

## Synthesis of Ferric Oxide Urea Formaldehyde Nanocomposite for Adsorptive Removal of Malachite Green Cationic Dye from Aqueous Media

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### ABSTRACT

The main objective of current research is to synthesise ferric oxide nanoparticles and prepare their nanocomposite from urea formaldehyde resin. Characterization techniques such as FTIR, XRD, and FESEM-EDX were used to obtain the specifications of the synthesised nanoparticle. Synthesised ferric oxide urea formaldehyde nanocomposite was used for the adsorption of malachite green (MG) dye from wastewater. The adsorption tests were implemented at various parameters. The adsorption capacity could reach 98% within a contact time of 80 min at pH 7 and an initial dye concentration of 50 ppm. It was finally retained that the adsorption rate of malachite green dye by ferric oxide urea formaldehyde nanocomposite follows pseudo second-order kinetics with the adsorption isotherm fitted by the Langmuir isotherm model well. All the above results demonstrated that ferric oxide urea formaldehyde nanocomposite has a significant potential for the removal of malachite green dye from wastewater.

**Keywords :** Ferric Oxide, Ferric Oxide-UF, Malachite Green, Langmuir Isotherm, Pseudo Second Order.

### I. INTRODUCTION

In the recent past, the environmental crisis has been a great challenge for living creatures. One of the examples is dyes, which are an important common pollutant in water pollution. In the early 19<sup>th</sup> century, dyes often arose naturally from plants and animals. But after this period, due to rapid industrialization and other human activities, the use of dyes has

increased. The industrial production of dye was performed in 1977, and gradually synthetic dyes replaced natural dyes[1], [2], [3], [4]. Dyes are considered to be the first pollutants in wastewater because of their complex structure, slow degradation, poisonous nature, and prolific production from industries[5], [6]. Malachite green (MG) is a triarylmethane dye that is highly water-soluble. It is highly cytotoxic to mammalian cells. It is a cationic

dye. Malachite green is widely used in the textile, paint, and painting industries, medicine, and food production. It is also directly used as a colour in the wood, silk, jute, leather, and paper industries. So, there is a significant amount of sewage in such industries, which contaminates the surrounding area every day. However, the negative effect will come into play if excessive concentrations of malachite green are discharged into the water resources, resulting in carcinogenic and mutagenic effects on living creatures[1], [7], [8], [9]. Considering the necessity and difficulty of the removal of toxic dyes, many physicochemical methods are available, such as physical adsorption, chemical precipitation, oxidation/reduction, filtration, electrolysis and ion exchange, coagulation, membrane filtration adsorption, and photocatalysis[10], [11], [12], [13]. In spite of that, some of these methods have the limitations of being time-consuming, costly, complex, and less sensitive. However, adsorption is recognised as a promising approach because of its simple operation, low cost, good removal performance, low generation of residues, and the fact that adsorbents may be regenerated and reused[11], [14], [15].

Some materials are economically infeasible due to their relatively high costs. Therefore, developing countries can't afford these composites. To overcome these challenging points, there is a need to investigate a low-cost and economically feasible alternative method for water decontamination[1].

In recent years, innovation in nanotechnology has generated effective materials due to the large surface area-to-volume ratio needed to remove pollutants from wastewater[1], [2]. Besides, the problem of stabilisation and agglomeration of nanomaterials constrained their effectiveness and potential applications[1]. To overcome this problem, the encapsulation of nanomaterials in polymer matrix has been reported[1], [2], [3]. Numerous nanoscale materials with a stabilised polymer matrix are reported for water decontamination, but their

dispersion in a polymer matrix still needs investigation[1], [4]. Metal oxide nanocomposite with polymer has an effective capacity to remove pollutants from wastewater if the properties of nanocomposite constituents are synergized[1], [5].

In this research work, we have synthesised the ferric oxide urea formaldehyde nanocomposite in situ by polymerization and chemical functionalization methods. Which was effectively used for the removal of malachite green dye from an aqueous source. The impact of influential factors such as initial dye concentration, contact time, adsorbent dose, and pH was studied. The mechanism of malachite green over the ferric oxide urea formaldehyde nanocomposites, adsorption kinetics, and adsorption isotherm were studied. The objective of the present work is to study the use of ferric oxide, urea, and formaldehyde nanocomposite for the effective removal of malachite green from wastewater.

## II. EXPERIMENTAL METHODS

### A. Material

Ferric nitrate [ $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ] (MERCK INDIA), ethylene glycol( $\text{C}_2\text{H}_6\text{O}_2$ ) (A R grade), urea (99%), and formaldehyde (A R grade) were used without further purification. Throughout the experiment, double-distilled water was used.

### B. Preparation of magnetite nanoparticle

The synthesis of ferric oxide nanoparticles is described as follows:

To create a sol, ferric nitrate was first mixed in 100 ml of ethylene glycol and heated to 40 °C while being rapidly agitated for one hour. The brown colour solution was then heated to a constant temperature of 80 °C until a dark brown colour gel was produced. After being aged for four hours, this gel was dried for five hours at 120 °C. Under vacuum, the resulting xerogel was annealed at a specific temperature. In the end, magnetite nanoparticles were produced effectively. To improve their magnetic qualities,

acetone and ethanol were used to wash the synthesised  $\text{Fe}_3\text{O}_4$  nanoparticles.

### C. Synthesis of Ferric oxide –Urea formaldehyde nanocomposite

In a 250-ml beaker, 20 ml of 40% formaldehyde and 10 g of urea were combined in a molar ratio of 2:1 (w/w). The mixture was magnetically agitated at 60 °C for 30 minutes to dissolve the urea in the formaldehyde. 100 mg of ferric oxide were added to this mixture and stirred. Five minutes later, 0.5 ml of concentrated  $\text{H}_2\text{SO}_4$  was added while being constantly stirred. After getting a white precipitate, it was washed with distilled water, dried in an oven, and put in desiccators.

### D. Preparation of Dye Solution

One gramme of powdered malachite green dye (1.00 g) was used to create the stock solution. A one-litre measuring flask was quantitatively filled with the dye and then topped off with distilled water to get a dye concentration in the solution of 1000 mg/L. Separately prepared stock dye solutions (1000 mg/L) were kept in distilled water at 4 °C for storage. To prepare the working solutions, dilute the stock solutions with distilled water.

### E. Estimation of Dye concentration

Using a UV-Vis spectrophotometer (Schimadzu UV-Spectrophotometer, Model UV-1800), the dye concentration and removal efficiency of the  $\text{Fe}_3\text{O}_4$ -UF nanocomposite were calculated. Absorbance was measured at 617 nm against blank, using malachite green as the standard, to estimate the dye in the synthetic effluent.  $\text{Fe}_3\text{O}_4$ -UF nanocomposites: the impact of experimental conditions on the elimination of malachite green dye.

## III.RESULTS AND DISCUSSION

The characterization of nanostructured  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4$ -UF was carried out by using the Bruker

ALPHA FTIR Spectrometer in the Department of Organic Chemistry at RTM Nagpur University Nagpur, Scanning Electron Microscope JEOL Model No. JSM7610FPLUS (75000X and 8000X) equipped with energy dispersive X-ray spectroscopy at RUSA Manipal University Jaipur, and the Rigaku Mini Flex 300/600 Benchtop X-Ray Diffractometer (using Cu-K radiation, with an operating voltage of 45 kV and a current of 40 Ma with a range of  $2\theta$  10 to 70 degrees) at RUSA RTM Nagpur University Nagpur.

### A. FTIR Analysis

Fig. 1 shows  $\text{Fe}_3\text{O}_4$  FTIR studies were carried out to determine the metal-oxygen bond. The adsorption bands at 428.23  $\text{cm}^{-1}$  and 540  $\text{cm}^{-1}$  show the vibration of Fe-O. The adsorption bands at 1641.56  $\text{cm}^{-1}$  and 3565.14  $\text{cm}^{-1}$  correspond to C=O and O-H modes, respectively[6].

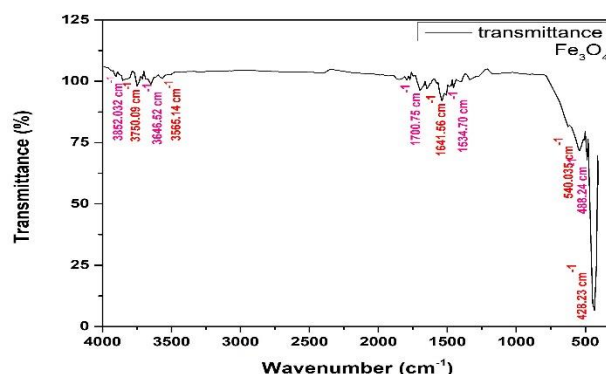
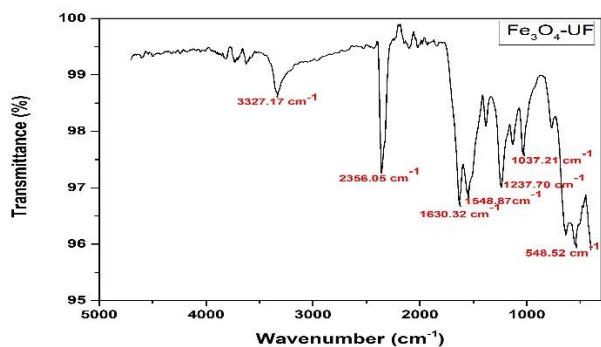


Fig. 1 FTIR of  $\text{Fe}_3\text{O}_4$

Fig. 2 shows  $\text{Fe}_3\text{O}_4$ -UF. Shifting of bands at higher wavenumbers indicates the formation of composites. The sharp peak at 548  $\text{cm}^{-1}$  of the Fe-O bond and the carbonyl group peak are shifted to 2356  $\text{cm}^{-1}$ .

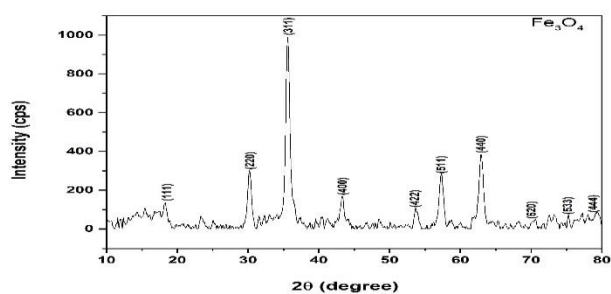
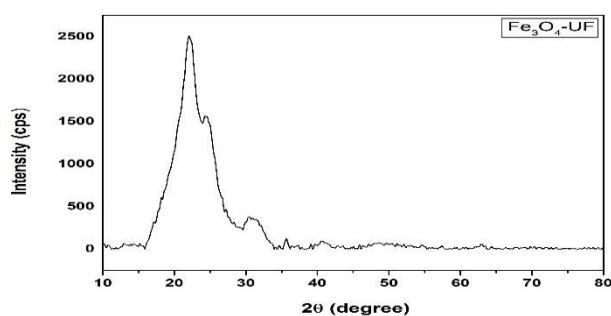
Fig. 2 FTIR of Fe<sub>3</sub>O<sub>4</sub>-UF

### B. XRD Analysis

Fig. 3 shows that the diffraction peaks at  $2\theta = 19^\circ, 30^\circ, 36^\circ, 43^\circ, 54^\circ, 57^\circ, 63^\circ, 71^\circ, 75^\circ,$  and  $79^\circ$  can be assigned to the (111), (220), (311), (400), (422), (511), (440), (620), (533) and (444) planes of Fe<sub>3</sub>O<sub>4</sub> (PCPDF # 391346). The crystallite size of the nanoparticle is calculated by the Scherrer formula.

$$D = \frac{K \cdot \lambda}{\beta \cdot \cos \theta}$$

Where K is the dimensionless shape factor,  $\lambda$  is the x-ray wavelength,  $\beta$  is line broadening at half the maximum intensity (FWHM), and  $\theta$  is the Bragg angle. The mean crystallite size of the Fe<sub>3</sub>O<sub>4</sub> is 14.43 nm.

Fig. 3 XRD spectra of Fe<sub>3</sub>O<sub>4</sub>Fig. 4 XRD spectra of Fe<sub>3</sub>O<sub>4</sub>-UF

### C. SEM Analysis

Figs. 5 and 6 show the same images of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles at 400 °C. It is indicated that the agglomeration of nanoparticles is because of xerogel.

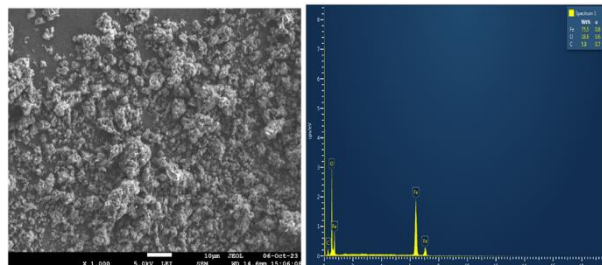
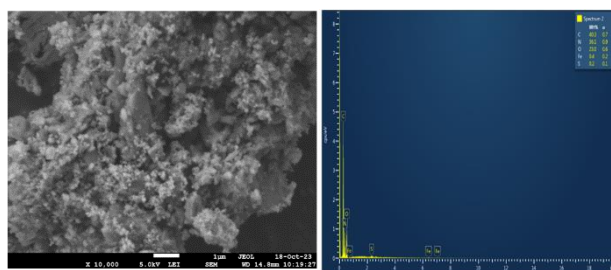
Fig. 5 SEM of Fe<sub>3</sub>O<sub>4</sub>Fig. 6 Fe<sub>3</sub>O<sub>4</sub> EDX imageFig. 7 SEM of Fe<sub>3</sub>O<sub>4</sub>-UF  
Fe<sub>3</sub>O<sub>4</sub>-UF EDX

Fig. 8

## IV. BATCH STUDY

To understand the effective adsorption behaviour of malachite green onto Fe<sub>3</sub>O<sub>4</sub>-UF, batch studies were executed with optimised parameters such as initial MG concentration (10–100 ppm), adsorbent doses (0.01–0.1 g), contact time (10–100 min), and working pH values (4–10). The general procedure was as follows: The desired quantity of Fe<sub>3</sub>O<sub>4</sub>-UF adsorbents was taken in a 50-ml Erlenmeyer flask containing a 25-ml solution of MG with a given concentration, and then the sample solution was shaken at 100 rpm on a NAVYUG (India) rotary shaker for a specific time. After that, the sample was filtered using Whatman filter paper no. 40, and the residual MG concentration was measured using a Shimadzu UV/Vis

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

$$q_e = (C_0 - C_e) \times \frac{V}{m} \quad \dots (2)$$

spectrophotometer at 624 nm. The adsorption percentage and adsorption capacities were calculated (eq<sup>n</sup> 1 and eq<sup>n</sup> 2) as follows:

Where  $C_0$  is the initial concentration in the dye solution (mg/L), and  $C_e$  is the final dye concentration in the aqueous solution after adsorption (mg/L),  $V$  is the volume (ml) of the solution taken, and  $W$  (g) is the mass of the adsorbent used.  $R\%$  is the adsorption percentage, and  $q_e$  is the maximum adsorption capacity.

## V. BATCH EXPERIMENTS

### A. Effect of initial concentration

The adsorption capacities of the  $Fe_3O_4$ -UF adsorbent at different initial MG concentrations (10–100 ppm) keep other parameters fixed. The results indicate that with increasing concentration, the adsorption percentage increases (Fig. 9). This is because of the high driving force for mass transfer at higher concentrations range[7], [16]. No more uptake was seen above 70 ppm. This is because of the saturation of all available active binding sites. The Langmuir adsorption coefficient is reported in the appropriate section.

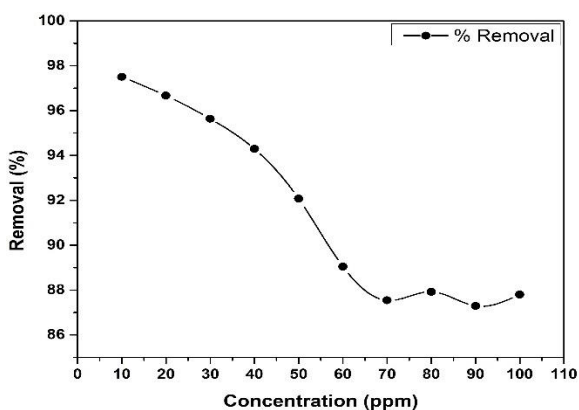


Fig. 9 Effect of initial concentration

### B. Effect of adsorbent Dose

With increasing adsorbent doses, the percentage of adsorption increases. This is because of the higher availability of more adsorption sites at high adsorbent doses (batch study 5). However, no significant increase in the adsorption efficiency above the 0.07 g

dose was observed (Fig. 10). The improvement in the adsorption percentage is because of the increase in the accessibility of the active sites for the adsorption of dye molecules[8], [17]. As a result, under the examined conditions, the optimal adsorbent dose was 0.05 g.

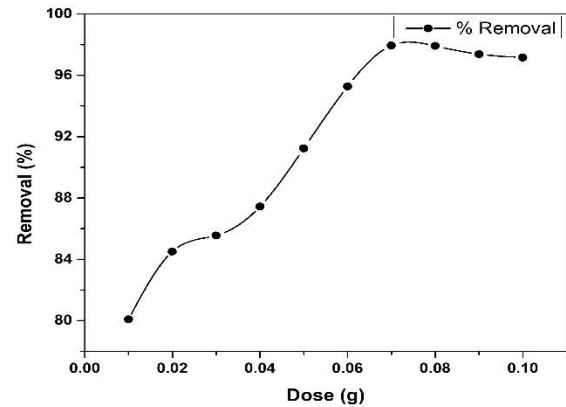


Fig. 10 Effect of Doses

### C. Effect of contact time

The impact of the contact time on the MG adsorption by  $Fe_3O_4$ -UF was achieved over a time interval of 10–100 min under fixed conditions (MG: 40 ppm, dose: 0.05 g) (Fig. 5.3). At an initial period of 60 minutes, the adsorption rate was high. This indicates the existence of available active sites on the  $Fe_3O_4$ -UF surface. A perusal of Fig. 11 indicates that the efficiency of the dye adsorbed is rapid in the initial stage up to 70 min and after that remains almost constant due to saturation of the active sites, which do not allow further adsorption to take place [8], [9], [10], [11]. The optimal contact time to attain equilibrium was experimentally found to be about 60 min.

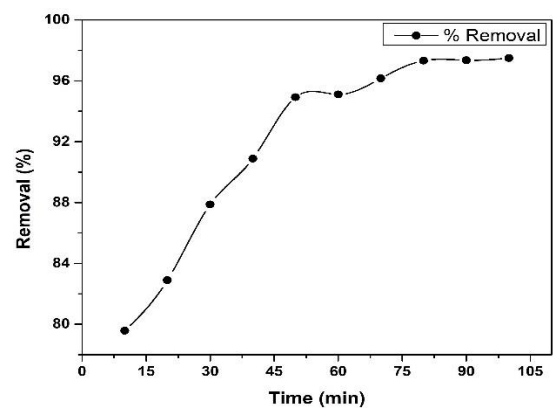


Fig. 11 Effect of contact time



### D. Effect of pH

The pH of the solution was found to influence the adsorption of the adsorbate on the adsorbent. The study was concluded at a fixed concentration of adsorbate (40 ppm), dose (0.05 g), and contact time (60 min). pH was adjusted by adding either 0.1 M HCl or 0.1 M NaOH, and the change in adsorption of dye was studied over a pH range of 4.0–9.0. The results obtained are presented in Fig. 12, which shows that the adsorption of malachite green increases with an increase in pH from 4.0 to 8.0, compared with pH 7, with an almost similar performance[11], [12], [13], [14], [15].

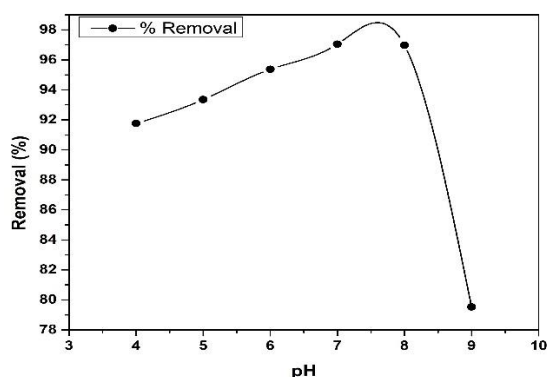


Fig. 12 Effect of pH

## VI. ADSORPTION ISOTHERM

Using two adsorption models, such as the Langmuir and Freundlich models (Fig. 13 and 14) in their formats, the experimental adsorption equilibrium data were evaluated in order to investigate the mechanism of adsorption onto ferric oxide urea formaldehyde nanocomposite. From the slopes and intercepts of these models, the correlated constants are evaluated (tables no. 1 and 2). Upon fitting the study data to both isotherm models and accounting for the higher correlation coefficient values ( $R^2 \sim 1$ ), it can be concluded that the Langmuir isotherm model provides the most accurate explanation for the adsorption of malachite green onto ferric oxide urea formaldehyde nanocomposite.

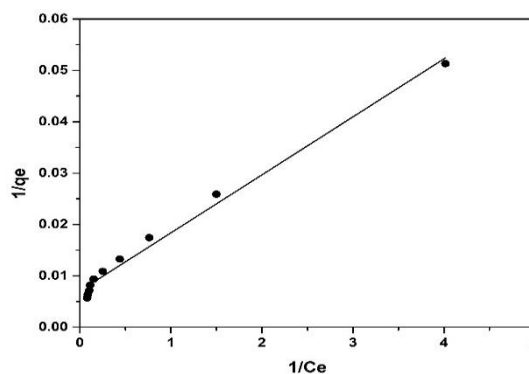


Fig. 13 Langmuir isotherm

TABLE I

Langmuir adsorption parameter

Intercept	Slope	$q_{\max}$ (mg/g)
0.00706	0.01129	141.6430595
$K_L$	$R_L$	$R^2$
0.625332152	0.030991792	0.98725

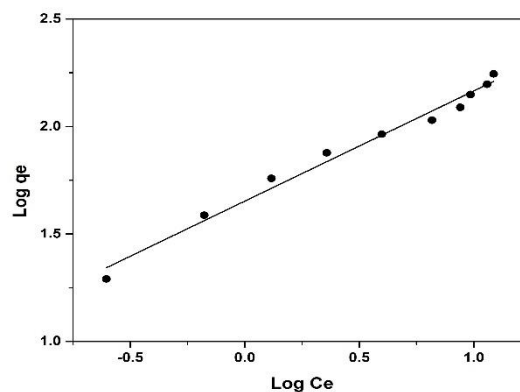


Fig. 14 Freundlich isotherm

TABLE II

Freundlich adsorption parameter

Intercept	Slope	$1/n$
1.65261	0.5129	0.5129
$K_f$	$R^2$	
44.93761302	0.98247	

## VII. ADSORPTION KINETIC

The adsorption kinetics of malachite green onto the ferric oxide urea formaldehyde surface (Fig. 15 and 16) were assessed through the application of various

kinetic models, including pseudo-first-order and pseudo-second-order models. The plots of the kinetic model equation were used to compute the variable parameters (Tables 3 and 4). The correlation coefficient ( $R^2$ ) and concurrence between the computed and experimental values of  $q_e$  are the two models' main application requirements. The system is believed to follow a pseudo-second-order kinetic model, as indicated by the higher values of ( $R^2 \sim 1$ ) and nearly identical experimental and calculated values of  $q_e$  (tables 3 and 4).

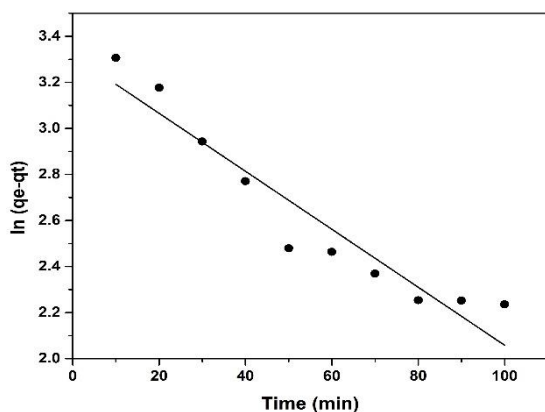


Fig. 15 Pseudo first order

TABLE III

Pseudo first order Parameter

Intercept	Slope	$q_e(\text{mg/g})$
3.31734	-0.01254	27.5868718
$K_1$	$R^2$	
-0.000179857	0.90243	

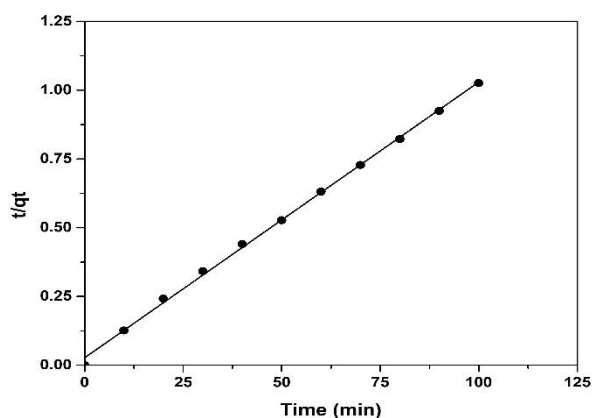


Fig. 16 Pseudo second order

TABLE IV

Pseudo second order Parameter

Intercept	Slope	$q_e(\text{mg/g})$
0.02649	0.01003	99.709
$q_e^2$	$K_2$	$R^2$
9940.269	0.003798	0.99865

## VIII.CONCLUSION

The goal of this effort is to characterise and synthesise ferric oxide using the sol-gel method. The synthesised ferric oxide is coated with urea formaldehyde resin in the ratio 1:2 to boost its effectiveness. The prepared  $\text{Fe}_3\text{O}_4$ -UF nanocomposite offers a low-cost, effective, and environmentally safe method of eliminating malachite green from wastewater. To fully understand how the various parameters affected the adsorption of MG onto  $\text{Fe}_3\text{O}_4$ -UF, tests were conducted on the  $\text{Fe}_3\text{O}_4$ -UF nanocomposite. 50 ppm of initial MG concentration, 0.05g of adsorbent, 60 minutes of contact time, and pH 7 were shown to be the optimal adsorption factors. It was found that the adsorption isotherm and kinetic model fit the pseudo-second-order kinetic model and Langmuir isotherm model better. All things considered; it seems likely that the synthesised  $\text{Fe}_3\text{O}_4$ -UF adsorbent will work well as an adsorbent to remove malachite green dye from aqueous solutions.

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