RASĀYAN *J. Chem.*
Vol. 11 | No. 1 |219-227 | January - March | 2018
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

MALACHITE GREEN DYE DEGRADATION USING $ZnCl_2$ ACTIVATED *RICINUS COMMUNIS* STEM BY SUNLIGHT IRRADIATION

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ABSTRACT
The degradation capacity of Malachite Green is tested with ZRCS using Sunlight irradiation by batch mode experiments such as the effect of pH, the effect of contact time, the effect of adsorbent dosage and initial dye concentration. The result indicates that the maximum degradation of Malachite Green is obtained as 85.30% at pH 6 in 90 minutes. The optimum conditions for the degradation of Malachite Green dye are 40ppm initial dye concentration and optimum dose of the carbon is 0.2g. The isotherms and isotherm constants are described by using Langmuir and Freundlich isotherm models for the degradation of Malachite Green using ZRCS. The Langmuir and Freundlich Models are very well fitted with the equilibrium data. The value of q_e is 16.6mg/g for Malachite Green on ZRCS. From the value of q_e, it is fitted well with a pseudo first order kinetics. ZRCS could be used as an effective adsorbent in cationic dye degradation.
Keywords: *Ricinus Communis* stem, $ZnCl_2$, degradation capacity, Malachite Green, Adsorption isotherms, Kinetics.

INTRODUCTION

Water is the most important compound for the survival of human beings, animals and plants. But the continuous increase in various activities by human beings like urbanization and industrialization is the main reason for causing pollution of water bodies.[1,2,3] The aqueous streams are contaminated by dyeing process carried out in leather, paper, textile, printing, cosmetics and food industries.[4] Discharge of the organic dyes into the environment cause serious problems such as Chemical Oxygen Demand, Biological Oxygen Demand, Increase of toxicity and human health issues.[5,6,7] Malachite green is a basic triphenylmethane dye ($C_{23}H_{25}N_2Cl$) used for dyeing of anionic fabrics bearing negative charge such as nylon, silk, acrylics and wool for a bright appearance.[8] The structure of Malachite Green has amino group and chromophores with positive ions and it is soluble in water.

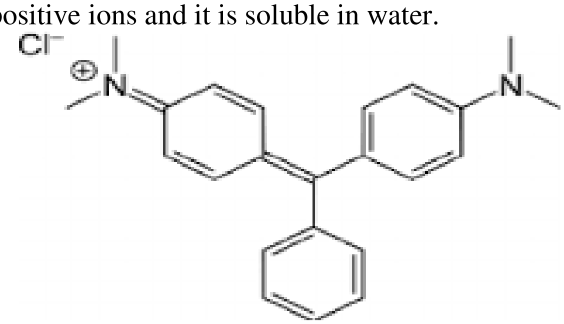

Fig.-1: Chemical Structure of Malachite Green

http://dx.doi.org/10.7324/RJC.2018.1111986

Even at very low concentration it is highly visible and has high brilliance and intensity of color. The release of Malachite Green into the water bodies cause environmental pollution such as undesirable color to the water and it reduces the Sunlight penetration into water. It affects the aquatic plants and animals. The presence of nitrogen in malachite green causes numerous harmful effects due to its genotoxic, teratogenic, carcinogenic and mutagenic characteristics.[9]

Generally, wastewater can be treated by using reverse osmosis, electrocoagulation, filtration, evaporation, membrane separation, adsorption, chemical precipitation, photocatalytic degradation and degradation using Sunlight irradiation.[10,11] When compared to other methods the degradation using Sunlight irradiation is simple and efficient to degrade the dye pollutants in aqueous media.[12]

The main advantage of solar irradiation method is to overcome the secondary waste generation from wastewater treatment and satisfy the permissible water quality standard and its use. This technique is a visible cleaning process for dyes.[13]Activated carbon is the widely used adsorbent for the degradation of pollutants from wastewater because of its high adsorption capacity towards a variety of dyes. Comparatively the cost and regeneration of the activated carbon is expensive than other adsorbents.[14,15] Because of the economic reason, it is examined for a long time that agricultural waste and its by-products are used for the preparation of activated carbon. These agricultural wastes include Neem Sawdust[16], Rubber Wood Dust[17], Commercial Activated Carbon[18], Wood Apple Shell[19], Cellulose Powder[20], TamarindFruit Shell[21], Unsaturated Polyester Ce(IV) Phosphate[22], Carbon prepared from Arundo donuts fruit[23]etc. *Ricinus Communis* is an agricultural waste and its common name is castor bean. It is an important drought resistance shrub belongs to the family Euphobiaceae.Physical and chemical activation are the two methods employed for the preparation of activated carbon. The carbonization and activation are carried out separately in physical activation, but both carbonization and activation takes place simultaneously in chemical activation. The raw material is initially activated by chemical and then carbonized at ambient temperature that depends upon the activating chemical used.[24] The chemical activation develops the pores of the adsorbent when compare to the raw material.[25]

The dehydrating reagents such as KOH, K_2CO_3, NaOH, $ZnCl_2$, and H_3PO_4 are used for the chemical activation. At low temperature, the Chemical activation gives a higher yield than the physical activation. $ZnCl_2$ activation results in high surface area and high yield.[26] The objective of this study is to know the degradation ability of ZRCS for degradation of Malachite green. The various batch parameters like the effect of pH, contact time, initial dye concentration and adsorbent dosage is determined and the experimental results are fitted with kinetic and Isotherm models.

EXPERIMENTAL

Materials and Methods

Zinc Chloride, Hydrochloric acid and Malachite green dye are purchased from Universal Scientific Company, India. The entire synthesis is carried out using Double distilled water. The procured chemicals and reagents are analytical grade which can be used without further purification. The preparation, physiochemical and surface characterization of ZRCS is already reported in our previous paper.[27]

Adsorbate

A stock solution of 1000mg/L of Malachite green is prepared by dissolving 1gram of the dye in double distilled water. All experiments are carried in duplicate and the mean values are reported.

Photo degradation of Malachite green

Batch mode parameters such as the effect of adsorbent dosage, initial dye concentration, pH and contact time are used to find out the degradation capacity of ZRCS onto Malachite green. The stock solution of Malachite Green is prepared and it is further diluted to 20-140 mg/ liter concentration for the experiments. 0.1M HCl/NaOH are employed to adjust the pH of the dye solution. The experiments are carried out by using 250ml borosil flasks, 0.2g of ZRCS and 50 ml of Malachite Green dye solution with different concentration at pH 6 and the solutions are kept in a shaker to attain the equilibrium in dark place. After attaining equilibrium the dye solutions are exposed to direct Sunlight irradiation.

The UV –VIS spectrophotometer model 119 is used to measure the absorbance in the range of 200-800nm. At regular intervals, the absorbance is taken to know the quantity of dye degraded using UV-VIS spectrophotometer. The absorbance obtained from the photodegradation experiments are then used to determine the percentage of degradation efficiency and it is calculated by the following relation:

$$D = \frac{C_0 - C_t}{C_0} \quad (1)$$

Where D is the Degradation efficiency, C_0 (mg/L) is the initial concentration of the dye and C_t (mg/L) is a concentration of dye after particular time interval[28].

RESULTS AND DISCUSSION

Effect of contact time

The effect of contact time is carried out to study the degradation capacity of the ZRCS by batch mode experiments. When the contact time increases the removal efficiency of ZRCS is also increased before the equilibrium is reached are shown in fig.2.The equilibrium condition is attained at 90 minutes which is fixed as an optimum contact time for Malachite Green dye degradation onto ZRCS. After the equilibrium time the degradation is more or less constant. This may be attributed to the initial stage of degradation and the availability of excess surface area sites and once saturation is reached, the uncovered sites are difficult to be filled, which is caused by the impervious forces between the cationic dye molecules and ZRCS[29].

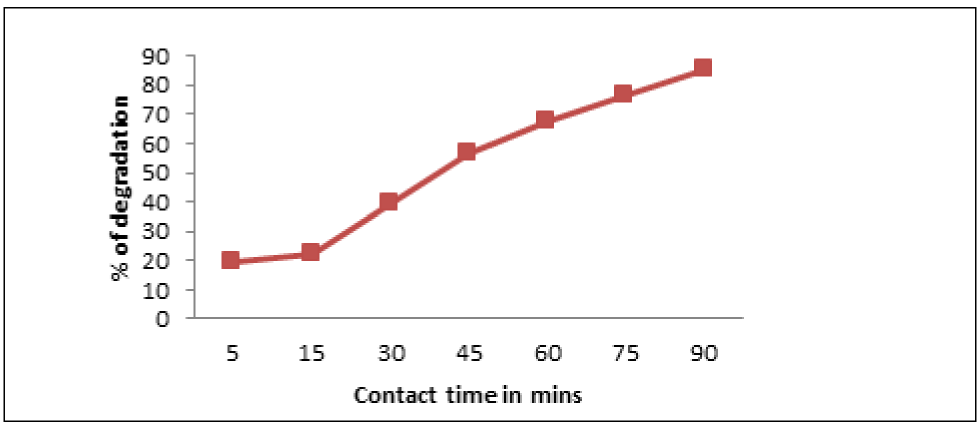

Fig.-2: Effect of Contact Time on the degradation of Malachite green dye using ZRCS.

Effect of pH

The pH is an important parameter is used to analyze the degradation of the Malachite green onto ZRCS. The ionization of the surface functional groups is influenced by solution pH. The degradation efficiency of ZRCS on photodegradation of Malachite Green is studied by varying the pH from 2-9[30]. In the graph when the pH increases from 2-6 the degradation ability also increases due to the number of the negatively charged site is available on the adsorbent surface at this pH. At pH 6 the strong electrostatic attraction created between the OH^- ions present in the adsorbent and cationic dye leads to utmost degradation of Malachite Green from wastewater.[31] At pH 2 the lowest degradation occurs and highest degradation occurs at pH 6. The surface of the ZRCS is positively charged to pH<5 and heterogeneous in the pH level 5-6, in this pH range the surface is negatively charged.The degradation increases with the increase of solution pH because of the accumulation of high OH^- ions on the ZRCS surface.[32] When the pH increases the attraction between the cationic dye and excess OH^- ions in solution increases, which enhances the Malachite Green dye degradation using ZRCS. In addition, the solution pH is higher than the zpc (zpc=4.2 pH). So the negative charge density of ZRCS is increased which supports the degradation of Malachite Green.[33] At pH 6 the maximum degradation of Malachite Green is achieved as 85.30%. The graph is plotted between pH and percentage of degradation to describe the degradation efficiency, is shown in the Fig.-3.

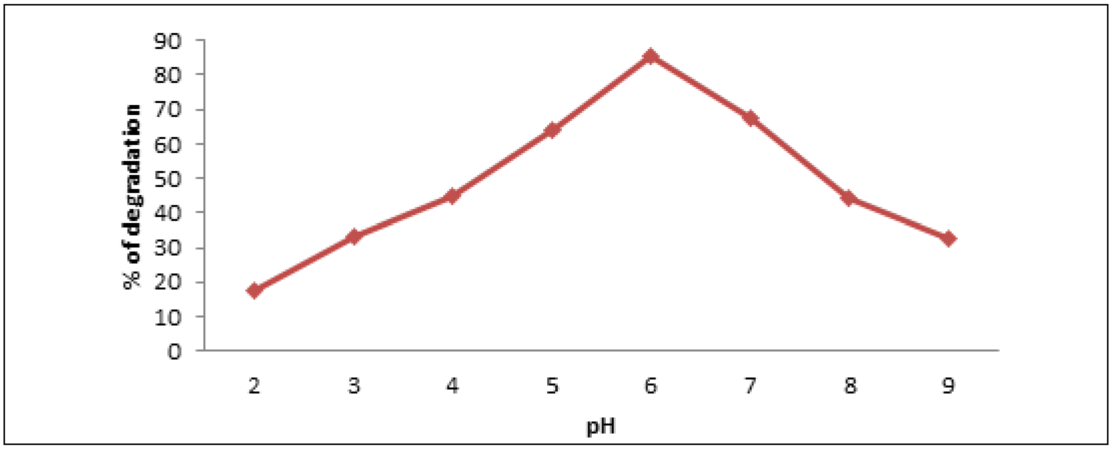

Fig.-3: Effect of pH on the degradation of Malachite green using ZRCS.

Effect of Adsorbent Dose

From the batch mode experiments the effect of adsorbent dose on Malachite Green is studied.The consequences are observed by the optimum pH at equilibrium time, for each degradation process. The degradation increases with increasing the adsorbent dose from 0.05g to 0.300g. The percentage of removal of Malachite Green depends upon the amount of adsorbent dose. If the adsorbent dosage increases the rate of degradation is also increasesupto0.2g. The enhanced degradation with adsorbent dose can be attributed to increasing the adsorbent surface and availability of excess adsorbent sites. The maximum dye removal of Malachite green is 85.30% occurs at 0.2g. Further, the increase in adsorbent dose does not cause any change in degradation ability. It can be characterized by the overlap of adsorption sites which decreases the availability of the total surface area of the dye and the diffusion path length is longer[34].The effect is explained by plotting a graph between adsorbent dose and percentage of degradation as shown in the Fig.-4.

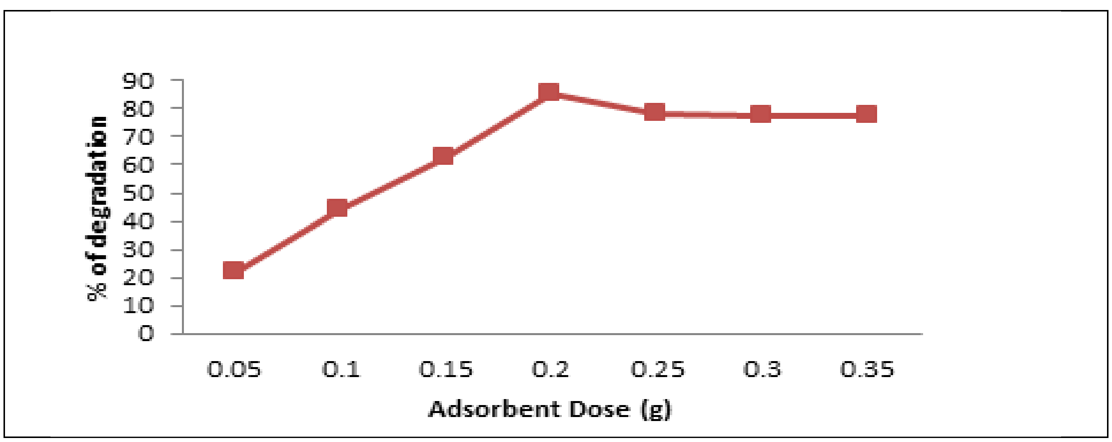

Fig.-4: Effect of adsorbent dosage on the degradation of Malachite green using ZRCS.

Effect of Initial Dye Concentration

The effect of initial dye concentration is carried out by using batch mode experiments and by varying the concentration ranges from 20 ppm to 140 ppm remaining parameters are kept constant as optimum values.[35] At lower concentration, the presence of dye molecules is low and the degradation site of the adsorbent is high, so the degradation is maximum at a lower concentration.[36] If the concentration of the dye is high then the excess dye molecules are available for excitation and energy transfer.[37] When the concentration of the dye solution increases the degradation ability of ZRCS is decreased. The relationship is given in the Fig.-5.

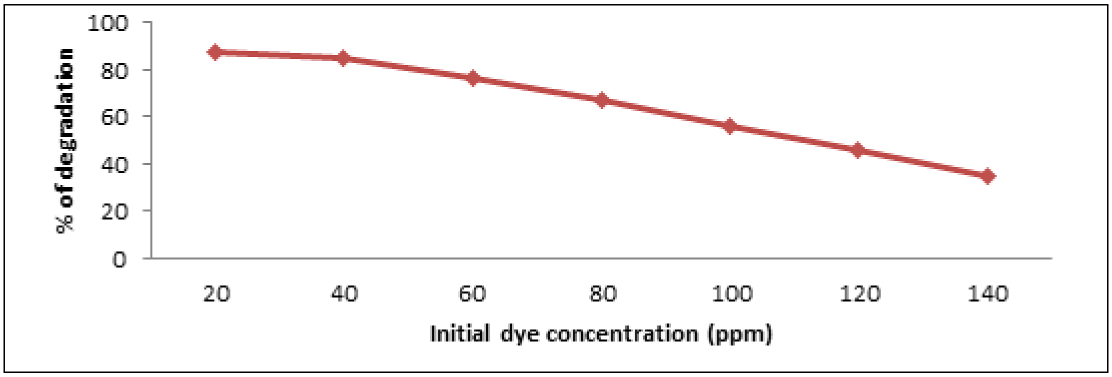

Fig.-5: Effect of initial dye concentration on the degradation of Malachite green using ZRCS.

Evidence for the degradation of Malachite Green onto ZRCS

UV spectra of Malachite Green onto ZRCS

The rate of degradation is measured with respect to change in intensity of adsorption peaks at 663nm for Malachite Green. The absorbance decreases gradually when the contact time increases with Sunlight irradiation; it shows that the dye has been degraded. The relationship between Wavelength and Absorbance is plotted in the Fig.-6.

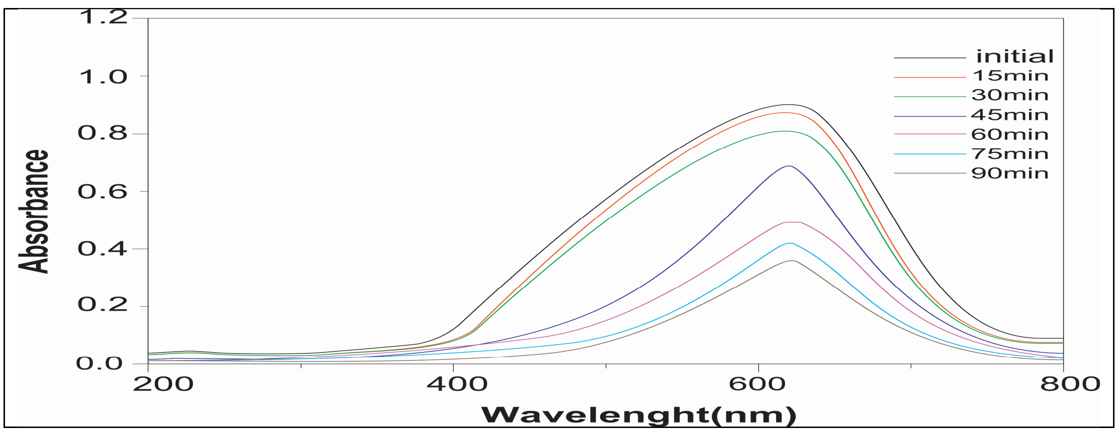

Fig.-6: UV spectra of Malachite Green onto ZRCS

Malachite Green degradation by ZRCS before and after treatment is shown in Fig.-7. The degradation of malachite green dye onto ZRCS is confirmed by the decolorisation of dye color after treating with ZRCS which is shown in Fig.-7.

Malachite Green Degradation on ZRCS is quantitatively analyzed using batch mode parameters by optimizing different parameters. The maximum percentage of degradation of Malachite Green in ZRCS is achieved at pH 6, 0.2g of adsorbent, 90 minutes contact time and 40 ppm of initial dye concentration.

Adsorption Isotherms

Langmuir Isotherm model is used to determine the adsorption equilibrium data. It is the most used Isotherm for designing the adsorption equilibrium and it is only applicable for monolayer adsorption on the surface with a definite number of adsorption sites[38]. The linear form of Langmuir model is expressed as follows:

$C_e/q_e= 1/q_{max} b+ C_e/ q_{max}$ (2)

Hence C_e is the concentration of Malachite Green dye solution (mg/L), q_e is the Malachite Green dye concentration (mg/g), q_{max} is the maximum degradation capacity (mg/g) and b is the Langmuir equilibrium constant.

Fig.-7: Malachite Green degradation by ZRCS before and after treatment.

A plot of C_e vs C_e/q_e for the adsorption of malachite green onto ZRCS is indicating a linear form of Langmuir Isotherm is shown in the fig.8. From the Table.1 the Q_m value of Malachite Green onto ZRCS is 12.64(mg/g), shows that the surface of the dye has very strong monolayer adsorption. The correlation coefficient (R^2) for the adsorption of Malachite Green onto ZRCS is equal to 0.9911 indicates a favorable adsorption of Malachite Green onto ZRCS.

Freundlich Isotherm

The heterogeneous system is explained by using Freundlich Isotherm. This Isotherm used for reversible adsorption is not restricted by the monolayer formation[39]. It is represented as follows:

$Logq_e =1/n \log(C_e)+\log K_f$ (3)

Where n is the Freundlich exponent, K is the Freundlich constant (mg/g),b is the constant associated energy of degradation (L/g) and 1/n is the heterogeneity factor.

The values of 1/n and K_f are calculated from the slope and intercept of the plot of log $q_e$vs log C_e is shown in the Fig.-9. The calculated parameters of Freundlich are summarized in the Table-1. From the table the correlation coefficients of Langmuir and Freundlich isotherms are more or less equal. So it is favorable for adsorption.

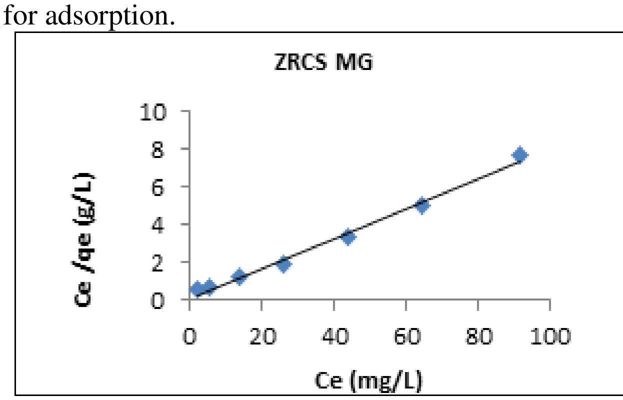

Fig.-8: Langmuir isotherm

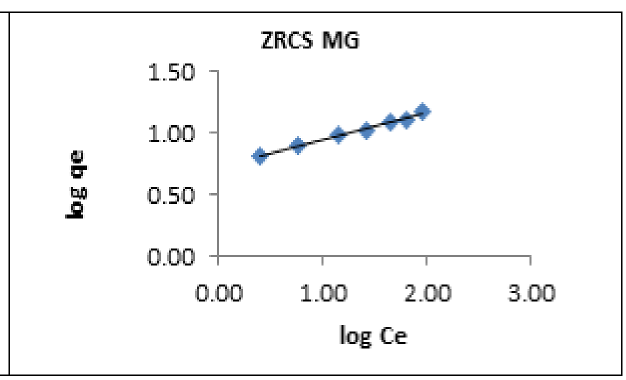

Fig.-9: Freundlich isotherm

Table-1: Langmuir and Freundlich Isotherm Models

Isotherm model	Parameters	ZRCS
Langmuir Isotherm	Q_m (mg/g)	12.64
	b (L/mg)	8.55
	R^2	0.9911
Freundlich Isotherm	1/n	4.504
	K_F (mg/g)	5.278
	R^2	0.9913

Table-2: Adsorption capacity of Malachite Green with various adsorbents

Adsorbents	Adsorption capacity (mg/g)
Neem Sawdust	4.35
Rubber wood Dust	36.45
Commercial Activated Carbon	8.27
Wood apple shell	34.56
Cellulose powder	2.42
Tamarind fruit shell	1.95
Unsaturated polyester Ce(IV) Phosphate	1.01
Carbon prepared from Arundo donuts fruit	8.69
Zinc chloride activated *RicinusCommunis* stem powder(present study)	12.64

Adsorption Kinetic Studies

Chemical kinetics study for the adsorption system is to find out the rate constant of the reaction and to know how the reaction is proceeding. In order to determine the kinetic parameter pseudo first order is employed to analyze the experimental data. The pseudo first-order kinetics linear form is as follows:

$$\ln (q_e-q_t)=\ln qe-k_1t \quad (4)$$

Where q_t(mg/g) is the amount of dye adsorbed at time t, q_e(mg/g) is the amount of Malachite Green dye adsorbed at the equilibrium phase and k_1(min^{-1}) is the rate constant of the pseudo first-order adsorption model.[40,41]

The pseudo first-order rate constant (0.0447 min^{-1}) reveals that the adsorption process of Malachite green is well fitted by the use of ZRCS. The linear regression coefficient value R^2 is equal to 0.99. This indicates the adsorption of Malachite Green onto ZRCS follows pseudo first-order kinetics is shown in the Fig.-10.

Table-3: Kinetic Data for the degradation of Malachite Green onto ZRCS

Kinetic model	Parameter	ZRCS
Pseudo first order kinetic model	k_1(min^{-1})	0.0447
	q_e(mg/g)	16.6
	R^2	0.99

CONCLUSION

In this study, Zinc chloride activated carbon is prepared from *Ricinus Communis* stem powder which is used as an adsorbent for the efficient degradation of Malachite Green from dye wastewater. The degradation of Malachite green onto ZRCS depends on the Initial dye concentration, Contact time, Adsorbent dosage and pH. The percentage of degradation of Malachite Green increases with a decrease in initial dye concentration. The adsorption data are well fitted with the Langmuir and Freundlich isotherm models. The results show an appreciable degradation of Malachite Green dye on ZRCS. At optimum condition, the maximum percentage of degradation of Malachite green is 85.30. The experimental studies have proved that the ZRCS can be used as a feasible and useful material to degrade Malachite green from dye wastewater.

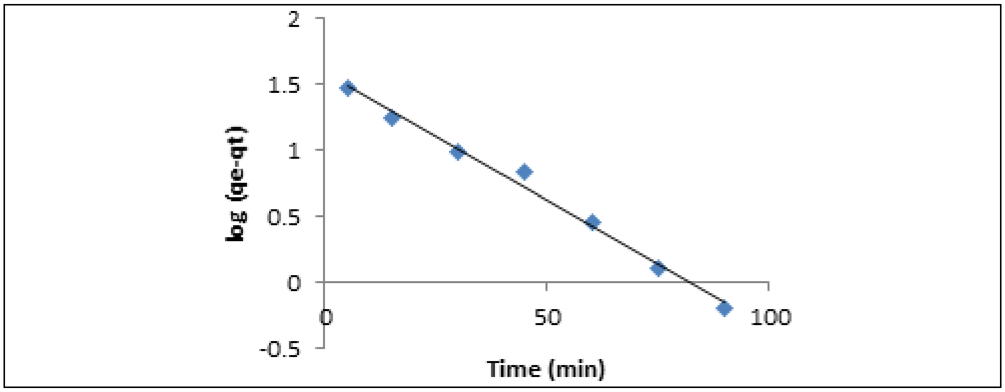

Fig.-10: Pseudo First order Kinetics for the degradation of Malachite green onto ZRCS

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[RJC-1986/2018]