

V. References

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