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Photo Catalytic Deprivation to Methylene Blue via ZnO Nano Particles by Advanced Oxidation Process

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Abstract

Photo catalytic degradation of dye work was studied using ZnO nano particles under UV irradiation. Chemical precipitation method was used for synthesis of zinc oxide and characterization studies were done by XR-diffraction technique (XRD), scanning electron micro scope (SEM) and band gap was determined using UV-visible spectrophotometer. Studies were conducted varying the photo catalyst, methylene blue concentration and residual concentration of methylene was monitored using spectrophotometer. The products were found by high performance liquid chromatography (HPLC). The peak photo degradation of methylene blue at concentration [0.75x10^{-5}] M was observed with dosage of 0.05g/100ml. In addition reusability aspects of nano particles where also studied which revalue's that reused nano particles exhibited same results as that of virgin particles.

Keywords: AOP, contaminants, degradation, methylene blue, ZnO Nano particles.

Introduction

Clean unadulterated water does not occur in the environment. Water contamination is a any undesirable alter in the state of water, contaminated with destructive substances. It is the second mainly vital environmental concern next to air pollution[1]. Any alteration in the physical, chemical and biological characteristics of water that has a harmful consequence on the existing things is termed as 'water pollution. As a outcome of the unwanted human activities, water pollution is a mounting hazard in several developing countries. One more staid aspect of water pollution is that which is caused by human activity and industrialization. There are also various micro genetic agents that include bacteria, viruses and protozoa which can also origin water pollution and many cause a variety of water borne diseases. With upward urbanization and increasing population, pollution has become the prevalent environmental challenge[2].

Dyes are normally used in the many industries including printing process, textile, plastic, cosmetics and the overload dyes are released into the effluent stream as waste after colouring the fabric. Most of the unspent dyes produces undesirable effluents and usually discharged without treatment[3]. The released wastes are in high concentrated and complex state causing difficulty in handing for future treatment. Most modern synthetic dyes are fairly stable even to the sunlight with some of them being carcinogenic[4]. The main objective of the study was degradation of methylene blue through reaction oxidative process.

Application of nano science to water treatment proves to be hopeful technology. As it can efficiently eliminate finest contaminants upto 300nm also they are capable for immobilising pathogenic organic lethal compounds. Nanotechnology is art of controlling and manipulating matter at individual atomic level as well as at super molecular levels. There by creating materials with fundamentally new properties as well as function due to their small structure. Nano structures exhibits numerous development over their regular sized materials and their by assist in environmental remediation[5]. Since the decay of water into hydrogen and oxygen on zinc oxide photo catalysis has been reputable as an efficient progression for the mineralization of contaminated organic compounds, harmful inorganic constituents and bacteria disinfection outstanding to the strong oxidizing agent, i.e., hydroxyl radical (OH•). Several metal oxide semiconductors like titanium dioxide (TiO_2), zinc oxide (ZnO), tungsten oxide (WO_3), strontium titan ate ($SrTiO_3$), and hematite (Fe_2O_3) are confirmed to be energetic photo catalysts. Mainly of these semiconductor photo catalysts have band gap in the ultraviolet (UV) section, i.e. corresponding to or larger than 3.2 ev (λ = 387 nm). Therefore they promote photo catalysis upon illumination with UV radiation[6]. Conversely the basic mechanism that takes place in photo catalytic reaction is the production of electron hole couple and its purpose, Which process as when a photo catalyst is illuminated by the light stronger than its band gap energy, electron–hole pairs diffuses out to the face of photo catalyst and participates in the chemical response with electron donor and acceptor. Individual's free electrons and holes convert the contiguous oxygen or water molecules into OH free radicals with super tough oxidization. It can oxygenolyse different kinds of organic compounds and some parts of minerals. This response can also deoxidize harmful substances like benzene, formaldehyde, and ammonia into CO_2 and water

complimentary of poisons, destructive, and malodorous material. There by achieving numerous treatment goals in a single process[7-9].

Material and Methods

Zinc oxide nano particles were synthesized by soaked chemical precipitation system using zinc nitrate and sodium hydroxide (1:2) M. ZnO particles were cleaned three times with deionised water and ethanol to eliminate the former impurities which are bound with the nano particles and then dehydrated in air atmosphere at about 60^0C. The obtained product is calcined at 500^0C in air atmosphere for 3 hr by means of muffle furnace. During aeration, Zn $(OH)_2$ formed into ZnO[10].

Characterization: These prepared ZnO is taken up for characterization studies.

X-ray diffraction (XRD): Figure-1 represents the prototype of ZnO nano fine particles. XRD peaks shows that the equipped material consists of particles in nano size range. XRD outline analysis is done using Siemens X-ray diffracto meter (AXS D5005), the peak strength location and width, full width at half maximum (FWHM) data ie.0.3858°. The diffraction peak was found to be 36.2549° and further it also confirms the prepared nano powder was of majorly containing zinc oxide particles. Nevertheless it do not contain significant XRD peaks other than ZnO peaks. Diameter of these nano particles was calculated using Debye scherrer formula.

$$d = 0.89\lambda / \beta \cos\theta$$

Where 0.89 is Scherrer's constant, λ is the wavelength of X-rays, θ is the Bragg diffraction angle, and β is the full width at half-maximum (FWHM) of the diffraction peak corresponding to plain. The particles size was found to be 21.65nm.

Scanning Electron Microscopy (SEM): The SEM pictures of ZnO nano particles are shown in figure-2 at dissimilar magnifications by means of SEM JEOL (JSM 6360). These films confirm the structure of ZnO nano particles. These pictures substantiate the approximate oval in shape and are arranged in groups to form a needle like structure. The particular area electron diffraction pattern shows distinct bright rings which conform preferential orientation of nano crystals as an alternative of asymmetrical.

UV–Vis Spectroscopy: Zno nano particles elucidation was equipped by ultrasonically dispersed them in absolute ethanol the greatest peak was found to be 374nm. Figure-3 represents the band gap (Eg) of ZnO nano particles is premeditated by using the formula Eg = hc/λ, where h = Planck's constant, c = velocity of light and λ = wavelength. The resultant band gap was found to be 3.32eV[11].

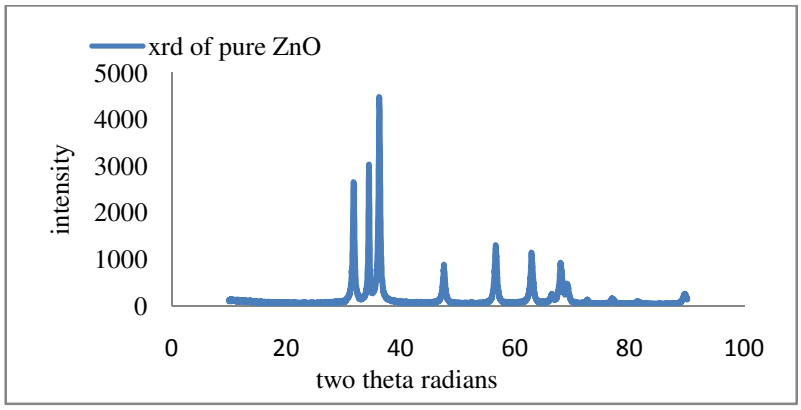

Figure-1
XRD plots of pure ZnO shows maximum peak

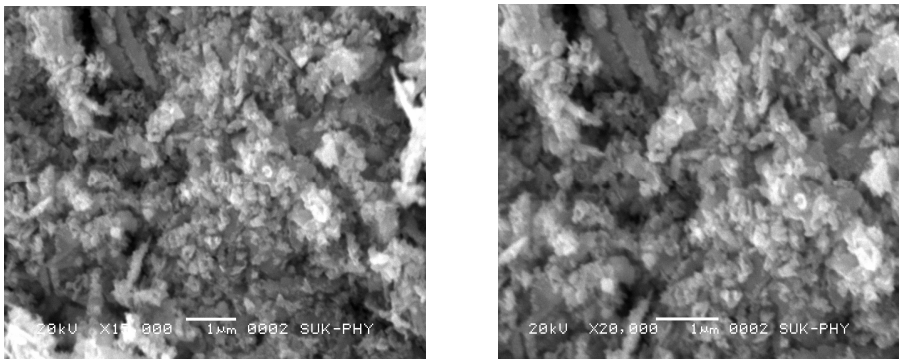

Figure-2
SEM images of ZnO at higher magnification

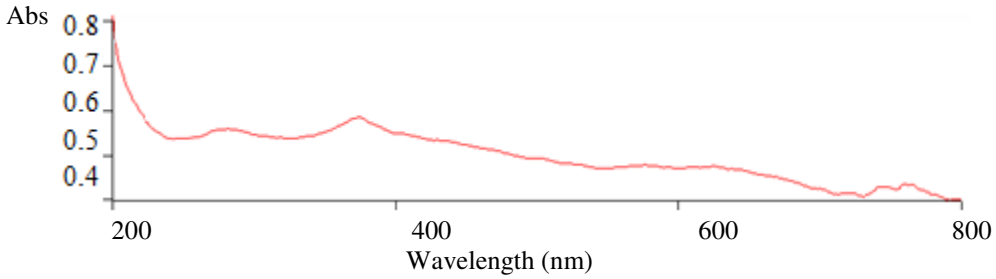

Figure-3

System generated UV visible spectro scopy of ZnO nano particles shows maximum peak to calculate energy gape of ZnO

Results and Discussion

Variation of Methylene Blue Concentration by UV Alone Without Catalyst: It is imperative from mechanistic and submission points of vision to study the reliance of photo catalytic response speed on the methylene blue concentration. Therefore, the control of substrate concentration on the degradation rate was deliberate at different concentrations altering from [$0.25x10^{-5}$]M to [$1x10^{-5}$]M in 100ml. The rate of response is calculated for maximum degradation i,e $1.53508E^{-06}$ M/sec. The degradation rate for the putrefaction and mineralization of the dye as a role of substrate concentration employing UV. It is observed that the degradation rate is originated to increase with the increase in substrate concentration from [$0.25x10^{-5}$] M to [$0.5x10^{-5}$] M. A additional increase in substrate concentration leads to diminish in the degradation rate of the dye. This might be due to that as the early concentrations of the dye increase the colour of the irradiating combination becomes additional and additional strong which prevents the dispersion of light to the surface of the substrate molecule. Their concentrations will decrease with increase in concentration of the dye as the beam photons are smaller amount then the molecules of dye and also all molecules of drug or dye do not approach in contact with light. Subsequently, the degradation efficiency of the dye decreases as the dye concentration increases[12-14]. Graphical representation is shown in figure-4.

Effect of Methylene Blue Concentration with photo catalyst: Consequence of variation of dye concentration was also intentional by taking different concentrations of dye [$0.25x10^{-5}$] M to [$1x10^{-5}$] M. The marks are represented in graph. From the observed data, it is apparent that the rate of photo catalytic degradation increases with increasing concentration of the dye. The rate stable is found optimum at [$0.75x10^{-5}$] M. It is decreased on additional increasing the dye concentration. Rate of reaction is calculated for maximum degradation i, e $1.12278E^{-05}$ M/sec.

This can be qualified to the statement that as the concentration of dyes is increased, more dye Molecules are obtainable for excitation then by inter system passage and hence there is an increase in the rate. The rate of photo catalytic degradation is observed to decrease with an increase in the concentration of dye further. At this point, the dye molecules starts performing as sieve for the incident light supply and they do not allow the wanted light intensity to reach the photo catalytic particles and therefore, results in decline in the rate of the photo catalytic degradation of dye. Hence, the production of comparative amounts of OH and O_2 on the plane of the catalyst does not increase, as the intensity of light and the irradiation time are constant. On the other hand, their concentrations will decrease with increase in concentration of the dye as the light photons are mainly absorbed and prohibited from touching the catalyst surface by the dye molecules. Therefore, the degradation efficiency of the dye decreases as the dye concentration increases[12-15]. Graphical representation is shown in figure-5.

Effect of photo catalyst loading: Amount of photo catalyst moreover affects the process of dye degradation. Dissimilar amounts of photo catalyst are worn (0.025 to 0.2 g) and the results are shown in figure -6.

It have been observed that as the quantity of catalyst is increased, the rate of photo degradation of dye increases but routinely the response rate become practically constant after a definite amount (0.025 g) of the semiconductor. This might be due to the truth that as the amount of semiconductor is increased, the existing surface area also increases, but after a definite limit, if the amount of photo catalyst is further increased there will be no increase in the showing surface area of the photo catalyst. It may be considered like a saturation point over which any increase in the quantity of semiconductor has insignificant or no consequence on the rate of photo catalytic degradation of dye, as any increase in the amount of semiconductor after this saturation point will only increase the width of the layer at the bottom of the clarification[11-14]. It is observed that the saturation point is increased on by means of vessels of higher dimensions. Rate of reaction is calculated for maximum degradation i.e. $3.07613E^{-6}$M/sec.

Reusability: The reusability of photo catalyst is noted in direct to set up the constancy while studying reclaimed photo catalyst, every parameters together with irradiation time, methylene blue concentration, amount of photo catalyst were kept constant. The photo catalyst is removed from the solution mixture through filtration. The well again photo catalyst is washed five times with deionised water, desiccated at 97°C in oven and reused in degradation process[12].

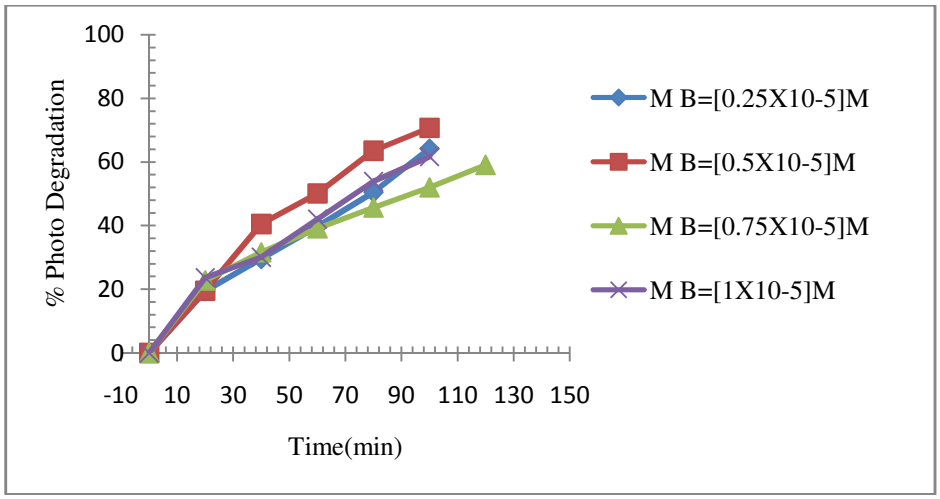

Figure-4
Effect of methylene blue concentration under UV alone

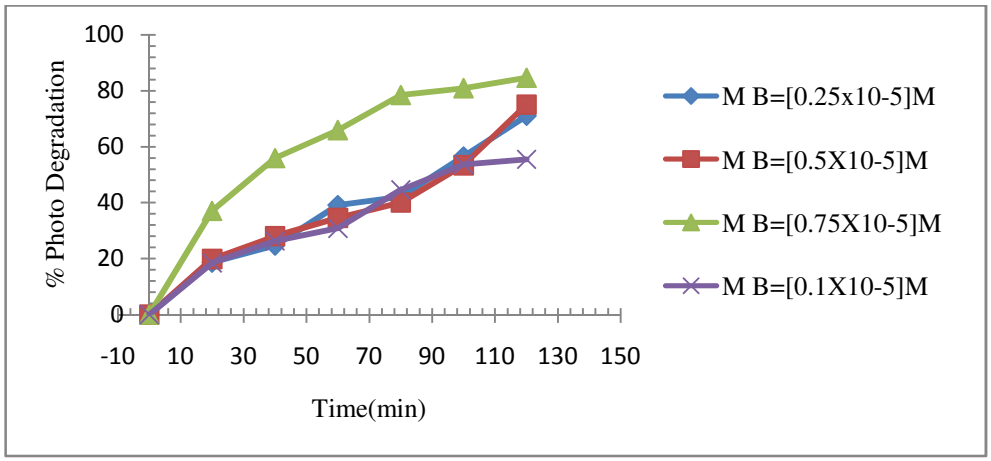

Figure-5
Effect of methylene blue variation under UV irradiation with constant catalyst of 0.1gm

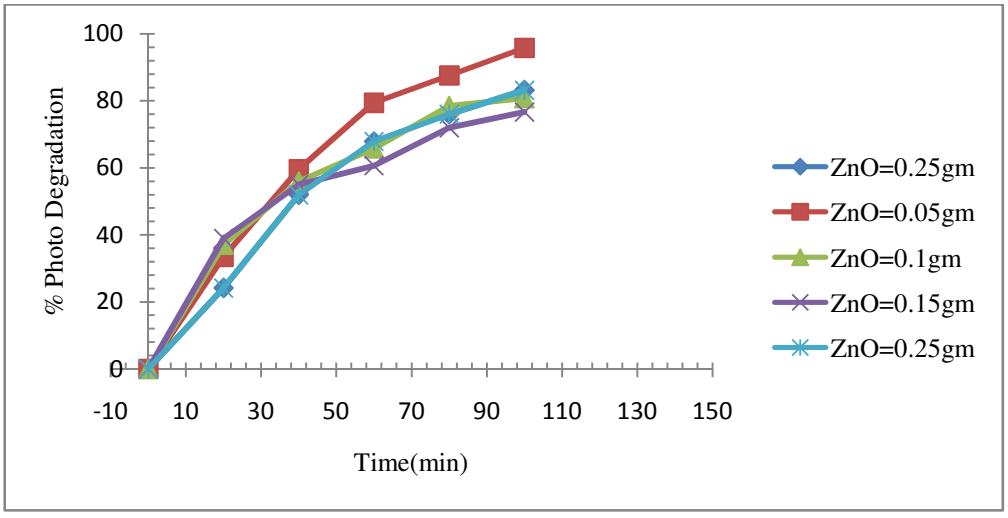

Figure-6
Effect of varying photo catalyst loading with constant methylene blue [0.75x10^{-5}] M under UV

Grade demonstrate no major lessening in photo catalytic act in photo degrading methylene blue, accordingly this indicates the constancy of ZnO as a photo catalyst. Stability of ZnO is shown through graphically in figure-7.

High Performance Liquid Chromatography Methylene blue reference sample: Methylene blue solution was taken for HPLC without degrading shown in figure-8.

Methylene blue (degraded): Degraded solution of methylene blue with ZnO is taken for product analysis and the five different degraded products were obtained is shown in figure-9.

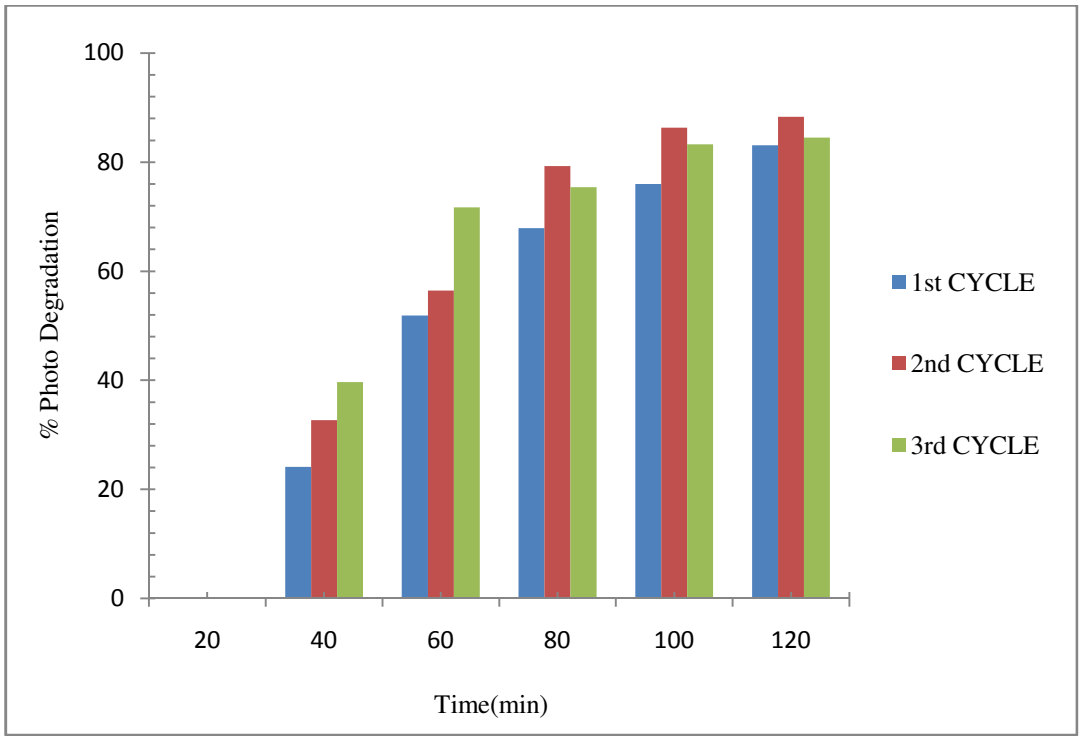

Figure-7
Reusability of ZnO photo catalyst keeping methylene blue[0.75x10^{-5}]M, of photo catalyst weight 0.05g/100ml, under UV irradiation time upto 100min

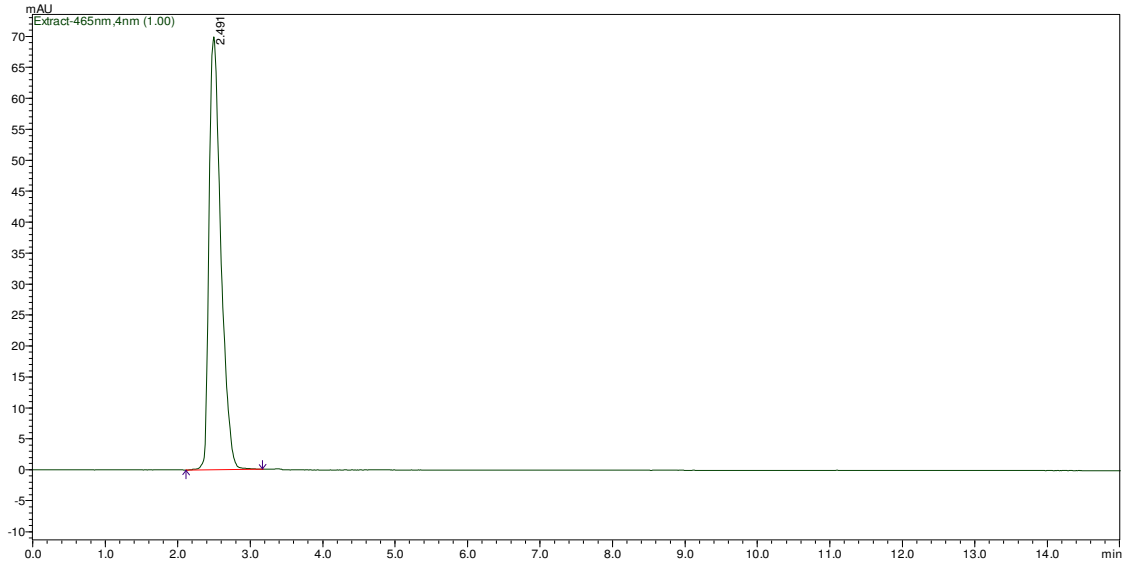

Figure-8
Methylene Blue reference sample without degradat

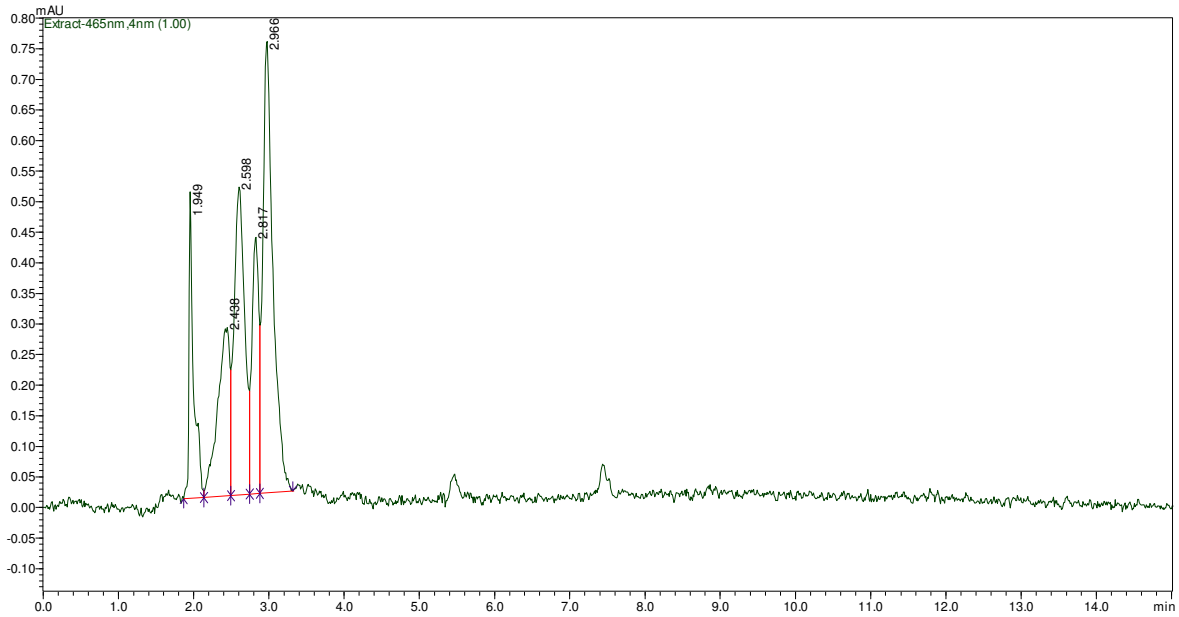

Figure-9

Methylene Blue High Performance Liquid Chromatography (HPLC) Peaks at Different Times, Initial Concentration of Methylene Blue= [0.75x10^{-5}] M and Photocatalyst of 0.05g In 100ml

Conclusion

Photo catalytic progression can powerfully degrade the organic contaminants using artificial UV light. The remarks, clearly demonstrates the significance of choosing most favourable degradation parameters to get hold of high degradation rates which is most necessary for any practical applications of photo catalytic oxidation processes. The percentage of purity of photo catalyst plays a vital role in bringing about degradation. Hence the studies on characterization of the same were done using XRD and SEM. The results of these test further conformed the obtained sample is ZnO, by characterization particle size is calculated and come to know the prepared ZnO is pure and does not contain any other impurities other than ZnO. These studies also conform the doped particles and its extent. This photo catalysts prepared by chemical precipitation were studied by investigating their photo degradation competence of vigorous organic drug or dye beneath artificial UV irradiation. The resulted show that performance of ZnO nano particles were better up to 95.77% degradation. Regeneration studies revealed that highest removal efficiency of 88.31% was obtained for zinc oxide. This study has shown that the nano particles which have undergone refluxing process exhibit superior photo catalytic capability in the photo breakdown of methylene blue, it's almost same amount of efficiency is obtained even after the 3rd cycle of regeneration. Using high performance liquid chromatography products were analysed and it was found that five degraded products were formed. This study indicates the enormous possible of ZnO to eliminate aqueous methylene blue beneath UV irradiation.

Future Scope of the Work: Degraded products can be identified using LCMS and their toxicity effects on humans and environment can be taken up.

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