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Photocatalytic Degradation of Methylene Blue Dye using Green Synthesized Iron Oxide Nanoparticles (Fe_3O_4) from *Gracillaria edulis*

G. Subhashini*, P. Ruban
[1*]Department of Biotechnology, SNMV College of Arts and Science, Coimbatore, India
Corresponding author email ID: **subhag4@gmail.com**

ABSTRACT
The present study was carried out to assess the photocatalytic degradation capacity of Fe_3O_4 nanoparticles using various concentrations of dyes and to assess the degradation processes with best fitted kinetic model.Fe_3O_4 Nanoparticles (NPs) were bio synthesized from Gracilaria edulis seaweed, photocatalytic (presence of UV irradiation) activities of green synthesized Fe_3O_4 nanoparticles were studied for degradation of methylene blue dye at different concentrations of aqueous dye, parallel with Nano particle concentration, time and pH. The dye samples before and after photo catalysis, were subjected to HPLC analysis and FTIR analysis and the changes that has occurred during photo catalysis were observed. In the presence of UV irradiation, the rate of decolourization increased with increase in Fe_3O_4 Nanoparticles and here 9 mg was the optimum concentration. When effect of time was checked with 90 mg/ml aqueous dye solution and 9 mg Fe_3O_4-NPs, it was noticed that after 18th hr, there was no change in rate of degradation, indicating that 18 hrs. was the required optimum time . The optimal pH was found to be 6 for methylene blue. In HPLC analysis the presence and absence of different types of aromatic compounds, hydroxyl and amide groups before and after treatment represents that constituents of the dye had undergone mineralization. FTIR analysis shows the presence and absence of many functional groups before and after treatment. The green synthesized Fe_3O_4-NPs catalyst from G. edulis was found to promote Photocatalytic degradation of methylene blue and fitted with various kinetic models. The Fe_3O_4 Nanoparticles size and its anatase phase property was conducive for effective removal of dye.
***KEYWORDS**: FTIR, Green synthesis, iron oxide nanoparticles, Photocatalytic degradation, textile dye, UV irradiation and Kinetic studies.*

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INTRODUCTION

It is known that clean water is becoming scarcer. The main pollutants of surface water were dyes. There are more than 10000 commercially available dyes, they are used in various business most often in the textile industry. Most dyes were not biodegradable, even little concentration as 1 µg can be more harmful. Convectional technologies relating to UV radiation and hydrogen peroxide oxidation are not effective with degradation of dyes as dye pollutants are chemically stable. Nowadays, photocatalytic dye degradation method have got extensive attention due to its effective decolourization of dyes [1].

Photocatalytic degradation is relatively easy; it can be reused and also release less toxic waste than adsorbents [2].Photocatalytic degradation can be carried out effectively with various forms of Nano particles [3]. Due its large surface area [4], Nanoparticles provide cost effective solution to some of the most challenging Environmental cleanup problem. The most commonly used compound were Iron oxide nanoparticles, as it is relatively cheap and safe for use. The nanoparticles shows efficient degradation of methylene blue dye under sunlight irradiation [5]. These Nanoparticles are stable and reusable, so can be ascertained many times for potential photocatalytic activity and remediation of polluted water [6]. Magnetic properties of iron oxide nanoparticles allow active adsorption, and effective removal of dye from aqueous system [7].

Biosynthesized Nanoparticles using Seaweed was found to be impressive in degrading dyes [8]. To improve degradation, recovery and safety Nanoparticles were immobilized with a solid structure [9]. When compared to other irradiation techniques, photocatalytic degradation was found to be faster in decolorizing methylene blue with the presence of Nanoparticles [10]. The self-degradation ability of methylene blue dye under visible light was found to be negligible in the absence of photo catalyst [11].

The aim of this study was to assess the ability of photocatalytic degradation of methylene blue dye by green synthesized Fe_3O_4 nanoparticles under UV irradiation conditions. To assess the adsorption and degradation reaction rate and kinetic models.

MATERIAL AND METHODS

Green synthesized Fe_3O_4 nanoparticles, methylene blue dye were purchased from sigma Aldrich. All glassware's were cleaned with sterile distilled water and rinsed with deionized water.

Preparation of extract:

Gracilaria edulis seaweed were collected, washed with sterile distilled water and dried, then made to powder. 1g of powder was mixed with 100 ml of water and kept on orbital shaker at 120 rpm for 12hrs. Then, the extract were filtered through WhatMann No1 filter paper and stored at 40°C in refrigerator for further use [12].

Synthesisof Iron OxideNanoparticles:

Iron oxide nanoparticles have been synthesized by [13] method with slight modification. 0.1M Ferric chloride solution was prepared by dissolving 1.62g of ferric chloride in 100ml of distilled water. Fe_3O_4-NPs were obtained with the reduction process, by adding 0.1 M Ferric chloride solution to the seaweed extract in a 1:1 volume ratio. The formation of Fe_3O_4-NPs was indicated by the appearance of brick red colour precipitate formed within 5 min [14]. To obtain a colloidal suspension the mixture was stirred for 60 min and kept at room temperature for 30minutes.Then it was centrifuged and washed several times with ethanol and dried at 40°C under vacuum to obtain Fe_3O_4 Nanoparticles. Seaweed extract have the best reduction capability against ferric chloride when compared to other plants that is observed by the external colour change. After the visual confirmation test the Fe_3O_4-NPs were synthesized by using the above procedure for further characterization.

Characterization

UV–visible spectrophotometric analysis was performed with methylene blue dye, before and after treatment with nanoparticles and the absorption maxima were analyzed using UV–visible spectrophotometer (UV-160 v, Shimadzu, Japan) at a wavelength of 200–800 nm.

Photo catalytic studies of Iron Oxide Nanoparticles

The photocatalytic (in presence of UV irradiation) activities of green synthesized Fe_3O_4 nanoparticles were assessed for degradation of methylene blue at different concentrations of aqueous dye (30 mg/ml, 60mg/ml, 90mg/ml, 120mg/ml). Similar optimization studies were carried out with Nanoparticle concentration (3mg, 6mg, 9mg, and 12 mg), time (2 hrs. – 24 hrs.) and pH (3, 6, 7, 9 and 11). The dye samples before and after photocatalysis, were subjected to HPLC and FTIR analysis to observe changes that have occurred with the presence and absence of Nanoparticles.

Effect of Nanoparticle and Nanocomposite dose on dye concentration

Varying concentrations of Fe_3O_4NPs (3, 6, 9, and 12 mg) were added to 30 ml each of the aqueous dye solutions of various concentrations (30, 60, 90, and 12mg) and subjected for photocatalytic activity under UV irradiation. Respective controls were maintained for each dye concentration. Absorbance was recorded at a time intervals of 6 hrs, for a period of 24 hrs and percentage of decolorization was calculated. The dye concentration and, dose of nanoparticles and nanocomposite, with maximum decolorization values was selected for optimization.

Effect of time on decolorization

The optimum dye concentration, nanoparticle dose and composite dose, along with controls were subjected for photocatalysis under UV irradiation for a period of 24 hrs. and absorbance was noted every 3 hrs. for calculation of time of decolorization.

Effect of PH:

Different pH solutions (3, 6, 7, 9 and 11) of the optimum concentration of dye and nanocomposite were added. It was allowed for decolorization under UV irradiation. The absorbance was noted at time intervals of 6hrs for 24 hrs.

Kinetic models

The mathematical suitability of the photocatalytic activity under UV irradiation mediated by the green synthesized iron oxide nanoparticles were analyzed by using various kinetic models in terms of the optimized parameters. The analyzed kinetic models were Langmuir isotherm, Elovich plot and fractional power model.

RESULTS AND DISCUSSION

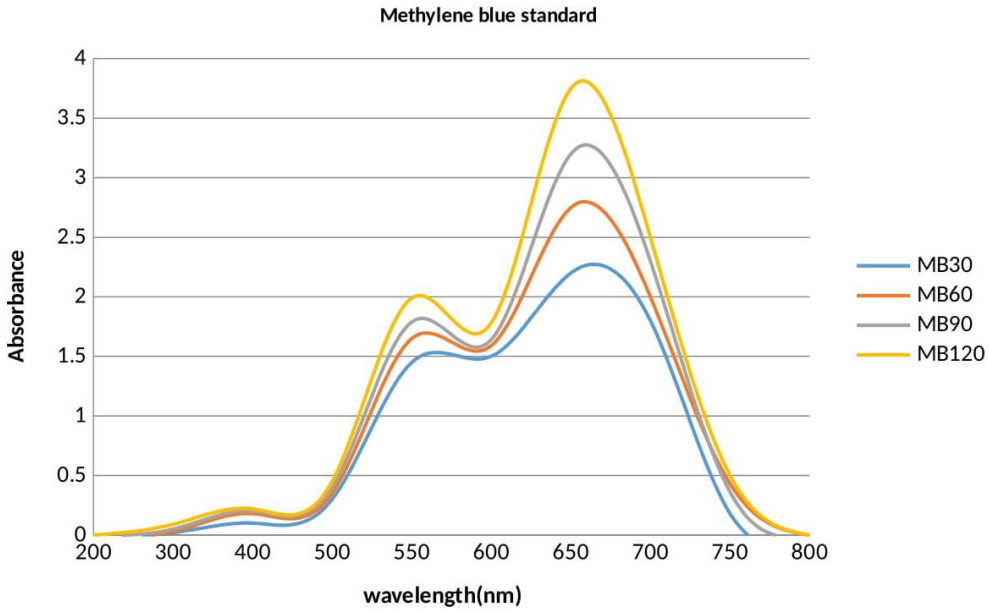

Fig 1: UV absorption of methylene blue dye standard

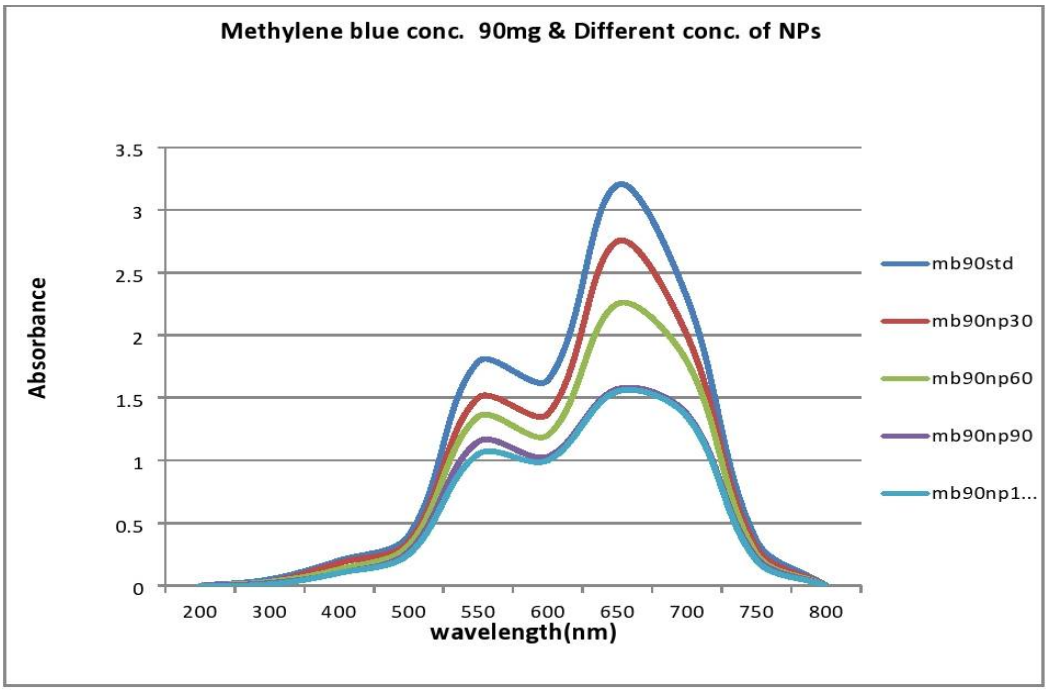

Fig 2: UV absorption of methylene blue conc. 90mg with different conc. of FE_3O_4nanoparticles

Characterization

Absorption is a conventional but efficient technique to remove dyes from aqueous solution[15]. The absorption of a photon of energy creates electrons and holes on the surface. The charged carriers do not recombine and these free radicals cause the oxidation of the dyes [16].Under UV-light irradiation, Iron oxide nanoparticle has been employed as photocatalytic agent to degrade the organic dye, viz. Methylene Blue (MB) in presence of visible light by taking 5 mL aliquot sample, and the absorption of the samples was recorded.

The rate of decolourization was observed with intensity of λmax (665 nm) of the dye. Under UV irradiation, the percentage of decolourization increased with increase in Fe_3O_4-NPs for all concentrations and here up to 9 mg was found to be the optimum concentration for decolourization. The reason for high catalytic activity of synthesized Nanoparticles was due to the high surface area, the main active site of the

catalyst and accelerates the photo degradation[17]. Effect of time was checked with 90mg/ml aqueous dye solution and 9 mg Fe_3O_4-NPs, it was noticed that after 18th hrs. There was no change indicating that 18 hrs. Was the optimum time. When the Nanocomposite size and dye concentration increase beyond the optimum, the photocatalytic activity decreases due to decrease in surface area [18].

The optimal pH observed for methylene blue was 6, which matches with the original pH of the dye. At extreme pH values, there will be reduction in the photocatalytic efficiency consistently with the establishment of coulombic repulsions between homologous charge states [19].The photocatalytic degradation capacity has been reported to be increased with increase in photocatalyst loading regardless of particle morphology [20].

HPLC and FTIR analysis of methylene blue dye before and after photo catalysis

The dye methylene blue contains many characteristic functional groups. The peaks at 1635.64 cm^{-1}, 2075.41 cm^{-1}, 3466.08 cm^{-1} are indicative of alkenes with C-H. Methylene blue dye resulted in nitrate with NO2 bending (420.48 cm^{-1}), sulphides and disulphides with C-S stretching (478.35cm^{-1}), β-substituted naphthalene with C-H out of plane bending (1637.56cm^{-1}), lactams with C-N stretching and sulphones with SO_2 asymmetric stretching (3450.65cm^{-1}), UV mediated photocatalysis of methylene blue in the presence of Fe_3O_4/Nanoparticles resulted in the formation of phenol due to oxidation of the dye [21].

Aromatic hydrocarbons corresponded to the peaks at 732.95 cm^{-1}, 779.24 cm^{-1}, 825.33 cm^{-1}, 979.84 cm^{-1}, 1018.41 cm^{-1}, 1087.85 $cm^{1,}$ 1219.01 cm-1, 1296.16 cm-1 and 1357.88 cm-1. Peaks at 732.95 cm-1 (O-H out-of-plane bending), 1296.16 cm-1 (coupled C-O stretching and O-H in-plane bending), 1357.88 cm-1 (O-H in plane bending, C-O stretching and O-H in-plane bending), 2939.52 cm-1 and 3163.26 cm-1 (conjugate chelation) indicated hydroxyl compounds [22]. Amides are represented by 732.95 cm-1 (OCN deformation), 1743.65 cm-1 (coupled C=O vibrations of acid anhydrides) and 3348.42 cm-1 (N-H asymmetric stretching). HPLC and FTIR analysis helped in understanding whether the dyes constituents had undergone mineralization.

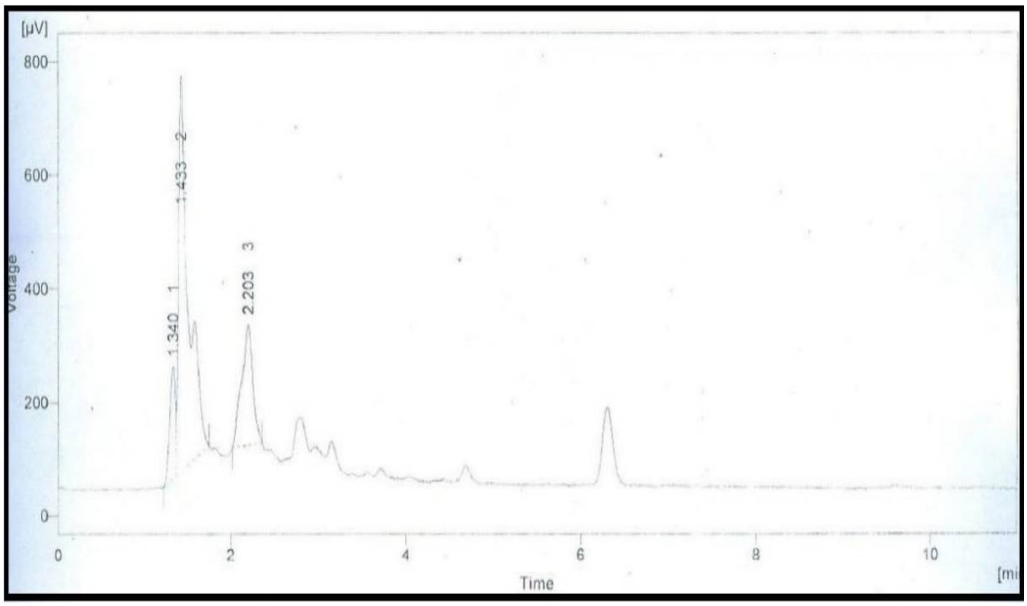

Fig 3: HPLC spectrum of methylene blue dye before UV mediated photo catalysis in the absence of nanoparticles

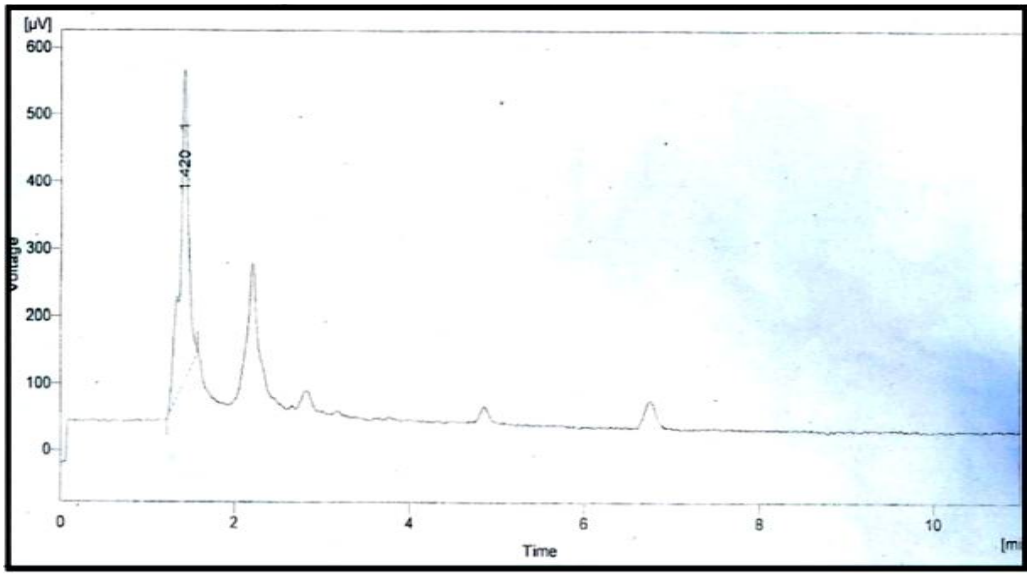

Fig 4: HPLC spectrum of methylene blue dye after UV mediated photo catalysis in the presence of nanoparticles.

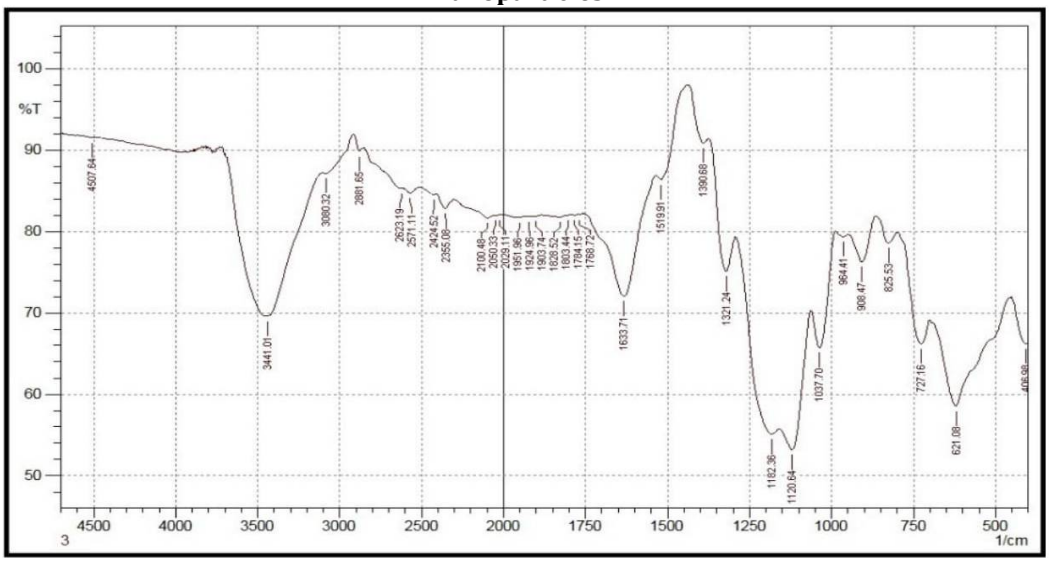

Fig 5: FTIR spectrum of methylene blue dye before UV mediated photo catalysis in the absence of nanoparticles

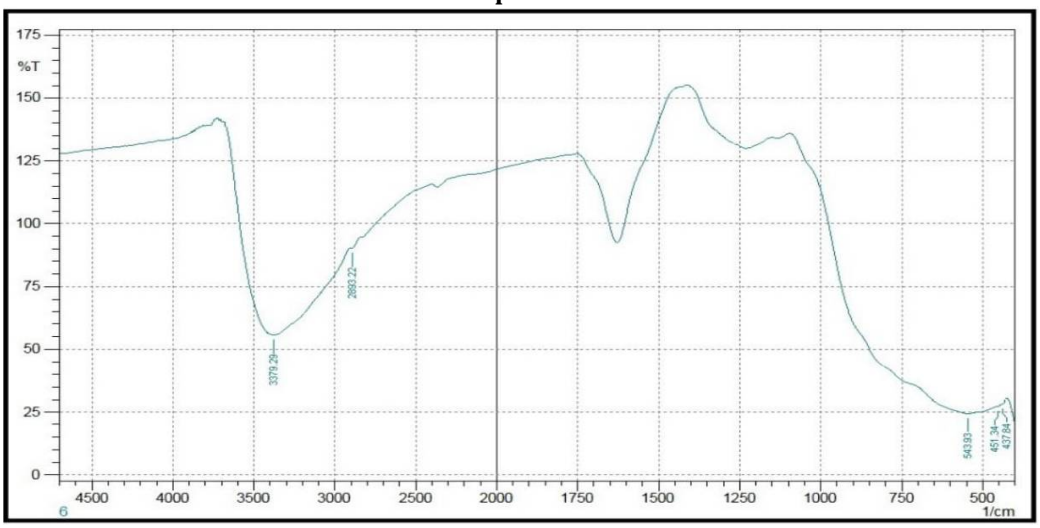

Fig 6: FTIR spectrum of methylene blue dye after UV mediated photo catalysis in the presence of nanoparticles

KINETIC ANALYSIS

The mathematical suitability of the photocatalytic activity under sunlight and UV irradiation mediated by the green synthesized nanoparticles and composite were analyzed by using various kinetic models in terms of the optimized parameters.

Langmuir isotherm

LANGMUIR ISOTHERM

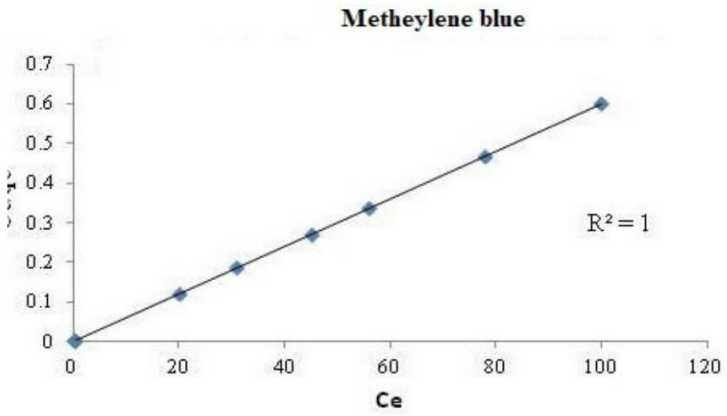

Fig 7: Langmuir isotherm for UV-mediated photocatalysis

UV mediated photo catalysis of the textile dye methylene blue via the presence of nanoparticles was indicated by the value of R2 which was found to be 1 in all cases. The influence of the initial concentration of the solute on the photocatalytic degradation rate was described by a pseudo-first-order kinetics, which is rationalized in terms of the Langmuir model modified to accommodate reactions occurring at a solid–liquid interface [23, 24]. The adsorption constant obtained from dark adsorption isotherms are usually significantly different to those determined by Langmuir model.

Elovich plot

ELOVICH PLOT

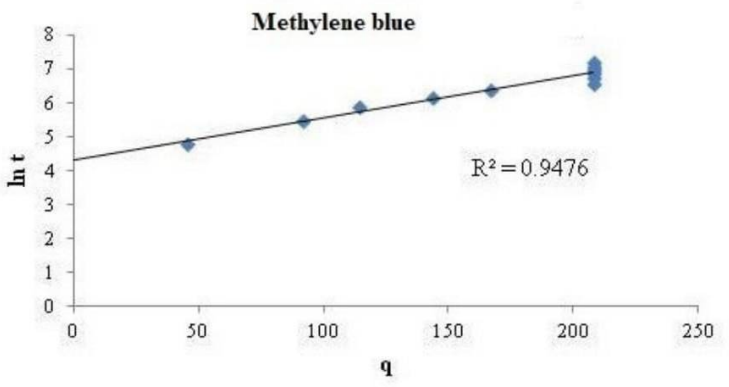

Fig 8: Elovich plot for UV-mediated photocatalysis

The Elovich plot for UV mediated photocatalysis agreed that the nanoparticles and composite were good photocatalysts for the photocatalysis of the textile dye Methylene blue as indicated by the R2 values which were all above 0.8. The R2 values confirmed the chemical nature of adsorption. Elovich model has been correctly applied for describing chemical adsorption[25].

Fractional power model

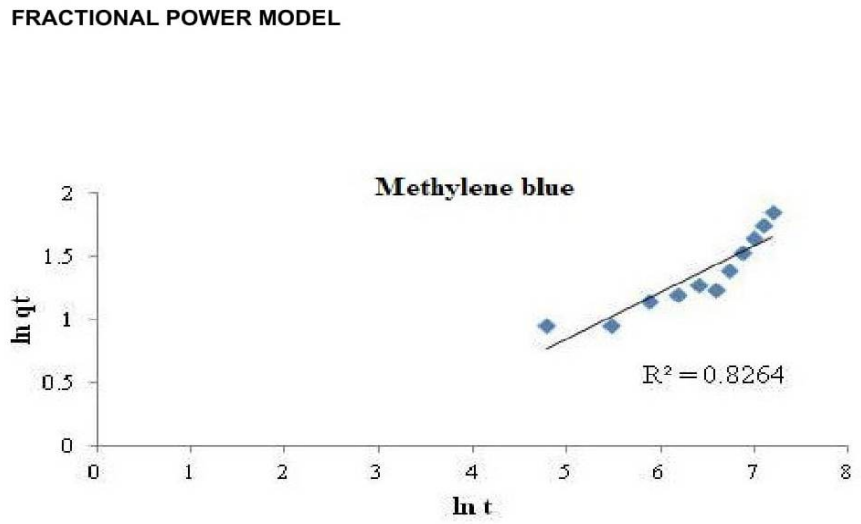

Fig 9: Fractional power model for UV mediated photocatalysis

As per R2 values, UV-mediated photocatalysis was best within the presence of the nanoparticles was ascertained by experimentation too. However, the photocatalysis mediate by Fe_3O_4 didn't consider divisional power model although it absolutely was found to be effective by experimentation. Thus green synthesized - Fe_3O_4 nanoparticles demonstrated high capability as catalyst, both in terms of kinetics and percentage of degradation [26]**.**

CONCLUSION

Pollution by textile dyes has drawn attention on the vital need for developing new Eco friendly purification technologies like photocatalysis by metal oxide nanoparticles. The present study has emphasized that Seaweeds can be put into use for development of efficient photocatalysts. The various experiments carried out indicted that UV is a better light source for optimum decolorization and the Fe_3O_4 nanocomposite was the best catalyst. The various kinetic models also supported these observations thereby citing that "green" Nano catalysts are the solution to the ever-growing water pollution menace.

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CONFLICT OF INTEREST

The authors do not have any conflict of interest.

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