

**CATALYTIC OXIDATION OF VOLATILE ORGANIC COMPOUNDS (ETHYL
BENZENE AND CHLOROBENZENE) CONTAMINATED WATER USING
MOLYBDENUM IMPREGNATED CARBON**

**Submitted in partial fulfilment of the requirements for the award of
Master of Science in Chemistry**

By

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39910015



DEPARTMENT OF CHEMISTRY

SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

Accredited with Grade "A" by NAAC | 12B Status by UGC | Approved by AICTE

JEPPIAAR NAGAR, RAJIV GANDHI SALAI, CHENNAI - 600 119

MARCH – 2021



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DEPARTMENT OF CHEMISTRY

BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of **Ms. PRATHYUSHA. C (39910015)** who carried out the project entitled "**CATALYTIC OXIDATION OF VOLATILE ORGANIC COMPOUNDS (ETHYL BENZENE AND CHLROBENZENE) CONTAMINATED WATER USING MOLYBDENUM IMPREGNATED CARBON**" under our supervision from January 2021 to March 2021.

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Submitted for Viva-voce Examination held on _____

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DECLARATION

I **C. PRATHYUSHA (39910015)** hereby declare that the Project Report entitled “**CATALYTIC OXIDATION OF VOLATILE ORGANIC COMPOUNDS (ETHYL BENZENE AND CHLROBENZENE) CONTAMINATED WATER USING MOLYBDENUM IMPREGNATED CARBON**” done by me under the guidance of **Dr S. SUPRIYA**, Associate Professor, Department of Chemistry, Sathyabama Institute of Science and Technology, Semmancheri, Chennai – 600119 and **Dr S. SWARNALATHA**, Senior Scientist, Environmental Science Lab, CSIR – Central Leather Research Institution, Adyar, Chennai – 600 020 is submitted in partial fulfilment of the requirements for the award of Master of Science in Chemistry.

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ACKNOWLEDGEMENT

I am pleased to acknowledge my sincere thanks to the Board of Management of **SATHYABAMA** for their kind encouragement in doing this project and for completing it successfully. I am grateful to them.

I convey my thanks to **Dr M. SUNDARESWARI**, Prof. and Dean, School of Science and Humanities and **Dr J. KARTHIKEYAN**, Head of the Department, Dept. of Chemistry for providing me necessary support and details at the right time during the progressive reviews.

I would like to express my sincere and deep sense of gratitude to my Project Internal Guide **Dr S. SUPRIYA**, Associate Professor, my External Guide **Dr S. SWARNALATHA**, Senior scientist, my mentor Mr N. PRABHAKARAN PhD scholar CSIR-Central Leather Research Institution for their valuable guidance, suggestions and constant encouragement paved way for the successful completion of my project work.

I wish to express my thanks to all Teaching and Non-teaching staff members of the Department who were helpful in many ways for the completion of the project.

C. PRATHYUSHA

ABSTRACT:

Volatile Organic Compounds (VOCs) has properties of toxicity, volatility and diffusivity possess a serious threat to human health and the eco-environment. Ethylbenzene and chlorobenzene VOCs are widely used in industrial sectors and discharged in wastewater without any proper treatment. The catalytic oxidation technology has been considered a highly efficient option for the treatment of VOCs. Molybdenum impregnated carbon matrix (Mo- CM) was prepared by the incipient wetness impregnation method and used for the catalytic oxidation of ethylbenzene and chlorobenzene (model VOC compounds) in presence of a strong oxidizing agent, hydrogen peroxide. This project also discusses the preparation of simulated VOC (ethylbenzene and chlorobenzene) containing water, with process optimization.

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CHAPTER – 1

INTRODUCTION

1.1 VOLATILE ORGANIC COMPOUNDS

Everyone is familiar with the word air pollution. The harmful contaminant that affects the environmental atmosphere is known as an air pollutant. Pollutants can be either natural or created by human activity such as trash or run-off waste produced by industries. A major contributor to air pollution is the evaporation of volatile organic solvents (VOCs) from untreated industrial wastewater discharge. Wastewater is extremely toxic that not only contaminate air but also water and soil. At present, wastewater treatment has received extensive research and scientists all over the world are studying the effects of these VOCs on ecosystems and trying to find ways for proper disposal. Volatile Organic Compounds are dominant pollutants with the characteristic of high vapour pressure at room temperature, low boiling point, easy diffusivity, toxicity and high volatility into the environment. The VOCs can be halogenated hydrocarbons, alcohols, aldehydes, aromatics, alkanes, ketones, olefins, ethers, esters, paraffin and sulfur-containing compounds etc., emits spontaneously from wastewater and react with NO_x to form photochemical smog, ground-level ozone and high global warming possibilities. The effect of VOCs on the atmosphere depends on the nature of VOCs, their concentration and emission sources. Ethylbenzene and chlorobenzene are widely used VOC in industries such as pharmaceuticals and discharged as wastewater into the environment. The emission of VOCs can be controlled by using methods based on recovery and destruction.

1.2 AROMATIC COMPOUNDS

Aromatic compounds such as benzene, toluene and ethylbenzene occur naturally in petroleum products, including gasoline and other fuels produced from crude oil. These compounds are also used in various products and formulations such as petrochemical, paints, perfume and detergents. Aromatic compounds are toxic, carcinogenic, mutagenic and also cause severe damage to the ozone layer by producing photochemical smog. Aromatic solvents commonly used in paints, thinners, gums, adhesives, lacquers and printing inks are classified as

priority pollutants. Inhalation of high-level aromatic compounds can cause unconsciousness, dizziness and even death.

1.3 ETHYL BENZENE

Ethylbenzene (C_8H_{10}) is an aromatic organic compound with the formula of $C_6H_5CH_2CH_3$. It is a colourless liquid with a gasoline odour and molar mass of 106.167 g/mol. Ethylbenzene is used primarily to make other chemicals mainly styrene. Ethylbenzene is found in manufactured products such as printing inks, insecticides, lacquers, paints, solvents in the rubber and chemical manufacturing industries. In this project, a high concentration of ethylbenzene was dissolved in water then catalytically oxidized using molybdenum catalyst. Initially, ethylbenzene was dissolved in distilled water by a stripping process then samples were taken at certain time intervals for analysis. The compressed atmospheric air used to strip out ethylbenzene from the liquid state to the vapour state. The ethylbenzene vapour dissolved in distilled water at optimum conditions, then the samples were analyzed in a UV-Visible spectrophotometer. The optimization of pH, LPM and time were studied to dissolve ethylbenzene in water.

1.4 HALOGENATED VOCs:

Halogenated VOCs are hazardous compounds due to their acute toxicity and resistance to degradation (Alonso et al.,). Halogenated VOCs includes chlorobenzene, dichloroethane, dichlorobenzene, chloromethane, chloroethylene, etc. generally these compounds are used in the formulation and processing of chemical extractants, paints, polymer synthesis, drug manufacturing, as cleaning agents and adhesives. These compounds are highly volatile and often have long atmospheric lifetimes (Aranzabal et al., 2014). Humans can be exposed to halogenated VOCs by drinking water, inhalation and adsorption during swimming (Huang et al.,). Halogenated VOCs have a significant impact on the destruction of the ozone layer and as a source of radicals in the atmosphere, which contributes to the greenhouse effects. The 100-years global warming potential (GWP) of halogenated VOCs range from 10 to 1800, which is much higher than that of CO_2 with a GWP of only one (Abedi et al.,).

1.5 CHLOROBENZENE:

Chlorobenzene is an aromatic organic compound with the molecular formula C_6H_5Cl . Its molecular weight is 112.56 g/mol. It is a colourless solvent, flammable liquid and widely used as an intermediate in the manufacture of other chemicals. Chlorobenzene is also known as chlorobenzol, monochlorobenzene and benzene chloride found in products like paints, waxes, polishes, used in the production of chloronitrobenzene, diphenyl ether, as a solvent in rubber and as an inert solvent. In this project, a high concentration of the chlorobenzene is dissolved in water by orbital shaking process and the samples were taken at certain time intervals for UV analysis. The chlorobenzene was dissolved in distilled water at optimum conditions then samples were analyzed in a UV-Visible spectrophotometer. The optimization of pH, LPM and time were studied to dissolve chlorobenzene in water.

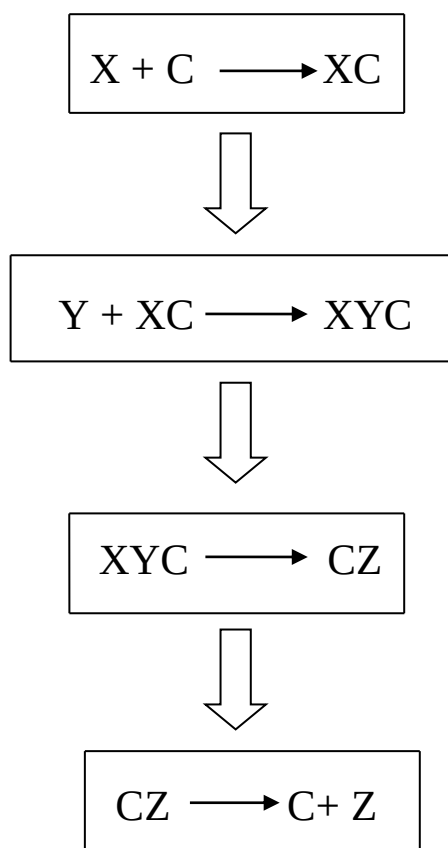
1.6 CATALYSTS:

Catalyst is a substance that is added to a reaction to increasing the rate of the reaction, which is not consumed by the catalyzed reaction and can continue to act. In general, chemical reactions occur faster in the presence of a catalyst because the catalyst will provide an alternative reaction pathway with lower activation energy than the non-catalyzed mechanism. In the catalytic mechanism, the catalyst usually reacts to form a temporary intermediate, which then regenerates the original catalyst in a cyclic process. A substance that provides a mechanism with higher activation energy does not decrease the rate because the reaction can still occur by the non-catalyzed route. An added substance that does reduce the reaction rate is not considered as a catalyst but as a reaction inhibitor.

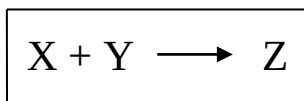
In the presence of a catalyst, less free energy is required to reach the transition state, but the total free energy from reactants to products does not change. A catalyst may participate in multiple chemical transformations. The effect of a catalyst may vary due to the presence of other substances known as inhibitors (which reduces the catalytic activity) or promoters (which increases the activity and also affect the temperature of the reaction).

Catalyzed reactions have lower activation energy (rate-limiting free energy of activation) than the corresponding non-catalyzed reaction, resulting in a higher reaction rate at the same temperature and for the same reactant concentration. As in the case of any other chemical reaction, the reaction rate depends upon the frequency of contact of the reactants in the rate-determining step.

Usually, the catalyst participates in the slowest step. The rate of the reaction depends upon the amount of catalyst. Although catalyst is not consumed by the reaction itself and they might be inhibited, deactivated and destroyed by a secondary process.



Hence, the overall reaction is



Whereas, X is the reactant material

C is the catalyst

Y is another reactant material

XYC is the formed intermediate

Z is the product

1.6.1 MOLYBDENUM IMPREGNATED CARBON MATRICES (Mo-CM):

Activated carbons are materials of great importance in technological applications of multidisciplinary fields ranging from adsorption to catalytic processes. Its extensive use is known from the combination of a well-developed pore network along with the presence of heteroatoms. Conventional activation methodologies can be physical (using steam or CO₂) or chemical (KOH, ZnCl₂ and H₃PO₄) methods commonly used. Carbon matrix is doped with molybdenum to increase its catalytic properties. The Mo-CM are used as catalysts to degrade the ethylbenzene contaminated water and it was compared with CM (without molybdenum). Molybdenum content in the prepared catalyst was analyzed using ICP-OES.

1.7 TREATMENT OF VOCs:

Several different technologies have been developed to control the emission of VOCs into the atmosphere including thermal oxidation, adsorption, absorption and condensation. One of the best options is the process of catalytic oxidation. Catalytic oxidation is a process in which compounds are oxidized using catalysts. Common applications of catalysts involve the oxidation of organic compounds into water and carbon dioxide. The oxidation of ethylbenzene by the addition of hydrogen peroxide produces hydroxyl radical with Mo-CM. The catalyst absorbed the ethylbenzene then the hydroxyl radical cleaves the bond of the organic compounds.

CHAPTER – 2

LITERATURE SURVEY

2.1 Literature survey on oxidation of ethylbenzene

The oxidation of ethylbenzene is an important raw material for the production of perfumes, pharmaceuticals, resins and alcohol. It is also an important route to utilize ethylbenzene effectively in the xylene stream of the petrochemical industry. Muhannad Shahzad Kamal et al. reported catalytic oxidation of VOCs and the elimination of volatile organic compounds using catalysts in the presence of hydrogen peroxide. Chaudhary and Sharma, (2020) reported a Study of ethylbenzene oxidation over polymer- hybrid supported Co (II) and Cu (II) complexes. They reported ethylbenzene conversion (83.65 %), the temperature at 100 °C with reuse of catalyst was three times. Liu et al., (2019) reported in situ fabrication of highly active γ -MnO₂/SmMnO₃ catalyst for deep catalytic oxidation of gaseous benzene, ethylbenzene, toluene, and o-xylene. They reported the BTEX oxidation resulted in the generation of numerous by-products. Xie et al., (2016) reported on hierarchical flower-like Co-Cu mixed metal oxide microspheres as highly efficient catalysts for selective oxidation of ethylbenzene. They reported a good catalytic conversion of ethylbenzene and other alkanes at a temperature from 100-400°C. The high-temperature oxidation methods require special equipment whereas the liquid phase does not. The liquid-phase oxidation of ethylbenzene by oxygen or air using heterogeneous transition metal catalyst was reported in this study. These reactions were found to proceed under relatively mild conditions and feasible.

2.2 Literature survey on oxidation of chlorobenzene:

Chlorinated VOCs are the most harmful chemicals. The catalytic behaviour of the reaction was the interaction between the catalyst and the reactant itself. Because of high volatility and toxicity, strong stability and low reactivity CVOs are considered to be an important group of VOC pollutants. Liu et al., (2020) reported on enhanced catalytic oxidation of chlorobenzene over MnO₂ grafted in situ by rare earth oxide: surface doping induces lattice oxygen activation, the chlorobenzene oxidized up to 325°C for a long time of 18h. Weng et al., (2017) reported on Catalytic Oxidation of Chlorobenzene over MnxCe_{1-x}O₂/HZSM-5

Catalysts. They used reaction temperature from 100 to 400°C for the oxidation of chlorobenzene. Liu and Pan, (2012) reported supercritical water oxidation of chlorobenzene in an anticorrosive fused- capillary reactor at a temperature of 450 °C. Tian et al., (2010) reported the Preparation of MnOx/TiO₂ composites and their properties for catalytic oxidation of chlorobenzene at a temperature between 100-300°C. The catalytic oxidation of chlorobenzene at high temperature is not a feasible method for industrial-level scale. The liquid-phase oxidation of chlorobenzene using heterogeneous transition metal catalyst is low cost and feasible method to implement at the industrial level. This work deals with the catalytic oxidation of chlorobenzene over carbon matrix and molybdenum carbon matrix.

CHAPTER – 3

SCOPE AND OBJECTIVES OF THE PROJECT

Scope:

Preparation of VOC contaminated water using ethylbenzene and chlorobenzene and to treat the prepared VOCs contaminated waters through catalytic oxidation using CM and Mo-CM catalysts.

Objectives:

- To prepare ethylbenzene contaminated water and its optimization studies.
- To prepare chlorobenzene contaminated water and its optimization studies.
- To synthesis Mo- CM catalyst.
- To study the catalytic oxidation of ethylbenzene contaminated water using CM and Mo-CM.
- To study the catalytic oxidation of chlorobenzene water using CM and Mo-CM.

CHAPTER – 4

EXPERIMENTAL SECTION:

4.1 MATERIALS USED:

Hot air oven (Swathi enterprises) used to dry samples at 110°C, Muffle furnace (Indfurr Superheat Furnaces) used for the calcination of catalyst at 500-700°C. All chemicals of ethylbenzene, chlorobenzene and hydrogen peroxide 30% bought from AR grade SDFINE chemicals. The molybdenum chloride bought from Alfa Acer chemicals of 99.99% pure. All chemicals are used without further purification.

4.2 PREPARATION OF MOLYBDENUM IMPREGNATED CARBON MATRIX (Mo- CM):

The Mo- CM catalyst was prepared using rice husk by incipient wetness impregnation method. The Molybdenum chloride solution was soaked with rice husk and then it was kept overnight for the absorption of molybdenum by capillary action. The metal-soaked husk was dried in a hot air oven at 110°C until completely dry then it was pre-carbonized at 400°C for 4h at a heating rate of 5°C/min. The pre-carbonized molybdenum carbon was subject to activation, it was mixed well with phosphoric acid then activated at 700°C for 1h at a heating rate of 5°C/min after cooling it was labelled as Mo- CM. The plain carbon matrix (CM) was prepared side by side without the addition of molybdenum in the husk by following the procedure reported by Maharaja et al (2017).

4.3 FABRICATION OF REACTOR FOR THE DESTRUCTION OF ETHYLBENZENE AND CHLOROBENZENE:

The two catalytic reactors (CR) were fabricated using a PVC tube as shown in Fig.1 with a total volume of 200ml and a working volume of 100ml. The CR bottom was packed with coarse quartz aggregate followed by fine aggregate packed then the catalyst of CM or Mo-CM was packed. The VOC water was sprinkled on top of the reactor and treated water was collected from the bottom of the reactor for analysis. The optimization studies such as pH, time

and different LPM were studied for treatability. The VOCs contaminated water treated through CR which was packed with Mo CM, the treatability was compared with CM packed CR.

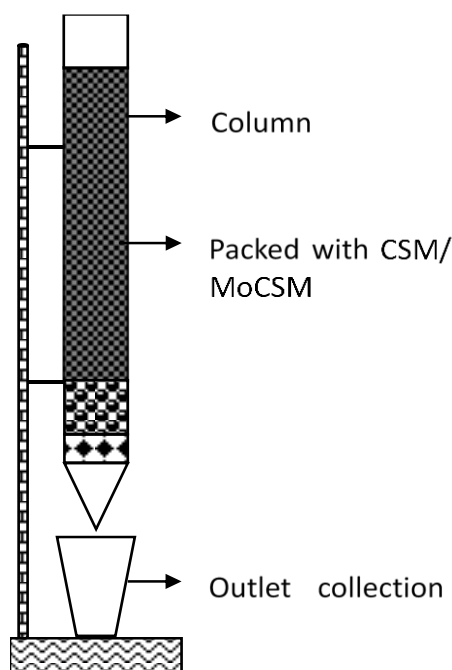


Fig.1: catalytic oxidation reactor for the destruction of VOCs

4.4 PREPARATION OF ETHYLBENZENE CONTAMINATED WATER:

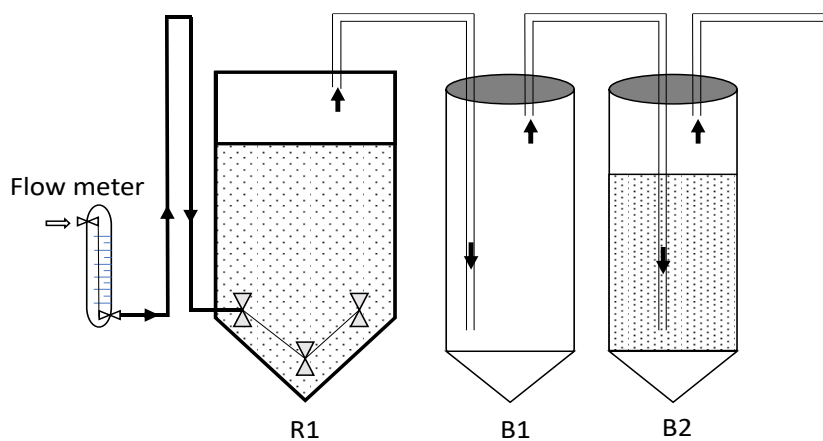


Fig. 2: stripper reactor to dissolve ethylbenzene in water

The closed stripper reactor was designed as reported by Natarajan et al., (2020). Ethylbenzene was dissolved in distilled water by the stripping process (Fig.2). 100 ml of Ethylbenzene was taken in a stripper reactor (R1) and dissolved in 500 ml of distilled water taken in a glass bottle (B2). The optimization of pH, LPM and time were studied by taking samples for certain intervals of time and analyzed under a UV-Visible spectrophotometer. On observing the intensity of the absorption peaks the optimum pH, LPM and time was fixed.

At first, 100 ml ethylbenzene was dissolved in 500 ml of distilled water which was of different pH values (4, 7,9,11.6) and aeration about 1 LPM. The 11.6 pH selected as the pharmaceutical wastewater pH was 11.6. The samples are taken for 450 minutes. Those samples are analyzed under a UV-Visible spectrophotometer and on observing the peaks, the optimum pH value was fixed. Similarly, ethylbenzene was dissolved in distilled water which has the optimum pH but by varying the aeration (0.5, 1, 1.5, 2) LPM. Again, the samples that are taken for certain time intervals have been analyzed under a UV-Visible spectrophotometer and the optimum LPM was fixed. The absorption peaks of ethylbenzene contaminated water at optimum pH and optimum LPM showed that the maximum intensity was reached at a particular time. That time has been noted for optimization of time.

4.5 PREPARATION OF CHLOROBENZENE CONTAMINATED WATER:

1 ml of chlorobenzene was added to 100 ml of distilled water which taken in a conical flask and dissolved by shaking process. The solution was kept in a shaker and optimum conditions studied. At first, 1 ml of chlorobenzene was dissolved in 100 ml of distilled water by shaking at 25°C and 100 rpm, the samples are collected at different intervals of time for analysis. These samples are analyzed under a UV-Visible spectrophotometer. The optimization of the volume of Chlorobenzene was studied by varying the volume of CB (0.1, 0.2,0.4,0.8, 1). Similarly, the samples are taken at intervals of time and examined for UV analysis. The optimization of RPM and temperature was also studied by varying the RPMs (50, 70, 120, 100) and temperatures (20, 25, 30, 35) similarly in different intervals of time samples are collected. These samples are studied under a UV-Visible spectrophotometer.

4.6 CATALYTIC OXIDATION OF ETHYLBENZENE CONTAMINATED WATER:

The ethylbenzene contaminated water at optimized condition was treated with the catalyst of CM and Mo-CM. The catalysts CM and Mo-CM are packed separately in two different columns. The ethylbenzene contaminated water was allowed to pass through the catalyst columns at different HRT (60 minutes, 40 minutes, 20 minutes, 10 minutes) with various RPM (1.3, 2, 4, 8). Similarly, H_2O_2 as an external oxidant was added to the ethylbenzene contaminated water and allowed to pass through the catalyst columns with 0.2 ml/L of peroxide. The optimum HRT was fixed by observing the absorption peaks obtained from the UV-Visible spectroscopy analysis. The optimization studies for the volume of peroxide and pH for the degradation of ethylbenzene were also performed. The degradation of ethylbenzene with the addition of peroxide was performed at optimum HRT and the collected samples are analyzed under UV-Visible spectrophotometer and HPLC.

4.7 CATALYTIC OXIDATION OF CHLOROBENZENE CONTAMINATED WATER:

The chlorobenzene contaminated water at optimized condition was treated with the catalyst of CM and Mo- CM. The catalysts CM and Mo- CM are packed separately in two different columns. The chlorobenzene contaminated water was allowed to pass through the catalyst columns at different HRT with various RPM. Similarly, H_2O_2 as an external oxidant was added to the chlorobenzene contaminated water and allowed to pass through the catalyst columns with 0.2 ml/L of peroxide. The optimum HRT was fixed by observing the absorption peaks obtained from the UV-Visible spectroscopy analysis. The optimization studies for the volume of peroxide and pH for the degradation of chlorobenzene were also performed. The degradation of ethylbenzene with the addition of peroxide was performed at optimum HRT and the collected samples are analyzed under UV-Visible spectrophotometer and HPLC.

CHAPTER – 5

RESULTS AND DISCUSSIONS:

Characterization of Mo- CM

Fourier-transform infrared spectroscopy (FT-IR)

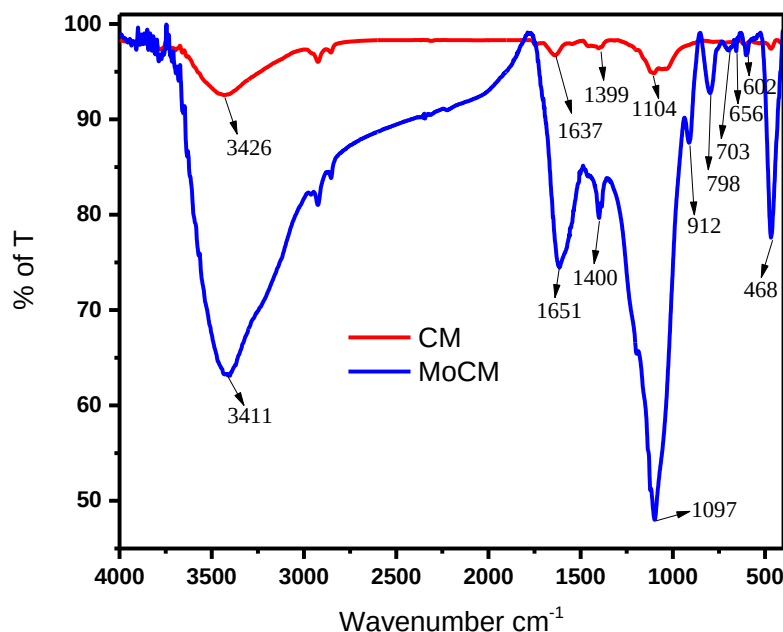


Fig 3: FT-IR analysis

The FT-IR spectrum of CM (Fig.3) shows a peak at 3426 cm⁻¹ due to stretching of -SiOH groups, it was shifted to 3411cm⁻¹ in Mo CM due to metal addition. The C-O group present in CM (1637 cm⁻¹) gets shifted in Mo CM (1651cm⁻¹) because of the carbon atom bonded with the metal atom (Bhaisare et al., 2016; de la Puente et al., 1998; Karthikeyan et al., 2015). The peak at 1104 cm⁻¹ of CM corresponds to the Si-O-Si stretching which gets shifted in Mo CM to 1097 cm⁻¹ due to metal incorporation. There are no peaks in the region of 900-500cm⁻¹ in CM but five new peaks formed in Mo CM of 602, 656,703,798,912cm⁻¹ because of the Mo ion incorporation. It has been reported by many researchers that the peaks between 500-991cm⁻¹ correspond to the MoCx, M=O, Mo-O-Mo vibrations of crystalline MoOx (Federation, 2004; Kumar et al., 2010; Rathod et al., 2010; Sohn et al., 2007). The sharp peaks in the region 800–600cm-

1corresponding to the stretching vibrations of Mo-O-Mo (Bhaisare et al., 2016). The FT-IR spectrum confirms the presence of molybdenum oxide on the carbon matrix.

OPTIMIZATION STUDIES FOR THE PREPARATION OF ETHYLBENZENE WATER

OPTIMIZATION OF pH:

100 ml of ethylbenzene was stripped to dissolve in 500 ml of distilled water with different pH values (4, 7, 9, 11.6) with constant aeration of 1 LPM. The samples are taken at different time intervals and analyzed under a UV-Visible spectrophotometer. On observing the absorption peaks, the maximum intensity that goes above 0.3 (absorption)obtained for pH 7 than other pH. So, it was fixed as optimum for pH (Fig.4).

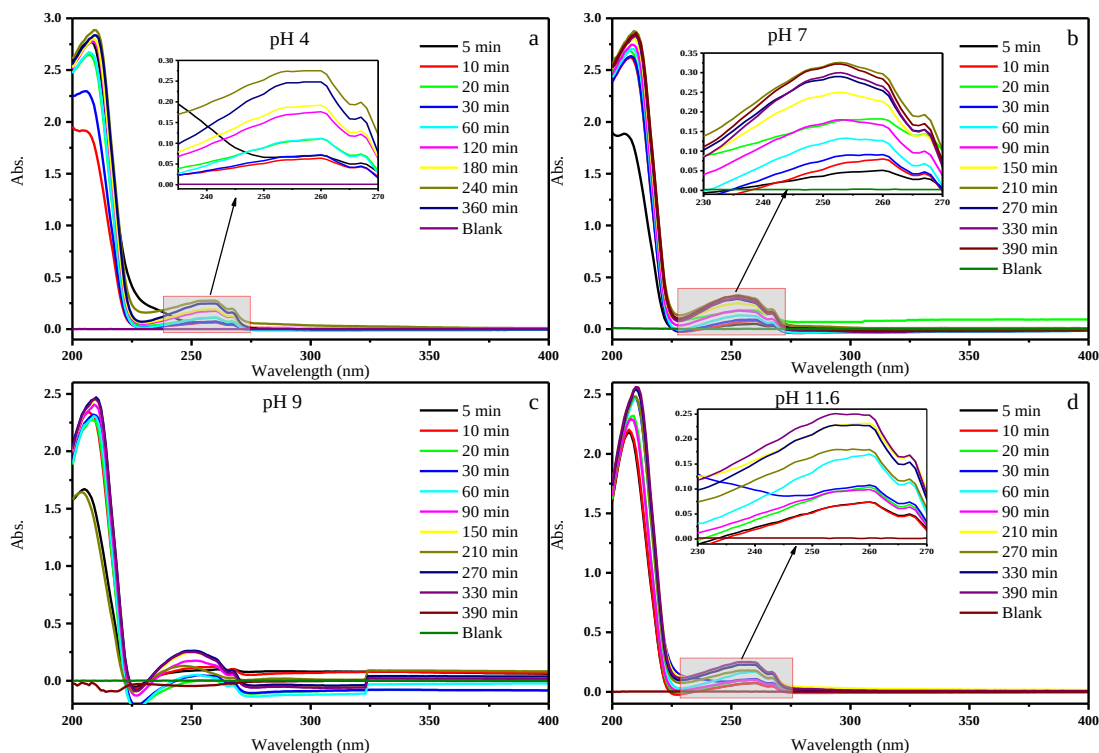


Fig 4: UV analysis for optimization of pH

OPTIMIZATION OF LPM:

The optimization of LPM was studied by varying LPMs (0.5, 1, 1.5, 2). The 100 ml of ethylbenzene was stripped to dissolve in 500 ml of distilled water at optimum pH (neutral). The samples are taken at different intervals of time and analyzed under a UV-Visible spectrophotometer. On observing the absorption peaks, the maximum intensity that goes up to 1.3 was obtained around 450 minutes for 2 LPM. Thus, the optimum LPM has been fixed (Fig.5).

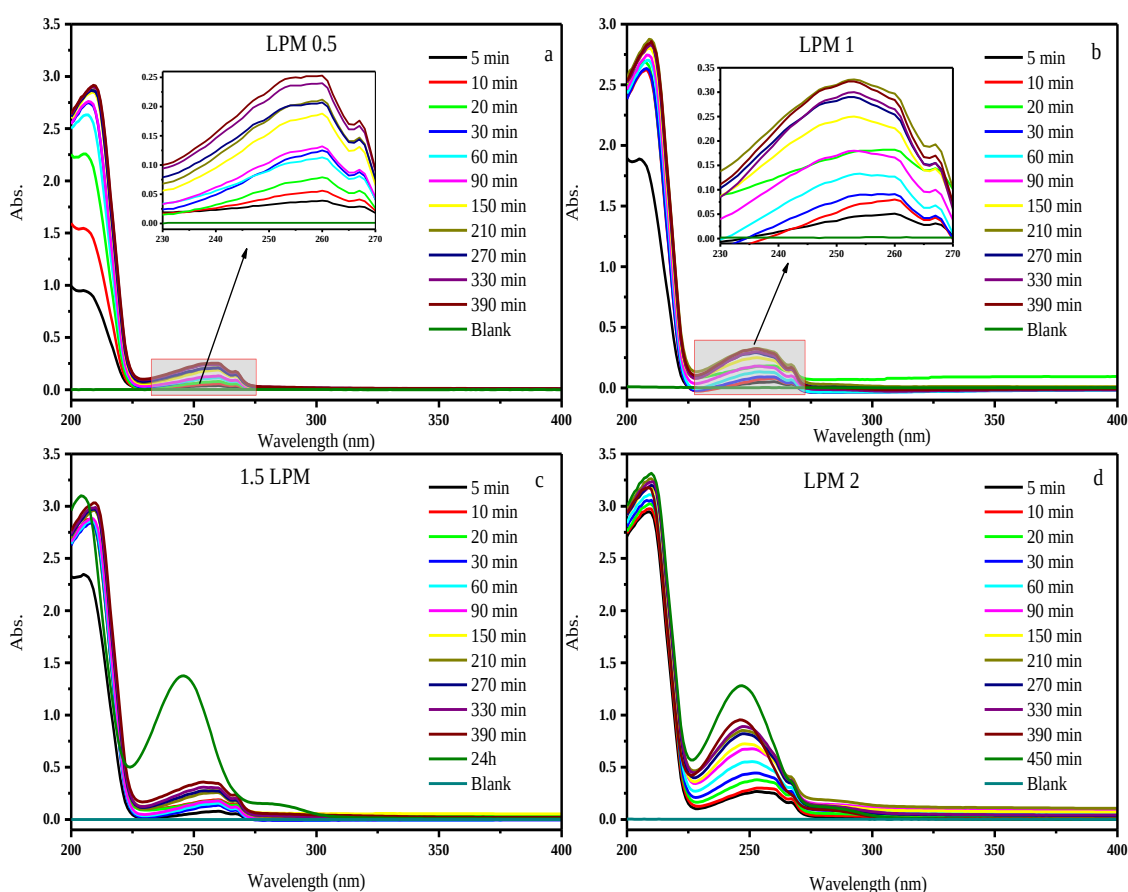


Fig 5: UV analysis for optimization of LPM

OPTIMIZATION OF TIME:

100 ml of ethylbenzene dissolved in 500 ml of distilled water at optimum pH and optimum LPM. The samples are taken at different time intervals and analyzed under a UV-Visible spectrophotometer. From the above graphs, the maximum intensity was found at 450 minutes. So, it was fixed as optimum for time for further studies.

OPTIMIZATION STUDIES FOR TREATMENT OF ETHYLBENZENE

OPTIMIZATION OF HRT FOR THE TREATMENT OF ETHYLBENZENE CONTAMINATED WATER WITH CM AND Mo- CM:

The ethylbenzene contaminated water with and without the addition of peroxide was treated with Carbon matrix and Molybdenum Carbon matrix at different HRT with various RPM. The samples are taken at different HRT (60 minutes, 40 minutes, 20 minutes, 10 minutes) with RPM of (1.3, 2, 4, 8) respectively and analyzed under a UV-Visible spectrophotometer. On observing the absorption peaks, the great performance on the degradation of ethylbenzene was found to be at 10 minutes HRT with 8 RPM after peroxide was added (0.2ml/L) (Fig.6).

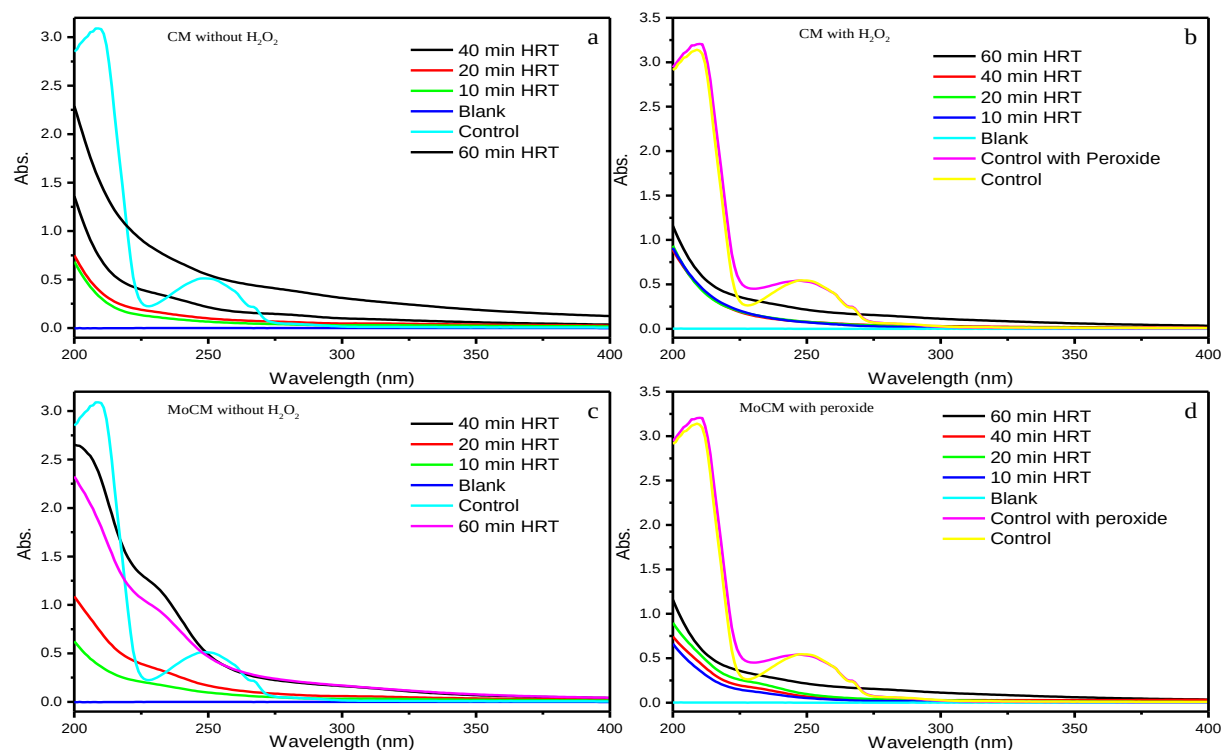


Fig 6: UV analysis for optimization of HRT for the treatment of ethylbenzene

OPTIMIZATION OF PEROXIDE DOSAGE IN Mo-CM:

The hydrogen peroxide addition was optimized by varying the H_2O_2 dosage such as 0.1 ml/L, 0.2 ml/L, 0.3 ml/L, 0.4 ml/L to dissolved ethyl benzene water through the Mo- CM column at optimum HRT i.e., 10 minutes. The samples with different volumes of peroxide are taken at optimum HRT and are analyzed under a UV-Visible spectrophotometer. On observing the absorption peaks of degradation of ethylbenzene with the addition of peroxide with different volumes, 0.2 ml/L of H_2O_2 was fixed as an optimum.

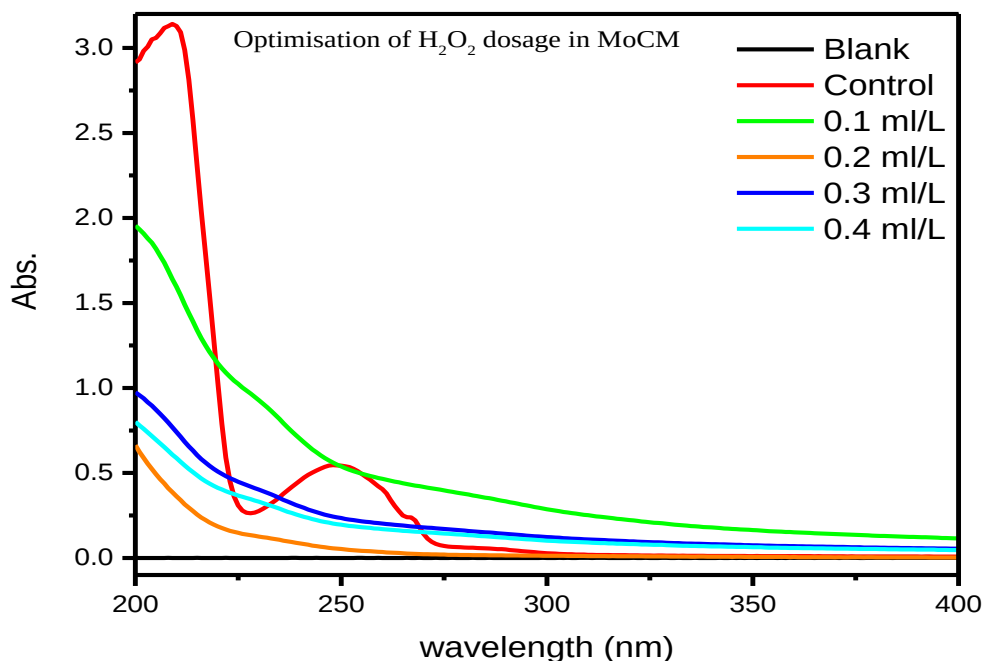


Fig 7: UV analysis for optimization of peroxide dosage in Mo-CM

OPTIMIZATION OF pH FOR DEGRADATION OF ETHYL BENZENE:

Optimization of pH for degradation of ethylbenzene was studied at different pH through Mo- CM column at 10 minutes HRT. The samples are taken at different optimum HRT and are analyzed under a UV-Visible spectrophotometer. Observing the absorption peaks of ethylbenzene water adjusted to different pH levels allowed to degrade after the addition of an optimum volume of peroxide. Neutral pH was fixed as the optimum pH for degradation of ethylbenzene with peroxide in Mo- CM.

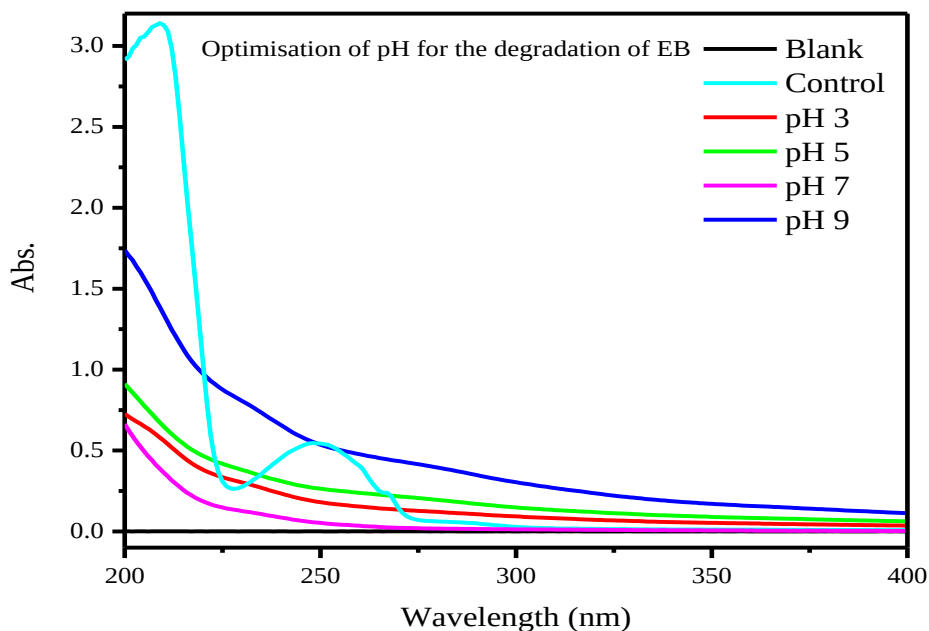


Fig 8: UV analysis for optimization of pH for the degradation of EB

HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY ANALYSIS:

The HPLC analysis for EB contaminated water and treated water were studied (Fig.6). It was found that the EB standard gave a broad peak at RT of 8.2 whereas the EB contaminated water at optimum conditions obtained at RT of 6.9. The decrease in RT due to the increase in polarity of the EB in the dissolved state resulted in quick elution. The EB water was added with hydrogen peroxide and kept for 1h after that the HPLC spectrum recorded. The same peak of RT 6.9 was also observed in peroxide addition, which indicates the EB has not degraded in presence of hydrogen peroxide alone. . In catalytic oxidation of EB using Mo CM, the EB was completely oxidized which was indicated by elimination RT at 6.7 and formation of degraded products at RT 5.4, lower molecular weight compound. Whereas the CM ethylbenzene treated water provides numerous degraded compounds along with non-degraded EB. Thus, it can be concluded that the molybdenum impregnation in the matrix can only able to degrade the EB completely (Fig.9).

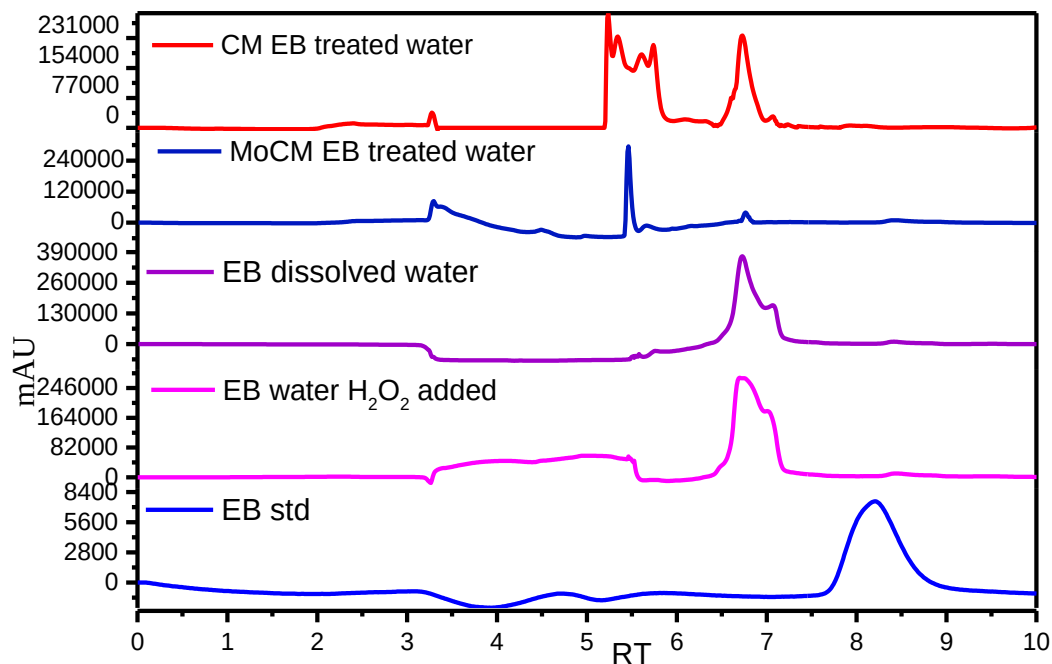


Fig 9: HPLC analysis for the treated EB contaminated water

On analyzing COD, it was found that Mo-CM has a removal efficiency of 89% in degradation of ethylbenzene at the time of 10 minutes.

OPTIMIZATION STUDIES FOR TREATMENT OF CHLOROBENZENE

OPTIMIZATION OF TIME:

1 ml of chlorobenzene was added to 100 ml of distilled water and kept on a shaker at 25°C and 100 rpm. The samples are taken at different intervals of time. As the peak obtained at 100 minutes gives maximum intensity it was fixed as optimum (Fig.10).

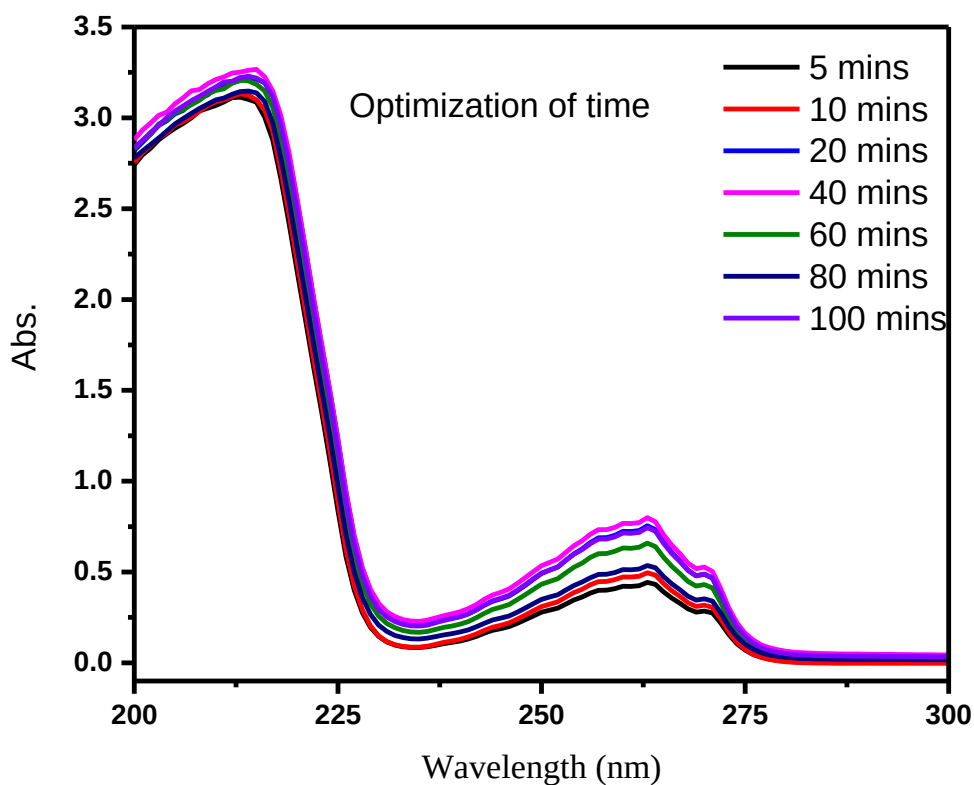


Fig 10: Optimization of time with 1 ml CB and 100 ml distilled water at 25°C

OPTIMIZATION OF VOLUME OF CHLOROBENZENE:

A different volume such as 0.1ml, 0.2ml, 0.4ml, 0.6ml, 0.8ml and 1 ml of chlorobenzene was added to 100 ml of distilled water and kept on the shaker at 25°C and 100 rpm. The samples are taken at different intervals of time. As the peak obtained by 0.4 ml of CB showed maximum intensity. It was fixed as optimum for volume (Fig.11).

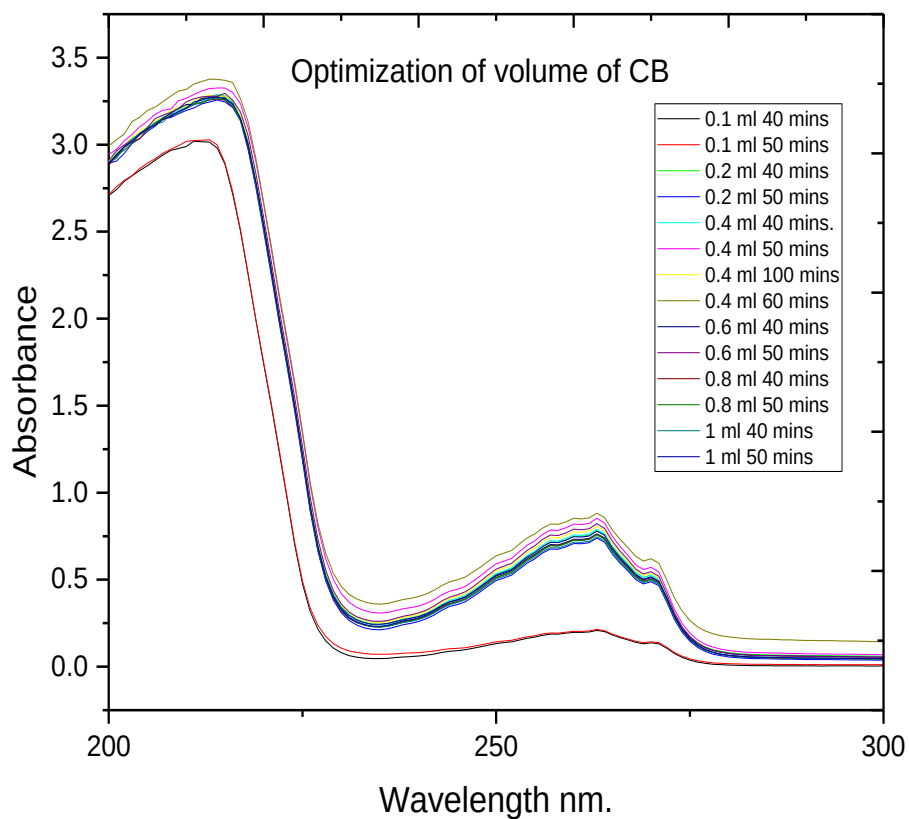


Fig 11: Optimization of the volume of CB dissolving in 100 ml distilled water at 25°C

OPTIMIZATION OF RPM:

The optimization of RPM for dissolving the CB studied at different RPM of 50, 70, 90 and 100 with a constant of CB 0.4ml and temperature 25°C. The samples were analyzed at different time intervals it was found that the 70 RPM gave maximum intensity when compared with other RPM so it was fixed as optimum for further studies (Fig.12).

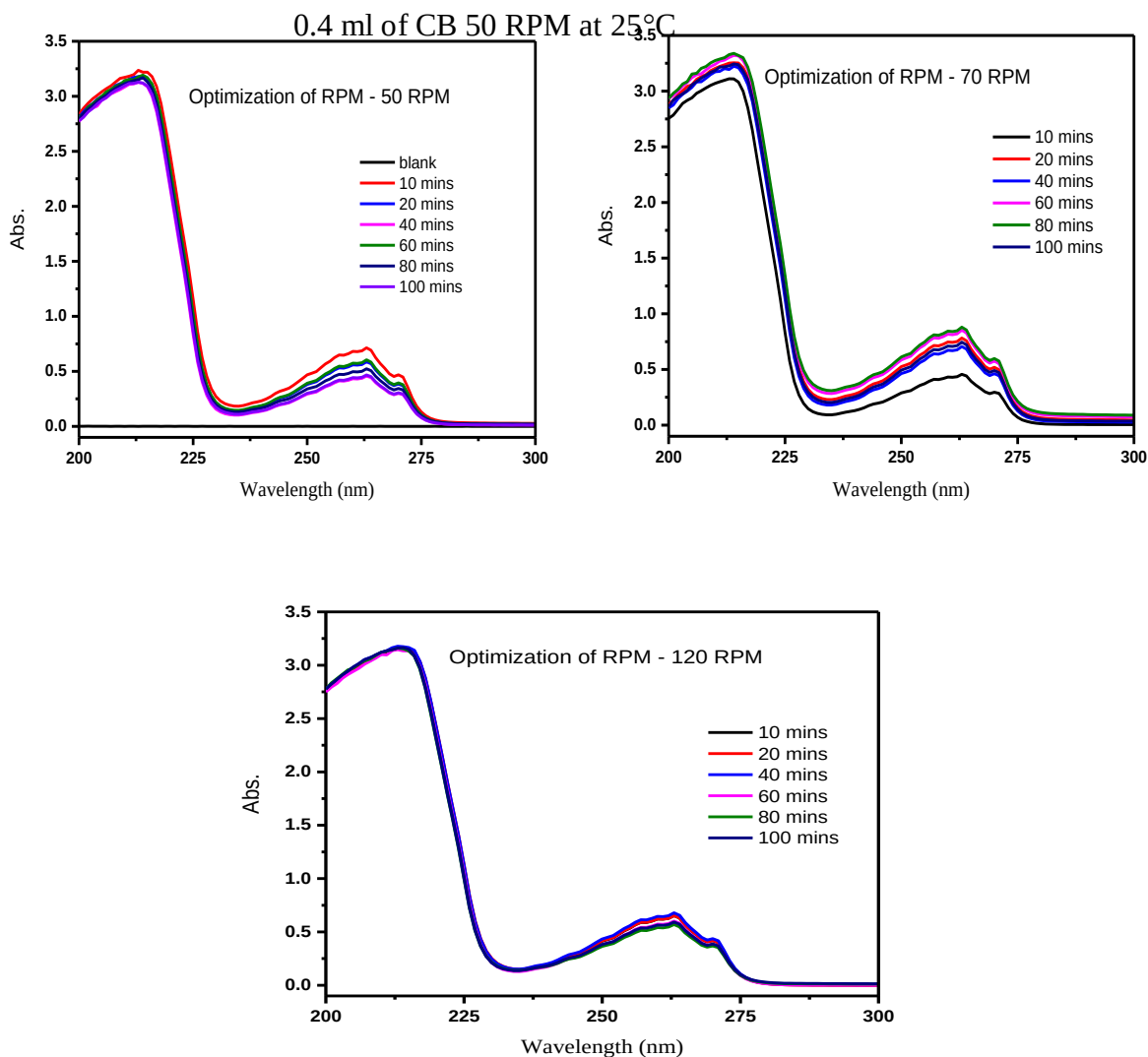


Fig.12: Optimization of RPM at 50, 70 and 120 with constant of 0.4 ml of CB and 25°C

OPTIMIZATION OF TEMPERATURE:

The optimization of temperature for dissolving the CB studied at different temperature of 20°C, 25°C, 30°C and 35°C with a constant of CB 0.4ml and temperature 70 RPM. The samples were analyzed at different time intervals it was found that the 25°C gave maximum intensity when compared with other temperatures so it was fixed as optimum for further studies (Fig.13).

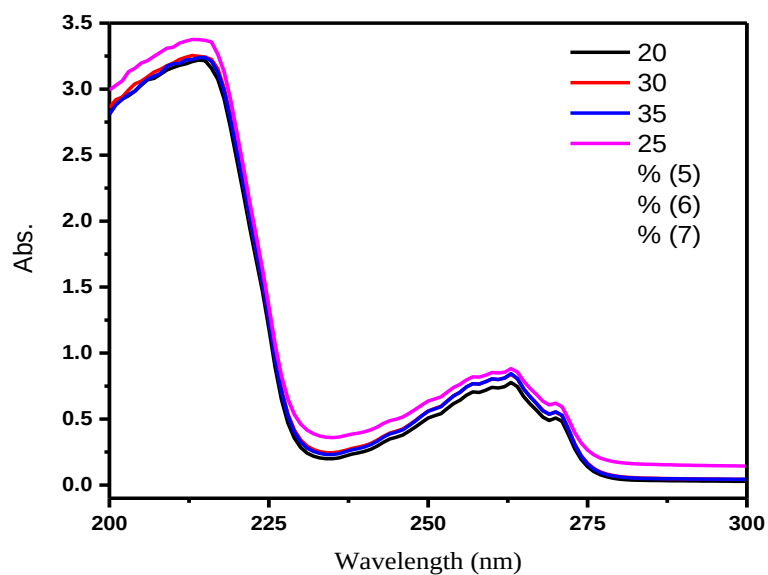


Fig 13: Optimization of temperature to dissolve constant volume 0.4 ml of CB at 70 RPM.

OPTIMIZATION OF HRT FOR THE DEGRADATION OF CB:

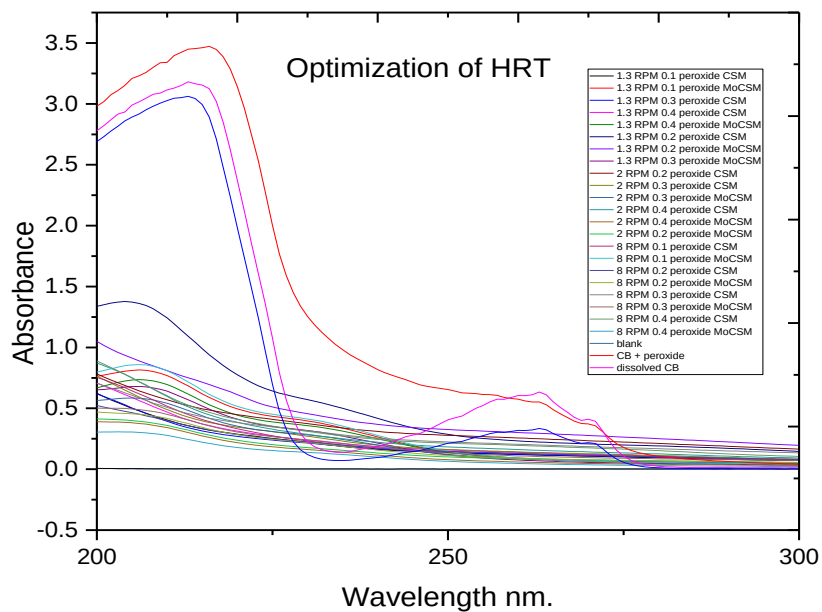


Fig 14: Optimization of HRT to degrade chlorobenzene.

The optimization of HRT for the degradation of chlorobenzene performed by adding peroxide and passing the chlorobenzene dissolved water through CM and Mo-CM columns at different hydraulic retention time (1.3, 2, 8) RPMs. The samples were analyzed under UV-Visible spectrophotometer and the peaks were absorbed. The peak of 0.4 ml H₂O₂ at 8 RPM showed the highest degradation. Hence, 8 RPM and 0.4 ml of peroxide is fixed as optimum.

HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY ANALYSIS:

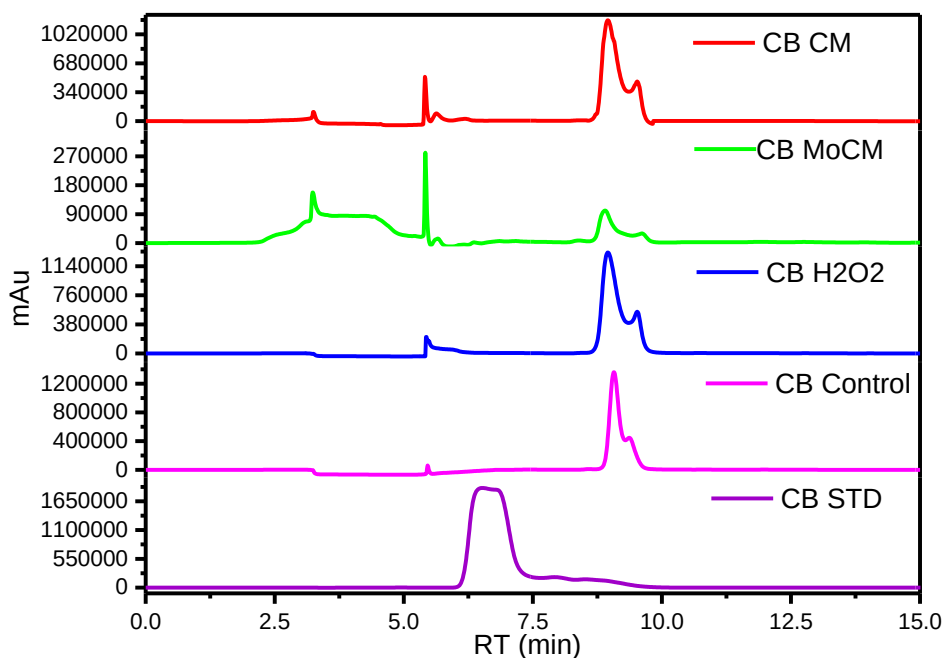


Fig 15: HPLC analysis for the treated CB contaminated water

The HPLC analysis for CB contaminated water and treated water was studied. It was found that the CB standard gave a broad peak at RT of 6.9 whereas the CB contaminated water at optimum conditions obtained at RT of 8.7. The increase in RT due to the decrease in polarity of the CB in the dissolved state resulted in quick elution. The CB water was added with hydrogen peroxide and kept for 1 hour after that the HPLC spectrum recorded. The same peak of RT 8.5 was also observed in peroxide addition, which indicates the CB has not degraded in presence of hydrogen peroxide alone. In catalytic oxidation of CB using Mo-CM, the

chlorobenzene was completely oxidized which was indicated by elimination RT at 8.7 and formation of degraded products at RT 8.4, lower molecular weight compound. Whereas the Mo-CM chlorobenzene treated water provides few degraded compounds along with non-degraded CB. Thus, it can be concluded that the molybdenum impregnation in the matrix can only able to degrade the CB completely (Fig.15). On analyzing COD, it was found that Mo-CM has a removal efficiency of 88% in degradation of chlorobenzene at the time of 10 minutes.

FUTURE WORK TO DO:

Proceed the same with toluene, dichlorobenzene and few other volatile organic compounds.

GEO-TAGGED PHOTOS:

Image (a): HPLC

Image (b): UV-Visible spectrophotometer

Image (c): Catalyst columns for the treatment of EB and CB contaminated water.

Image (d): Molybdenum impregnated Carbon matrix

GEO-TAGGED PHOTOS



CHAPTER – 6

CONCLUSION:

The toxic VOCs were oxidized using a heterogeneous catalyst, MoCM at room temperature. The molybdenum carbon matrix was synthesized from rice husk. The model VOC contaminated water using ethylbenzene and chlorobenzene were prepared along with optimization studies. It was found that optimum conditions for preparing EB contaminated water were 2 LPM, time 450 min and pH 7. The optimum condition for the oxidation of EB contaminated water was recorded as time 10 min, peroxide 0.2ml/L and pH 7. It was found that the treatment efficiency of EB over Mo- CM was 89% at room temperature. The HPLC spectrum and UV spectrum supported the complete degradation of EB oxidation. Similarly, the preparation of chlorobenzene contaminated water was recorded at the optimum condition of 0.4ml of CB, RPM 70, temperature 25°C, and pH 7. The optimum oxidation conditions for the treatment of chlorobenzene were recorded as 10 min, 0.4 ml/L hydrogen peroxide and pH 7.0. Thus, the VOCs contaminated water was successfully treated using a synthesized molybdenum impregnated carbon matrix.

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