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Research Article

ADSORPTIVE REMOVAL OF MALACHITE GREEN DYE FROM AQUEOUS SOLUTION USING A NON CARBON ADSORBENT: EQUILIBRIUM, KINETICS AND THERMODYNAMICS

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ABSTRACT

In this paper, studies for the removal of malachite green dye from aqueous solution using adsorption technique are presented. There are different adsorbent available for malachite green dye removal from water effluents. Hence, the recent literature in the area is categorized according to the cost, feasibility, and availability of adsorbents. An extensive survey of the adsorbents, derived from various sources such as low-cost biological materials, waste material from industry, agricultural waste, polymers, clays, nano-materials, and magnetic materials, has been carried out. Adsorbent unsaturated polyester resin is case effective for the removal of malachite green dye from aqueous solution. The research paper studies different adsorption factors, such as pH, concentration, adsorbent dose, contact time, temperature. The fitting of the adsorption data to various models, isotherms, kinetic and thermodynamic parameter is also reported.

Keywords: Adsorption, Malachite Green, Unsaturated Polyester Resin, Aqueous Solution.

1. INTRODUCTION

Till the nineteenth century, shells, flowers, roots, insects, and mollusks were used to extract all the colorants. But, with the historic discovery of the primary artificial dye, most of the works of natural dyes are substituted with synthetic dyes as they will be made on an oversized scale [1]. The treatment of dye, containing industrial waste product could be a worldwide environmental case round-faced by government agencies and therefore the scientific community. It's necessary because of adverse effects on the atmosphere and individuals. The presence of dyes in water sources grime natural place and represent health issues as a result of they're not perishable and sophisticated naturally [2, 3].

Malachite green (MG) could be a cationic dye that's soluble in water that like as green crystalline powder and belongs to the triphenylmethane category [4]. It had been discovered that the intensive usage of MG dye has caused many health hazards and thus, the correct treatment of effluent containing MG dye is very necessary. An oversized range of dyes is discharged into the waste stream by the textile industries. Several color effluents are composed of non-biologically reactive organic compounds. Dye imparts toxicity and reduces the biological activity of water; there's a very important demand for the removal of dyes from industrial water before they're mixed with water streams. These may be with efficiency separated by the sorption technique.

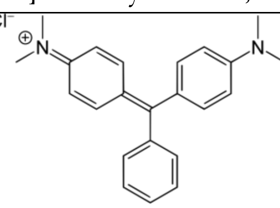
Malachite green (MG), is that the most generally used dye for coloring functions [5]. This tri aryl methane series dye is wide utilized in the cultivation trade as a biocide also as within the cotton, wool, paper, leather, and acrylic industries quite it, the malachite green dye is additionally utilized as a therapeutic agent to treat parasites, fungal, associated microorganism infections in fish and fish eggs and as an antiseptic for external application on the tissue. MG could be an extremely disputed compound because of its in-depth use, its reportable toxic properties, that area unit acknowledged causing metabolism toxicity, cause, and carcinogenesis. Its oral uptake is additionally dangerous and carcinogenic [6]. The removal of dye from an aqueous solution of their binary mixture is extremely out of print. Therefore we've got administrated the studies on the removal of malachite green dye from their mixture. Factors influencing adsorption embody particle size distribution, nature of adsorbent and adsorbate, the surface area of the adsorbent, initial concentration, dose adsorbent, temperature, pH, contact time, etc. Isotherms are empirical relations that are accustomed product what proportion substance will absorb by unsaturated polyester resin adsorbent. The foremost unremarkably used isograms are chemist isograms and Freundlich isotherm. The Kinetic of adsorption is sort of vital because it decides the residence time of adsorbate at the solid-solution interface and helps in determining the speed of the adsorption method. This study includes an adsorption rate study. In this study, the removal of MG dye from wastewater is done by the adsorbent unsaturated polyester resin, in which dye is adsorbed on the surface of UPR. The effects of initial adsorbate, concentration, pH, contact time, and capacity of adsorbent on the removal of MG dye have been studied.

2. EXPERIMENTAL

2.1. Target compound and chemicals

The Malachite green dye is the adsorbate, its color is green. Table 1 represents the important physicochemical properties of malachite green (MG chloride) dye. It gives the green colored solution in the aqueous phase. It is a basic cationic dye and has a chemical formula is $C_{52}H_{54}N_4O_{12}$. The aqueous solutions of varying concentrations of malachite green dye were prepared by dilution from its stock solution and the study was done by varying different parameters. Various solutions at desired concentrations were prepared from standard solutions. All reagents used in this work were of analytical grade. Adsorbent UPR were obtained from M/s Naphtha Resins, Bangalore, India, and were used without any purification.

Table 1: Physicochemical properties of malachite green dye

Parameters	Malachite green chloride
Molecular formula	$C_{23}H_{25}ClN_2$
Molecular weight	364.911 g/mol
IUPAC name	[4-[[4-(Dimethylamino)phenyl]]-phenylmethylidene]cyclohexa-2,5-dien-1-ylidene]-dimethylazanium, chloride
Molecular structure	
Other name	Aniline green, Basic green 4, Diamond green B, Victoria green B
Color index number	42000
Maximum wavelength	618 nm

2.2. Instrumentation

Adsorption measure was studied with a 1.0 cm light path quartz cells exploitation photometer (systronics photo-meter 166 India, over the wavelength vary 325-900 nm) at λmax 618nm. Before the measure, an activity curve was obtained by exploiting the quality of malachite green dye resolution with noted concen-trations. All hydrogen ion concentration measurements were disbursed with a dB 1011 digital hydrogen ion concen-tration meter, fitted with a glass electrode. Sartorius CP224S beam balance (Gottingen, Germany) and ultra sonic cleaner (Frontline FS four, Mumbai, India) were used throughout the study.

2.3. Experimental design

Based on the operational and method factors, namely, result of pH scale, adsorbent dose, malachite green dye concentration, temperature, pH scale and contact time were studied with the foremost important impact on the surface assimilation of malachite green dye. However, it's quite tough to hold out associate degree experi-mental style as well as of these factors as a result of large number of experiments and complex information analysis is needed. Therefore, the foremost vital factors were chosen. It absolutely was found that the four factors result of concentration of dye, pH, temperature, and adsorbent dose have the foremost important result on malachite green dye adsorption rate.

2.4. Preparation of analytical solutions

A stock solution of malachite green dye was prepared by dissolving 1.16 g in 1000 ml of distilled water. A working solution of desired concentration was prepared by diluting stock solution in distilled water. Britton-Robinson buffers in the pH range 2.48 to 12.3.

2.5. Simple colorimetric method for malachite green dye

This method is based on the color formation when it was dissolved in alkaline media. When malachite green dye is dissolved in aqueous solution at pH 9.5, a green colored chromogen was formed and it has given the absorption maximum at 618 nm. Stock solution of dye (1.16 g/L) was transferred into 50 ml volumetric flask and made up to the mark with 0.1N sodium hydroxide as reagent black.

2.6. Adsorption studies

Adsorption was determined by a batch method, which permits convenient evaluation of parameters that influence the adsorption process. In the batch method, 1.16 g/L unsaturated polyester resin is mixed with 30 ml of a solution of known concentration (0 - 50 g/L at pH 9.5) in 250 ml Erlenmeyer Flasks for the removal of MG at room temperature. Flasks were agitated on a water bath shaker for identified time intervals, then centrifuged and analyzed. UV spectrophotometer is used for the analysis of MG concentration. The amount of analyte adsorbed at any time was calculated by the difference in their initial and final concentrations. Each experiment was repeated and the result is obtained by average values. According to equation (1), the obtained data were deputed to calculate the equilibrium analyte uptake capacity

$$qe = v(C_0 - Ce) / m \quad (1)$$

Where qe (mg g-l) is the equilibrium amount of analyte in the adsorbed phase, C_0 and Ce are the initial and equilibrium concentrations of analyte (mg L-l) in the aqueous solution, v is the volume of the solution (L), and m is the sorbent dose (g) in the mixture. The removal percent of the analyte (Re %) in the solution was calculated using equation (2).

$$Re\,\% = [(C0 - Ce)/\ C0] \times 100 \quad (2)$$

2.7. Isotherm studies

To study the adsorption behavior of malachite green onto UPR and to achieve the most effective fitting of the theoretical model, the experimental records from the batch experiment were analyzed victimization two-parameter (Langmuir, and Freundlich), In these models, linear regression analysis was wont to evaluate whether the theoretical models have better or worse fit the experimental information.

2.8. Quality assurance/quality control

Accuracy and precision are necessary in an experiment so all of the batch isotherm tests were replicated thrice to establish the accuracy, reliability, and reproducibility of the collected data. In different experiments, blanks were run and corrections made wherever necessary. All glasswares used in the study were prepared by soaking in 5 % HNO_3 solution for a period of 3 days before being doubly rinsed with distilled, demonized water, and oven dried.

3. RESULTS AND DISCUSSION

3.1. Adsorbent characterization

In the present study, an SEM photograph of UPR reveals surface texture and porosity. SEM was performed using a Zeiss EVO 50 instrument. Powder X-ray diffraction (XRD) measurements were performed on the Diffracto-meter system XPERT-PRO X-ray powder diffract meter using graphite monochromatic with Cu Ka radiation (k = 1.54 Å). X-ray diffraction (XRD) pattern at 2θ ranges between 10°-70° was used to phase characterization.

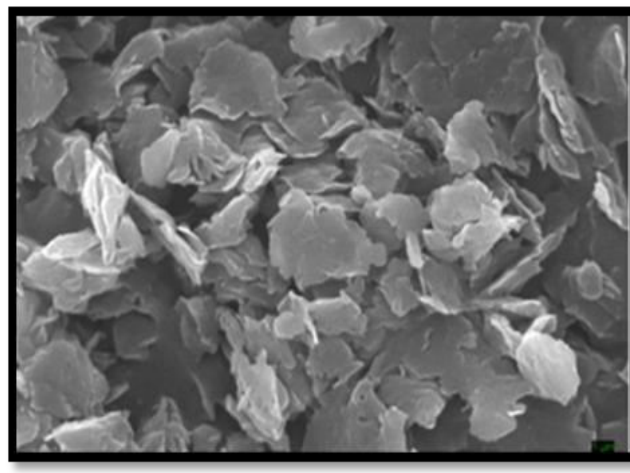


Fig. 1: Scanning Electron Microscope of UPR

3.2. The effect of adsorbent dose on adsorption process

To renovate the adsorbent dose for the removal of Malachite green dye from its aqueous solutions, adsorption was carried out with different adsorbent dosages at different temperatures. The dose of adsorbent was varied from 0.16 g/L to 1.66 g/L for UPR at a fixed temperature, pH, and adsorbate concentration. The study shows as the dosage of the adsorbent increases, it increases the rate of adsorption. As the adsorbent dosage increases, the adsorbent sites available for the dye molecules also increase and consequently better adsorption is considered [7]. Thus, in all subsequent studies, the optimum amount of UPR was chosen as 1.16 g/L. At this amount the adsorption over UPR is efficient and saves unnecessary use of an excess of adsorbent quantity-wise. As shown in (fig.2) for the unsaturated polyester region, with the increasing amount of adsorbent, % sorption of the dye is also increased gradually. About 95% of dye sorption was observed for 1.16 g/L. of adsorbent dosage. After that, the increase is very little. Such a trend is mainly due to the increase in availability and sportive surface area of more exchangeable sites for dye.

3.3. Effect of initial dye concentration

The dye concentration has an apparent influence on its removal from the aqueous phase. The effect of malachite green dye concentration on the efficiency of adsorption was also investigated in the initial concentration range as shown in the fig.3. The adsorption capacity of UPR at equilibrium increases with an increase in initial dye concentration. This trend could be attributed to the fact that at a high concentration of dye, there is a high driving force for mass transfer. Besides if the dye concentration in the solution is higher, the active sites of the adsorbent are surrounded by a higher number of dye molecules which leads to more efficient adsorption.

3.4. Effect of Temperature

Temperature is additionally a notable dominant think about the important applications of the adsorbent for the dye removal method. Fig. 4 represents the sorption of mineral inexperienced by UPR at totally different temperatures. The temperature affects the dye sorption potency completely which suggests that the proportion removal of dye increase on increasing the temperature of the system. This trend is often attributed to the actual fact that the chemical interactions going down between mineral inexperienced dye and also the adsorbent square measure endothermic in nature. This is often additionally urged by the calculations of natural philosophy parameters.

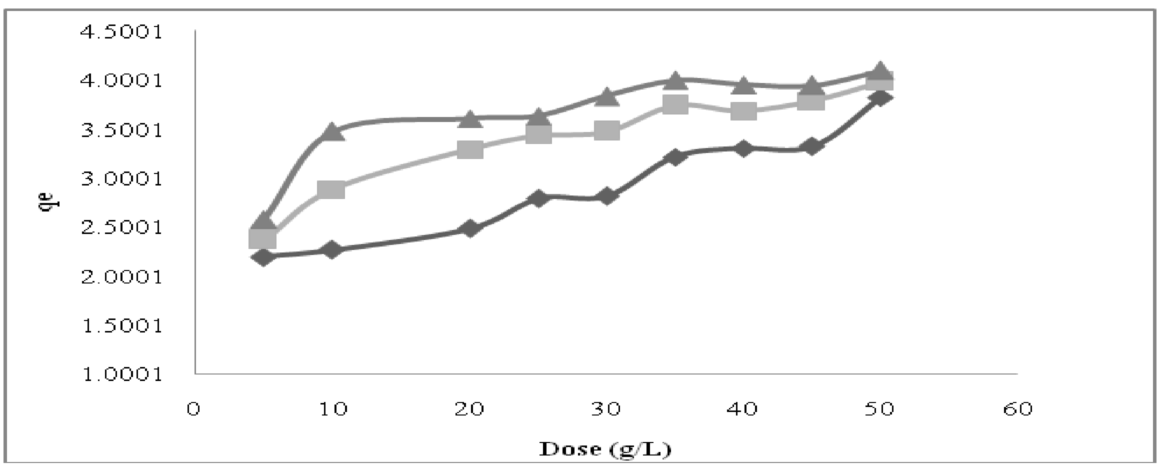


Fig. 2: Effect of amount of adsorbent (UPR) for the removal of Malachite Green at 5×10^{-5} M at pH 9.5 and different temperatures

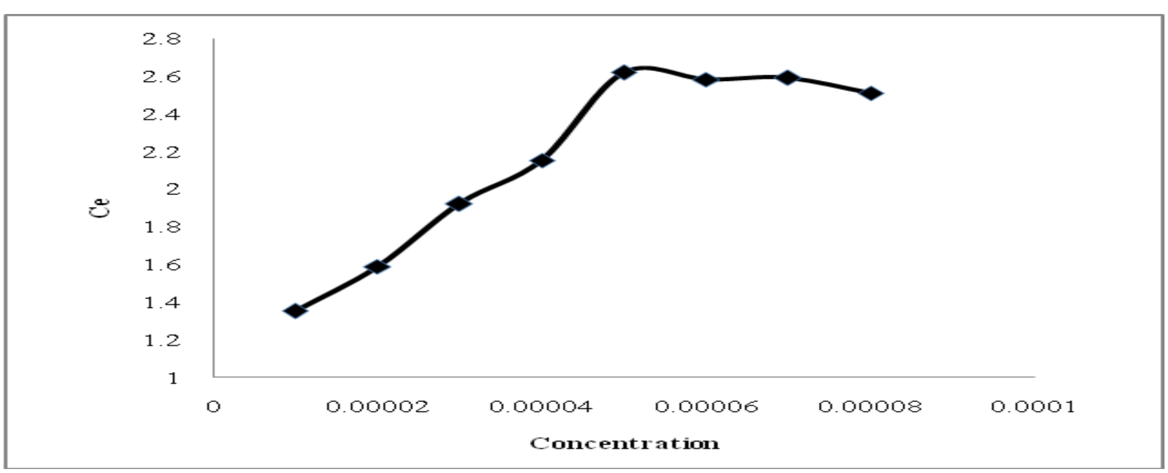


Fig. 3: Effect of concentration of the dye for the removal of Malachite Green by UPR at 1.16 g/L at pH 9.5 at 30°C

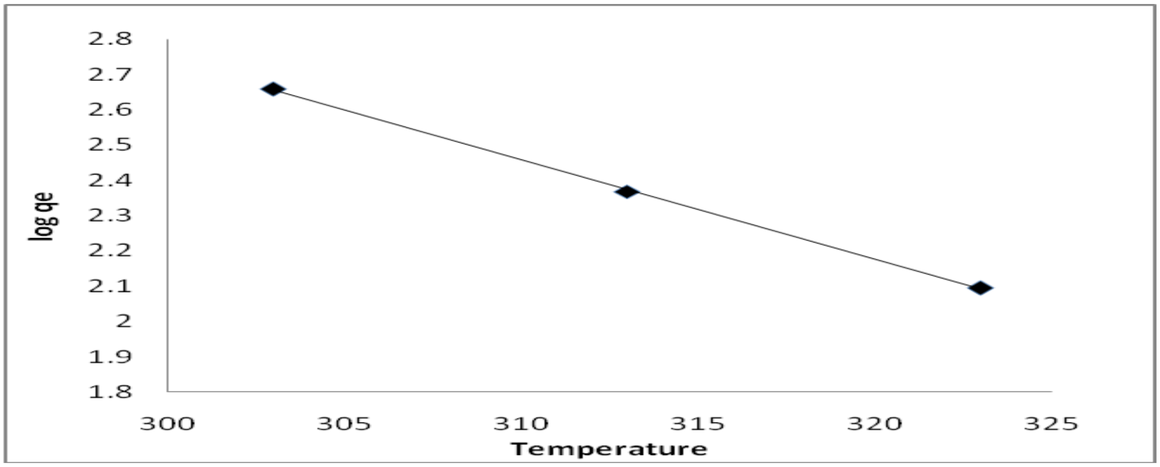


Fig. 4: Effect of temperature for the removal of Malachite Green (5×10^{-5} M) over UPR (1.16 g/L) at pH 9.5 and different temperatures

3.5. Effect of Contact Time

The impact of contact time on surface assimilation of malachite green is clearly diagrammatic within the fig. 5 that originally the speed of adsorption is extremely high, however, the rate of adsorption decreases when it is slow. The equilibrium time for adsorption is half-hour as a result of the concentration of dye doesn't modification considerably when half-hour. It's primarily to the saturation of the active sites that don't allow what is more surface assimilation to occur. This can be explained by the actual fact that originally, the surface sites area unit terribly massive that permits adsorption to require place terribly simply. However, as time passes, the active sites get saturated so decrease the rate of adsorption.

3.6. Effect of Initial pH of the solution

The initial pH of the dye resolution includes a strong impact on the surface properties of adsorbents yet because the degree of ionization of dye molecules. Thus the effect of pH on the adsorption process is an imported point for study. In the experiment, 100ml of 5×10^{-5} M dye solutions in the pH range 2.48 to 12.3 have been studied. The results are shown in the fig. 6 below and it is depicted from the graph that the removal efficiency of dye is reasonably high in the pH range 7-9 and declined at a higher pH value. The higher adsorption at very acidic media could be due to the interactions between the positively charged dyes cations with surface functional groups present in UPR. On the contrary, at higher pH values, the adsorption decreases which maybe because of the formation of soluble hydroxyl complexes.

3.7. Adsorption isotherms

Adsorption isotherm helps to supply vital data on the sorption mechanisms, the surface properties, and affinities of the adsorbent at equilibrium. The Langmuir and Freundlich isotherms equations were applied during this study. The simple regression is usually wont to confirm the best-fitting isotherm and also the relevance of isotherm equations is compared by checking the correlation coefficients.

3.7.1. Langmuir isotherm

Adsorption isotherm information is represented by the Langmuir adsorption isotherm [8]. Langmuir isotherm presumes monolayer surface assimilation onto a surface containing a finite range of adsorption sites of uniform steps while not transmigration of adsorbate within the surface plane. The linear type of the isotherm was analyzed consistent with the Langmuir model.

$$1/q_e = 1/Q^0 + 1/\, bQ^0C_e \quad (3)$$

Where qe is the amount adsorbed (mol g-1) and Ce is the equilibrium concentration of the adsorbate (mol L^{-1}). Q^0 and b are the Langmuir constants related to maximum adsorption capacity and energy absorption, respectively. When we plot a graph between 1/qe verses 1/Ce a straight line is depicted with slope $1/bQ^0$ is obtained, which shows that the adsorption of malachite green dye over UPR follows the Langmuir isotherms. Langmuir constants were calculated and values of these constants at different temperatures are given in Table 2. It must be pointed out that Q° and b are empirical constants and are really secondary parameters obtained graphically using Equation (3). So a definite conclusion regarding the trend cannot be obtained by comparing b and the Q° values separately. In such cases, the better alternative is to compare bQ° value which shows the same trend as shown in table 2.

Langmuir isotherm can be reported in terms of the dimensionless constant separation factor for equilibrium parameter RL [9], defined as follows:

$RL = 1/(1 + bC_0$ (4)

Where C_0 is the initial concentration of the dye and b is the Langmuir constant. The values of RL indicate the type of isotherm to be irreversible (RL = 0), favorable (0 < RL < 1), linear (RL = 1) or unfavorable (RL >1). Values of separation factor for the adsorbent are found to be less than unity, confirming thereby the favorable adsorption process. The same method has already been adopted [10] to confirm the favorability of a Langmuir type of adsorption.

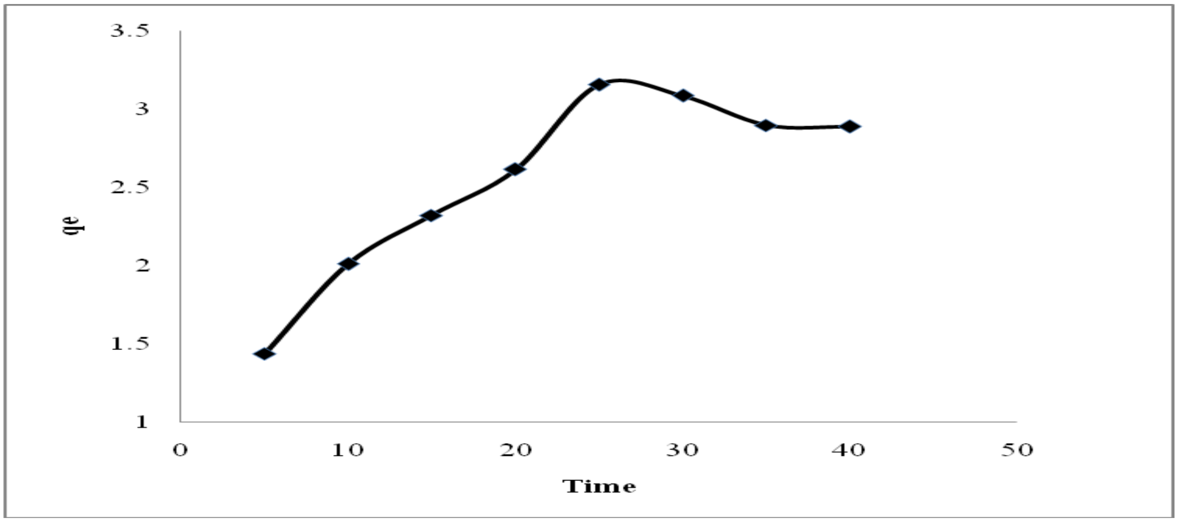


Fig. 5: Effect of contact time for the removal of Malachite Green over UPR at 1.16 g/L at pH 9.5 at 30°C

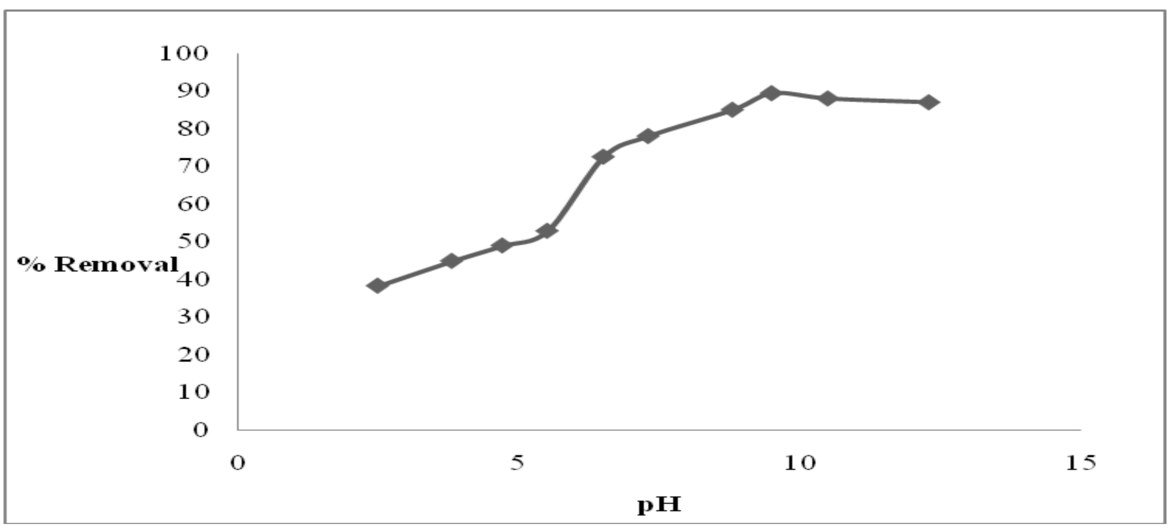


Fig. 6: Effect of pH for the removal of Malachite Green by UPR 1.16 g/L at pH range 2.48 to 12.3 at 30°C

Table 2: Langmuir Constants for MG over UPR

Temp.(°C)	b ($mol\ g^{-1}$)	Q° ($L\ mol^{-1}$)	bQ°	R^2	%RSD
30°C	9.693	0.023	328.90	0.995	1.17
40°C	8.705	0.029	280.11	0.932	0.83
50°C	7. 678	0.017	303.53	0.963	1.09

3.7.2. Freundlich isotherms

The adsorption data for adsorption over UPR were also found to be fitted to the linear form of the Freundlich equation (5) [11]. The logarithmic form of Freundlich isotherm is given by the following equation:

$$\log q_e = \log K_f + 1/n \log C_e \quad (5)$$

Where q_e is the adsorbed amount (mol g^{-1}) and C_e is the equilibrium concentration of the adsorbate (mol L^{-1}). 'K_f' and 'n' are Freundlich constants where 'n' giving an indication, how favorable the adsorption process and 'K_f' [mg/g $(l/mg)^{1/n}$] represents the adsorption capacity of the adsorbent. K_f can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto UPR for a unit equilibrium concentration (table 3). The slope of 1/n ranging between 0 and 1 is a measure of adsorptivity or adsorption intensity, as its value gets closer to zero becoming more heterogeneous [12]. The value of 1/n below one indicates a normal Langmuir isotherm while 1/n above one is indicative of cooperative adsorption. This experiment result shows the n values ranging between 1 and 10 indicating beneficial adsorption. Linear plot of log qe versus log Ce shows that the sorption of malachite green dye from an aqueous solution on UPR additionally follows Freundlich isotherms [13].

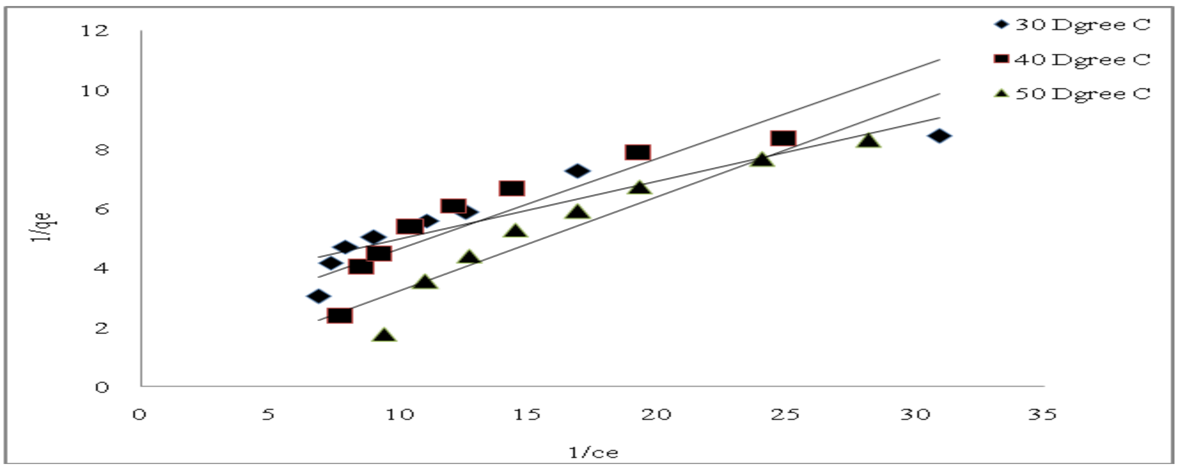


Fig. 7: Langmuir adsorption isotherm for the adsorption of Malachite Green over UPR

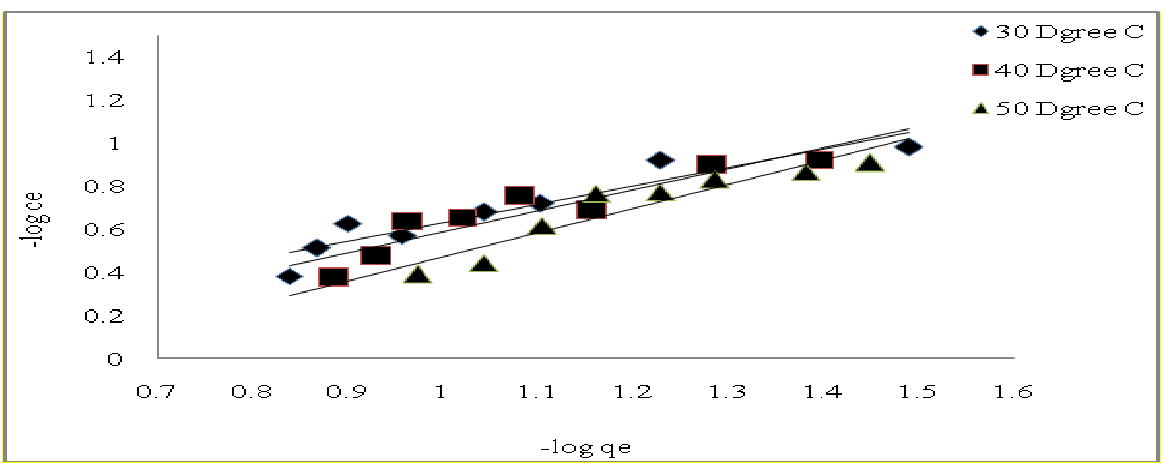


Fig. 8: Freundlich adsorption isotherms for adsorption of the MG over UPR

Table 3: Freundlich constants for the MG over UPR

Temp.(°C)	K_f	N	R^2	%RSD#
30°C	9.925	1.152	0.929	1.18
40°C	19.150	3.038	0.935	0.89
50°C	29.143	4. 169	0.907	1.25

3.8. Thermodynamics parameters

Thermodynamic parameters were estimated to confirm the adsorption nature of the present study. The thermodynamic constants, entropy change ($\Delta S°$), enthalpy ($\Delta H°$), and Gibbs free energy ($\Delta G°$) are calculated to obtain the thermodynamic feasibility and the spontaneous nature of the process. The change in enthalpy ($\Delta H°$), and change in entropy ($\Delta S°$) can be calculated from the variation of Langmuir constant with temperature (T) using the following thermodynamic relations equation (6), (7), and (8). [14].

$$\Delta G° = -RT \ln b \quad (6)$$

$$\Delta H° = -R\,(T_2T_1)/T_2-T_1)\ \ln (b_2/b_1 \quad (7)$$

$$\Delta S° = (\Delta H° - \Delta G°)/\,T \quad (8)$$

Where, b, b1, b2 are the equilibrium constants at different temperatures, which are obtained from slopes of straight lines in the case of Langmuir adsorption isotherms at different temperatures.

Negative values of free energy for the UPR system show the spontaneity of the adsorption process. It was also seen that with increasing temperatures, $\Delta G°$ values decreases, which once again reveals higher adsorption at higher temperatures (table 4). The endothermic nature [15, 16] of the process was all over again confirmed by getting positive values of $\Delta H°$ and sensible affinity of the UPR towards the malachite green is shown by positive $\Delta S°$.

3.9. Adsorption kinetics

The kinetic study of adsorption processes provides useful data regarding the efficiency of the adsorption and the feasibility of scale-up operations. The kinetic data of adsorption can be obtained by using different types of mathematical models of which the one mostly used model is Lagergren's rate equation. The kinetics of the adsorption process was calculated using the first-order rate equation [17].

$$\text{Log}\,(qe - qt) = \log qe - k_{ad} \times t/\ 2.303 \quad (9)$$

Where qe and qt indicates the amount adsorbed at equilibrium and at any time t, respectively. Lagergren's plots for malachite green dye adsorption over UPR at pH 9.5 and different temperatures for UPR obtained for log (qe-qt) versus t depict straight lines and confirm the adsorption process to follow first-order rate kinetics (fig. 9). The k_{ad} values evaluated, from the respective Lagergren's plot are presented in table 3. The correlation coefficients for the pseudo-second-order kinetic model are < 0.95, indicating a poor pseudo-second-order fit to the experimental data.

Table 4: Thermodynamics parameters of MG over UPR

dsorbent	$\Delta G°$(kJmol^{-1})			$\Delta H°$(kJ mol^{-1})	$\Delta S°$ (Jk^{-1}mol^{-1})
	30°C	40°C	50°C	30°C	30°C
UPR	-16.281×10^3	-17.243×10^3	-18.810×10^3	1.613×10^3	17.055

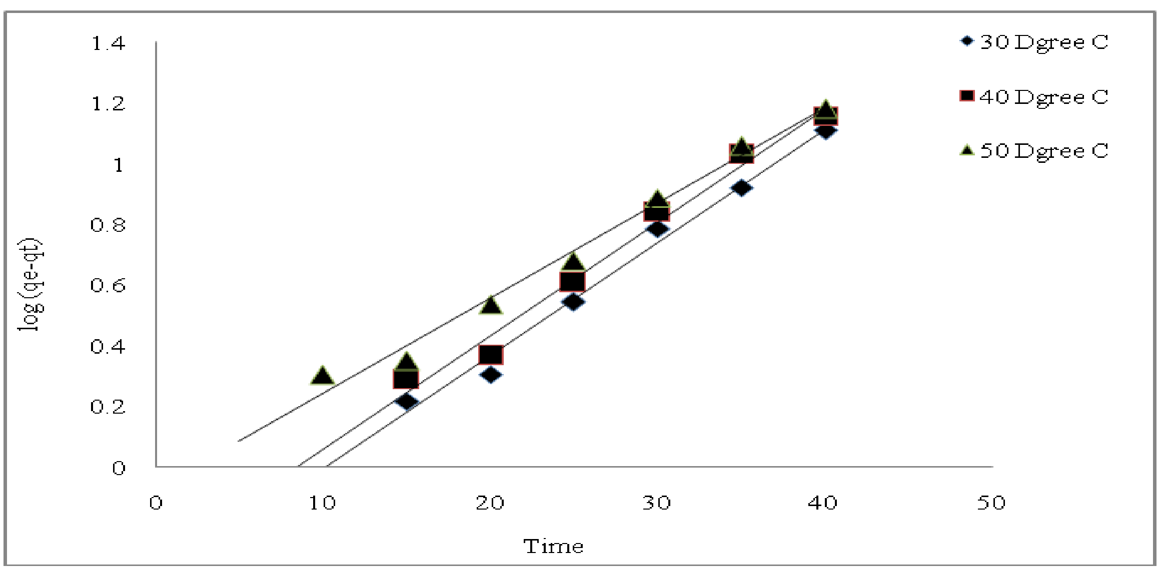


Fig. 9: Lagergren pseudo first order plots for adsorption of MG over UPR at pH 9.5 and different temperatures

Table 5: Rate constant k_{ad} for MG over UPR

Temp (°C)	k_{ad}	% RSD
30°C	0.04210	0.909
40°C	0.05952	0.914
50°C	0.08653	0.928

 # Average of three replicate measurement

4. CONCLUSION

Adsorption of Malachite green on the surface of adsorbent is a potential and economically inexpensive process. In the present study, UPR was used as an adsorbent for the removal of Malachite green dye from an aqueous solution. The UPR has a very high adsorption capacity to remove the dye, with monolayer adsorption efficiency. The rate of adsorption increases with the increase in amount of adsorbent. Freundlich and Langmuir's equations followed very well with the equilibrium isotherms. A pseudo-first-order kinetics model agreed well with the dynamical behavior for the adsorption of Malachite green dye on UPR under different temperatures, consistent with physical adsorption being the rate-determining step.

Conflict of interest

None declared

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