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Research Article

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Enhanced activity and reusability of ZnO loaded magnetic activated carbon for the removal of organic pollutants under sunlight

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ABSTRACT

The removal of organic dyes such as Methylene Blue, Thymol Blue, Malachite Green and Methyl Violet from aqueous solution have been attempted by ZnO doped magnetic activated carbon. The phase compositions and morphology of the composite were characterized by using XRD, SEM, EDAX and FT-IR. The influence of various parameters such as effect of agitation time, dye concentration and pH has been studied. The ZnO-Fe_3O_4/Activated Carbon composite attained a maximum removal efficiency of almost 95% under natural sunlight irradiation for 90 min as compared with pure ZnO (58%). First and Second order kinetic models were evaluated to study the adsorption kinetics in case of Methylene Blue. The adsorption system follows second order kinetics. Even Langmuir isotherm has also been studied for 1st cycle as well as 2nd cycle of the composite used for removal. As far as the Langmuir Isotherm is concerned, it gives the best data correlation based on homogeneous surface i.e surface consists of identical sites, equally available for adsorption. The theoretical monolayer removal capacity Qo of the composite is found to be 34.84mg/g and 33.55mg/g for 1st cycle and 2nd cycle respectively. The effect of desorption at different pH shows that the adsorption is very less. However, the results shows that the composite is quiet effective as there is a vast reduction in COD of industrial effluent samples which has been collected from Hosur, India. After the careful study of photocatalytic activity and reusability of ZnO loaded magnetic activated carbon, it can be a promising photocatalyst under sunlight for practical use in wastewater treatment to control water pollution.

Keywords: Dyes, Composite, Removal capacity, COD.

INTRODUCTION

The textile and organic dyes, with largest groups of organic compounds, are mainly dumped directly in the environment. These dyes are toxic to microorganism, aquatic life and human beings, by constituting a serious concern to the ecosystem. Therefore, many efforts have been devoted to remove these dyes from the waste water. These are discharged into the water body and the colour tends to persist even after the conventional removal processes. Methylene blue, Thymol Blue, Malachite Green and Methyl Violet are the most toxic and carcinogenic in nature which may cause skin irritation and allergic disorder. It is estimated that around 10–15% of organic dyes are discharged in various ways in to the environment which has vary adverse effect on public health as well as on aquatic life [1].The removal of all the dyes from the industrial waste water before they are discharged into the water bodies is therefore very important from health and environmental protection point of view [2]. Several conventional technologies such as membrane filtration, liquid- liquid extraction adsorption have been used to separate organic dye from water. [3-5].

Adsorption is one of the most important technique due to the availability of wide range of adsorbents and it is proved to be the efficient method for the removal of non-biodegradable pollutants (including dyes) from waste water. The common adsorbent is activated carbon which is having good capacity of removal of dyes and organic

pollutants due to its high adsorption capacity, high surface area and micro porous structure but desorption and reusing is difficult under common conditions and unfortunately the overall process becomes expensive.

However in this project activated carbon has been prepared from lignucellulosic bio-waste material i.e. Walnut shells to make it cost effective. Even iron has been impregnated to activated carbon in order to make it as magnetic in nature. This magnetic activated carbon can be reused upto 3 cycles with good removal efficiency. Moreover a new composite has been prepared where magnetic activated carbon has been doped in ZnO because doping with metal ion (Fe) may extend the photo response of ZnO in visible light region. Furthermore it introduces additional energy and reduced the band gap of ZnO. Then this composite has been subjected to different sophisticated instrumentations such as SEM, EDAX, FT-IR and XRD for characterization purpose. Owing to the challenging task for synthesis of highly efficient ZnO based composite, this review focuses on various current synthetic strategies used to produce ZnO-Fe_3O_4/Activated Carbon based composite for waste water treatment.

The knowledge of this review offers us valuable insight and inspiration to synthesize an efficient recyclable ZnO based composite. The composite materials were found to exhibit very interesting photocatalytic properties for removal of Methylene Blue under sunlight. Even this composite have been used for the removal of other dyes such as Thymol Blue, Melachite Green and Methyl Violet under visible sunlight.

The composite ZnO- Fe_3O_4/Activated Carbon showed enhanced catalytic activity compared to conventional ZnOphotocatalyst. After the preparation of the composite, Methylene blue dye has been removed by using different concentration. As far as the scope and objective is concerned removal of other toxic dyes has been attempted in this project and finally reduction in COD has also been observed by using this composite. First and Second order kinetic models were used to study the adsorption kinetics Even Langmuir isotherm has also been studied for 1st cycle as well as 2nd cycle of the composite used for removal. As Langmuir Isotherm gives the best data correlation based on homogeneous surface i.e surface consists of identical sites, equally available for adsorption. Even the cost effectiveness has also been calculated so that it can be used in future for waste water treatment.

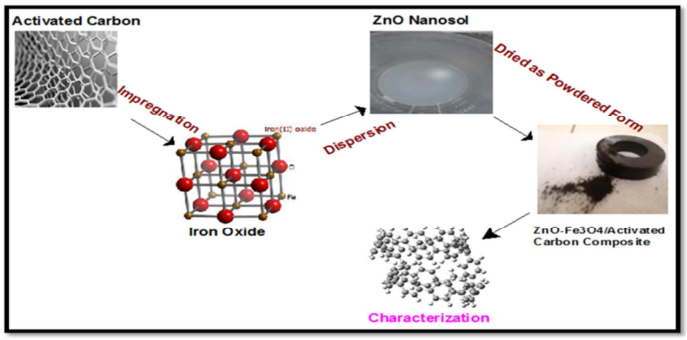


Fig 1 : Process for preparation of ZnO-Fe_3O_4/Activated Carbon Composite

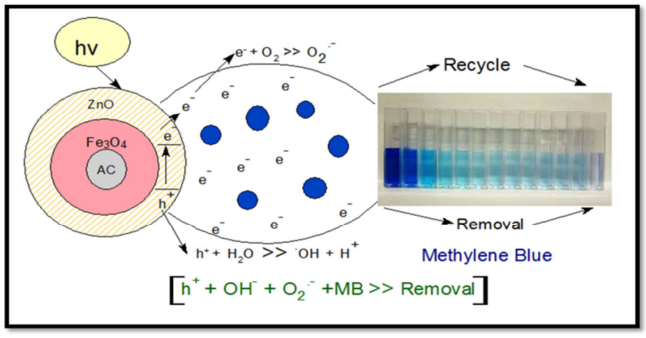


Fig 2: Mechanism Pathway for Removal of Dye

EXPERIMENTAL SECTION

2.1 Preparation of Activated Carbon

Walnut Shells have been crushed into very tiny pieces and treated in Tubular Muffle Furnace in Nitrogen Atmosphere for 2hr in 600°C and finally it has been crushed in crucible and made it in powdered form. This

powdered material was washed with deionised water and kept in Hot air oven for overnight for drying and particle sieved at 100 Mesh Size [6,7].

2.2Impregnation of Iron in Activated Carbon

At first 1M of $FeCl_3$ solution has been prepared. Then 5gm of Activated Carbon has been dispersed into 25 ml of 1M of $FeCl_3$ solution, which is also known as impregnation. Finally the solution was dried for 6hrs in 100°C. Then the powdered Material mixed with Ethylene Glycol (150mM) for reduction. Samples were treated to Tubular Muffle Furnace in Nitrogen Atmosphere for 2hrs in 550°C. The powdered material has been collected and kept in desiccator [8, 9].

2.3Preparation of ZnOnanosol

In order to prepare ZnOnanosol, two precursors has been prepared. In Precursor A, 0.2 M Zinc Acetate Dihydrate has been prepared in 50 ml Methanol and kept in magnetic stirrer maintained temperature of about 50°C and stirred for 30 min. Whereas in Precursor B, 0.4 M NaOH solution has been prepared in 50 ml Methanol and kept in magnetic stirrer maintained temperature of about 50°C and stirred for 30 min. Now Precursor B has been added into Precursor A in drop-wise manner under constant stirring for 30 min. Finally the sol has been heated for 30 min while maintaining temperature of about 50°C. Then it has been stirred for 2hrs in Magnetic stirrer and cooled [10].

2.4Preparation of ZnO-Fe_3O_4/Activated carbon composite

At first Iron impregnated activated carbon composite was dispersed in ZnOnanosol and sonicated for 1hr. After that it was washed with double distilled water for 2 to 3 times. Then the particles were dried at 120°C for overnight. Finally it has been crushed into fine powdered form and sieved in 100 Mesh Size. The composites have been collected and kept in desiccator for photocatalytic activity.

2.5Characterization of ZnO-Fe_3O_4/Activated carbon composite

After the successful synthesis, the composite has been given for characterization by the use of different sophisticated instruments such as XRD, SEM, EDAX and FT-IR. The morphology of the activated carbon and composite has been investigated by SEM. Furthermore the composite has been subjected for EDAX analysis which gives the clear picture of the composition. The inorganic composition has been confirmed by XRD analysis and it has been matched with the standard available in JCPDS number. Moreover the metallic oxide has been confirmed by FT-IR data**.**

2.6Photocatalytic activity for removal of dyes

Methylene Blue, Thymol Blue, Melachite Green and Methyl Violet dye were collected of Analytical Grade. Then different concentration (ppm) solutions were prepared and after that 20 ml has been taken in conical flask. Simultaneously 30 mg of composite was added into it and kept in shaker for 20 min. Then those conical flasks were subjected to sunlight for 2 hr. Finally the solution was centrifuged and filtered and then the absorbance has been evaluated by UV visible spectrophotometer (Monitoring wavelength range: 200 nm to 800 nm). Then effect of pH and effect of Contact time has been studied in case of Methylene Blue dye [11,12,13].

RESULTS AND DISCUSSION

3.1 Characterization of Zn0-Fe_3O_4/Activated carbon composite

3.1.1 XRD data interpretation

XRD pattern of FexOy/Activated Carbon shows that iron oxide corresponds to hematite and finally it has been matched with the standard JCPDS #039-1346. Similarly in case of ZnO(0.01M)-FexOy/Activated Carbon, the iron oxide corresponds to magnetite and matched with the standard JCPDS #99-200-3876. Finally for ZnO(0.2M)-FexOy/Activated Carbon composite ZnO corresponds to Wurtzite and successfully matched with the standard JCPDS #036-1451 which confirms the presence of ZnO in the composite**.**

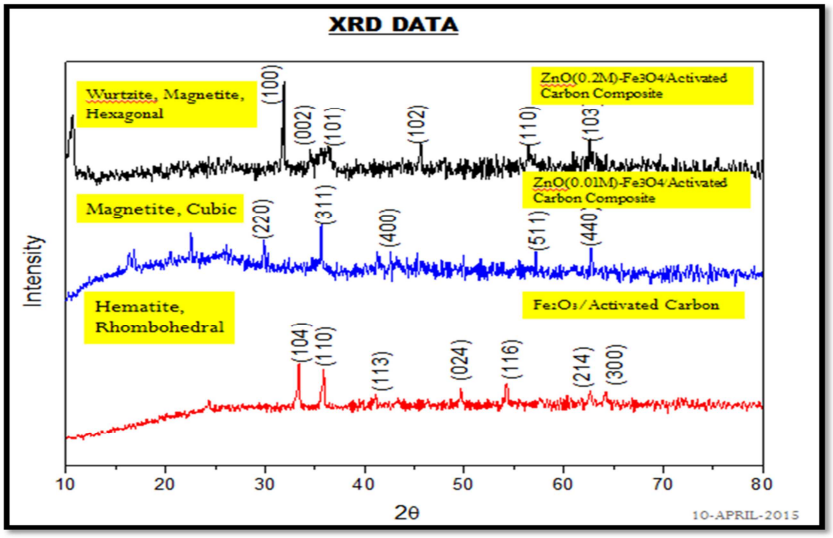


Fig 3: XRD pattern of Fe_2O_3/Activated Carbon, ZnO(0.01M)-Fe_3O_4/Activated Carbon and ZnO(0.2M)-Fe_3O_4/Activated Carbon

3.1.2 FT-IR data

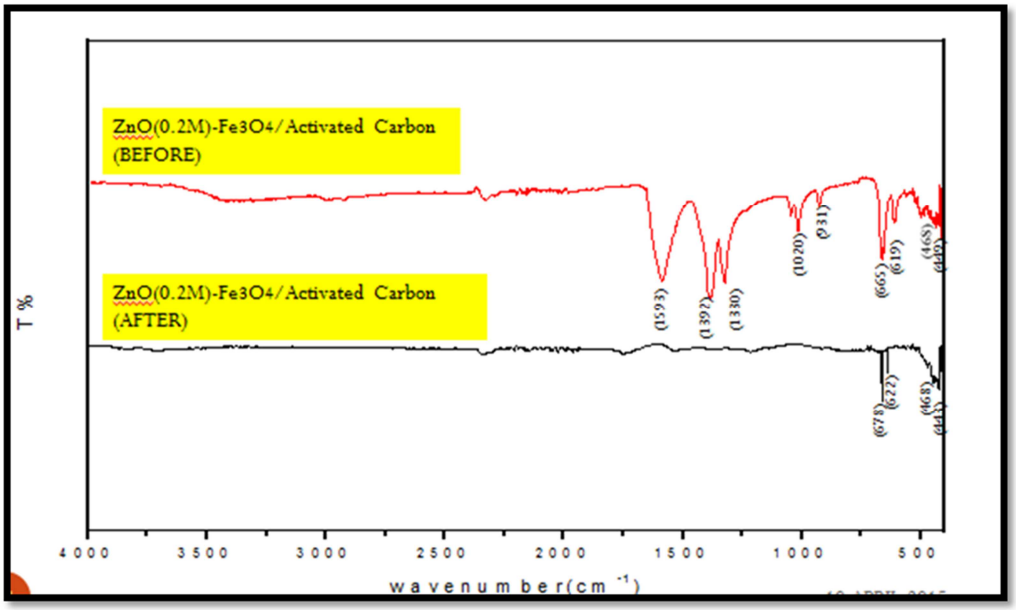


Fig 4: FT-IR Pattern of the composite before and after removal

FT-IR study confirms the presence of metal oxides in the composite. Even the peak of FT-IR also shows the presence of ZnO and Iron Oxide before and after removal of dyes. Table No. 1, shows the detailed study of FT-IR data.

Table No. 1: FT-IR data to confirm the Metal Oxide in composite

Sr. No.	Metal Oxide	Wavenumber
1.	ZnO	445-470 cm^{-1}
2.	Fe_xO_y	620-678 cm^{-1}

3.1.3 SEM images

The morphology of Activated Carbon, Iron Impregnated Activated Carbon and ZnO(0.2M)-Fe3O4/Activated Carbon Composite is clearly distinguished in given SEM images. The layered structure of ZnO(0.2M)-Fe_3O_4/Activated Carbon Composite is clearly distinguished in SEM image (Fig.5-7). High loading concentration of Fe_3O_4 and ZnO gave severe aggregation of the composite and uneven dispersion across the Activated Carbon surface.

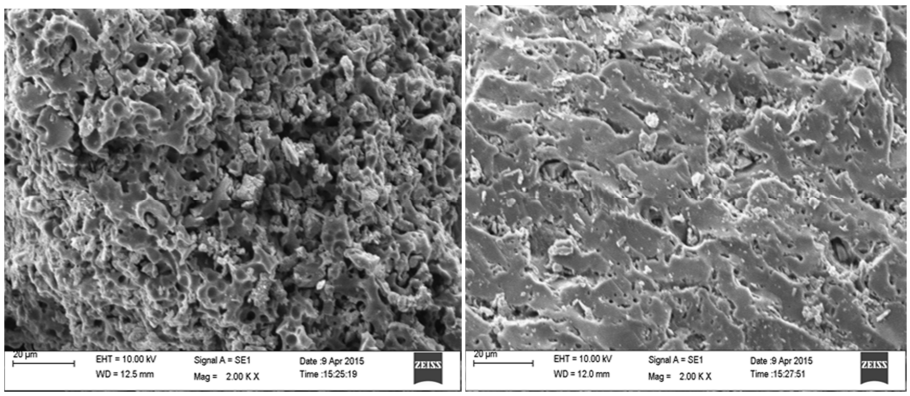


Fig 5: SEM images of Activated Carbon

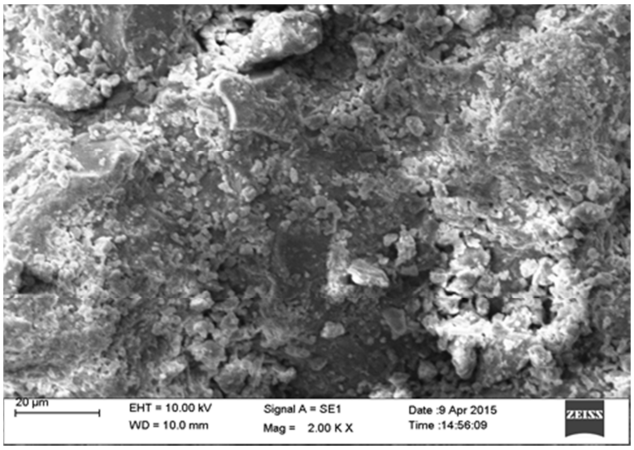


Fig 6: SEM image of Iron Impregnated Activated Carbon

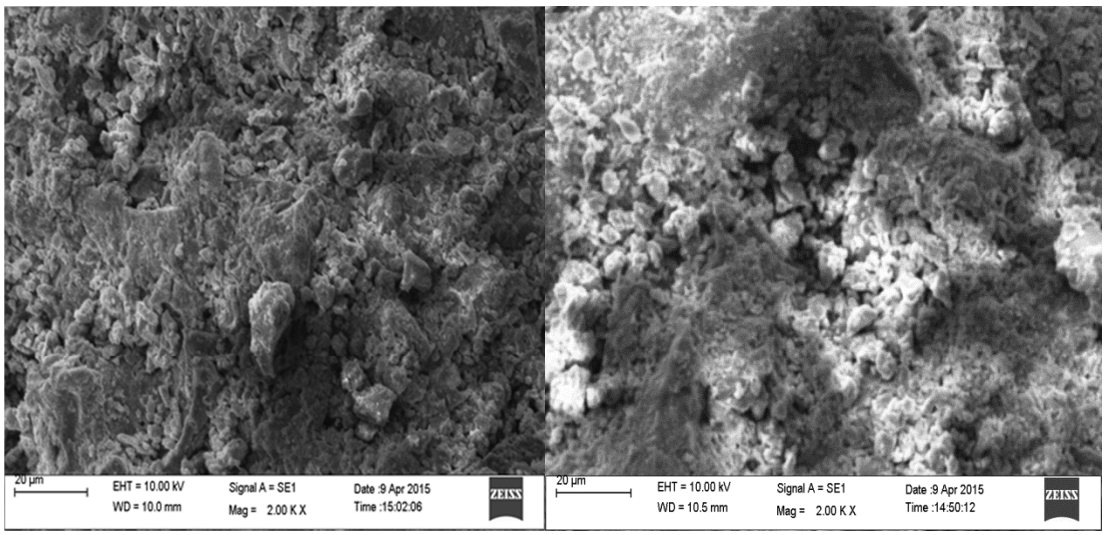


Fig 7: SEM images of ZnO(0.2M)-Fe_3O_4/Activated Carbon Composite

3.1.4 EDAX analysis of Activated Carbon

The peak of EDAX (Fig.14) confirms the existence of C element in Activated Carbon. Furthermore the appearance of C, Zn and O confirms the constituents of the ZnO(0.2M)-Fe3O4/Activated Carbon Composite. But the disappearance of Fe element in EDAX analysis (Fig.9) of the composite is may be due to coating of the composite by ZnO.

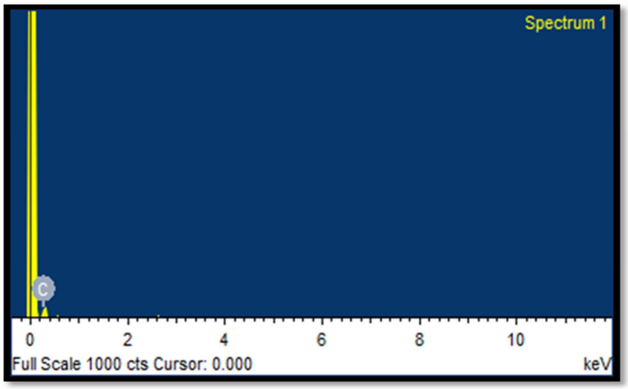


Fig 8: EDAX Analysis of Activated Carbon

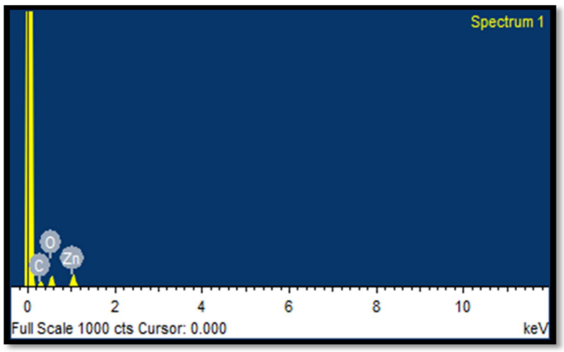
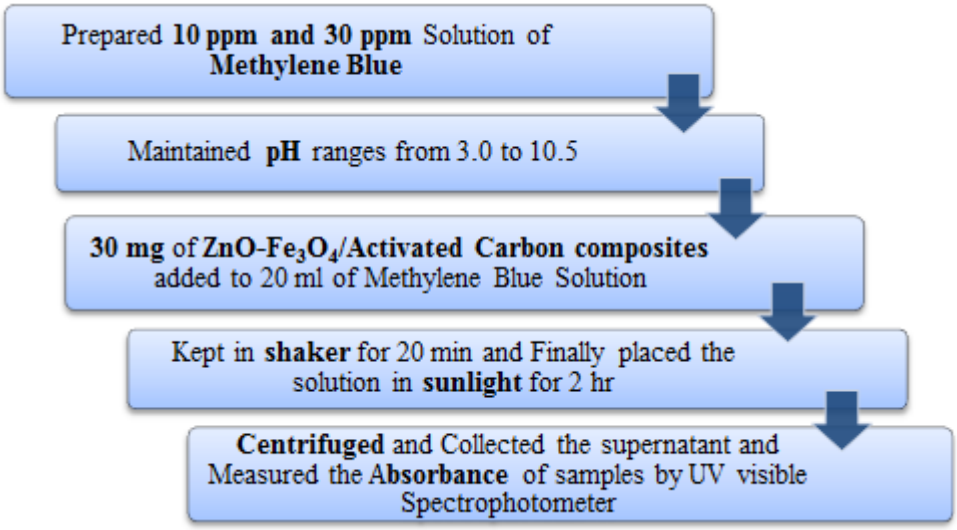


Fig 9: EDAX Analysis of ZnO(0.2M)-Fe_3O_4/Activated Carbon Composite

3.2Properties of Methylene Blue dye

1. Empirical formula C16H18ClN3S
2. Cationic Azo dye
3. λmax: 663 nm
4. Toxic Textile Dye

3.2.1 Experimental methodology for removal of Methylene Blue dye



3.2.2 Removal percentage

% Removal = A_o – At/ A_o × 100

Where A_o= Absorbance at initial time

At= Absorbance at final time (After Removal)

3.3Effect of pH

The initial concentration of 10 and 30 ppm of Methylene Blue have been taken for the study of effect of pH. The composite used for removal of Methylene Blue is 30mg per 20 ml of dye. For the further study of the effect of pH, pH ranges from 3.0 to 10.5 have been maintained. So it has been found out that the removal percentage of Methylene Blue dye increases as the pH increases. In general terms the removal minimum in pH 3.0 whereas removal maximum in case of pH 10.5. The effect of pH has been shown (Table No. 2 and 3).

Table No. 2: Effect of pH for the removal of Methylene Blue dye using ZnO-Fe3O4/Activated Carbon Composite (10 ppm)

Sr. No.	Initial pH	Final pH	Removal %
1.	3.0	3.3	64.69%
2.	5.0	5.4	81.06%
3.	7.0	7.8	86.82%
4.	9.0	9.2	88.51%
5.	10.5	10.6	91.46%

Condition Maintained:

Initial Concentration of Dye: 10 ppm, Composite Used: 30mg, Volume of Dye: 20ml, Agitation Time: 2hrs, pH: 3.0 to 10.5, Monitoring Wavelength: 663 nm

Table No. 3: Effect of pH for the removal of Methylene Blue dye using ZnO-Fe3O4/Activated Carbon Composite (30 ppm)

Sr. No.	Initial pH	Final pH	Removal %
1.	3.0	3.3	53.26%
2.	5.0	5.4	70.57%
3.	7.0	7.6	69.78%
4.	9.0	9.2	72.03%
5.	10.5	10.5	80.21%

Condition Maintained:

Initial Concentration of Dye: 30 ppm, Composite Used: 30mg, Volume of Dye: 20ml, Agitation Time: 2hrs, pH: 3.0 to 10.5, Monitoring Wavelength: 663 nm

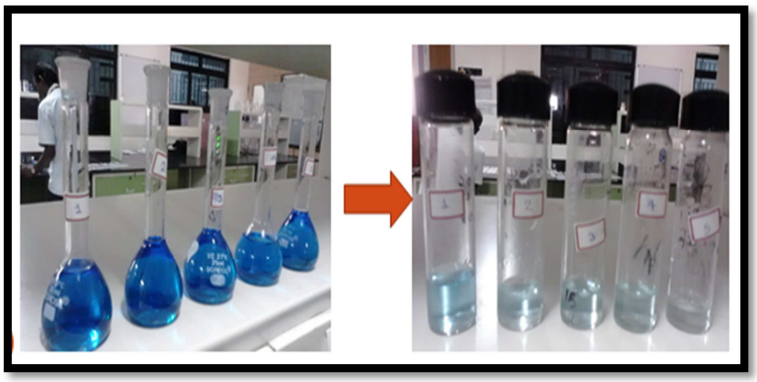


Fig 10: Image shows before and after Removal of Methylene blue

5.4 Effect of contact time

The effect of contact time has also been examined by maintaining certain conditions. Thus the effect of contact time has been studied for different concentration of methylene blue dye. The analysis is done for 10ppm, 30ppm, 40ppm and 50ppm methylene blue solution. The contact time ranges from 30min to 180min. So the effect of contact time is shown below in tabulation form.

Table No. 4: Effect of contact time for the removal of Methylene Blue dye using ZnO-Fe3O4/Activated Carbon Composite

Sr. No	Time (min)	Removal % (10ppm)	Removal % (30ppm)	Removal % (40ppm)	Removal % (50ppm)
1.	30 min	79.45	61.11	60.32	50.93
2.	60 min	82.21	62.18	70.97	53.22
3.	90 min	85.88	67.89	73.21	59.21
4.	120 min	91.46	80.11	76.86	70.88
5.	150 min	93.25	84.79	80.14	77.48
6.	180 min		85.53	80.22	78.21

Condition Maintained:
Initial Concentration of Dye: 10, 30, 40 and 50ppm, Composite Used: 30mg, Volume of Dye: 20ml, Agitation Time: 30min to 180min, pH:9.0, Monitoring Wavelength: 663 nm

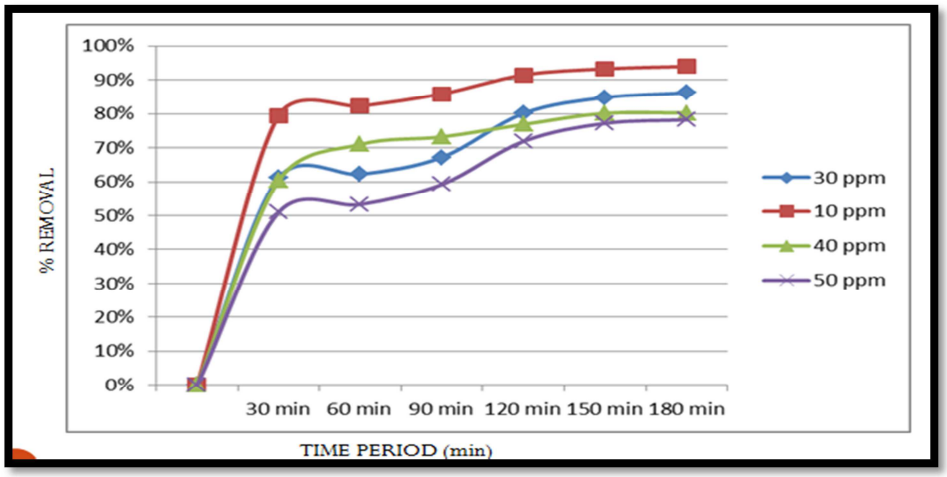


Fig 11: Graphical Presentation of Removal % of Methylene Blue at Different Time

The figure gives the clear idea of the effect of contact time in which it has been shown that the % removal increases with time period for different concentration of Methylene Blue. Furthermore the % removal is maximum in case of 10 ppm Methylene Blue solution and minimum in case of 50 ppm.

3.5 Kinetic study

3.5.1 First order kinetic study model*:*

The Lagergren First Order Model can be represented as:

$dq/dt= k_1(qe-q)$

Integrating equation for the boundary conditions for t=0 to t=t and q=0 to q=q, gives

$\log(qe-q)= \log qe- k_1t/2.303$

whereqe and q are the amounts of Methylene blue adsorbed (mg/g) at equilibrium and at time t respectively and k1 is the rate constant of first order kinetics (min-1). Values of qe and k1 are calculated from the slop of the intercept of the plot log(qe-q) vs t (Table No. 5)

3.5.2 Second order kinetic study model*:*

The second order kinetic is represented as:

$dq/dt= k2 (qe-qt)^2$

Integrating both side for the boundary condition t=0 to t=t and qt=0 to qt=q gives.

$1/(qe-q)= 1/qe + k_2t$

This equation can be rearranged as

$t/q = 1/k_2qe^2 + t/qe$

where k2 is equilibrium rate constant of second order model. Values of k2and qe were calculated from the slop and intercept of the plots t/q vs t (Table No. 6).

[q= % R/100 × Conc. of MB × Volume taken/1000 × 1000/Dose]

where, q is Amount removal (mg/g)
% R is % removal of Methylene Blue
Dose is amount of adsorbent used.
q_e denotes the amount of removal at equilibrium which has been calculated by plotting graph.

Table No. 5: First Order Kinetics Model for comparison of calculated and experimental qe values

Sr. No.	Concentration of Methylene Blue (ppm)	qe (Experimental)	k_1	qe (Calculated)	R^2
1.	10 ppm	6.06	0.0119	1.0882	0.9632
2.	30 ppm	16.958	0.0124	8.175	0.8251
3.	40 ppm	21.36	0.0184	9.5499	0.974
4.	50 ppm	24.48	0.0227	20.5353	0.7718

Table No. 5: Second Order Kinetics Model for comparison of calculated and experimental qe values

Sr. No.	Concentration of Methylene Blue (ppm)	qe (Experimental)	k_2	qe (Calculated)	R^2
1.	10 ppm	6.06	0.034	6.256	0.9959
2.	30 ppm	16.958	0.004	17.76	0.9787
3.	40 ppm	21.36	0.0064	21.97	0.9959
4.	50 ppm	24.48	0.0020	27.39	0.9617

As qe values calculated from the second order kinetic model are close to the experimental qe values with good correlation coefficients. Hence it follows the second order kinetic model on the assumption that the rate determining step may be through sharing or exchange of electrons between adsorbate and adsorbent.

Table No. 7: Pseudo Second Order Kinetic Model showing t vs t/q for different concentration

Sr. No.	Agitation Time (min)	10 ppm		30 ppm		40 ppm		50 ppm	
		q	t/q	q	t/q	q	t/q	q	t/q
1.	30 min	5.23	5.73	12.22	2.45	16.08	1.86	16.97	1.76
2.	60 min	5.48	10.94	12.43	4.82	18.92	3.17	17.74	3.38
3.	90 min	5.72	15.73	13.57	6.42	19.52	4.61	19.73	4.56
4.	120 min	6.06	19.80	15.42	7.78	20.46	5.86	23.62	5.08
5.	150 min	6.21	24.15	16.95	8.84	21.36	7.02	24.48	6.12
6.	180 min			17.10	10.52	21.39	8.41	26.69	6.74

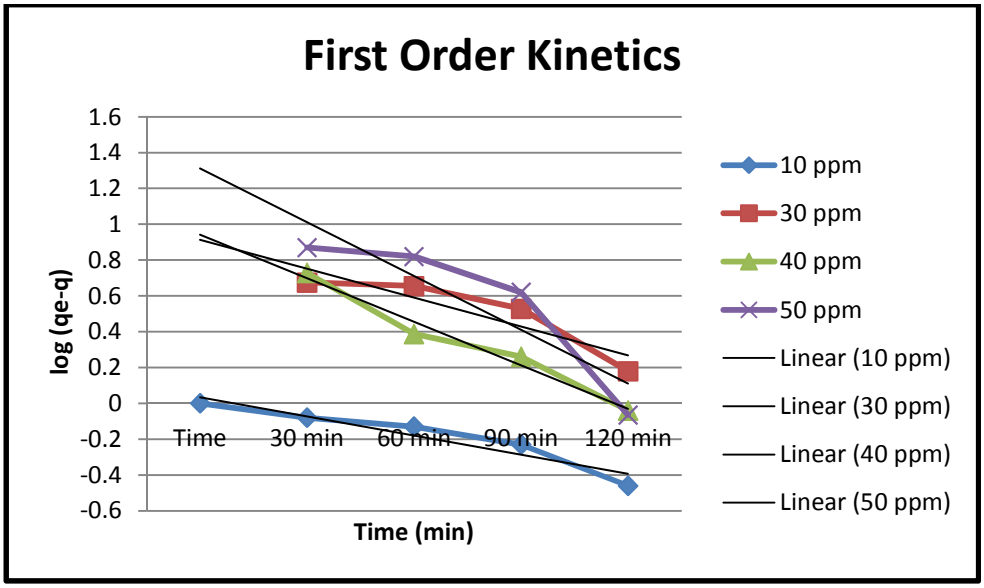


Fig 12: First Order Kinetic Model for different concentration

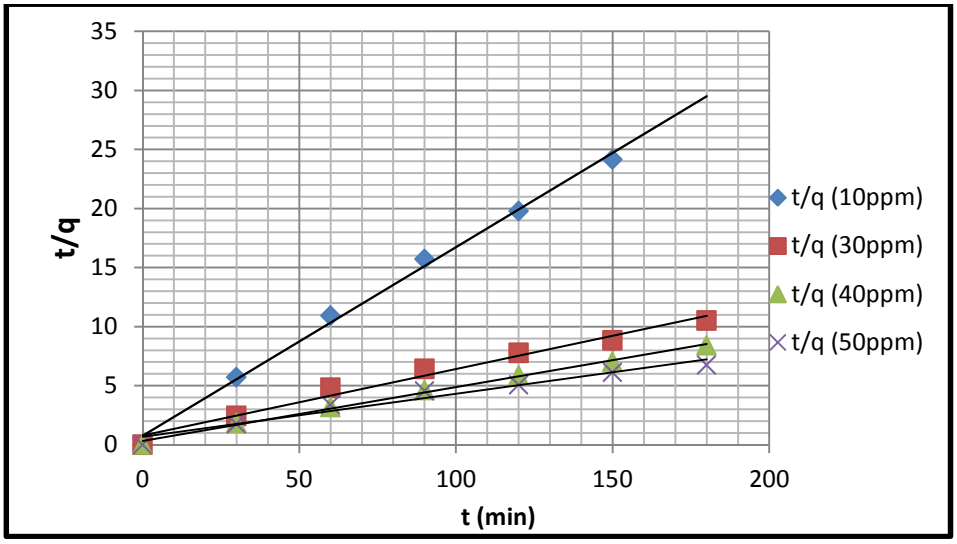


Fig 13: Second Order Kinetic Model for different concentration

3.6 Removal capacity and Isotherm study

Even the removal capacity as well as Isotherm study has been done in order to know the efficiency of the composite when compared to other adsorbents and composites.

$C_e = C_o - (C_o \times R\%)/100$

Where C_e is Equilibrium Concentration
C_o is Initial Concentration
qe is Amount removal at equilibrium

Table No. 8: Removal Capacity for 1st Cycle

Sr. No.	Concentration of Methylene Blue	C_e	q_e	C_e/q_e
1.	10 ppm	0.854	6.06	0.14
2.	30 ppm	4.563	16.958	0.27
3.	40 ppm	8.744	20.80	0.42
4.	50 ppm	17.410	21.72	0.80

$Q_o = 1/m$
$= 1/0.0287 = 34.84$ mg/g
where Q_o is Theoretical Monolayer Removal Capacity
$b = 1/ I Q_o = m/ I = 0.224$ L/mg
where b is Langmuir Constant

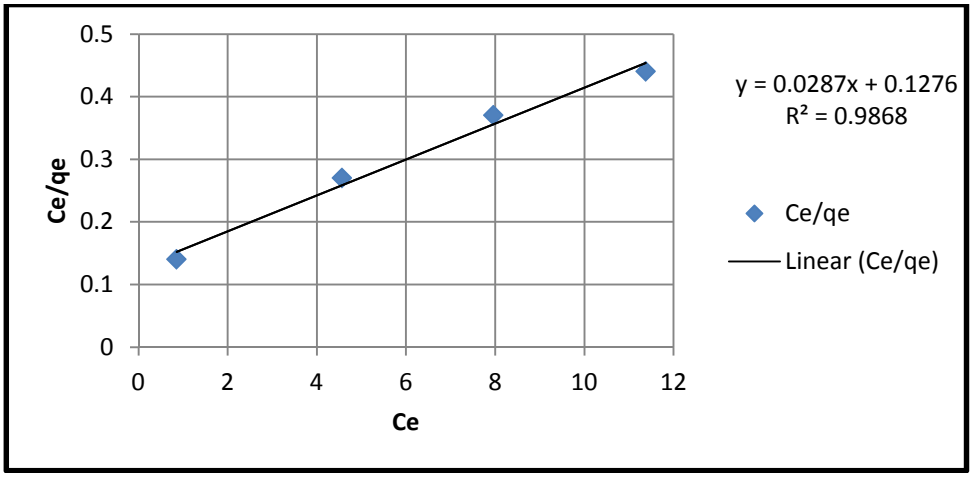


Fig 14: Graph between C_e vs C_e/q_e for calculation of Q_o

3.7 Langmuir Isotherm for 1st cycle

Langmuir Isotherm is based on the adsorption on a homogeneous surface i.e. consists of identical sites and equally available for adsorption. Langmuir Isotherm also gives the best correlation with homogeneous equal site for removal.

C_e/q_e(calculated) = $1/Q_0$ b + C_e/Q_0

q_e (calculated) has been evaluated from above formula and finally it has been compared with q_e (experimental) value

Table No. 9: Langmuir Isotherm Study

Sr No.	Concentration of Methylene Blue	C_e	q_e(Experimental)	q_e (Calculated)
1.	10 ppm	0.854	6.06	6.71
2.	30 ppm	4.563	16.95	16.53
3.	40 ppm	7.964	21.36	22.75
4.	50 ppm	11.375	24.48	25.27

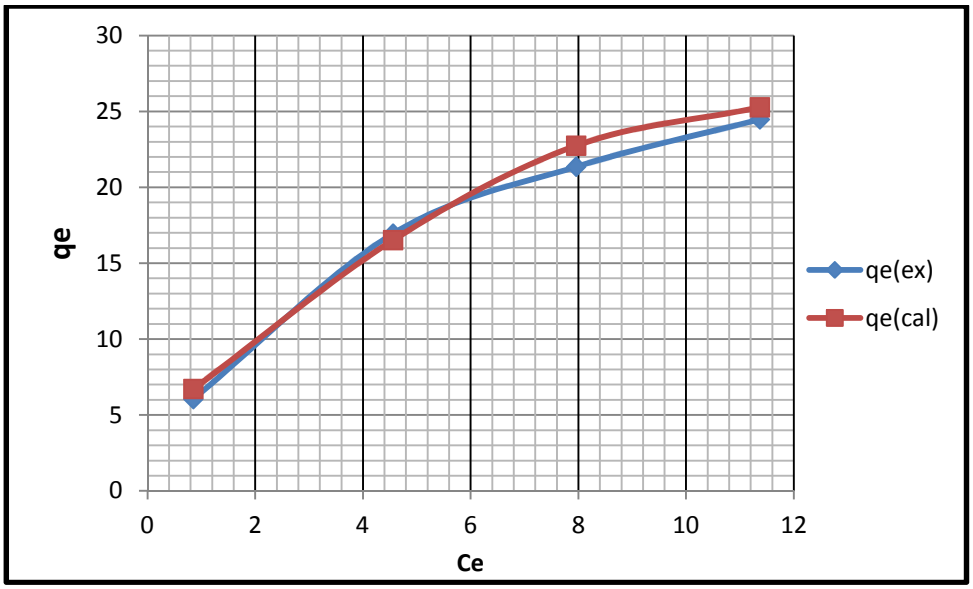


Fig 15: Langmuir Plot for comparison of q_e (experimental) and q_e (calculated)

3.8 Equilibrium Parameter (R_L)

The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter RL, which is a dimensionless constant referred to as separation factor or equilibrium parameter [14].

$R_L = 1/(1+ bC_o)$

Where, R_L is Equilibrium Parameter
C_o is Initial Concentration
Significance: If R_L is in between 0 to 1 (Favourable for removal)

Table No. 10: Evaluation of R_L value

Sr. No.	Concentration of Methylene Blue	Q_o	b	R_L
1.	10 ppm	34.84	0.224	0.308
2.	30 ppm			0.129
3.	40 ppm			0.100
4.	50 ppm			0.081

After the careful study of equilibrium parameter (RL) in 10, 30, 40 and 50 ppm Methylene blue solution. Therefore as per the significance of equilibrium parameter, values of RL in different concentration ranges from 0.308 to 0.081 so it can be referred that the composite is favourable for removal.

5.9 Reusability of the composite for waste water treatment

After the careful study of Kinetic model as well as Isotherm study, the reusability of the composite has also been studied for evaluation of the efficiency of composite. Thus the removal percentage of Methylene Blue has been evaluated for 2nd cycle and it has been compared with the 1st cycle. The detailed study has been shown in Table No. 11

3.9.1 Methodology for evaluation of reusability of the composite

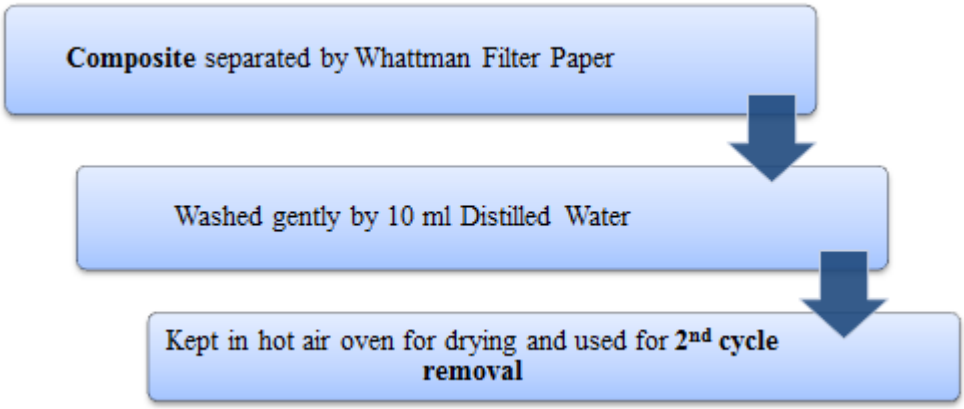


Table No. 11: Comparison of 1st Cycle and 2nd Cycle Removal %

Sr. No.	Concentration of Methylene Blue	1st Cycle Removal %	2nd Cycle Removal %
1.	10 ppm	91.46%	66.25%
2.	30 ppm	84.79%	63.19%
3.	40 ppm	80.14%	58.40%
4.	50 ppm	77.48%	52.18%

Condition Maintained:

Initial Concentration of Dye: 10, 30, 40 and 50ppm, Composite Used: 30mg, Volume of Dye: 20ml, Agitation Time: 120min, pH:9.0, Monitoring Wavelength: 663 nm

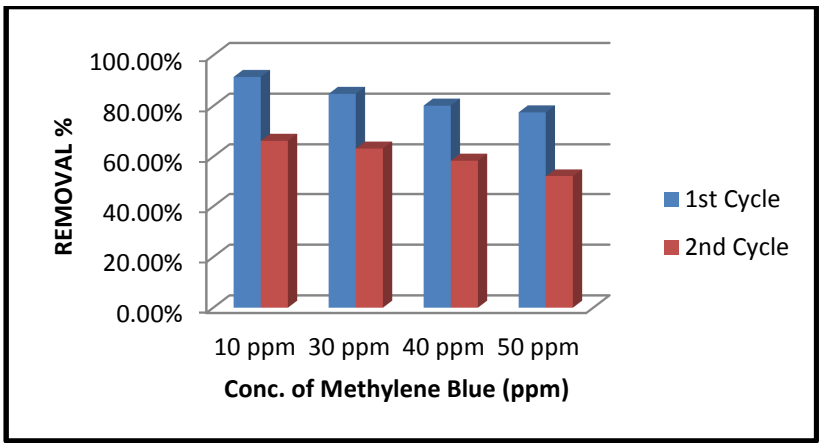


Fig 16: Bar Graph shows the Comparison between 1st cycle and 2nd cycle removal %

3.10 Langmuir isotherm for 2nd cycle

The detailed study of Langmuir Isotherm for 2nd cycle has been shown in table no. 12. Even for 2nd cycle the Langmuir isotherm obeys as q_e (experimental) and q_e(calculated) are close to each other.

Table No. 12: Langmuir Isotherm Study for 2nd Cycle

Sr. No.	Concentration of Methylene Blue	C_e	q_e (experimental)	C_e/q_e	q_e(Calculated)
1.	10 ppm	3.375	4.416	0.764	4.27
2.	30 ppm	11.04	12.638	0.873	10.93
3.	40 ppm	16.64	15.573	1.068	14.34
4.	50 ppm	23.91	17.393	1.374	17.71

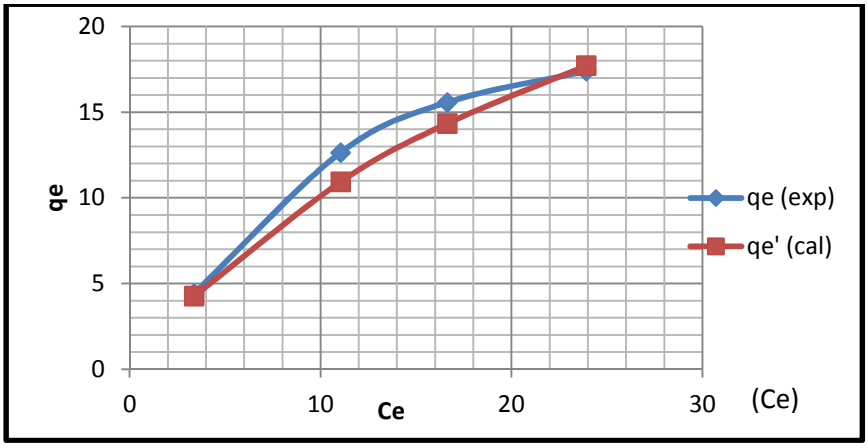


Fig 17: Langmuir Plot for 2nd Cycle

For 2nd Cycle Removal by plotting graph $C_e$vsC_e/q_e
Q_o= 1/m= 1/0.0298= 33.55mg/g
b=m/I= 0.048 L/mg

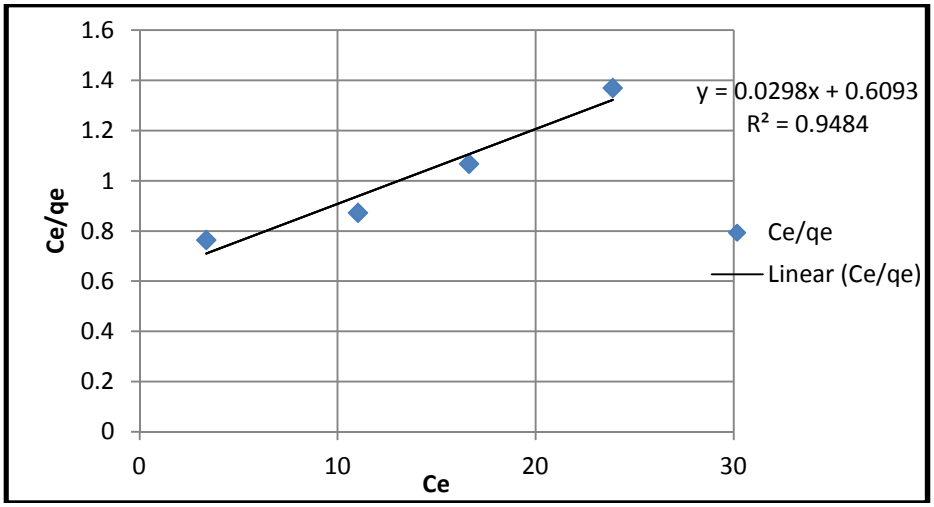
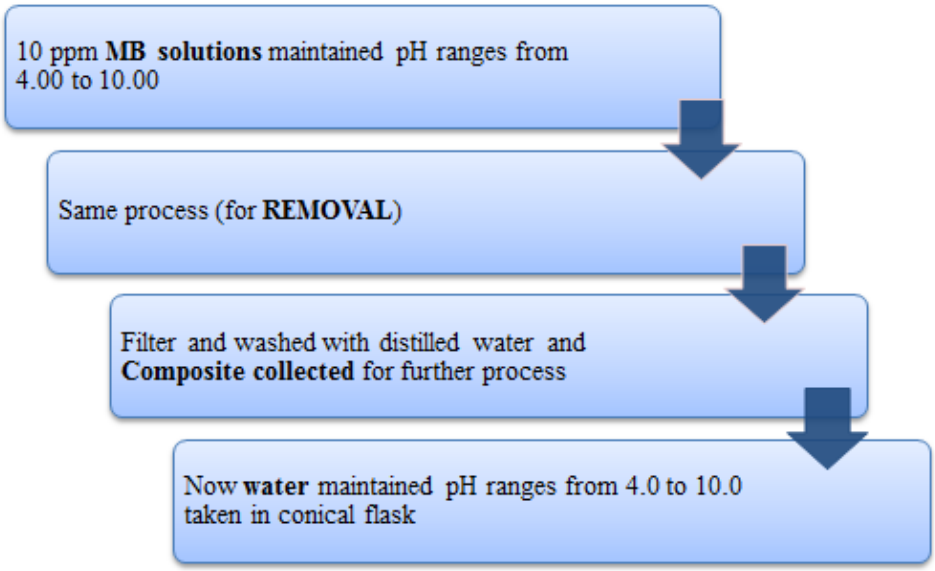


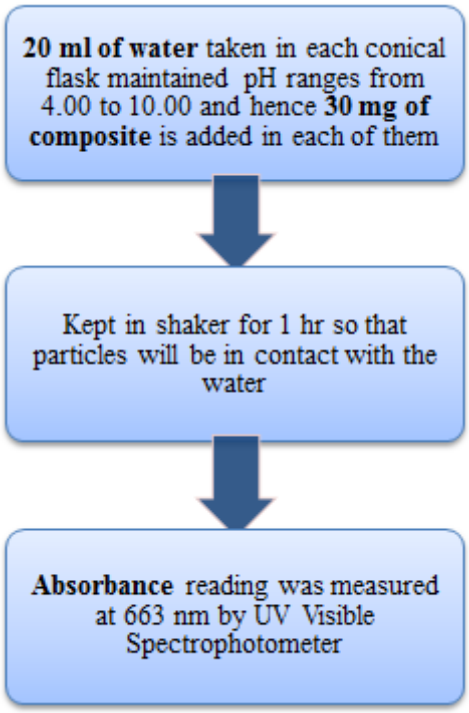
Fig 18: Graph between CevsCe/qe for calculation of Qo

3.11 Effect of desorption at different pH

3.11.1 Methodology for the study of desorption effect



Now next half process for the study of desorption at different pH can be elaborated as follows



To make the removal process more economical, it is necessary to regenerate the spent dye. Desorption was higher in lower pH 4.0 (4.5 – 4%) for 10 ppm concentration as per the study. In the pH ranges from 7.0 to 10.0 desorption was found to be less than 3%. The detailed study has been shown in Table No 13

Table No. 13: Effect of Desorption Study at different pH

Sr. No.	pH	Desorption %
1.	4.0	4.03 %
2.	7.0	2.66 %
3.	9.0	2.11 %
4.	10.0	1.42 %

Condition Maintained:

Initial Concentration of Dye: 10 ppm, Composite Used: 30mg, Volume of Dye: 20ml, Agitation Time:60 min, pH:4.0 to 10.0, Monitoring Wavelength: 663 nm

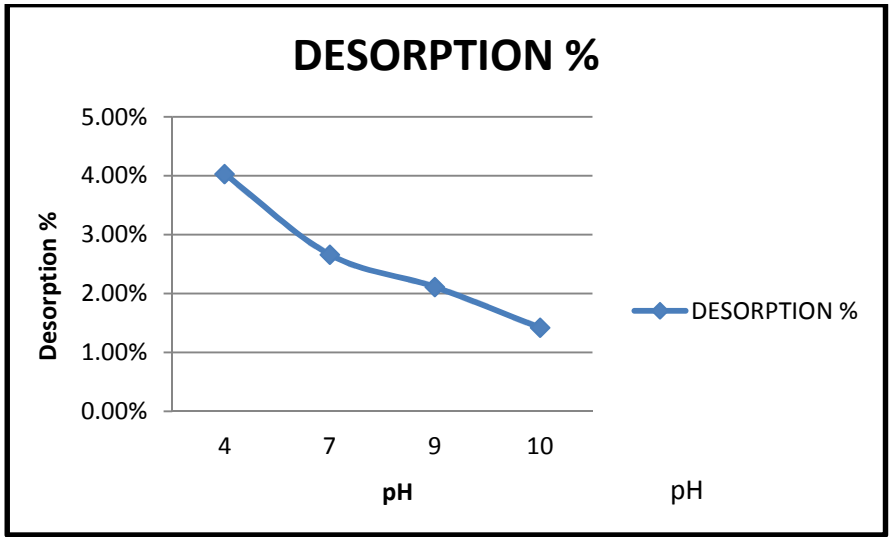


Fig 19: Graphical Presentation of % Desorption at different pH

3.12 Removal of different dyes

3.12.1 Methodology for removal of dyes

At first the different dyes were collected namely Thymol Blue, Melachite Green and Methyl Violet of Analytical Grade. Then 30 ppm solutions were prepared for each dye and after that 20 ml has been taken in conical flask. Simultaneously 30 mg of composite was added into it and kept in shaker for 20 min. Then those conical flasks were subjected to sunlight for 2 hr. Finally the solution was centrifuged and filtered and then the absorbance has been evaluated by UV visible spectrophotometer (Monitoring wavelength range: 200 nm to 800 nm). Table No. 14 shows the detailed study of the removal % of different dyes along with the lambda max of each dye.

Table No. 14: % Removal of different dyes

Sr. No.	Dyes	Concentration	Lambda max	Removal %
1.	Thymol Blue	30 ppm	434 nm	71.24 %
2.	Melachite Green	30 ppm	618 nm	64.19 %
3.	Methyl Violet	30 ppm	580 nm	72.01 %

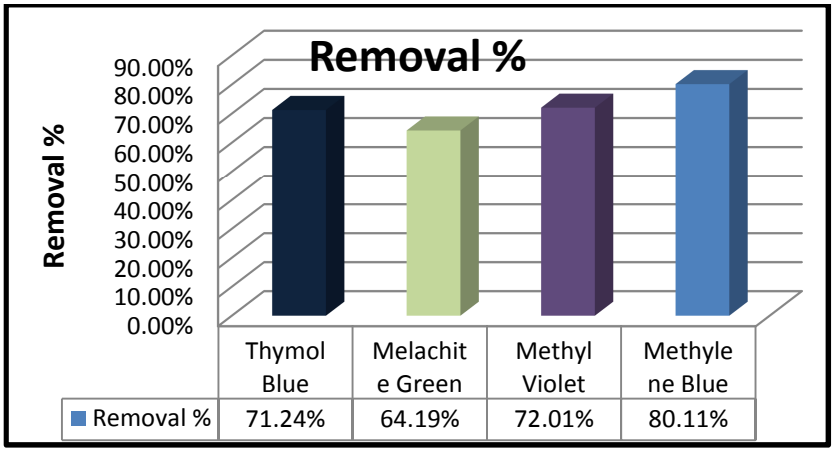


Fig 20: Comparative study of removal % of different dyes

3.12 Reduction of COD

In environmental chemistry, the chemical oxygen demand (COD) test is commonly used to indirectly measure the amount of organic compounds in water. Most applications of COD determine the amount of organic pollutants found in surface water (e.g. lakes and rivers) or wastewater, making COD a useful measure of water quality.

Industrial Waste Water Effluent were collected from 'PRINTED CIRCUIT BOARD 'Hosur, India. A lot of organic and in-organic by products are discharged in to waste water stream continuously. It mainly consists of chelators, organic acids, alkali, inks, photo resists and metal compound.

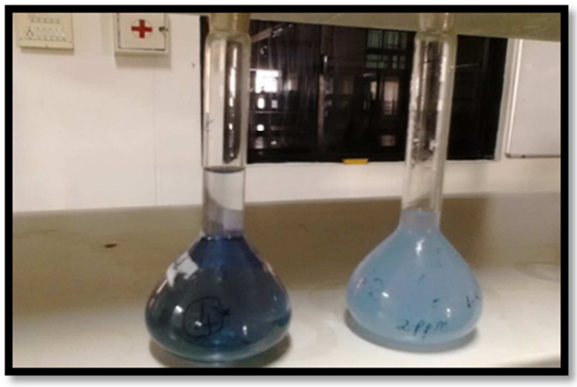
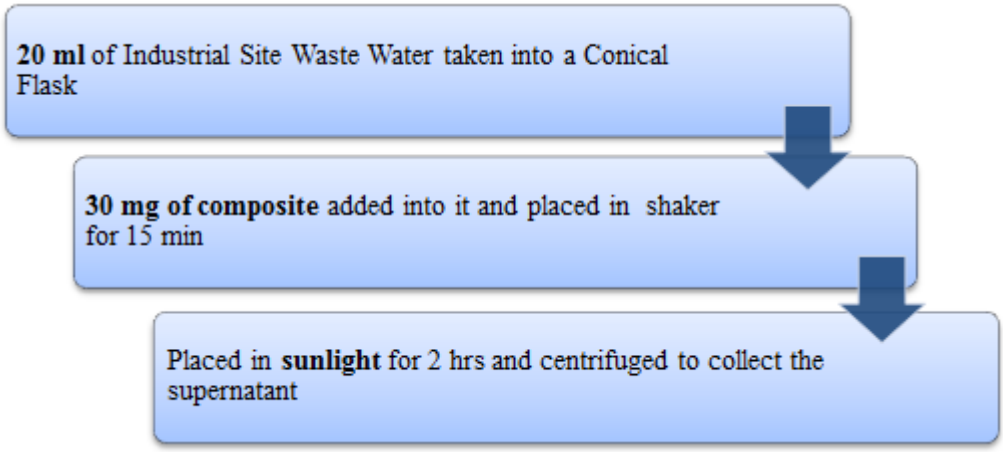


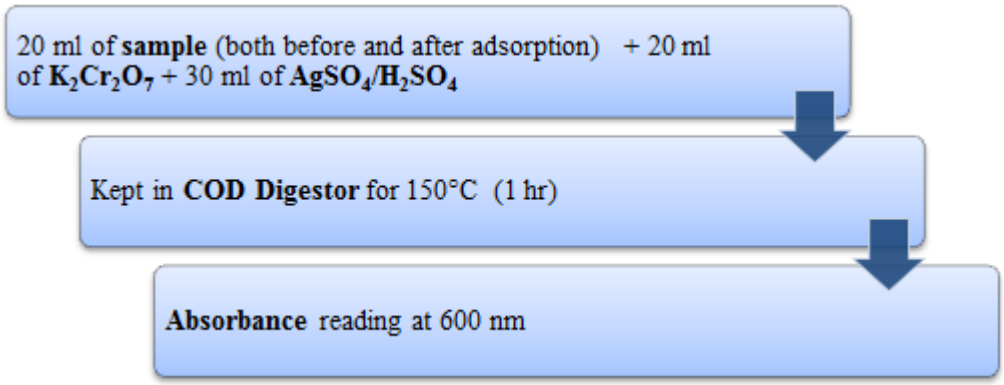
Fig 21: Industrial Effluent

Resistant Stripper Concentrate (RSC) : Initial **COD = 25450 ppm** {Diluted 2 times}
Resistant Developer Concentrate (RDC): Initial **COD= 5874 ppm {**Dilute 5 times}

3.12.1 Procedure for COD reduction



The next half procedure will be done by using COD Digester which is as follows:



3.12.2 Evaluation of COD reduction

COD Reduction % = A_o – At/ A_o × 100

where A_0 is Initial Absorbance of Sample before Removal

At is Final Absorbance of Sample after Removal

Table No. 15: COD Reduction in Industrial Effluent

Sr. No.	Industrial Effluent (Initial COD)	Final COD	COD Reduction
1.	RSC (COD = 12725 ppm)	4840.59 ppm	61.96 %
2.	RDC (COD = 1174.8 ppm)	726.024 ppm	38.20 %

3.13 Cost effectiveness

After Careful study of the cost of all the chemicals used of Analytical Grade, the cost of the composite has been evaluated per gram. Table no. 16 shows the cost effectiveness of the composite prepared for waste water treatment

Table No. 16: Cost Effectiveness of the Composite

- Ferric Chloride (Anhydrous) : Rs 0.67
- Ethylene Glycol : Rs 0.615
- Zinc Acetate Dihydrate: Rs 2.184
- Sodium Hydroxide : Rs 0.015
- Methanol : Rs 10

Total Cost : Rs 13.484

Now Yield is around 5 gm.

So Cost of the composite = Rs 13.484/5 gm

= Rs 2.69/gm

CONCLUSION

A facile method was developed and explored for synthesis of highly photocatalytic active magnetically recyclable composite. This study shows that ZnO-Fe_3O_4/Activated Carbon is the effective composite for the removal of Methylene blue dye from aqueous solution. The removal percentage increases with increasing contact time and decreases with increase in concentration of dye. Furthermore there is a sharp increase in removal percentage with increase in pH and percentage of desorption decreases with increase in pH. The formation of ZnO-Fe3O4/Activated Carbon was confirmed by XRD.

The adsorption of dye follows second order Kinetic model. The theoretical monolayer removal capacity were found to be 34.85mg/g and 33.55mg/g for 1st cycle and 2nd cycle respectively composite used for removal. The removal was found to be maximum in the pH ranges from 7.0 to 10.5. Even this composite is found to be very effective for the reduction of COD in industrial effluents. Finally from this study it has been concluded that ZnO-Fe3O4/ Activated Carbon composite is found to be cost effective compared to other adsorbents. In addition, the synthesised composite exhibits high removal efficiency for Methylene Blue under solar light, easy separation and good stability. These results suggest that the designed photocatalyst could be a general and competent platform for the removal of organic pollutants and dyes. After the careful study of photocatalytic activity and reusability of ZnO loaded magnetic activated carbon, it can be a promising photocatalyst under sunlight for practical use in wastewater treatment to control water pollution.

Acknowledgement
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