Photo catalytic degradation of Malachite Green using TiO_2 –Fly ash Nanocomposite

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Abstract

TiO_2- Chemically treated Fly ash(CFA) nanocomposite had been successfully synthesized via thermal hydrolysis process at 120^0C and 48 continuous reflux condensation. The product was characterized by XRD, SEM and FTIR spectroscopy and used to explore the possibility for photo catalysis to remove malachite green dye from water. The results of XRD and SEM demonstrated that the as prepared product was mainly TiO_2 –CFA nanoparticles having large surface area. The SEM images showed that the product was found to consist of a mixture of irregular spherical particles of nanoscale and whiskers of uneven length. FTIR spectrum of TiO_2 nanoparticles shows free bands corresponding to -OH, Ti-OH modes. Batch experiments were conducted to assess the degradation of the dye from aqueous media using TiO_2 –CFA nanocomposite.

The results showed that the nanocomposite can be effectively used for the removal of dyes. The facile synthesis method and the super photocatalytic performance derived from the TiO_2-CFA nanocomposite display its potential application for removal of malachite green dye from aqueous environment.

Keywords: TiO_2, Fly ash, hydrothermal treatment, photo catalysis, characterization. Malachite green dye.

Introduction

The scarcity of pure water is a major problem of our country. Most of us consume contaminated water for various purposes. As human needs are increasing day by day and the industries are born and grown, the problem of wastewater discharge has become more and more severe. Textile industries are the primary source that release synthetic dyes to the environment. In the present industrial scenario, textile dye removal from effluents is gaining importance to meet stringent regulations and to protect environment in a cost effective way. The global consumption of dyes and pigments accounts to $7x10^5$ tons/year, in which approximately two-third is being consumed by textile industry alone.

The textile dyes are having complex aromatic structures, which are tough to degrade into non-toxic materials. Textile waste waters normally need high chemical oxygen demand due to the high toxicity and high total suspended solids. The conventional methods used for decolouration of textile effluents include precipitation, adsorption, flocculation, reverse osmosis, ultrafiltration etc. Nowadays, photocatalytic degradation is found to be of great importance, as the complex structure of the dye degrades into simpler and less toxic compounds.[10] (TiO_2 is considered as the prominent photo catalyst due to its superior photocatalytic oxidation, thermal stability, non-corrosive and nontoxicity properties[8,9,12] and adsorptional photocatalyst.[7]

The present study aims at utilizing the potential of TiO_2 and chemically treated fly ash(CFA)nanocomposite for the degradation of malachite green dye from water and to develop a new and efficient technology for malachite green(MG)dye removal. Generally, TiO_2 is used in slurry form in photo catalysis. Experiments with nanocomposites containing TiO_2as one constituent showed excellent results on degradation of textile dyes[11,14,16]. But in the slurry form, the ultimate recovery of the photo catalyst is a costly process. When using TiO_2 nanoparticles, the photo catalysis is more efficient, as nanoparticles have large surface area compared to their bulk counterparts.

Malachite green (MG) and methylene blue (MB) are used for dyeing wood, cotton and silk. Malachite green is potentially harmful and exposure of it may cause increased vomiting, cyanosis, shock, heart rate, jaundice and quadriplegia and tissue necrosis in human. MG is used as biocide in the global aquaculture industry. It is also used as a food coloring agent, food additive, medical disinfectant, as well as in silk, wool, jute, leather, cotton, paper etc.[3] MG removal by photo degradation using ZnO,[20] electrochemical degradation[8], photocatalytic degradation with TiO_2[31] has also found researcher's attention.

Accelerated urbanization and industrialization led to an excessive release of dangerous wastes into the environment. One of them is fly ash resulted from coal combustion. Nowadays only 40% of the fly ash is used for cement production, therefore alternate solutions are looked after. Thus, fly ash as such or mixed with photo catalyst represents a complex substrate able to simultaneously remove of heavy metals and dyes. Advanced processes are already suggested such as ultrafiltration for heavy metals[6] or dyes. Adsorption (including the use of industrial wastes as substrates) represents another well-investigated path for heavy metals,[1] dyes[29] or surfactants[18] removal.

Various kinds of fly ash have been used as low-cost sorbents for removal of heavy metals, organics and dyes from water.[5] Fly ash is mentioned as a possible substrate for pollutants removal in advanced wastewater treatment[30]. Advanced oxidation process (AOP) is recognized for the ability to mineralize a wide range of organic compounds, involving the generation of highly reactive radical species, (mainly HO.), able to degrade the recalcitrant large molecules including dyes.[17,19] The widely reported photo catalyst is TiO_2 as it has high stability under UV and Visible irradiation, good resistance to microbial attack, very good chemical stability over a broad pH range, being actually nonreactive in wastewater.

Fly ash (FA) represents a mixture of unburned carbon and metal oxides; among these there are Fe_2O_3 and MnO that can act as *in situ* Fenton-systems.[25] Adsorption proved to be efficient on fly ash for the advanced treatment of multi cation wastewater.[24] Fly ash as such or mixed with photo catalysts[32] represents a complex substrate able to simultaneously remove heavy metals and dyes. The composite proved to be efficient in the simultaneous removal of pollutants from single-, bi- and tri-pollutants solutions and an activation effect is outlined when heavy metals (copper) are among the components and the photocatalytic experiments proved various paths for dyes removal[13,22,23] and heavy metals removal.[4]

Material and Methods

Materials: Titanium iso propoxide, Ethanol, HCl, Tween 20, Malachite Green, NaOH all chemicals used are of analytical grade (>98%). Raw fly ash was collected from Hindustan Newsprint Ltd., Kochi and was purified and used for the work.

Preparation of of TiO_2 nanoparticles: A 50 ml of Ethanol-Water mixture is prepared in 1:1 ratio maintaining a pH of 4. The mixture is then kept on the magnetic stirrer at 50°C. 1ml of Tween20 is added, which plays the role of surfactant. Then 100ml of titanium isopropoxide (precursor) is added and kept the reaction to continue for 3hrs, till a cloudy solution was obtained. The solution is filtered and washed thrice with distilled water. The final product obtained is dried for 24hrs and calcined at 240°C for 24hrs in Muffle furnace and ground in ballmill.

Preparation of chemically treated fly ash (CFA): Fly ash as received is sieved through 75 micron IS sieve and subjected to pretreatment by mixing 500 g fly ash (FA) with 1000ml double deionized water to remove the soluble inorganic matter present. The sample then was mixed with 1M HCl solution in the ratio of 1g fly ash to 2ml acid, filtered and heat treated at 105^0C for 12hrs

Preparation of TiO_2- CFA nano-composite: Chemically treated fly ash was mixed with TiO_2 in an optimized ratio CFA: TiO_2 = 3:1. The non-ionic surfactant Tween 20 is added to the slurry prepared in alkaline media (using NaOH) for surface charge control and as potential templating agent. The new nano-composite material was prepared from the slurry in the 1000 mL volumetric flask with reflux condenser under stirring at 300 rpm for 48 hr, at atmospheric pressure and at 100^0C on a thermoset heating plate with magnetic stirrer. The slurry was further washed with ultra-pure water till constant pH is obtained, followed by filtration and drying at $105\text{-}115^0$C and then calcined at 240°C.

Characterization of TiO_2 nanoparticles: The characterization of TiO_2 nanoparticle was done using scanning electron microscopy (SEM) and the analysis results are shown in fig 1. The image produced shows the surface morphology and size of particle. SEM can achieve resolution better than 1 nanometer. The SEM analysis shows that the TiO_2 particles are of rigid and mostly spherical in shape with relatively smooth surface.

The size of the particle was calculated from the XRD pattern of TiO_2 by Scherr'r equation.

The Scherr'r equation is $D=\frac{k\lambda}{\beta cos\theta}$ where D is the particle size in nm, k is a shape factor having a typical value of 0.9, λ is the X-ray wavelength 1.5406 A^0, β is the line broadening at half of the maximum intensity (of a peak) and θ is the diffraction angle. The results show the sizes 5.64nm, 6.48nm and 13.46 nm at major peaks.

FTIR spectra of TiO_2 (Fig. 3) show the major peaks identified stretches at wave numbers 3368.97 cm^{-1} attributed for absorption band for hydroxyl groups for the stretching vibrations in the Si-OH and Al-OH-and 1621.81 cm^{-1} which indicates the bending modes of water molecules.

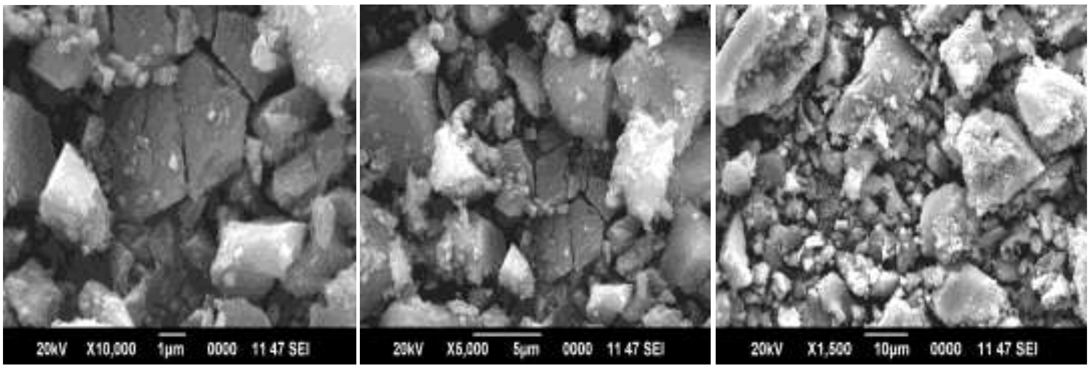

Figure 1: SEM image of TiO_2

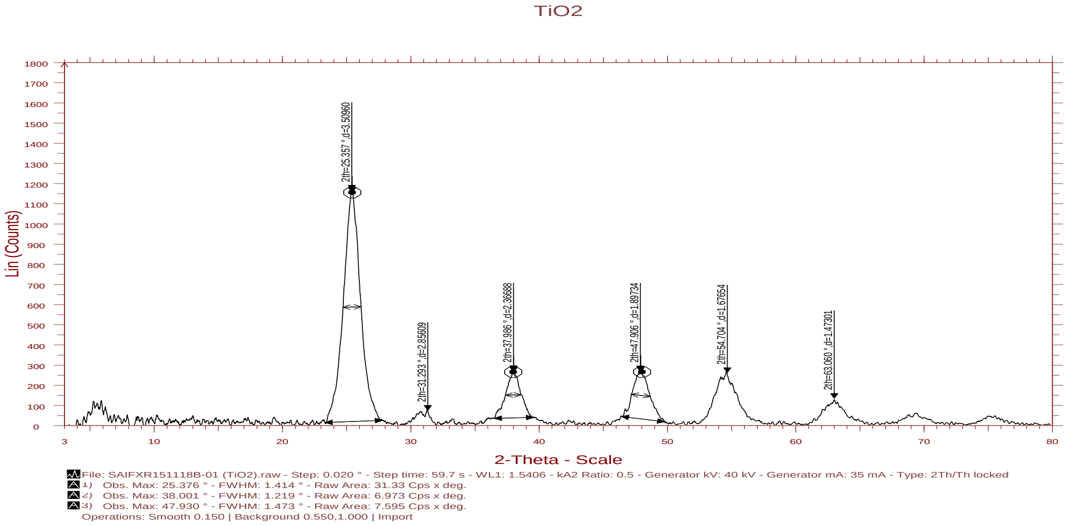

Figure 2: XRD of TiO_2

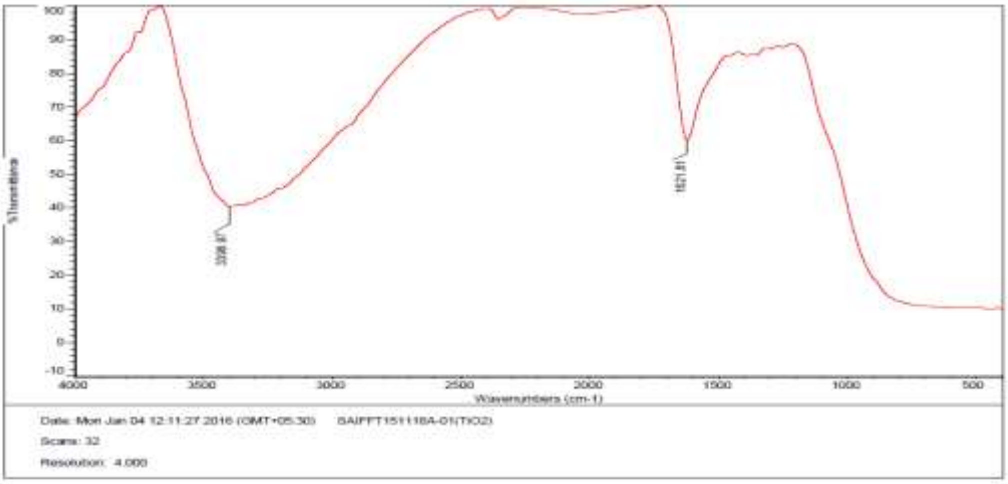

Figure 3: FTIR spectra of TiO_2

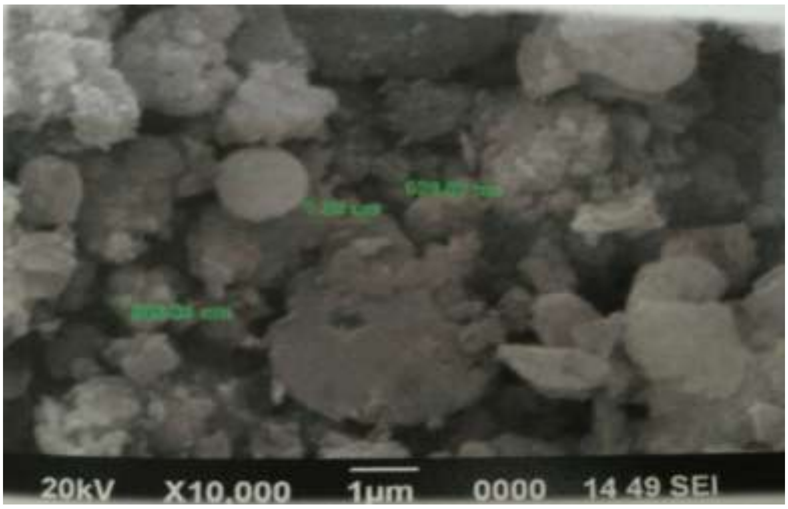

Figure 4: SEM Micrograph of CFA

The SEM analysis of chemically treated fly ash (fig. 4) shows that particles are spherical in shape and have a relatively smooth surface. It contains particles in the nano scale size. The normal fly ash is of lower activity and glassy surface layer. Particles will be dense and chemically stable. The reaction of HCl with fly ash rapidly disintegrates the glassy layer to encourage chemical activity by increasing the microporevolume.

Characterization of TiO_2- CFA nano-composite: TiO_2-CFA nanocomposite material was characterized by SEM, XRD and FTIR methods. The SEM image of TiO_2- CFA (Fig.5) shows that particles are relatively spherical in shape and has a smooth surface.

The XRD pattern (Fig. 6) demonstrates the mineralogical composition of the TiO_2-Fly ash. It was found that composite consists of TiO_2anatase and brookite crystalline phases. Also, it contains peaks of quartz (SiO_2).

XRD data shows that the hydrothermal process promotes surface interactions including dissolution, re-crystallization of the fly ash components, development of new components with TiO_2 by chemisorption etc. Thus, it may be concluded that during synthesis the nano-sized TiO_2 particles were embedded in the micro-sized fly ash grains.

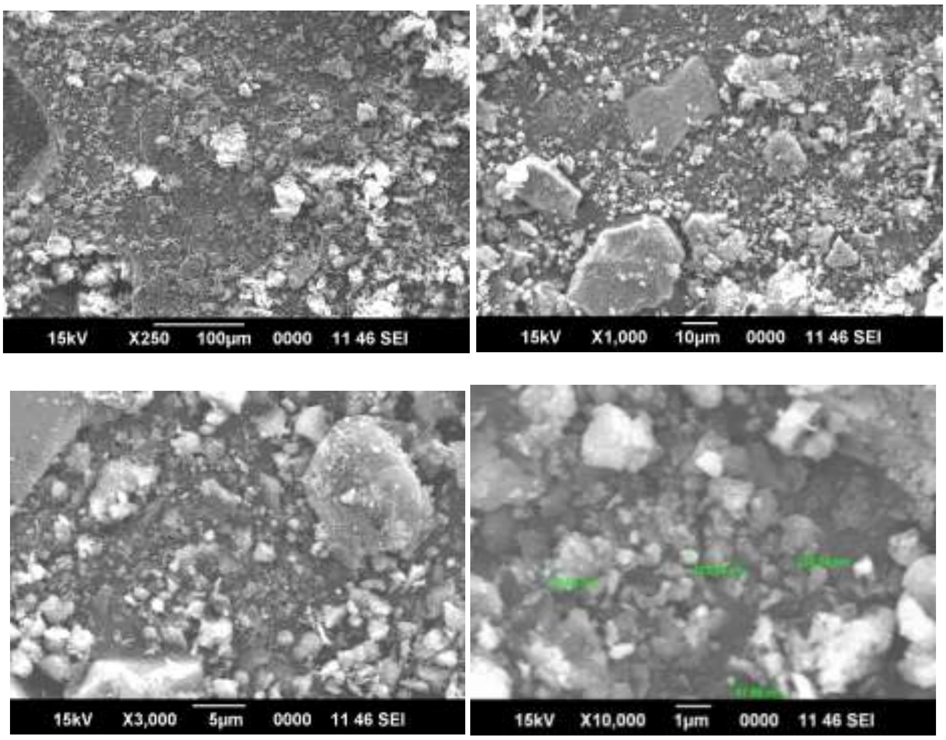

Figure 5: **SEM of TiO_2-CFA nanocomposite**

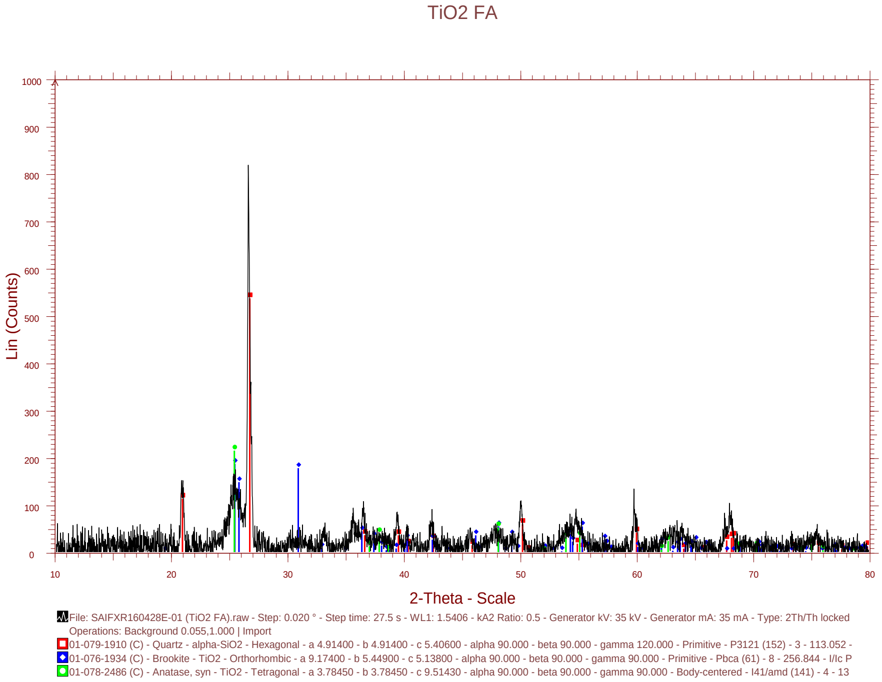

Figure 6: XRD pattern of TiO_2 -CFA

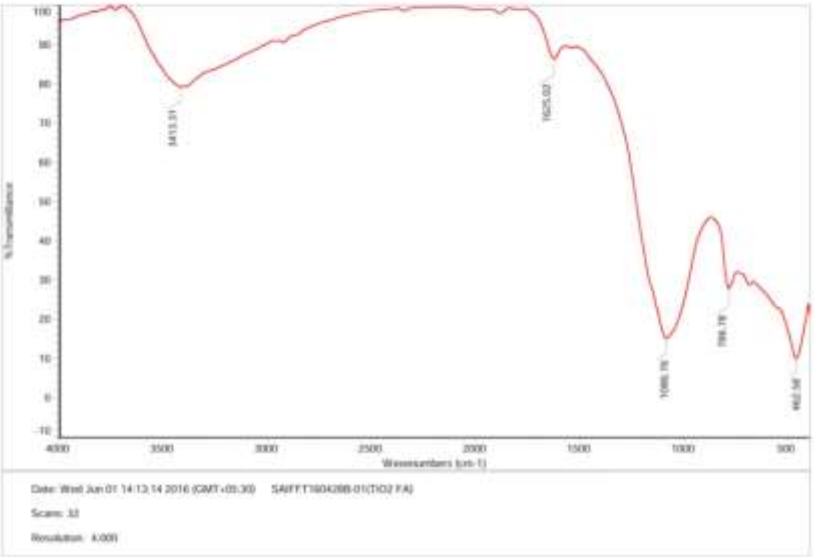

Figure 7: FTIR Spectra of TiO_2-CFA nano-composite

FTIR spectra of TiO_2 –CFA (fig.7) show the major peaks stretches at wavenumbers 3413.31^{-1} and 1625.02 cm^{-1}, 1086.76 cm^{-1} and 756.78 cm^{-1} which indicate the presence of functional groups OH- and Si-OH, C=O and C-H respectively.

Preparation and analysis of malachite green in water: 20mg/l malachite green solution was prepared and stored as stock solution. It was diluted to required concentrations of the dye for experiment. Each test was performed in a glass batch reactor under UV light in dark room. Hydrogen peroxide was used as an additional oxidant aiming to increase the hydroxyl radicals, since these radicals are produced by the interaction between hydrogen peroxide with transition-metal oxide. The malachite green concentration was monitored by a UV-Visible Spectrophotometer, micrometer based with wave length range 200 to 1100 nm, resolution 0.1 nm and accuracy 0.1 nm. (M/s Systronics India Ltd) with the help of a calibration curve. This method is applicable in the range of 30 to 20 000 μg/l of dye.

Batch experiments: 100 ml of aqueous solution of malachite green of concentration 20mg/l was taken in a Pyrex glass reactor and exposed to UV radiation at a height of 20 cm from top of sample surface under the following conditions:

a) varying quantities of catalyst (TiO_2 –CFA) at various pH and constant time of exposure.
b) varying quantities of catalyst TiO_2 –CFA) at constant pH and constant time of exposure.
c) fixed quantity of catalyst a (TiO_2 –CFA) at varying time of exposure.
d) fixed quantity of catalyst TiO_2 only, varying time duration.
e) fixed quantity of catalyst TiO_2 only, varying time duration without H_2O_2.
f) varying quantity of catalyst TiO_2 only with constant time.

All experiments were carried out at under room temperature (30± 5° C), pH range of 6 to 9 and a determined quantity of catalyst. These experiments were conducted to study the effect of contact time, effect of initial concentration and effect of pH. The samples are analyzed for concentration at frequent intervals. Percentage removal of malachite green was noticed after 30 minutes.

Removal rate is calculated using the equation:

$$q = (Co-Ce)/Ce*100$$

where Co and Ce are the malachite green concentrations at the beginning and end of each experiment respectively.

Results and Discussion

Effect of contact time: The effect of contact time on malachite green removal is as shown in fig. 8. The percentage removal of dye increases with increase in time.

Effect of catalyst dose: The percentage removal of malachite green increases with increase in catalyst dosage. The percentage removal of malachite green increases with increase in catalyst dosage and shows an optimum in the range 0.07-0.1 mg/100ml.

The percentage removal of malachite green increases with increase in time when catalyst TiO_2 only is used without hydrogen peroxide. The percentage removal of malachite green is highly dependent on pH. Maximum removal is at value of 5-6. The percentage removal of malachite green increases with increase in time when the catalyst used is TiO_2 only. The percentage removal of malachite green shows a gradual increase when we are using catalyst TiO_2 only and hydrogen peroxide oxidant. The percentage removal of malachite green increases gradually when we are using TiO_2-CFA nanocomposite instead of TiO_2 only, quantities of catalyst being same.

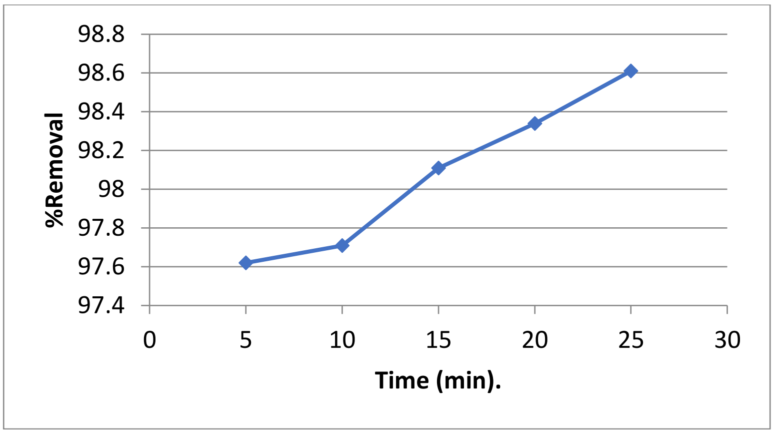

Figure 8: Effect of contact time on malachite green removal at varying pH using TiO_2-CFA nanocomposite.

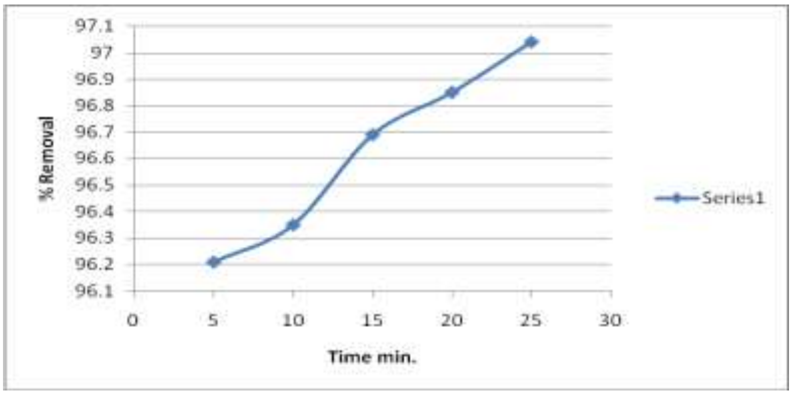

Figure 9: Effect of contact time on malachite green (pH constant) using TiO_2-CFA nanocomposite.

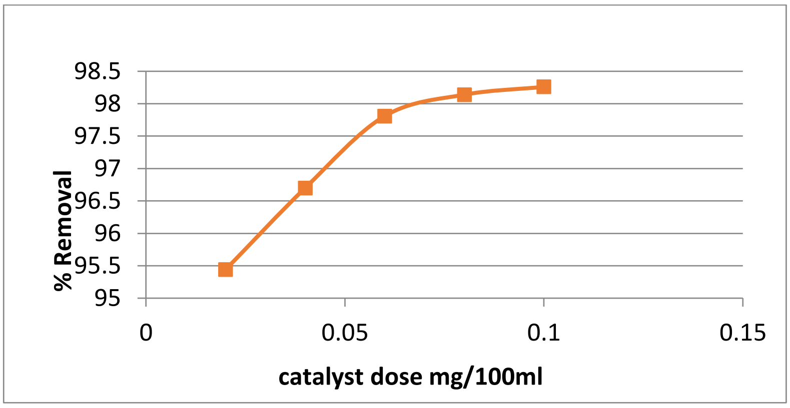

Figure 10: Effect of TiO_2 dose on malachite green

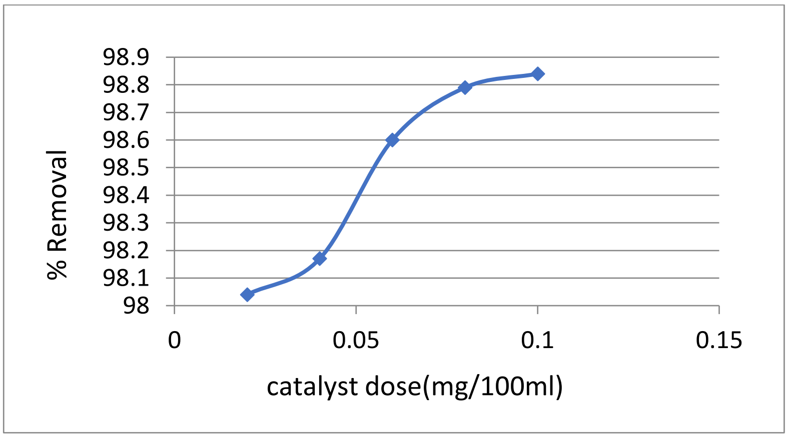

Figure 11: Effect of TiO_2-FA dose on malachite green

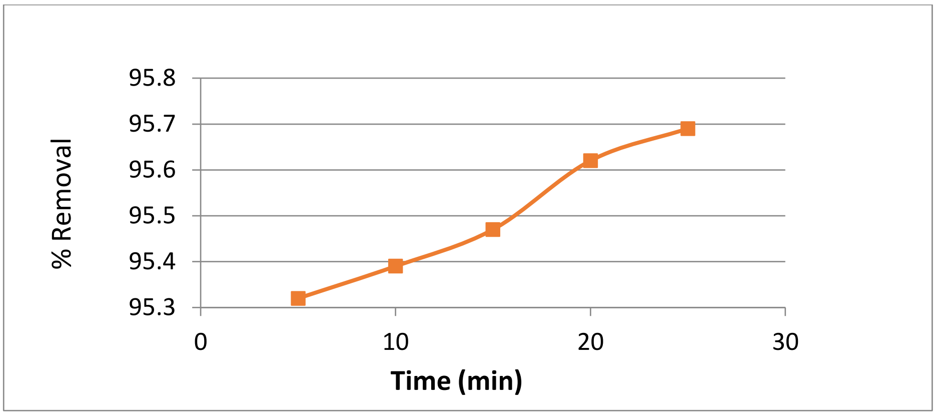

Figure 12: Effect of catalyst TiO_2 only on dye removal

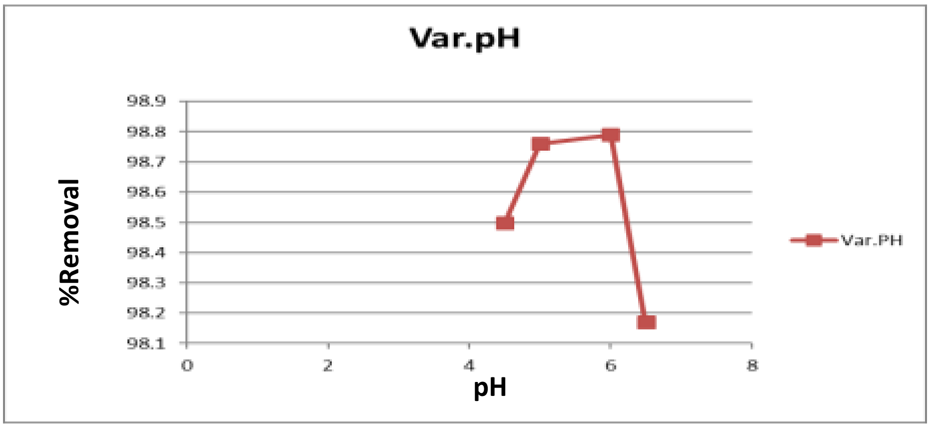

Figure 13: Effect of pH on malachite removal.

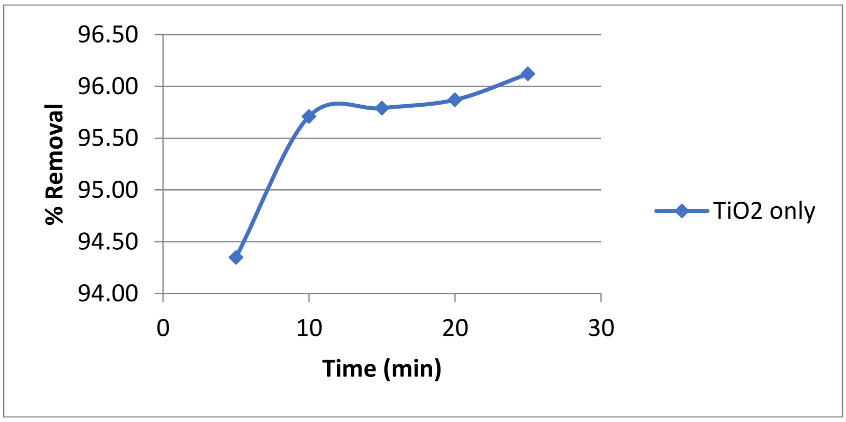

Figure 14: Effect of time on malachite removal, catalyst is TiO_2 only

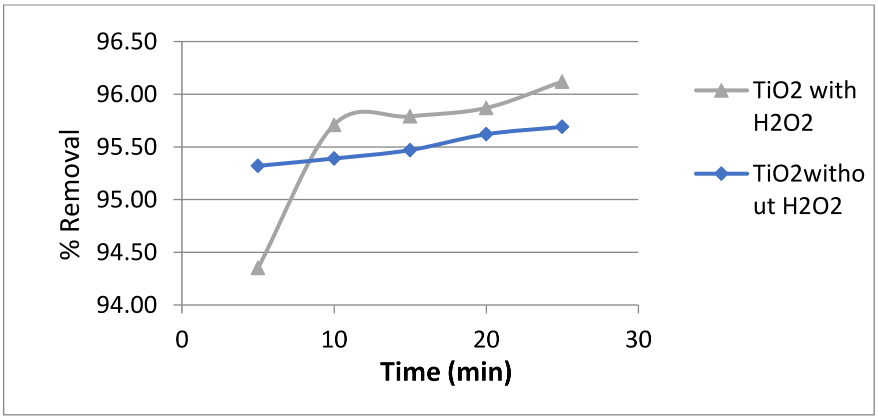

Figure 15: Effect of time on malachite green removal with or without hydrogen peroxide withcatalystTiO_2-CFA

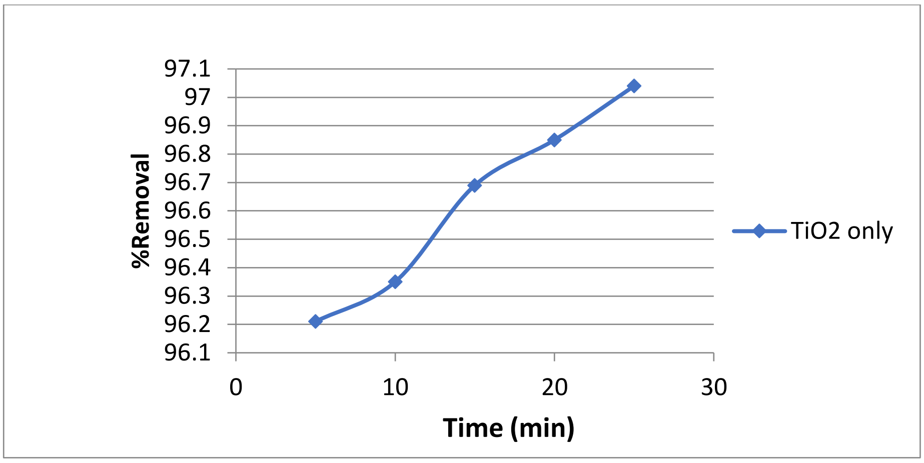

Figure 16: Effect of time on malachite green removal when catalyst is TiO_2 only and catalyst TiO_2-CFA composite.

The percentage removal of malachite green shows noticeable results when we are using TiO_2-FA nanoparticle as initial catalyst instead of TiO_2 only.

Conclusion

Batch studies on malachite green removal by photocatalytic degradation using TiO_2-CFA were carried out with significant effects on process variables such as catalyst dose, contact time, pH, effect of hydrogen peroxide etc. Percentage removal of dye was found. The removal rate of dye is about 2.5 % higher when TiO_2-CFA was used than with TiO_2 alone as catalyst even at dye concentration is 0.02 ppm. The dye removal rate increases with increase in contact time and initial concentration of dye. The removal rate increases rapidly at initial stages with increase in catalyst dose but shows steady state as the dose further increased.

The pH variation studies showed that the degradation process is highly dependent on pH. The percentage removal of malachite green increases with increase in pH. The efficiency of TiO_2-CFA to remove malachite green from water is found to be 98.8 % at a pH value of 6. Fluorescence quenching may also have resulted from the photo induced electron transfer process between MG and nanocomposite [21] when the organic pollutants are subjected to photo catalysis.

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