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Recovery of wastewater of textile industrial effluent by resin based photo catalyst in newly developed photo reactor

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ABSTRACT

Photo catalytic degradation of Chicago sky Blue 6 B (Direct Blue 1) (CSB-6B) in recently developed photo catalytic reactor using recently developed photo catalyst Methylene Blue Immobilized Resin Dowex-11. This is successfully applied for degradation of dye pollutants of wastewater of textile industries. The reactor is made of glass slides (tubes) coated with a thin-film of Methylene blue Immobilized Resin Dowex-11 with the help of suitable and non-reactive adhesive, the model dyes solution is continues recycles from reactor for 3 hour in a recirculation mode under various conditions (with/without catalyst, with/without light radiation, variation in: catalyst amount, dyes concentration, light intensities, pH). The removal efficiency was evaluated using UV/Visible spectrophotometer at λ_{max} = 618 nm for dye CSB-6B). The degradation efficiency was very good and we obtained 99.9% transparent water in 3 hour at pH 9.

KEYWORDS

Photo catalytic transformation;
Dowex-11;
Azo dyes;
Chicago sky blue 6B (CSB-6B);
Methylene blue.

INTRODUCTION

Azo-dyes; which contain one or more azo-bonds are widely used synthetic dyes and usually are major pollutants in waste water of textile industries. Azo-bonds are so strong and are therefore difficult to break and hence these azo-dyes are non-biodegradable in nature. Due to their toxicity and non-degradation property, these dyes are categorized as environmentally hazardous materials. The discharge of this colored, toxic and non- biodegradable wastewater from textile industries in the ecosystem has created a big environmental problem. During the last few years, several studies have been carried out for biological, physical and chemical treatment of dyes containing wastewater[1-4] the most common treatment methods including adsorption, biological degradation, chlorination or ozonation, are commonly used technics but these are not enough to remove these dye pollutent from water streams of textile industries. Recent developments of advance oxidation process were found as an emerging technology leading to the total decolorization of most of organic dye pollutants[5-12]. Heterogeneous Photo catalysis can be successfully

used to oxidize many organic dye pollutants present in aqueous systems. Advance oxidation processes are all characterized by the same chemical feature: production of radicals through a multistep process, although the different reaction systems are used. A lot of studies have been reported on the photo catalytic transformation of refractory organics. TiO_2, ZnO and some other such oxides have been used as photo catalyst for many systems either in suspended or in supported forms[13-17].

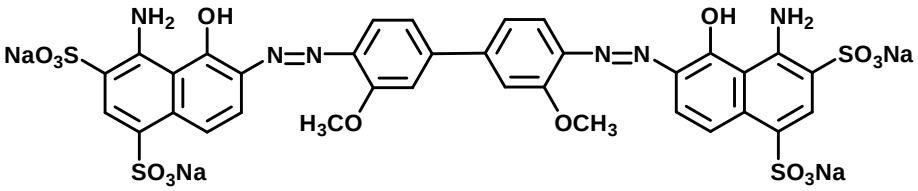
The fading of the dye solution was associated with cleavage of azo linkage in dye molecule. Azo dyes are characterized by nitrogen to nitrogen double bond (-N=N-that are usually attached to two radicals of which at least one but usually both are aromatic groups (benzene /naphthalene ring) The color of azo dye is determined by the azo bonds and their associated chromophore and auxochrome. Azo bonds of azo dyes molecules can be oxidized by these radical[18-20] the cleavage of –N=N- bonds leads to the de-colorization of dye.

Elimination of dye pollutants of wastewater of textile industries by photo catalyst in the presence of sunlight is the most environment friendly treatment method. Here we use Methylene Blue immobilized resin Dowex-11 as photo catalyst which is an efficient photo catalyst for degradation of dye pollutants in the presence of visible/Sun light irradiation. When methylene blue immobilized resin Dowex-11 is irradiated by visible light, it become activates self and due to intersystem crossing electronic transition occurs form catalyst to dye molecule due to it dye molecule become exited and rearranged, resultant degradation of dye molecule start and simultaneously hydroxide ions and superoxide ions also form they are also have high capacity to oxidized organic molecules so rate of degradation of dye molecules is so high comparatively old traditional technics and we get better result in small interval of time approx. 2 to 3 hour and we get 99.9% transparent water. We also done a comparative experiments with traditional and too costly photo catalyst like ZnO, TiO_2 and we find out that they takes day long time for degradation of dye molecules and efficiency of degradation is too less we get only 80 to 90 % transparent water in more than 12 hour study. Finally we choose newly developed photo catalyst Methylene Blue Immobilized resin Dowex-11 as future catalyst and it may be prove best at industrial level treatment of dye polluted waste water. One another major plus point is that size of catalyst particle is large (size ~20-50 mesh) so we can easily separate from water by simple filtration process with the help of common house hold cloth/ Net. ZnO, TiO2 are very fine powder so very difficult to separate from water.

EXPERIMENTAL

Materials

Azo dye, Chicago sky blue 6B (CSB-6B) was used as a model compound. Chicago sky Blue 6 B (Direct Blue 1).



Structure of Chicago sky blue 6B

This is a recalcitrant azo dye found in textile wastewater. Solution was prepared by dissolving a defined quantity of the dye in distilled water. (λ_{max} = 618 nm.) (Dye content about 80 %.). For the preparation of catalyst we use an anion exchange resin Dowex-11 (size ~20-50 mesh) and methylene Blue C.I.: 52015 also called Swiss Blue. One gm dissolves in an ml of water. (λ_{max} 668 and 609nm). (Dye content about 82 %.)

Photo catalyst

Used chemicals

We prepare Photo catalyst by following materials Dowex-11 Resin 20-50 mesh (Sisco Chemicals India Mumbai), Methylene Blue Hydrate For Microscopy, (C. I .No 52015) (Loba Chemicals India)

Preparation of photo catalyst

The photo catalyst was prepared by appropriate

amount of the Dowex-11 resin add to methylene blue solution of suitable concentration and place the container in dark for 2 days finally filter Dowex-11 resin from Methylene Blue solution and washed Dowex-11 resin by distilled water and use it for catalysis process for several times.

Role of methylene blue

Methylene blue is photosensitized dyes. When molecule of Methylene Blue immobilized in pores of resin (fill in pores of resin). Methylene blue (MB) is photosensitized dyes and becomes exited by absorbing photons of light radiations. In first electronic excitation, electron transfers into singlet state and through inter system crossing (ISC) electron can transfer to triplet state of Methylene Blue. Further inter molecule electronic interaction occurs between resin, Methylene blue and solution mixture and resultant is formation of holes, hydroxyl radicals and Supra oxide ions (o^-), these are highly oxidative in nature

Analytical methods

Change in dyes concentration is observed simply by Shimadzu-160 UV/Visible spectrophotometer. We pipette out 10 ml of solution by pipette at the time interval of 15 minutes and observe changes in percentage transparency of dyes solution. Dissolved oxygen and temperature.(YSI 550A), as well as pH (Fisher Scientific Accumet 50) is monitored during the experiments. Irradiation intensity is measured using a photometer (IL 1400A).

The reactor system

A photo catalytic reactor (PCR) was used to study the degradation of azo dye Chicago sky Blue 6 B (Direct Blue 1). The system consisted of the PCR, a 1 L open reservoir equipped with a stirrer to ensure complete mixing, and a peristaltic pump to force the solution from the reservoir to the reactor The PCR was made of 3 to 9 glass or more slide/tubes/cylinder with different amount of catalyst coating. Reactor height is 30 cm. and glass tubes, beakers were choosing because this kind of system is Visible light transparent and easy modals. Each glass tubes had an inner diameter of 50 mm, an outer diameter of 90 mm, Water was divided among the 3 or more glass tubes/cylinder and forced to follow a fixed route inside each tube before leaving the reactor, resulting in increased irradiation time. Tungsten lamp of 200 watt/Sunlight is used as light source; the intensity of radiation is of 10.4 mW/cm^2. All experiments were performed at room temperature. Detailed reactor set up shown in figure 1

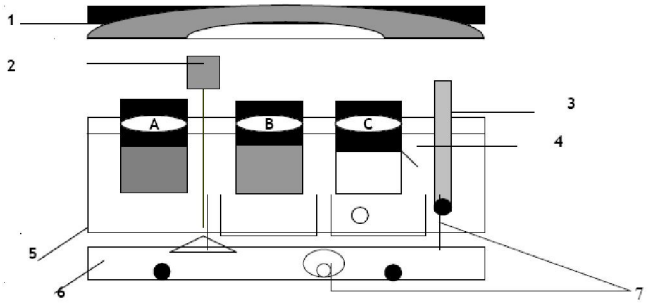


Figure 1 : Schematic diagram of the experimental setup: (1) light lamp; (2) stirrer; (3) Thermometer; (4) Glass reactor (beaker); (5) water bath; (6) magnetic stirrer. Beaker coated with Methylene Blue immobilized Resin Dowex-11 by non-reactive adhesive (a) Dyes solution without catalyst coated reactor shows no change in color (b) shows (degradation of dyes molecules) change in color by the action of photo catalyst (c), solution become colorless this shows the complete degradation occurs by the action of methylene blue immobilized resin dowex-11 (20-50 mesh) in three hour irradiation time duration. 7. Reactor pump and connecting tube to reservoir and reactor beaker.

RESULTS AND DISCUSSION

Probable chemical reaction of this degradation

Methylene Blue Immobilize Resin Dowex-11. This is newly developed photo catalyst. The dyes immobilize in porosity of resin is Methylene Blue. Methylene Blue is photo sensitive in nature, when light radiation is irradiated on this dyes electronic transition occurs from valance band (VB) to conduction band (CB) through intersystem crossing (ISC) electron reach in to triplet state of Methylene Blue. After it intermolecular electronic transition start between resin, Methylene blue dyes molecules, water molecules, dye (CSB-60 molecules and dissolved oxygen, resultant through chain process, holes, hydroxyl radicals and Supra oxide ions (o^-) are produced and these are highly oxidizing in nature, by the action of holes, hydroxyl radicals and Supra oxide ions (o^-) on Azo dyes, are transformed in simple organic compounds like CO_2, H_2O, SO_2, N_2, etc. The main factors influencing the photo catalytic degradation of Azo dyes is variation in catalyst loading, variation in

concentration of dyes, variation in pH of the solution, variation in light intensity, variation in dissolve oxygen.

Discussion on results

Photo catalytic destruction of the (CSB-6) solution was measured using UV/Visible spectrophotometer at (λ_{max} = 618 nm.). After 3-hour photo catalytic experiment at pH 9

The transparency is increases by 24, 40, 48, 85 and 95 and 99.9% after 30 minute, 1h,1.5h, and 2 h, 2.5h and 3h respectively. The increase in transparency is likely due to the degradation of the CSB-6. The temperature was almost constant during the experiments (30°C), while the dissolved oxygen concentration ranged from 6.0 to 6.9 mg/L (71–82% saturation). The highest removal rate of CSB-6B is observed at pH 9. In The First 24 hour experiment, the reactor operated with uncoated cylinder tube/slides and the 200 watt UV/Visible light/Sunlight. During this experiment, no variation in transparency is detected. Next, the Methylene blue Immobilized Resin Dowex-11 thin-film fixed in/on reactor cylinders /tubes/ slides and the reactor operated with the UV/VIS/Sun light for 3 hour. During this time, significant variation in transparency is observed. Thus, the removal of CSB-6B detected on (pH 9) can only be a result of photo catalysis and not a result of adsorption on the Methylene blue Immobilized Resin Dowex-11 surface. The rate of removal/degradation is reduce to much below pH 2.5 and above pH 13, almost dyes degraded and 99.9% transparency indicated fast rate of degradation of dyes. This represents higher removal efficiency than reported in previous studies photo catalyst TiO_2 and ZnO. In this study we recover (99.99%) transparent water from textile industries wastewater containing non-biodegradable dyes/azo dyes successfully. Degradation of dye CSB-6B using an immobilized Methylene blue Immobilized Resin Dowex-11 is achieved successfully. The dye CSB-6B degraded completely after 3 h at pH 9 and show 99.9% transparency. Effect of These parameters on the rate of degradation are (1) Variation in catalyst loading, (2) Variation in dyes concentration, (3) Variation in pH, (4) Dowex-11 ariation in light intensity, (5) effect of dissolve oxygen. All the sets are observed more than 3 hour.

Effect of catalyst

The amount of the photo catalyst affects the rate of photo catalytic degradation. We observe effect of variation in amount of photo catalyst on the rate of degradation at constant pH 7.5. We find out that as concentration of catalyst increases rate of degradation also‘ increases. Increase in the rate of degradation with increase in amount of catalyst is due to availability of more catalyst surface area for absorption of quanta and interaction of molecules of reaction mixture with catalyst, result is that number of holes, hydroxyl radicals and supra oxide ions (o^-) are increased. These are principle oxidizing intermediate in advance oxidation process and increases the rate of degradation. Effect catalyst loading on rate of degradation is graphically shown in figure 2

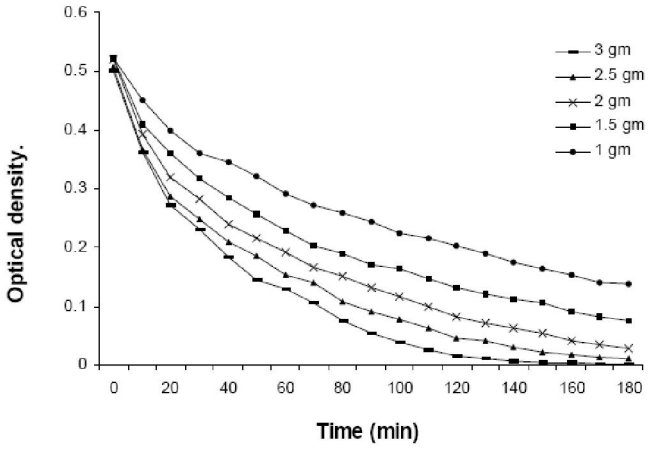


Figure 2 : Effect of catalyst loading on photo catalytic transformation (Temperature: 303 K, solution, Volume: 200 ml, initial dye concentration: 40 mg/l, pH 7.5, UV lamp: 10.4 $mWcm^{-2}$.)

Effect of initial dyes concentration

We observe the effect of change in dyes concentration on photo catalytic degradation and find out that as concentration of dyes increases the rate of degradation decreases. This effect may be caused due to following reason

1. As the concentration of dyes increases number of photons reaching to catalyst surface decreases result is that less number of catalyst molecules undergoes excitation and due to this effect rate of formation of holes, hydroxyl radicals and supra oxide ions (o^-) is decreased so rate of degradation also decreased.
2. Catalyst surface area is fixed so as the concentration of dyes increases rate of degradation decreases because limited number of dyes molecules attach

at the active site of the catalyst and remaining dyes molecules persist in solution until earlier attached molecules are degraded and number of active site of catalyst also decreases due less availability of photons for excitation of catalyst molecules. Competitions between dyes molecules to attach to the active site also effect rate of degradation. At higher concentration number of dyes molecules are also high so more will be the competition for attachment to active site of catalyst between the dyes molecules and result is reduction in the rate of degradation. Rate of degradation of dyes shown graphically in figure 3

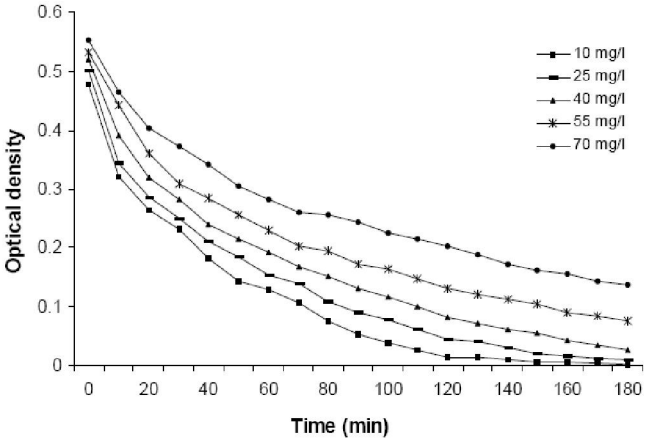


Figure 3 : Effect of initial dye concentration on transformation (Temperature: 30^{3}K, solution volume: 200 ml, pH 7.5, UV lamp: 10.4 mW cm^{-2}.)

Effect of pH

We observe that effect of pH on rate of degradation of dyes molecules is very interesting. The results shows that rate of degradation is very low in high acidic pH range, if pH is lower than 3.5 rate of degradation is very less, as pH increases rate of degradation also increases when pH reaches to basic range the rate of degradation increases fast, in pH range 7.5 to 9 rate of degradation is very good. On further increasing pH the rate of degradation also start to decrease after pH range 10 or above rate of degradation is less and decreases as pH increases. So we conclude that rate of degradation in basic medium is higher than acidic medium. The increase in rate of photo catalytic degradation may be due to the more availability of $^-$OH ions in pH range 7.5 to 9 which will generate more ·OH radicals by combining with the holes which are formed due to electronic excitation in catalyst. Formation of hydroxyl radicals are responsible more for the photo catalytic degradation than supra oxide ($^-$O). At higher pH the rate of degradation decreases. This effect is due to competition between $^-$OH groups to attach to the active site of catalyst, so rate of attachment of $^-$OH group decreases. Result is that formation of hydroxyl radicals (·OH) decreases and due to this reason rate of degradation also decreases.

Graphical representation of variation in pH is shown in figure 4.

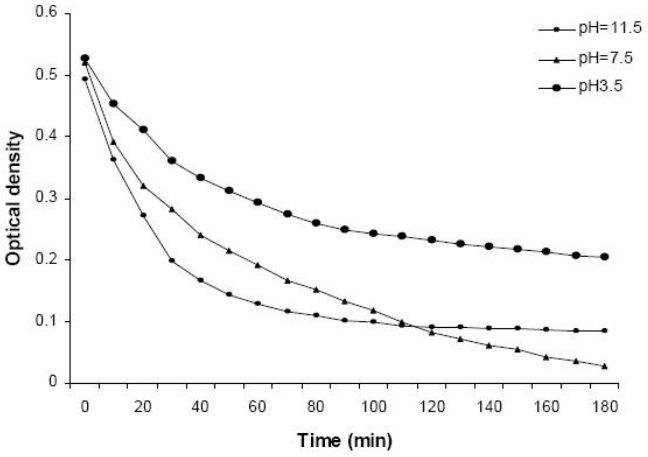


Figure 4 : Effect of pH on transformation (Temperature: 303 K, solution volume: 200 ml, initial dye concentration: 40 mg/l, UV lamp: 10.4 mW cm^{-2}.)

Effect of light intensity

We observe the effect of light intensity on rate of degradation. We find out that as light intensity increases the rate of degradation of dyes molecules also increases up to certain extent and after it no changes are observed in rate of degradation. These changes in rate of degradation of dyes molecules by variation in light intensity is due to the reason that as light intensity increases number of photons reaching the catalyst surface also increases so number of exited catalyst molecules increases and result is increase in the number of holes, hydroxyl radicals and Supra oxide ions (o^-) and rate of degradation of dyes molecules also increases.

We observe that after some extent of increase in light intensity there is no effect on rate of degradation on further increase in light intensity. The cause is that maximum numbers of photons which are required for excitation are available in fix range irradiating light intensity and after it if we further increase light intensity no considerable changes are observed in rate of deg-

radation because there is no requirement of more photons for excitation. Because all catalyst molecules become active (exited) in fix light intensity range after it if we increase light intensity to any range, the rate of degradation remains unchanged. Graphical representation of light intensity variation is shown in figure 5

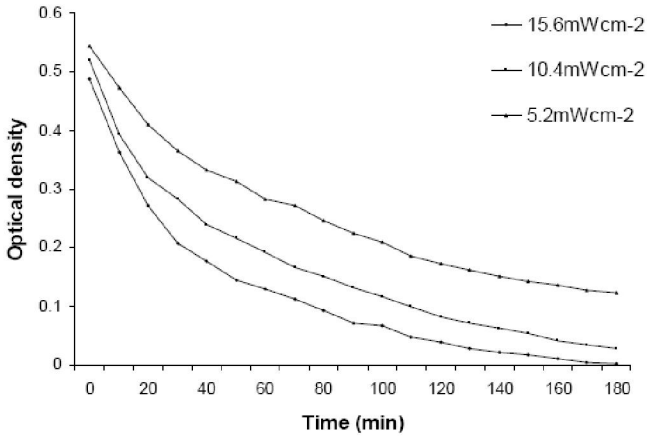


Figure 5 : Effect of variation of light intensity on transformation (Temperature: 303 K, solution volume: 200 ml, initial dye concentration: 40 mg/l, pH 7.5.)

Effect of dissolved oxygen on rate of degradation

We observed the effect of Dissolved oxygen on rate of degradation, as dissolved oxygen increase in dyes solution rate of degradation also increase. We observed that when oxygen gas is passed through reaction mixture the rate of degradation increases but when Nitrogen or any other non-reacting gas is passed through this solution no effect is observed on rate of degradation. This effect is may be due to more availability of oxygen for formation of supra oxide ($^{\cdot}O$) and hydroxyl radical. These are highly oxidative in nature and increase the rate of degradation of dyes molecules.

Kinetics of transformation

The Langmuie- Hinshelwood kinetics model can formally describe the Photo catalytic transformation of various organic molecules by means of illuminated photo catalyst. This model was used to describe the photo oxidation kinetics of the dye by a great number of researchers. The photo catalytic transformation of Chicago sky blue 6B dye containing immobilized resin obeys apparently pseudo-first order kinetics at low initial dye concentration. The dye is adsorbed on to the catalyst surface to be effectively oxidized due to the fast recombination of electron-hole pair. In Langmuir-Hinshelwood pseudo-first order kinetics model the rate of reaction is proportional to the surface coverage. Therefore, the initial rate r_0 ($mgl^{-1}min^{-1}$) of decolorization can be written as:

$$\mathbf{r_0 = -dc/dt = k_rKC/1+KC}$$

Where r^0 = initial rate of reaction, k_r = constant for photo catalyst, K = rate constant for adsorption, C = concentration of bulk solution at adsorption equilibrium, c = concentration of bulk solution at any time t, t = time in minutes.

The above equation can be rearranged in the following linear form:

$$\mathbf{1/r_0 = 1/krKC + 1/kr}$$

Decolorization of the dye solution obeys pseudo-first order kinetics with respect to the dye concentration. From the experimental results, it has been confirmed by the linear plot obtained by plotting optical density of the solution with time as shows in figure 6

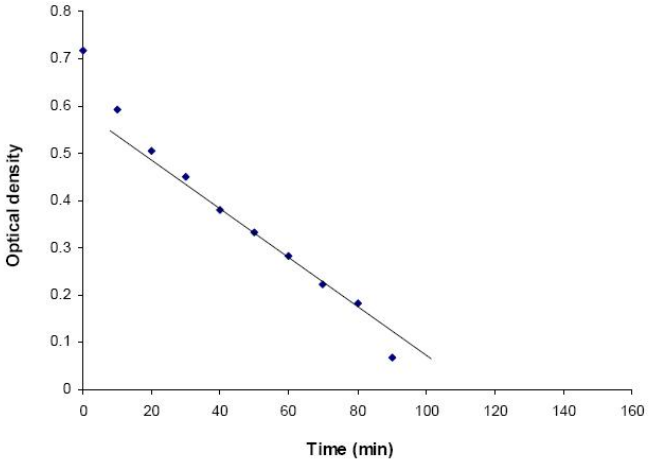


Figure 6 : Kinetics plot of photocatalytic transformation of Chicago Sky Blue 6B (Temperature: 303 K, solution volume: 200 ml, initial dye concentration: 40 mg/l, pH 7.5, Light intensity; 10.4 mW cm^{-2}.

Proposed mechanism for transformation

When a photo catalyst absorbs a photon of energy equal to or greater than its band gap width, an electron may be promoted from the valence band to the conduction band leaving behind an electron vacancy or hole in the valence band. On the other hand, the dye molecules are exited to first exited singlet state in the presence of solar radiation. Then these exited singlet molecule are transferred to the triplet state through intersystem crossing. Then these exited singlet molecule are transferred to the triplet state through intersystem crossing. The triplet dyes donate its electrons to the photo-

catalyst and the dye becomes positively charged. The dissolved oxygen of the solution will pull an electron from the conduction band of photocatalyst. The positively charged molecules of the dye will immediately react with hydroxyl ions to form ·OH radicals and superoxide ions these ·OH radicals and superoxide ions will oxidize the dye molecule (Chicago sky blue 6B) into the product. The probable mechanism for degradation of CSB-6B

$$Dye + Im\text{-}R + h\upsilon \longrightarrow Dye^{+} + Im\text{-}R(e^{-})$$

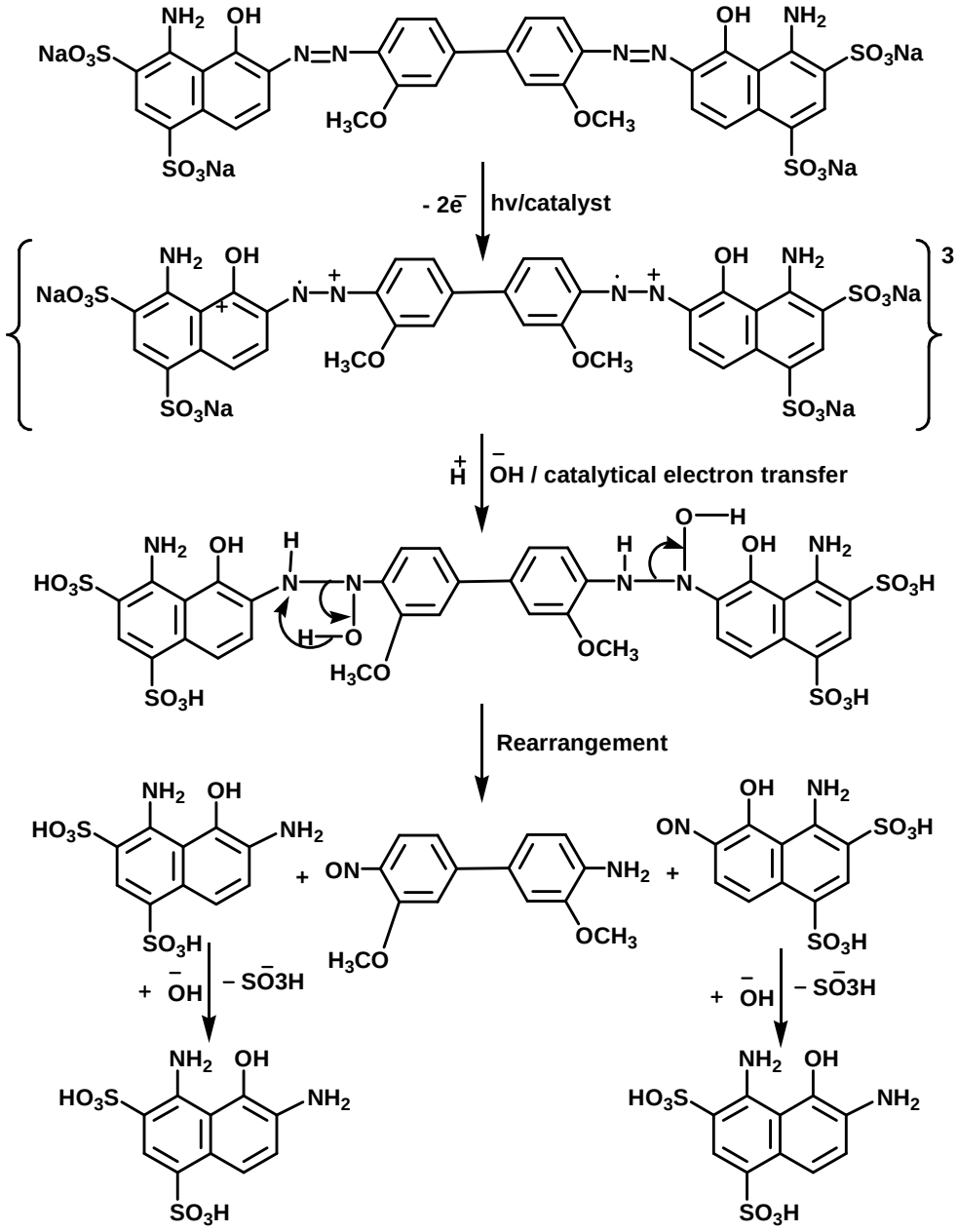
$$Im\text{-}R(e^{-}) + O_2 \longrightarrow Im\text{-}R + {\cdot}O_2^{-}$$

$$Dye^{+} + OH^{-} \longrightarrow Dye + OH{\cdot}$$

$$Dye^{+} + OH{\cdot} \longrightarrow Product$$

[Where Im-R=Immobilized-Resin]

Mechanism of photocatalitical degradation of Chikago sky blue -6B



CONCLUSION

This study focused on the evaluation of CSB-6B removal by means of a novel photocatalytic reactor with thin-film of Methylene blue immobilized resin dowex-11 prepared. The system operated in a recirculation mode under various conditions (with/without catalyst,

with/without UV/VIS radiation, different amount of catalyst, different dyes concentration, different light intensities, different pH conditions, and different dissolve oxygen percentage.) Changes in transparency of solutions from dark colored non-transparent solution to 99.9% transparent solution shows success of experimental set up of instrument with applying Methylene blue Immobilized Resin Dowex-11 photo catalyst. These results show that new reactor set up using Methylene blue Immobilized Resin Dowex-11 photocatalysis provides a promising technology to improve the quality of effluent from textile wastewater treatment plants. After long observation we conclude that this photo catalyst (Methylene Blue immobilized Resin Dowex-11) with new reactor has good potential of degradation of Azo dyes/ dyes into simple molecules and purify textile effluent (wastewater) which contains large amount of non fixed dyes mostly Azo dyes. These Azo dyes are non bio degradable.

We observe the effect of different parameters given in order

1. Effect of variation in dyes concentration: - As concentration of dyes increases the rate of degradation of dyes deceases.
2. Variation in amount of catalyst: - As concentration of catalyst increases the rate of degradation of dyes molecules also increases.
3. Variation in pH: - In acidic range of pH the rate of degradation is very less as pH increases rate of degradation also increases and between pH ranges 7.5 to 9 rate of degradation is faster on further increase in pH the rate of degradation decreases.
4. Variation in light intensity: - On increasing light intensity the rate of degradation of dyes molecules increases up to certain limit after it there is no further changes in the rate of degradation.
5. Effect of dissolved oxygen: - Rate of degradation increases up to some extent on increasing the dissolved oxygen in dyes solution.

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