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DEGRADATION OF HETEROCYCLIC AZO DYES DIRECT YELLOWY 27 USING METHYLENE BLUE IMMOBILIZED RESIN DOWEX-11

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ABSTRACT

Degradation of Direct Yellow -27 (DY 27) a heterocyclic azo dye by Methylene Blue Immobilized Resin Dowex 11 (MBIR Dowex-11) and the effect of different operating parameters like light intensity, amount of the catalyst (MBIR Dowex-11), pH of treated and untreated water. It has been found that MBIR Dowex-11 catalysts is capable to degraded DY 27 Heterocyclic azo dye up to 0.03 OD in presence of sun light of summer afternoon. We can use same catalyst again many time and it works well every time.

Key Words: Photocatalyst, MBIR Dowex-11, Azo Dyes, pH

1. Introduction

Degradation of the non-biodegradable and carcinogenic DY 27 heterocyclic azo dye is a challenging task for researchers. DY 27 is commonly used in different industries like, textile and paper and pulp industry etc. DY 27 is non-biodegradable so, conventional methods are not capable to eliminate it from water. Advance Oxidation Process (AOP) -Heterogeneous photo MBIR Dowex-11can prove a promising technology for degradation DY 27 azo dye. AOP-MBIR Dowex-11 Heterogeneous photo catalyst can be used for treatment of wastewater of textile industries; paper industries, food industries, chemical industries, Dyes industries etc. Some common wastewater treatment techniques are Adsorption, Sedimentation, Flocculation/Coagulation, Reverse osmosis etc. however these methods converts the phase of the pollution. These conventional methods also required huge amount of electricity and requires continues supply of chemicals. The solar energy or light energy based (MBIR Dowex-11) heterogeneous photocatalyst technique is capable to degrade DY 27, Dyes etc. We can reuse same catalyst many times. when we compare all parameters this technique will prove sustainable chipper in long run. I use MBIR Dowex-11 Heterogeneous photo catalyst for degradation of other Azo dyes.

It believes that during the process of sensitization of photo catalyst, electron migrates from balance band VB to conduction band CB and holes are formed at VB band. These holes produces hydroxyl radicals ($^{\cdot}OH$) which have high tendency of oxidation. These $^{\cdot}OH$ react with azo dyes and process of degradation start.

Large number of researcher reported use of photo catalytic degradation of Azo dyes, pesticides and Dyes etc.

Ever since 1977, when Frank and bard [i-ii] first examined the possibilities of using ZnO to decompose cyanide in water. Zhongbiao Wu et al [iii] worked on Alkali and alkaline earth tantalates, ZnO and other photocatalyst in different application. A new techniques have arisen as a new group of photocatalyst materials for water splitting into H_2 & O_2 and organic molecular degradation under ultra-violet/visible light irradiation. Tanaka K. et al. [iv] apply photocatalytic degradation technology for some commercial azo dyes. I. Husain and J Husain [v] in 2012 worked on pollution of ground water due to discharge of dyeing and printing industrial effluent in Bandi River, Rajasthan, India. Heller [vi] pointed out that, all the knowledge that was gained during the development of semiconductor photo electrochemistry in decades has greatly assisted the development of photocatalytic process. Legrini et al.[vii] in 1993 suggested that the purification with TiO_2 photo catalyst in presence of UV radiation has been known to have several advantages; effective removal of organic compounds dissolved or dispersed in water and inexpensive cost. Hsu Chin Cheng, Wu. L.[viii] carried out degradation of heterocyclic dye (Methyl Orange) under UV Light (300 nm) illumination using ZnO. Wang at al. [ix] worked to enhanced photocatalytic activity for degradation of Methyl orange SO_4^{2-}/ZnO/TiO_2. Stylidi et al.[x] proposed a TiO_2-mediated photo degradation of Acid Orange 7, they reported the degredation of the organic molecule like naphthalene and benzene into CO_2, $NH_4^+$and NO_3^-, sulfur into SO_4^{2-} ions. Ziyong Yu et al [xi] discoloration of Orange II by an innovative Co_3O_4/raschig ring photocatalyst (Co_3O_4/RR) is feasible and proceeds to completion using oxone as an oxidant within the short time of ∼5 min. Sakthivelet al.[xii] using ZnO with sunlight -the photo degradation rate decreased with an increase dye concentration. Poulios and Tsachpinis[xiii] ,investigated the photocatalytic degradation process of reactive black 5, using different semi conducting oxides, like TiO_2, UV-100 TiO_2, ZnO, and TiO_2/WO. D. Mendez-Pazetet al [xiv] is carried out anaerobic treatment of azo dyes acid orange 7 under fed batch and continues condition and he observed that the removal rate of dye pollutant is increase with high rate when some glucose is added to reaction mixture. Yiming Xu, et al[xv], does work on enhanced photocatalytic activity of supported TiO_2 : dispersing effect of SiO_2.

Aim of the presence work is to utilize renewable source of energy for degradation of water pollutants like heterocyclic azo dyes. MBIR Dowex-11 catalyst based wastewater treatment technique is capable to remove organic heterocyclic azo dye pollutants in a cheap, eco-friendly, way. I also observe the effect of different parameters on rate of degradation of organic heterocyclic azo dyes. These parameters are (1) variation in amount of catalyst (2) Variation in pH (3) variation in light intensity; all the sets are observed for 2-4 hour.

2. Materials and Methods:

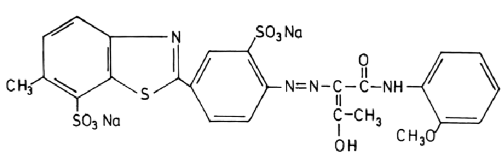
2.1 Dye Sample

Name of Heterocyclic dye : *Direct Yellow 27* (Sigma-Aldrich)

Molecular Formula : $C_{25}H_{20}N_4Na_2O_9S_3$

Absorption maximum : λ_{max} 393 nm

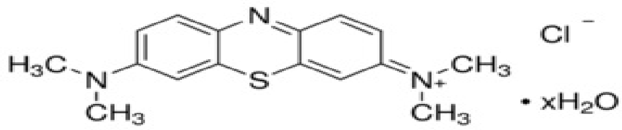
Molecular Structure :



IUPAC Name: Disodium;2-[4-[[1-(2-methoxyanilino)-1,3-dioxobutan-2-yl]diazenyl]-3-sulfonatophenyl]-6-methyl-1,3-benzothiazole-7-sulfonate.

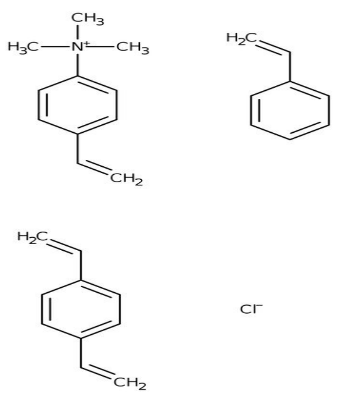
Molecular weight : 662.62
Color Index Number: 13950
CAS Number : 10190-68-8

2.2 *Methylene Blue* Dye (Sigma-Aldrich)
Molecular Formula : $C_{16}H_{18}ClN_3S \cdot xH_2O$
Molecular Weight : 319.85



IUPAC Name:3,7-bis(Dimethylamino)phenazathionium chloride,Basic Blue 9,Tetramethylthionine chloride
Colour Index Number : 52016
CAS Number : 122965-43-9

2.3 : *Dowex-11 Resin* (Sigma Aldrich)
Name : Dowex Marathon 11 chloride form
Molecular Formula : $(C_{10}H_{12}.C_{10}.H_{10}.C_8H_8.C_3H_9N)X$
Molecular Structure :



Particle Size: 25-30 mesh
CAS Number: 9049-12-1
Matrix active group : Trimethylbenzylammonium functional group
Moisture : 48-58 %

2.4 Analytical methods:
Preparation of Catalyst :
2.2 Photocatalyst:
Used Chemicals: To prepare Photocatalyst by following materials Dox-11 Resin 25-30 mesh, Methylene Blue Hydrate form (Sigma -Aldrich)
2.3 Preparation of Photo Catalyst:
We pour the Dowex Marathon 11 chloride resin in M/1000 solution of Methylene Blue solution (in double distilled water) and shake well. Put this mixture for 3 days for complete immobilization of Methylene Blue inside the pores of resin in dark place. After three days we

can filter Methylene blue immobilized resin from solution, wash this resin by double distilled water twice before used.

2.5 Analytical methods:

The change in dye concentration is observed simply by Shimadzu160 UV/Visible spectrophotometer. Takeout 10 ml of solution by pipette at the time interval of 15 minutes and observe changes in optical density (OD) of dye solution. We also monitored temperature as well as pH during the experiments. Irradiation intensity was measured using a photometer (IL 1400A).

2.4 Experimental set up and Experimental procedure

The photo reaction is carried out in glass reactor/acrylic sheet reactor which contains polluted water samples passes DY 27 dye and heterogeneous photo catalyst MBIR Dowex-11. Solution of reactor is continuously circulated by water pump during the experiment.

We followed following protocols for monitoring the experimental process.

(1**)** We observed bio degradability of pollutants present in water sample (without catalyst): We found No biodegradation

(2) We observed action of catalyst in dark. - In dark chamber - No change in dye concentration.

(3) We use AOP- Heterogeneous photo catalyst (MBIR Dowex-11). We observed that highly polluted and dark colour sample solution transform in to completely transparent water.

3. Result and discussion

3.1 Probable Chemical Reaction of This Degradation:

MBIR Dowex-11 is a photo sensitive in nature, when light radiation of desired wavelength strikes on its surface electrons get excited at balance band -VB and moves in conduction band-CB and through ISC electron reach in to triplet state after it intermolecular electronic transition start between catalyst, water, D.YELLOW -27, and dissolved oxygen, resultant a chain process of formation of holes, hydroxyl radicals and supra oxide ions (o$^-$) are produced they are oxidizing in nature, due to action of hydroxyl radicals and Supra oxide ions (o$^-$) on dyes, are transformed in simple organic compounds like CO_2, H_2O, SO_2, N_2,NO_x etc.

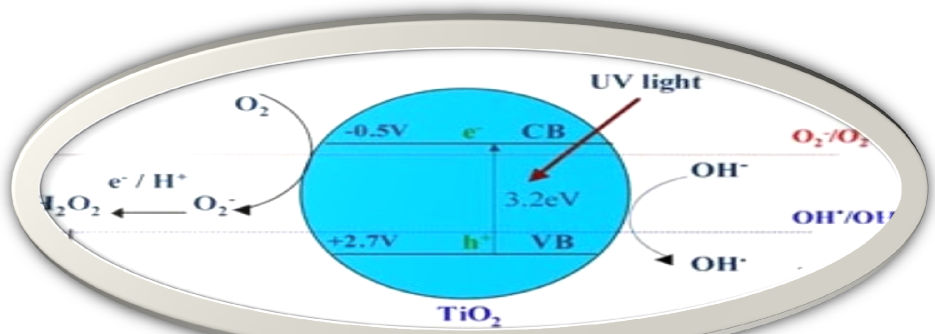
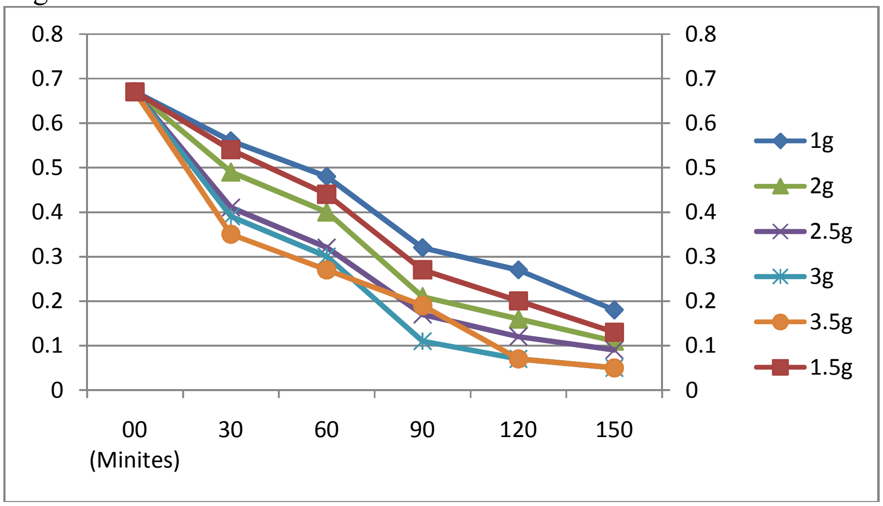


Figure : Mechanism of photocatalytic degradation Process

The few common factors which influences the catalytic degradation process are catalyst loading, concentration of DY 27, pH of the solution, April month10 am-1 pm.

3.2 Effect of catalyst. We observe the effect of amount of photocatalyst on rate of degradation of DY 27 Heterocyclic azo dye that the rate of degradation increase as amount of catalyst increases. This may be due to generation of more, hydroxyl radicals and supra oxide ions (o$^-$).

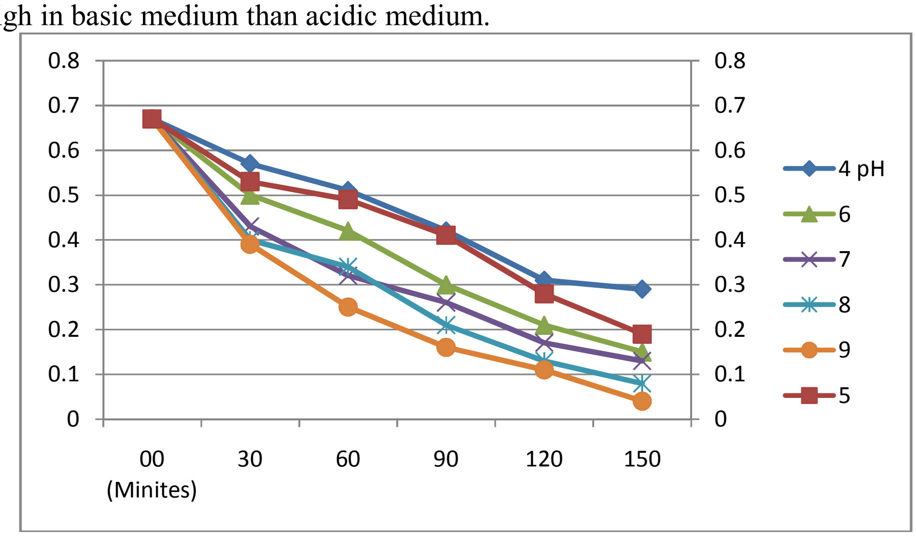
These are principle oxidizing intermediate in advance oxidation process resultant increases the rate of degradation.



Graph i- Effect catalyst loading on rate of degradation. Optical density (OD) -Vs- Time at pH 7, Dye concentration 1mg in one litter , Volume 1 litter, Summer afternoon10 am-1 pm.

3.3 Effect of pH.

The rate of degradation of DY 27 is very low in high acidic pH range below 4 and, as pH increases beyond 5 the rate of degradation also increases. The rate of degradation occur fasts fast, in pH range 7 to 10 .So we conclude that rate of degradation of DY 27 Heterocyclic azo dye is high in basic medium than acidic medium.

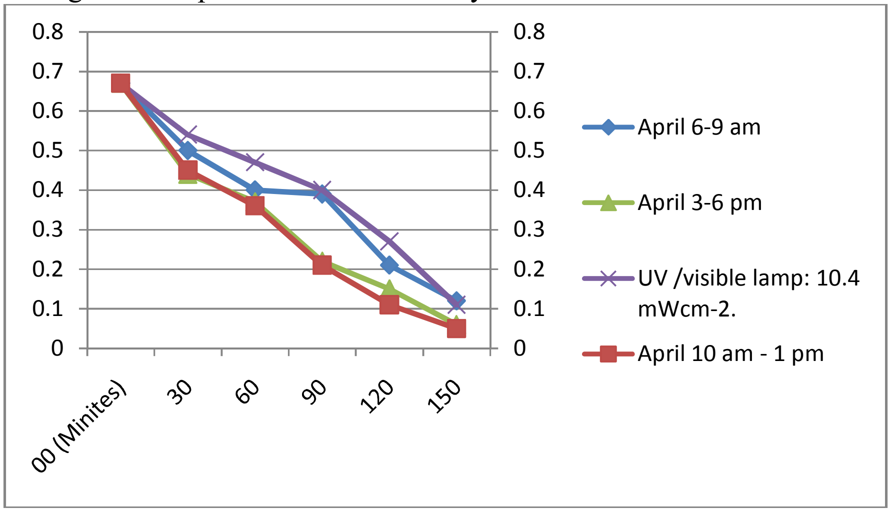


Graph ii: Effect of pH on rate of degradation OD -Vs- Time. Dye concentration 1mg/litter , catalyst 2 g in 1 litter, Summer afternoon 10 am -1 pm, pH 7.

3.4 Effect of light intensity

It has been observed that as light intensity increases the rate of degradation increase. The rate of degradation of DY 27 heterocyclic azo dye by variation in light intensity may be due to increases number of photons to reach on catalyst surface resultant number exited AOP-Heterogeneous photo catalyst MBIR Dowex-11 molecules increases and through chain process the number of holes, hydroxyl radicals and Supra oxide ions (o^{-}) increases.

We observe that rate of degradation of DY 27 Heterocyclic azo dye is higher in summer afternoon sun light as compare to winter and rainy session after noon



Graph iii: Effect of different light intensities on rate of degradation OD -Vs-Time at pH 7, catalyst 2g, dye concentration 1mg/l, volume 1 litter, Summer afternoon.

3.5 Effect of dissolved oxygen on rate of degradation

We observed the effect of Dissolved oxygen on rate of degradation. We observed that when we supply atmospheric air from bottom by using ban aeration pump (3 litter /minute) of the reaction mixture the rate of degradation increases.

4. Conclusion

After long observation we conclude that

A continues working model- dual treatment- solar energy based treatment in day time and UV Visible light treatment in night time. It is capable to degrade all DY 27 pollutants. We recover 99-99.99% transparent water from highly polluted industrial effluents including textile effluents. This photo catalyst AOP- Heterogeneous photo catalyst MBIR Dowex-11 has potential to degrade DY 27 Heterocyclic azo dyes like dy 27etc. into simple molecules such as CO_2 H_2O,N_2, NO_x etc.

I observe the effect of different parameters given in order

Effect of Variation in amount of catalyst: - As amount of catalyst increase the rate of degradation also increases.

1. Effect of Variation in pH:- I observe that rate of degradation between pH range 7.5 to 10 rate of degradation is good
2. Effect of Variation in light intensity: -.I observe that the rate of degradation of DY 27 Heterocyclic azo dye is higher in Afternoons.
3. Effect of dissolve oxygen: - I observed that when we supply atmospheric air from bottom of the reaction mixture the rate of degradation increases.

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