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# Photo catalytic degradation of textile Azo dye using newly developed photo catalyst

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**Abstract**
In the present work, degradation of azo dye polluted water is challenging for researchers and environmentalists. Azo dye polluted water is hazardous for living world. Many Techniques of photocataytic Degradation Physicochemical techniques include membrane filtration, coagulation/flocculation, precipitation, flotation, adsorption, ion exchange, ion pair extraction, ultrasonic mineralization, electrolysis, advanced oxidation (chlorination, bleaching, ozonation, Fenton oxidation and photo catalytic oxidation) are available in world. The most important dye removal techniques are Photo catalytic oxidation processes.
Degradation of these azo dye by recently developed photo catalyst Methylene Blue immobilized Resin Dowex-11 is cheaper and very good alternative to replace costly traditional treatment and less efficient technologies for industrial application. This catalyst has potential to degrade all dye molecules and we recover 100% clean and transparent water from dark color textile effluent wastewater within few hour treatments by Methylene Blue immobilized Resin Dowex-11, photo catalyst. We use Tropaeolin O (Acid Orange 6), Methyl Orange, and Orange Gas model dye for experimental purpose; this is Azo dye and used in textile industries.

**Keywords:** photo catalyst, degradation, Azo dyes, UV light, tropaeolin O, methyl orange methylene blue immobilized-resin dowex-11, orange G

## 1. Introduction
The Textile industry is one of the oldest industries in India. Textile industry is one of the most water and chemical intensive industries worldwide. The effluents are considered very complex since they contain salt, surfactants, ionic metals and their metal complexes, toxic organic chemicals, biocides and toxic anions. Azo dyes are regarded as the largest class of synthetic. Azo dyes are classified according to the presence of azo bonds (–N=N–) in the molecule. Azo dyes are the largest group of synthetic dyes and pigments with industrial application due to their relatively simple synthesis and almost unlimited numbers and types of substituent's (Balcioglu *et al*.) [1]. The worldwide production of these organic dyes is currently estimated at 450000 tons/year, with almost 50000 tons/year lost in effluent during application and manufacture (Lewis *et al*.) [2]. Azo dyes contain at least one N=N double bond and many different structures are possible. Monoazo dyes have only one N=N double bond, while diazo, triazo and polyazo dyes contain two, three or more N=N double bonds, respectively. The azo groups are generally connected to benzene and naphthalene rings, but can also be attached to aromatic heterocyclic or enolizable aliphatic groups (Zollinger *et al*.) [3]. The general structure of the azo dye molecule can be seen in Figure1


**Fig 1:** General structure of azo dyes (where R can be an aryl, heteroaryl or - CH = C (OH) - alkyl derivative).

These lateral groups are necessary for obtaining colors with different shades and intensities. Azo colorants range in shade from greenish yellow to orange, red, violet and brown. The colors depend largely on the chemical structure, whereas different shades rather depend on physical properties. However, the important disadvantage, limiting their commercial application, is that most of them are red and none are green. Synthesis of most azo dyes involves diazotization of a primary aromatic amine to give a diazonium salt. The diazonium compound is then coupled with one or more nucleophiles. Amino- and hydroxyl- groups are commonly used coupling components. The coupling reaction is generally in para position in respect to the amino or hydroxyl groups (Zollinger *et al*.) [3]. The general scheme of azo dye synthesis is shown in figure 2.

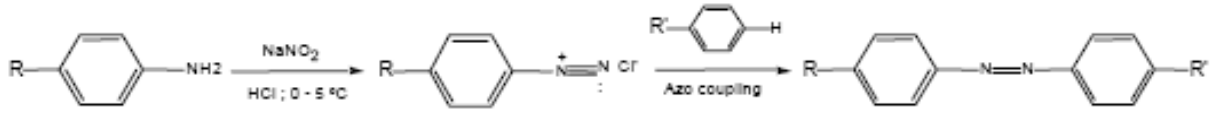


**Fig 2:** Azo dye synthesis

The azo linkage is considered the most labile portion of an azo dye. The linkage easily undergoes enzymatic breakdown, but thermal or photochemical breakdown may also take place. Degradation of azo dyes can be obtained by reduction or by oxidation. The reduction releases the colorless component amines (Figure 3).

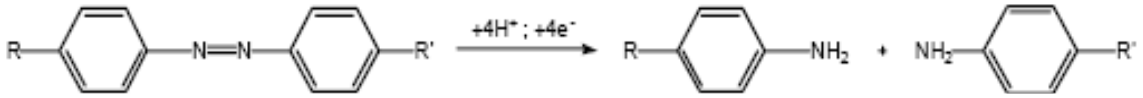


**Fig 3:** Azo dye reduction

### 1.1 Dye removal techniques

Various physical, chemical and biological pre treatment, main treatment and post treatment techniques can be employed to remove colour from dye containing wastewaters. Physicochemical techniques include membrane filtration, coagulation/flocculation, precipitation, flotation, adsorption, ion exchange, ion pair extraction, ultrasonic mineralization, electrolysis, advanced oxidation (chlorination, bleaching, ozonation, Fenton oxidation and photo catalytic oxidation) and chemical reduction. Biological techniques include bacterial and fungal biosorption and biodegradation in aerobic, anaerobic, anoxic or combined anaerobic/aerobic treatment processes.

Dye removal strategies consist therefore mostly of a combination of different techniques. The most important dye removal techniques are briefly discussed.

### 1.2 Membrane filtration

Nano filtration and reverse osmosis, using membranes with a molecular weight cut-off (MWCO) below 10,000 Dalton, can be applied as main or post treatment processes for separation of salts and larger molecules including dyes from dye bath effluents and bulk textile-processing wastewaters. Filtration with bigger membranes, i.e. ultra filtration and microfiltration, is generally not suitable as the membrane pore size is too large to prevent dye molecules passing through but it can be successful as pre treatment for further nano filtration or reverse osmosis (Rozzi *et al*.) [4]. Membrane filtration is a quick method with low spatial requirement.

### 1.3 Coagulation/flocculation

Coagulation/flocculation is often applied in the treatment of textile-processing wastewater, either to partly remove Chemical Oxygen Demand (COD) and colour from the raw wastewater before further treatment to polish the final effluents of biologically or otherwise treated wastewater, or even as the main treatment process (Timmons *et al*.) [5]. The principle of the process is the addition of a coagulant followed by a generally rapid chemical association between the coagulant and the pollutants.

Various inorganic coagulants are used, mostly lime, magnesium, iron and aluminium salts. Inorganic compounds are, however, generally not very suitable to remove highly soluble (= sulphonated) dyes from solution (Hazel *et al*. [6], Southern *et al*.) [7] unless rather large quantities are dosed (Hao *et al*.) [8]. Coagulation/flocculation with inorganic chemicals generates considerable volumes of useless or even toxic sludge that must be incinerated.

### 1.4 Sorption and ion exchange

Activated carbon or other materials can be used to remove dyes from wastewater, either by adsorption (anionic dyes) or by combined adsorption and ion exchange (cationic dyes). Sorption techniques yield waste sludge, i.e. dye-saturated material that should be disposed off or regenerated. As there are nonionic, anionic and cationic dyes, most adsorbents do not remove all different dye types. Activated carbon is capable of adsorbing many different dyes with high adsorption capacity but it is expensive and the costs of regeneration are high because desorption of the dye molecules is not easily achieved (McKay *et al*.) [9]. Various other (mostly low-cost) adsorbents have therefore been investigated as an alternative to activated carbon.

### 1.5 Electrolysis

Electrolysis is based on applying an electric current to the wastewater to be treated by using electrodes. The anode is a sacrificial metal (usually iron) electrode that withdraws electrons from the electrode material, which results in the release of Fe (II)-ions to the bulk solution and precipitation of Fe $(OH)_2$ at the electrode surface. Moreover, water and chloride ions are oxidized, resulting in the formation of $O_2$, $O_3$ and $Cl_2$. The cathode is a hydrogen electrode that produces $H_2$ gas from water. Organic compounds like dyes react through a combination of electrochemical oxidation, electrochemical reduction, electro coagulation and electro flotation reactions. At the anode sorption onto precipitated iron, direct electrochemical oxidation forming oxidized radicals and oxidation by the produced $O_3$ and $Cl_2$ gases. At the cathode electrochemical reduction forming reduced radicals and in the bulk solution chemical reduction or coagulation by the released Fe (II) ions, followed (in case of coagulation) by flotation by bubbles of the produced $H_2$ gas. In several studies, electrochemical methods have been successfully applied to achieve decolourisation of dye solutions and dye containing wastewaters. (Lin. *et al*.) [10].

### 1.6 Advanced oxidation processes

Advanced oxidation can be defined as oxidation by compounds with an oxidation potential ($E_0$) higher than that of oxygen (1.23 V), i.e. hydrogen peroxide ($E_0$ = 1.78 V), ozone ($E_0$ = 2.07 V) and the hydroxyl radical ($E_0$ = 2.28 V). Hydrogen peroxide alone is, however, usually not powerful enough. Advanced oxidation processes (AOPs) are therefore mostly based on the generation of highly reactive radical species (especially the hydroxyl radical $HO^{\cdot}$) that can react with a wide range of compounds, also with compounds that

are otherwise difficult to degrade, e.g. dye molecules. The four AOPs that have been most widely studied are ozonation, UV/$H_2O_2$, Fenton's reagent ($Fe^2+/H_2O_2$) and UV/$TiO_2$ (Aplin *et al*.) [11]. In the ozonation process, hydroxyl radicals are formed when $O_3$ decomposes in water.

Though ozone itself is a strong oxidant, hydroxyl radicals are even more reactive. Decomposition of ozone requires high pH (>10). Ozone treatment of organic molecules proceeds therefore faster in alkaline solutions than at neutral or acidic pH where ozone is the main oxidant (Ruppert *et al*.) [12]. Ozone rapidly decolorizes water-soluble dyes but non-soluble dyes (vat dyes and disperse dyes) react much slower (Gähr *et al*.) [13]. Textile-processing wastewater furthermore usually contains many refractory constituents other than dyes (e.g. surfactants) that will react with ozone, thereby increasing the ozone demand. It is advised; therefore, to pre-treat the wastewater before ozonation is applied (Vandevivere *et al*.) [14]. For example, in Leek, England, ozonation is used as the final stage (after biological treatment and filtration).

$$H_2O + O_3 \longrightarrow HO_3^+ + OH^- \longrightarrow 2\,HO_2 \xrightarrow{+2\,O_3} HO^{\cdot} + 2\,O_2$$

For treating textile-processing wastewater at full-scale (Churchley *et al*.) [15] this concept is, however, not logical as ozonation seldom leads to complete oxidation. Instead, ozone converts the organic compounds into smaller (usually biodegradable) molecules like dicaroboxylic acids and aldehydes (Peralta *et al*.) [16]. The reduction of COD is therefore low, while some of the ozonation products (especially the aldehydes) are highly toxic. It is better, therefore, to treat the effluent of the ozonation stage, logically by using inexpensive biological methods.

### 1.7 Photo catalytic oxidation processes

(UV/$H_2O_2$, UV/$TiO_2$; UV/Fenton's reagent; UV/$O_3$ and other) are all based on the formation of free radicals due to UV irradiation. Typically, as UV light does not penetrate sufficiently in highly coloured waste streams, application of photo catalytic processes is limited to the post-treatment stage (Vandevivere *et al*.) [14]. When UV is used in combination with hydrogen peroxide, hydroxyl radicals are formed according to the following (simplified) reaction:

$$H_2O_2 + h\nu \longrightarrow 2\,OH^{\bullet}$$

Drawbacks of the UV/$H_2O_2$ process are the relatively high costs and the occasional lack of effectiveness (Hao *et al*.) [17]. Faster, cheaper and more effective photo catalytic processes receive therefore increasing attention, especially those based on catalysis by solid semiconductor materials, mostly $TiO_2$ particles. When this material is irradiated with photons of less than 385 nm, the band gap energy is exceeded and an electron is promoted from the valence band to the conduction band. The resultant electron-hole pair has a lifetime in the space-charge region that enables its participation in chemical reactions (Gomes *et al*.) [18]. In general, oxygen is used to scavenge the conduction band electron to produce superoxide radical ($O_2^{\cdot-}$), while adsorbed water molecules are oxidized to hydroxyl radicals: With $TiO_2$ catalysed UV treatment; a wide range of dyes can be oxidized. The dyes are generally not only decolourised but also highly mineralized.

## 2. Newly developed photo catalyst

## Photo degradation of Azo-Dyes in the presence of Methylene Blue immobilized Resin Dowex-11 photo catalyst

### 2.1 Preparation of photo catalyst

We prepare approximately M/1000 concentration solution of Methylene Blue in Double distilled water and add Dowex-11 resin in this solution and shake well. Put this mixture for 3 days for complete immobilization of Methylene Blue In side the pores of resin. All the process is carried out in dark place. After three days we can filter Methylene blue immobilized resin from solution, wash this resin by double distilled water twice and used it as photo catalyst(Meena *et al*.) [19].

### 2.2 Role of methylene blue

Methylene blue is photosensitized dye. When molecule of Methylene Blue immobilized in pores of resin (fill in pores of resin). Methylene blue is photosensitized dye 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 (Meena *et al*.) [20].

### 2.3 Analytical Methods

The change in dye concentration is observed simply by Shimadzu-160 UV/Visible spectrophotometer. We suck out 10 ml of solution by pipette at the time interval of 15 minutes and observe changes in percentage transparency of dye solution.

### 2.4 Experimental set up and experimental procedure

The photo reaction is carried out in glass reactor which contains mixture of Dyes (Sudan IV) and photo catalyst. Solution of reactor is continuously stirred by magnetic stirrer during the experiment. The solution is illuminated by 500W halogen lamp above the reactor. Schematic diagram of the setup shows in figure1.

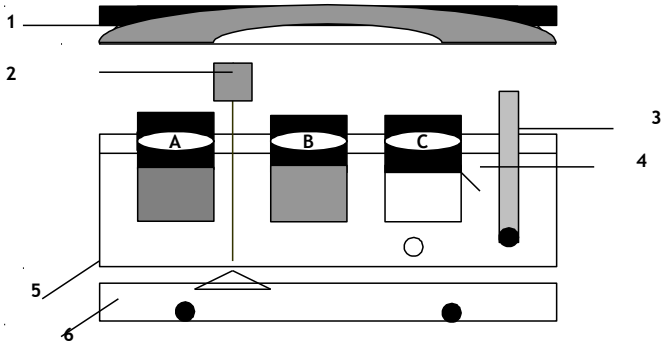


**Fig 4:** Schematic diagram of the experimental setup: (1) UV lamp; (2) stirrer; (3) Thermometer; (4) Glass reactor (beaker); (5) water bath; (6) magnetic stirrer. Beaker (a) Dye solution without catalyst shows no change in color (b) shows (degradation of dye molecules) change in color by the action 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.

At fixed time interval, 10 ml solution is taken out from reaction mixture. Filters catalyst particles and observe variation in transparency of colored water by the help of spectrophotometer (160UV/Visible spectrophotometer).
Following schedule of observation is followed in all experimental process.

1. In first experiment we observe bio degradability of dyes (without catalyst). We put dye solution in solar/lamp light for 3 days and after 3 days we observe changes in dye concentration. If no changes are found in dye concentration then we carry out next experimental step.
2. In second experiment which is carried out in dark for test action of catalyst in dark we put reaction mixture (dye solution and catalyst) in dark chamber there is no change observed in dye concentration.
3. In third experiment we add pure resin without immobilization of Methylene Blue. This experiment is carried out for test action of resin (without immobilized). We observe that absorption process occurs. Absorption efficiency is reduced after first absorption and stop after 2-3 time of use due to fill the pores of resin.
4. In fourth experiment we use Methylene blue immobilized resin and we observe that polluted and darkly colored mixture transform into transparent water like mineral water. This catalyst can be used many times as there is no effect on efficiency of degradation of dye molecules.

## 3. Result and discussion

### 3.1 Probable chemical reaction of this degradation

Methylene Blue Immobilize Resin Dowex-11. This is newly developed photo catalyst. The dye immobilize in porosity of resin is Methylene Blue. Methylene Blue is photo sensitive in nature, when light radiation is irradiated on it electronic transition occurs from valance band (VB) to conduction band (CB) and through intersystem crossing (ISC) electron reach in to triplet state of Methylene Blue. After it intermolecular electronic transition start between resin, Methylene blue dye molecules, water molecules, Tropaeolin O dye 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. (Meena *et al*.) [21].
The main factors influencing the photo catalytic degradation of Azo dyes is variation in catalyst loading, variation in concentration of dye, variation in pH of the solution, variation in light intensity, variation in dissolve oxygen.
The generation of holes, hydroxyl radicals and Supra oxide ions ($o^-$) can be explained better with the help of proposed diagram. This proposed diagram shows the action of photo catalyst and process of generation of oxidative intermediates. (Pachwarya *et al*.) [22].

## 4. Mechanism

On the basis of the observed data, the following tentative mechanism may be proposed for photocatalytic degradation of Azo Dye
The mechanism of this process is as follows-

$$\text{Dye} \xrightarrow{\text{Light Radiations}} \text{Dye}^{*1}$$

$$\text{Dye}^{*1} \xrightarrow{\text{ISC}} \text{Dye}^{*3}$$

$$\text{Dye}^{*3} + \text{I-R} \longrightarrow \text{Dye}^{+} + \text{I-R}\,(e^-)$$

$$\text{I-R}\,(e^-) + O_2 \longrightarrow \text{I-R} + {}^{-}O_2$$

$$\text{Dye}^{+} + {}^{-}\text{OH} \longrightarrow \text{Dye} + {}^{\bullet}\text{OH}$$

$$\text{Dye} + {}^{\bullet}\text{OH} \longrightarrow \text{Product}$$

When the solution of the dye was exposed to light, in presence of photo catalyst, initially the Dye molecules are excited to first excited singlet state (Dye $^{*1}$). Then these excited molecules are transferred to the triplet state through inter system crossing (ISC). The triplet dye (Dye $^{*3}$) may donate its electron to the photocatalyst and the dye becomes positively charged. The dissolved oxygen of the solution will pull an electron from the conduction band of the semiconductor, thus, regenerating the semiconductor.
The positively charged molecules of the dye (Dye $^+$) will immediately react with $OH^-$ ions to form $OH^{\bullet}$ radicals that will convert the dye molecules into products(Meena *et al*.) [23].

## 5. Conclusion

As compared to solar photo catalytic systems with other photo catalyst, Methylene Blue immobilized-Resin Dowex-11 used as solar photo catalysts gives very good results and successfully improved the degradation rate of organic dyes. It believed that the improved color degradation capability is due to the fact that the visible region of the solar radiation excites the Methylene blue immobilized resin, followed by a series of photosensitizing reactions. The photo catalytic degradation of Azo Dye has been studied using Methylene Blue immobilized-Resin Dowex-11 as photo catalyst. The photo catalytic degradation of the dyes follows first order kinetics for the system.
The photo catalytic degradation efficiency has been generally, found to increase with increase in catalyst loading. The Photo catalytic transformation decreases with increases in initial dye concentration. With the increase in the concentration of a dye solution, the number of photons decreases, to reach the catalyst surface, decreasing the number of photons absorbed by the catalyst and all the degradations occur at an optimal pH 7.5 value.
Therefore this technology has very good potential of organic molecular degradation from complex molecule into simpler molecules. Azo dyes which polluted water large part of textile effluent can transform into color less and non toxic compounds so this catalyst may applicable for industrial purpose for improvement in quality of the wastewater of textile industries and many others.

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