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Photocatalytic degradation of carcinogenic methylene blue dye by using polyaniline-nickel ferrite nano-composite

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ABSTRACT

The present work deals with the development of a novel method for the removal of color from textile dying wastewater by using conducting polyaniline-$NiFe_2O_4$ nano-composite. It is successfully synthesised in situ through self polymerisation of monomer aniline. Photocatalytic degradation studies are carried out for water soluble carcinogenic methylene blue (MB) dye by using polyaniline (PANI)-Nickel Ferrite ($NiFe_2O_4$) nanocomposite in aqueous solution. Different parameters like dye concentration, dose of photocatalyst, contact time and pH have been studied to optimise reaction condition. It is observed that photocatalytic degradation by PANI-$NiFe_2O_4$ nano-composite is a more effective and faster mode of removing Methylene blue(MB) dye than work done before. The optimum conditions for the removal of the MB dye are initial concentration 30ppm, photocatalyst dose 8gm\lt, pH 8.5.The EDS technique gives elemental composition of synthesised PANI-$NiFe_2O_4$.The SEM and XRD studies are carried for morphological feature characteristics of PANI-$NiFe_2O_4$ nano-composite. Also the kinetics studies have been carried out.

Keywords: Photocatalytic degradation, PANI-$NiFe_2O_4$ nano-composites, SEM, EDS, XRD.

INTRODUCTION

A wide range of methods have been developed for the removal of synthetic dyes from water and wastewater to decrease its impact on environment. Over 70,000 tons of approximately 10,000 types of dyes and pigments are produced annually worldwide. Out of which about 20 – 30% dyes are wasted in industrial effluents during the textile dyeing and finishing processes [1]**.** Dye effluents from textile industries are becoming a serious environmental problem because of its toxicity, high chemical oxygen demand content and biological degradation [2]. In the last decade, photocatalytic degradation processes have been widely applied as techniques for the destruction of organic pollutants in wastewater and effluents, especially degradation of dyes [3-14]. Among the new oxidation methods or advanced oxidation processes(AOP),heterogeneous photo-catalysis appears as an emerging destruction technology leading to the total mineralisation of most of the organic pollutants [15]. Semiconductor mediated photo-catalysis is a well-established technique for pollutant degradation and hydrogen (clean fuel) production by water splitting. Photo-catalysis can be defined as “catalytic reaction involving the production of a catalyst by absorption of light”[16]

In recent years, the use of semiconductor metal oxides as photo-catalysts for degradation of pollutants has attracted attention of scientific community. Semiconductor metal oxide nano-particles have been studied due to their novel optical, electronic, magnetic, thermal and mechanical properties and potential application in catalyst, gas-sensors and photo-electronics devices [17-18]. Dyes are not removed by traditional methods such as biological, physical and chemical methods. Advanced oxidation processes (AOPs) have been found to be promising alternative for detoxification of industrial effluents especially from the environmental point of view. Heterogeneous photo-catalysis consists on the non selective destruction of organic compound in presence of semiconductor materials as catalyst

and visible light. This process allows the complete mineralisation of organic pollutants to CO_2,H_2O and mineral acids [19]. Dramatic visible photo-catalytic degradation performances due to synergetic effect of TiO_2 and PANI [20].The photo-catalytic activity of the photocatalyst can be promoted by increasing the separation efficiency of photo-induced electron hole pairs. The combination of photo-catalyst and PANI with the delocalised conjugated structures may be an ideal system to achieve an enhanced charge separation by photo-induced carrier transfer. Recently some studies have been reported on the combination of PANI with TiO_2 to improve its performance of solar transfer [21,22].Also the different photocatalytic application get studied[23-24].

The present work investigation is a novel, simple and fast method for degradation of Methylene blue dye by conducting polyaniline(PANI)-$NiFe_2O_4$ nano-composites as a catalyst. experiment is carried out and the kinetics for degradation of Methylene blue on PANI-$NiFe_2O_4$ composites is studied. Photo-catalytic experiment is carried out and also studied the kinetics for degradation of Methylene blue by using PANI\$NiFe_2O_4$ nano-composite.

Photocatalytic Mechanism

To further confirm these results[see fig-1(a), 1(b), 1(c)], the ESR/DMPO spin trapping experiment are carried out to detect the active species in this system under visible light irradiation [25-26]. The relative energy levels of PANI(π-orbital and π*-orbital) and $NiFe_2O_4$[conduction band(CB),valence band(VB)] as shown in the Fig-1(a).Based on the results of photocatalytic mechanism under visible light irradiation can be proposed as, PANI absorbs visible light to induce π-π* transition, transporting the excited state electrons to the π* orbital. The d orbital conducting band of $NiFe_2O_4$ and have chemical bond interaction. According to the mechanism which shown in the fig-1(c), MB is adsorbed on the PANI-$NiFe_2O_4$ was excited by visible light irradiation. Subsequently, an electron is injected from the excited MB to the conducting band of the polyaniline with $NiFe_2O_4$ where the electron is scavenged by molecular oxygen.Fig-1(b) explained the results which are obtained with the PANI-$NiFe_2O_4$ as catalyst under visible light irradiation, where the PANI-$NiFe_2O_4$ and could serve to reduce recombination of photogenerated electron and holes by scavenging of electron. In this experiment ,excited state electrons is readily injected in to the d orbital(CB) of $NiFe_2O_4$ and subsequently transfer to the surface to react with water and oxygen which yield hydroxyl and superoxide radicals. This radical has oxidised the methylene blue (MB).

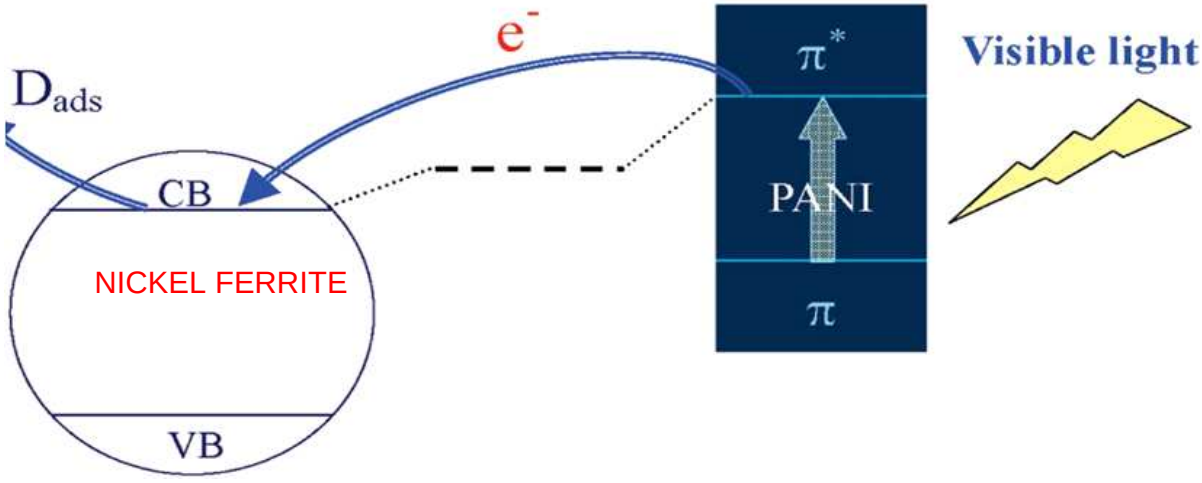


Fig-1(a) mechanism scheme of visible light photocatalysis process

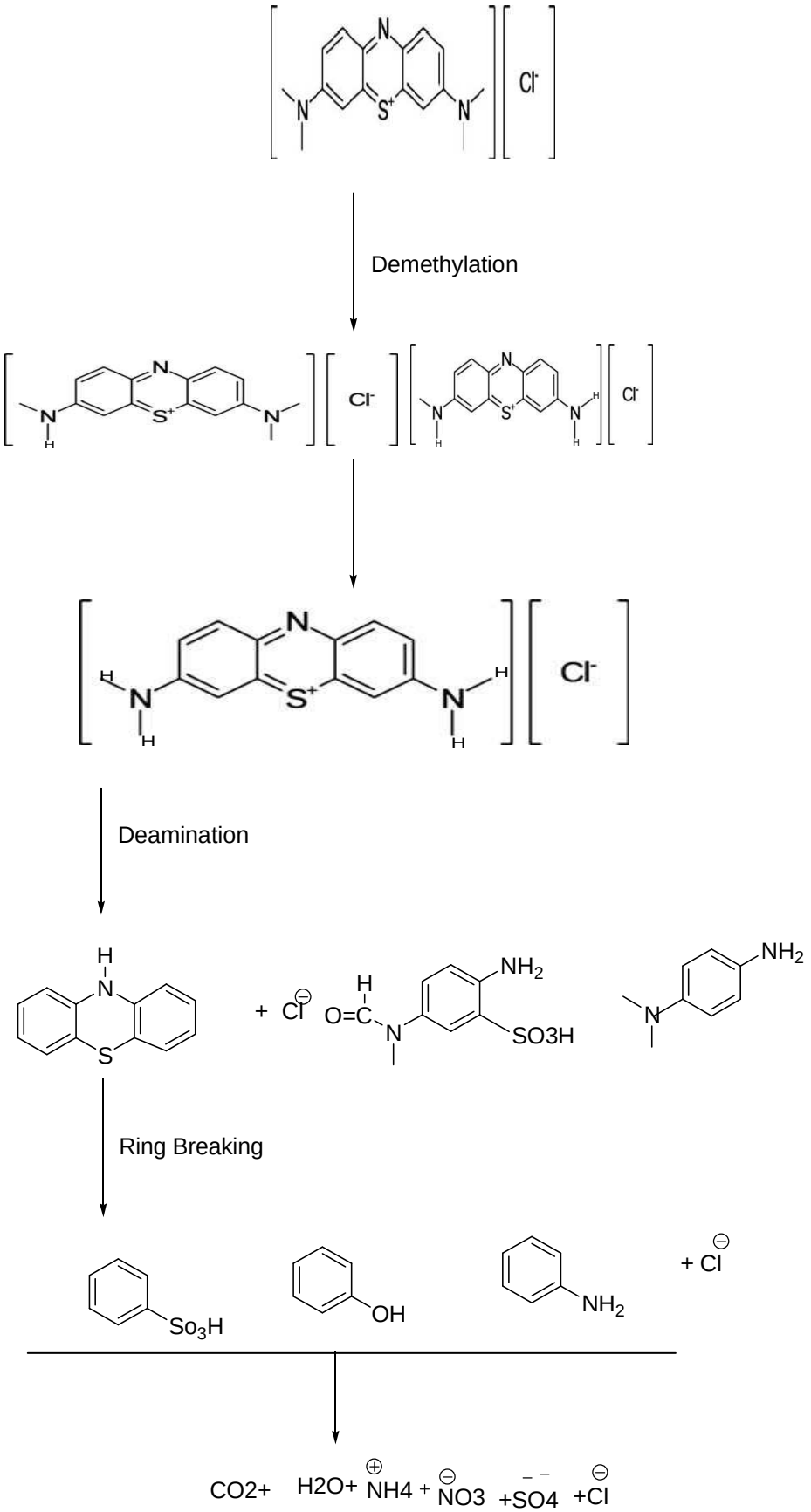


Fig 1(b)-suggested photocatalytic degradation scheme for methylene blue under visible light irradiation in the presence of PANI/$NiFe_2O_4$

$MB(Ads) \xrightarrow{\text{visible light}} MB^*(Ads)$ (1)

$MB^*(ads)+PANI/NiFe_2O_4 \longrightarrow PANI/NiFe_2O_4 + MB^+(ads)$ (2)

$PANI/NiFe_2O_4(e) + O_2 \longrightarrow PANI/NiFe_2O_4 + O_2^-$ (3)

$MB^+(Ads) + {}^-OH \longrightarrow MB^{\cdot} + {}^{\cdot}OH(\text{hydroxyl radical})$ (4)

Fig1(C) Photosensitisation effect by the Methylene Blue Dye

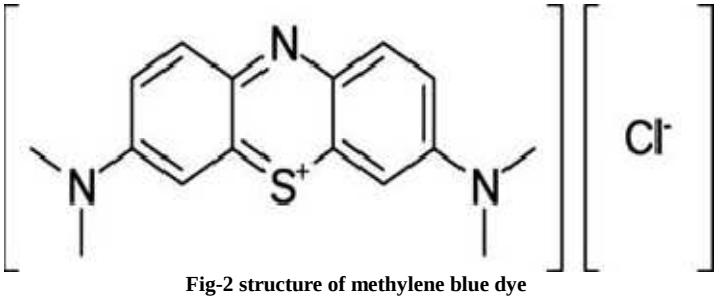


Fig-2 structure of methylene blue dye

MATERIALS AND METHODS

Methylene blue(MB)(as shown in fig-2),$NiCl_2$,$FeCl_3.6H_2O$,monomer aniline, Distilled water, Ammonium per-sulphate $(NH_4)_2S_2O_8$. The water soluble MB dye which has M.F. **$C_{16}H_{18}N_3SCl$**,M.W. **319.85g**/mole,M.P.**105C^0** and prepared nano-composite is used as catalyst. All chemicals and reagents were of analytical grade purity. The structure of dye presented in fig-2.The stock solution 100ppm of dye was prepared in double distilled water. In 100ml of dye solution of the desired concentration, of a different catalyst dose is added and irradiated with xenon lamp to provide energy to excited PANI-$NiFe_2O_4$ in the reactor. At specific time interval suitable aliquot of the sample is withdrawn and analyse after centrifugation. The changes of dye concentration are determined by UV-Visible double beam spectrophotometer (systronics model-2203) at λ max 665 nm in our laboratory.

Instrumentation

The photo-catalytic degradation study was carried out in photo-catalytic reactor. The reactor consist of xenon lamp, tin reflector and reaction flask. Irradiation was conducted using 500 W xenon lamp placed inside the tin reflector. The lamp emits pre-dominantly a visible radiation of 14 mW/cm^2 of intensity. Intensity of radiation was measured by illuminance meter. pH metric measurement are made on equip-tronics digital pH meter(Model-E610)fitted with glass electrode which is previously standardized with buffers of known pH in Acidic and basic media.

Preparation of PANI\\$NiFe_2O_4$ nano-composite

Synthesis of $NiFe_2O_4$ nanoparticles

$NiFe_2O_4$ nano-particles were synthesized according to the following procedures: 1.0 g of Nickel chloride ($NiCl_2.6H_2O$)(5mmol) in 5ml of deionized water and 1.63 g of ferric chloride ($FeCl_3.6H_2O$)(6mmol) in 5ml of deionized water were mixed at room temperature. The above mixture was dropped into 200 ml aqueous ammonia solution (0.6M) in 20 min with vigorous stirring .The pH values of the reaction mixture were kept in the range of 11-12 with the addition of a concentrated ammonium hydroxide solution. The resulting nano-particles were separated by centrifugation at 2800 rpm for 10 min .The product was washed with distilled water three times and then further washed with ethanol (C_2H_5OH) three times and dried in oven.

Synthesis of PANI-$NiFe_2O_4$ nano-composite

PANI-$NiFe_2O_4$ nanocomposite were synthesized via self-assembly method using ammonium persulfate (APS) as an oxidant without the aid of organic dopants or surfactants. The synthesis process is as followed: 0.64 mol/L aniline monomer into polymerization vessel containing 1g.$NiFe_2O_4$ in 100 ml of 1.14 mol / L H_2SO_4 acid solution at room temperature and magnetic stirring for 8 hours. Then 50 ml (1 M) of ammonium per-sulfate $(NH_4)_2S_2O_8$ was added to the above mixture reaction. Resulting precipitate was collected by filtration then washed with deionized water and methanol three times respectively. The product was dried in oven at 70oC for 24h to obtain green–black powder of PANI-$NiFe_2O_4$ nanocomposite[27-28].

RSEULTS AND DISCUSSION

Characterisation and Analysis

SEM Analysis

Scaning electron microscopy is widely used to study the morphological features and surface characteristics of adsorbent materials. The PANI-$NiFe_2O_4$ nano-composites is analysed by SEM before fig-3(a) and after photocatalytic degradation of MB dye as shown in the fig-3(b). It show SEM micrographs of PANI\$NiFe_2O_4$.Fig-3(a) shows surface texture and porosity on PANI\$NiFe_2O_4$.It has heterogeneous surface, micropores and mesopores as seen from its surface micrographs. Also its surface is black-greenish in colour. Fig-3(b) losses its somewhat texture and porosity of PANI-$NiFe_2O_4$ surface. Also its surface becomes somewhat faint black-greenish in colour.

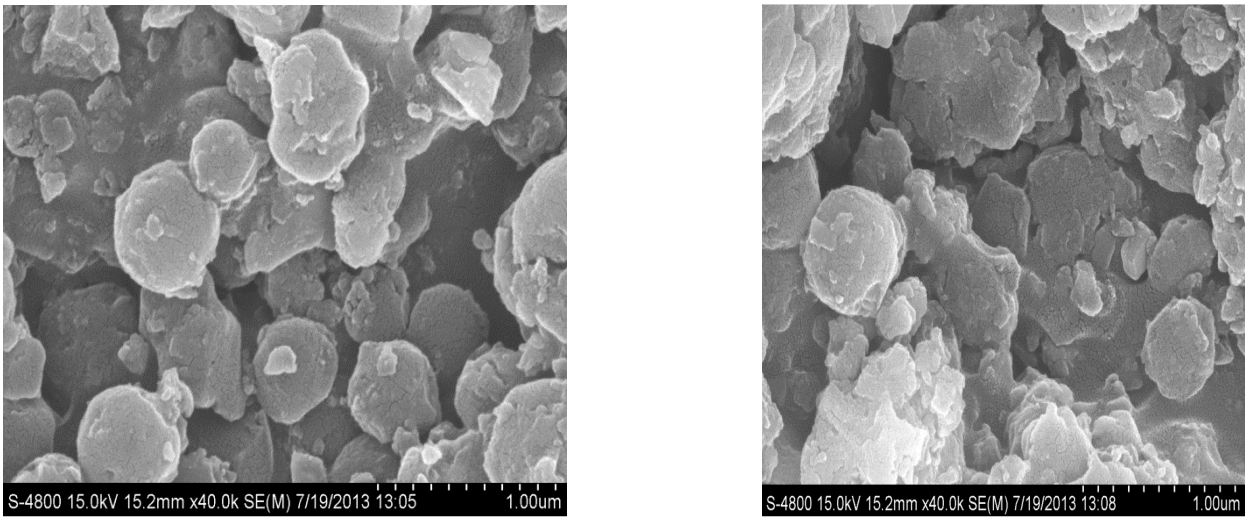


Fig-3(a) SEM images of prepared PANI/$NiFe_2O_4$ Nanocomposite before photocatalytic experiment

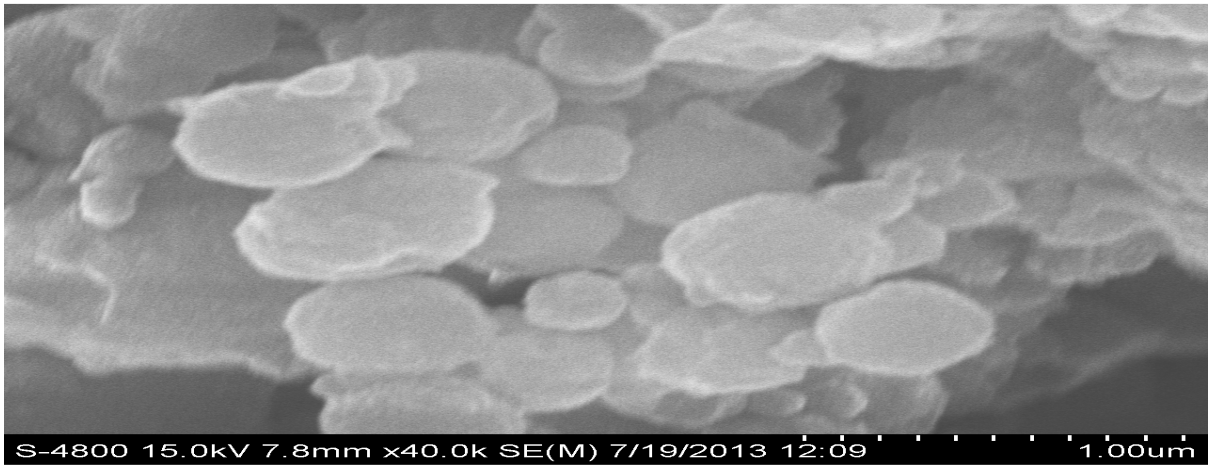
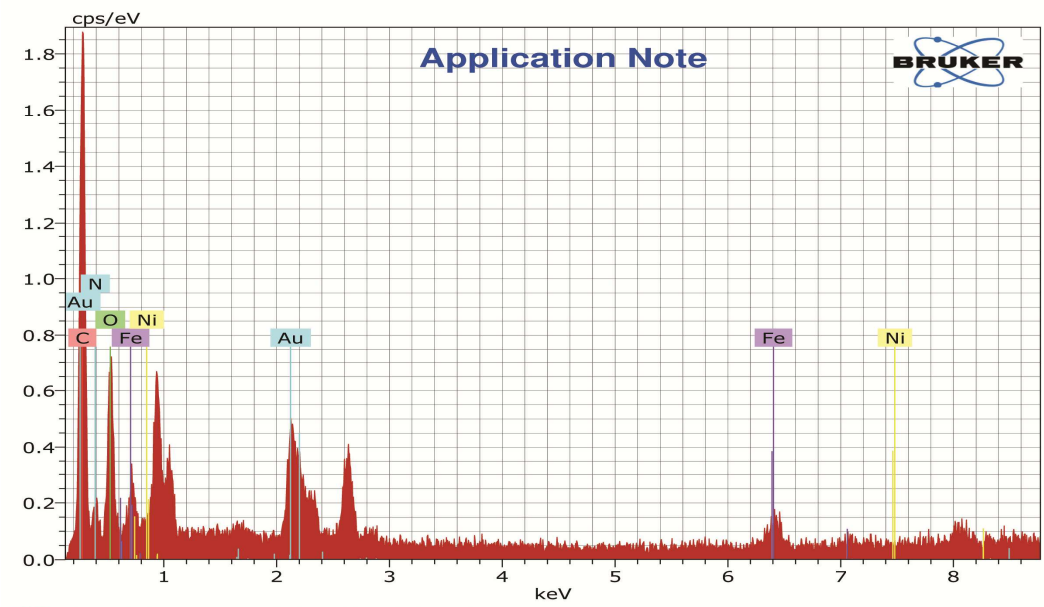


Fig-3(b) SEM image of PANI\$NiFe_2O_4$ Nanocomposite after photocatalytic degradation of dye

Electron Dispersive X-Ray Spectroscopy(EDS) Analysis

Interaction of electron beam with a sample target produces a variety of emissions. An energy-dispersive (EDS) detector is used to separate the characteristic x-rays of different elements into an energy spectrum, and EDS system software is used to analyze the energy spectrum in order to determine the abundance of specific elements. EDS can be used to find the chemical composition of materials down to a spot size of a few microns, and to create element composition maps over a much broader raster area. Together, these capabilities provide fundamental compositional information for a wide variety of materials. From the analysis known that PANI-$NiFe_2O_4$. Nano-composite consist of exact elemental compositon of specific element like Ni, Fe, N,O,C etc. as shown in the(fig.4). As PANI-$NiFe_2O_4$ is conducting material therefore it needs to coat with gold metal.



El AN Series unn. C [wt.%] norm. C [wt.%] Atom. C [at.%] Error (1 Sigma) [wt.%]

C	6	K-series	18.37	39.10	57.19	2.90
N	7	K-series	5.85	12.46	15.63	1.57
O	8	K-series	9.42	20.05	22.02	1.80
Fe	26	K-series	3.21	6.84	2.15	0.18
Ni	28	K-series	2.43	5.17	1.55	0.18
Au	79	M-series	7.70	16.38	1.46	0.37
		Total:	46.98	100.00	100.00	

Spectrum: 1308

El AN Series unn. C [wt.%] norm. C [wt.%] Atom. C [at.%] Error (1 Sigma) [wt.%]

C	6	K-series	18.37	39.10	57.19	2.90
N	7	K-series	5.85	12.46	15.63	1.57
O	8	K-series	9.42	20.05	22.02	1.80
Fe	26	K-series	3.21	6.84	2.15	0.18
Ni	28	K-series	2.43	5.17	1.55	0.18
Au	79	M-series	7.70	16.38	1.46	0.37

Fig-4.EDS image of prepared gold(Au) coated PANI-$NiFe_2O_4$ Nanocomposite

XRD Analysis-

The analysis is carried out by using D8 ADVANCE (Burker) model x-ray diffractometer using cukα wavelength 1.54 A^0.

By using Scherrer's formula, the size of PANI-$NiFe_2O_4$ nano-composite is calculated.

$$D = \frac{K\lambda}{\beta COS\theta} \quad (1)$$

Where
K=constant(0.89 to1.39)
ƛ=Radiation of wavelength
β=FWHM(Full Width Halfwave Maxima)
θ=Bragg angle in degree
D=Particle Size

The XRD pattern of PANI-$NiFe_2O_4$ shows the spectrum having main peak at 2θ of 33^0.From which calculated size of PANI-$NiFe_2O_4$ nanocomposite is **15.19nm**.The XRD diagram of PANI-$NiFe_2O_4$ as shown in the(fig-5).

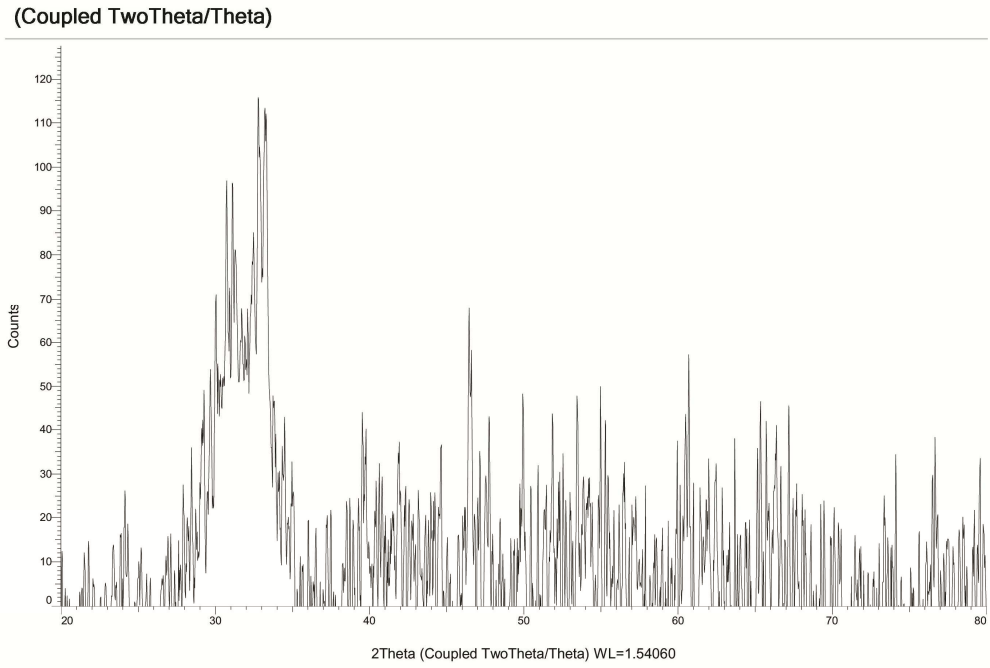


Fig-5 XRD image of prepared PANI-$NiFe_2O_4$ Nanocomposites

Parametric studies

The photocatalytic degradation of MB dye was studied at λ max 665nm.The optimum condition for removal of dyes is 30 ppm,pH 8.5,PANI-$NiFe_2O_4$ 8gm\lt.The results obtained during this study are being shown in(fig 6-9).

Effect of catalyst dose

The effect of catalyst dose on the degradation of MB is investigated by employing different doses of PANI-$NiFe_2O_4$ nanocomposite varying from 2 to 8 gm\lt. Photocatalytic degradation of MB is increases rapidly with an increasing amount of PANI-$NiFe_2O_4$ nano-composite. As the number of active sites of the catalyst increases, degradation of MB also increases as shown in the fig-6.

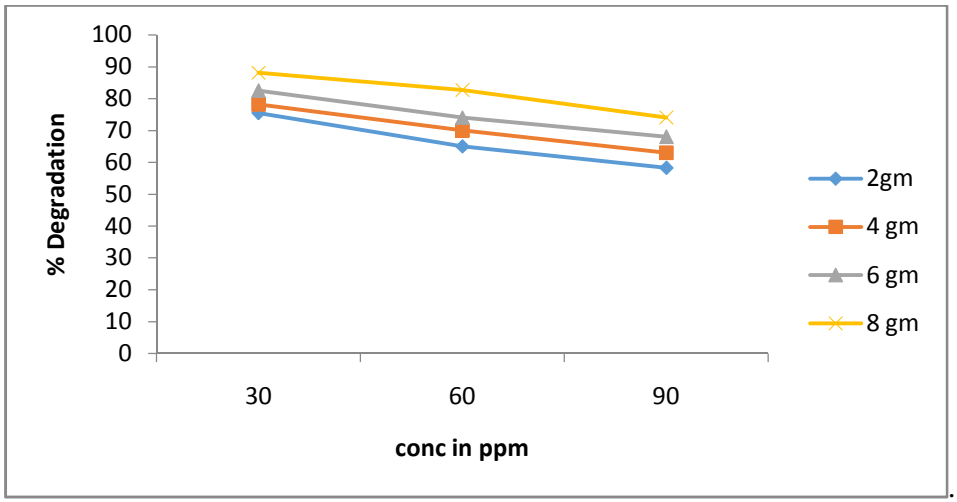


Fig-6 Effect of photocatalyst dose on % removal of acid methylene blue dye for different initial dye conc.With contact time 120 min,pH 8.5

Effect of $_{p}$H

The photocatalytic degradation of MB dye is studied at different pH values as it is an important parameter for reaction taking place on the particular surface. The role of pH in photocatalytic degradation of dye is studied in the pH range 0-12 at dye concentration 30ppm and PANI-$NiFe_2O_4$ concentration 8gm\lt. It is observed that the rate of photocatalytic degradation inhanced with an increase in pH up to 8.5 as shown in the (fig-7). As the pH increases, no.of anions increase. These anions form a bond with PANI-$NiFe_2O_4$ nano-composite. When the $_{p}$H increases onwards 8.5 the repulsion of the dye anions by negatively charged PANI-$NiFe_2O_4$ surface would result in reduction in efficiency of degradation of MB.

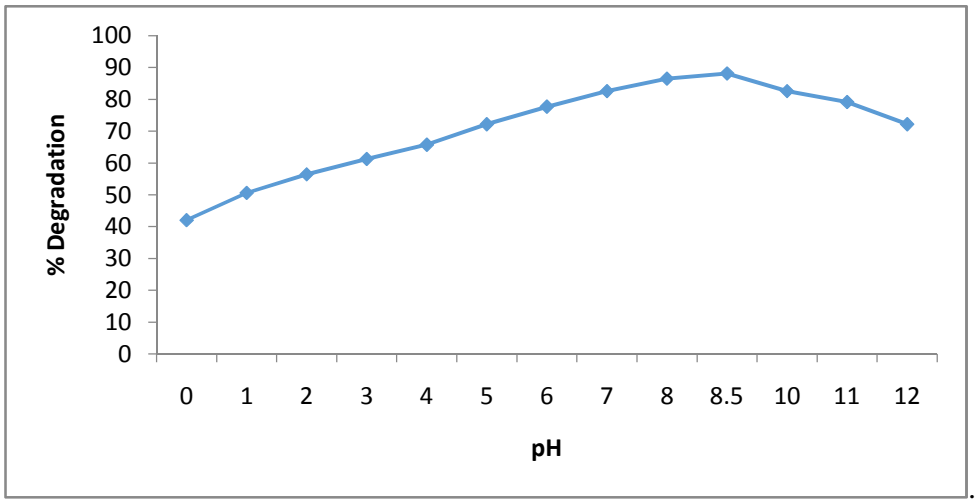


Fig-7 Effect of pH on degradation of methylene blue dye by PANI-$NiFe_2O_4$ catalyst dose 8g/lt at 30ppm

Effect of initial dye concentration

The rate of degradation of MB dye is studied by varying the dye concentration from 10 to 100 ppm because for fixed catalyst concentration active sites remains the same. With the increase of the initial MB concentrations, the MB molecules gets accumulate on the surface of PANI-$NiFe_2O_4$ catalyst. However, quenching between these excited methylene blue molecules irradiated by visible light will takes place . The quenching probability could also increase with the increase of the initial MB concentrations. Consequently, the photocatalytic efficiecncy of MB solutions is decreased with the increase of the initial MB concentrations as shown in the (fig-8).

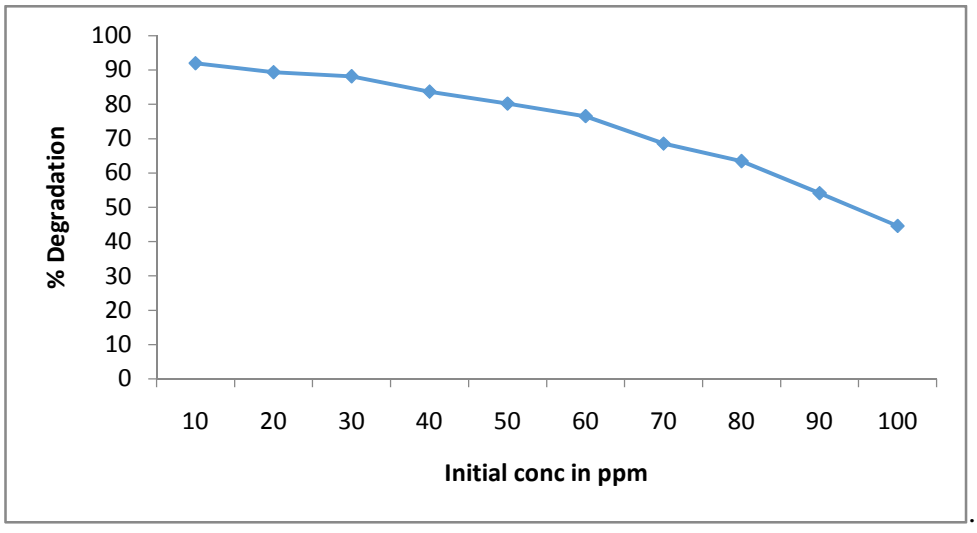


Fig-8 Effect of initial dye conc.on % degradation of methylene blue dye by PANI-$NiFe_2O_4$ catalyst dose 8 g/lt at PH 8.5

Effect of contact time

The effect of contact time for the photocatalytic degradation of methylene blue dye by PANI-$NiFe_2O_4$ nano-composite as shown in the (fig-9).The dye is slowly degraded in 1st 50min and then degradation rate increases rapidly and reaches equilibrium in about 120 min. The rate of degradation of dye is initially slowed because the surface of photocatalyst (conducting PANI-semiconducting $NiFe_2O_4$) is not efficiently activated, as the phocatalyst

surface get activated rate of degradation increases rapidly. As the maximum concentration of dye is degraded from aqueous solution the rate of degradation reaches at equilibrium.

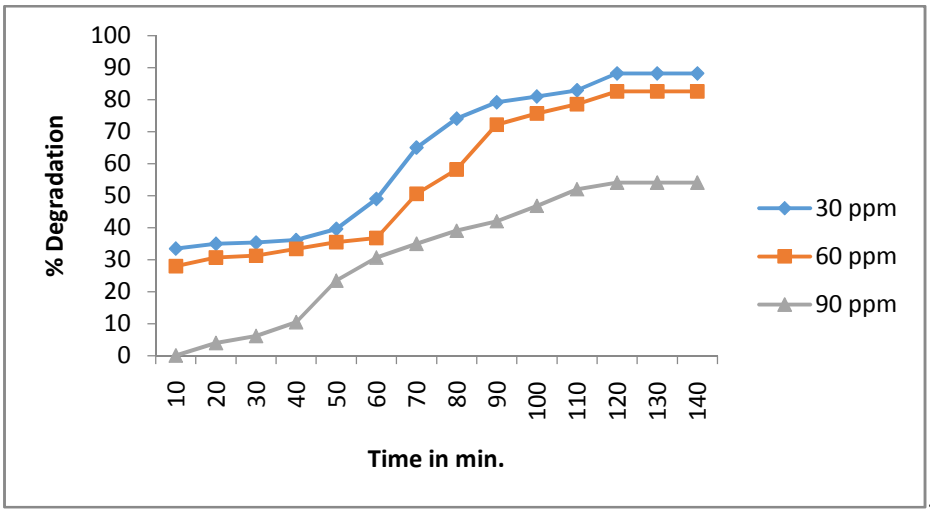


Fig-9.Effect of contact time on % degradation of methylene blue dye at catalyst dose 8g\lt and ₚH 8.5

Photoctalytic degradation kinetics study

Pseudo 1st Order

The photocatalytic degradation of MB dye on the surface of PANI-$NiFe_2O_4$ also follow a pseudo first-order kinetics. It can be expressed as, where C and C_0 are the reactant concentration at time $t = t$ and $t = 0$, respectively, k and t are the pseudo-first-order rate constant (reaction rate constant) and time, respectively [30]. The relationships between [ln (C/C_0)]and irradiation time (Reaction time) are as shown in the (fig-10).It is obvious that there exists a linear relationship between [ln(C/C_0)] and irradiation time. The pseudo-first-order rate constant k and linear regression coefficient (R^2) for MB solutions with different initial MB concentrations are summarized in **Table 1**, respectively. According to the Langmuir-Hinshelwood model, the fact that the decrease of reaction rate constant with the increase of the initial concentration of MB solutions obtained from **Table 1** could be explained as follows. The MB dye is firstly adsorbed on the surface of PANI-$NiFe_2O_4$, and then the photocatalytic degradation takes place under visible irradiation. With the increase of the initial MB concentrations, the MB molecules congregate on the surface of PANI-$NiFe_2O_4$ catalysts. However, quenching between these excited molecules irradiated by visible light will takes place . The quenching probability could also increase with the increase of the initial methylene blue concentrations. Consequently ,the photocatalytic efficiency of methylene blue solutions is decreased with the increase of the initial methylene blue concentrations.

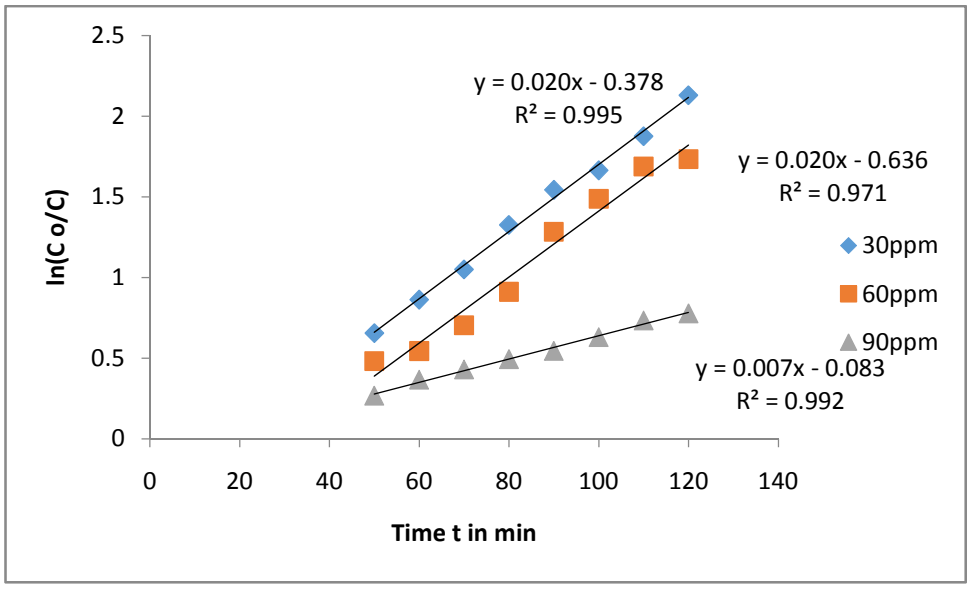


Fig-10. Pseudo 1st order kinetics for photocatalytic degradation of methylene blue dye with catalyst(PANI-$NiFe_2O_4$)dose 8 gm/ lt

Table 1: Reaction rate constant of MB photocatalytic degradation with different initial concentration

Amount of catalyst	Initial conc. ppm	Rate const. (k)	R2
8 gm	30	0.0208	0.9958
	60	0.0205	0.971
	90	0.0072	0.9929

CONCLUSION

1.PANI/$NiFe_2O_4$ nanocomposite is successfully synthesised in situ through self polymerisation of monomer aniline.
2.Photocatalytic degradation of methylene blue dye by using catalyst dose(PANI-$NiFe_2O_4$) is successfully applied. The photocatalytic degradation rate increased significantly by increasing amount of catalyst dose, while with an increasing dye concentration photocatalytic degradation rate decreases. Basic $_P$H condition is found ,which significantly affect the dye degradation efficiency of methylene blue dye is 88.13% and after elution the concentration of dye is 30 ppm.
3.The present study shows that conducting PANI-$NiFe_2O_4$ can be used as photocatalyst for the degradation of methylene blue dye from aqueous solution.
4.The rate of photo-degradation is found to confirm the pseudo first order kinetics with good correlation with R^2 values.

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