Chapter - 8

Description of Dye and its Removal Processes

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Abstract— *This chapter discussed the classification of dyes based on their origin and application. Different removal process using different state of the art technique in their removal process is also discussed.*

Introduction

Dye compounds are usually coloured due to the presence of the chromophoric groups. These are ionizing and aromatic organic compound which binds to different material and transmits colour. The release of wastewater from various industry into natural water bodies hampers the human being as well as the aquatic life. It also affects the human life as well as the environment due to their toxic and carcinogenic nature. The cleaning of wastewater is one of the most noteworthy environmental problems. This contamination of pollutant also increases the biochemical oxygen demand (BOD) and cause lack of dissolved oxygen to sustain

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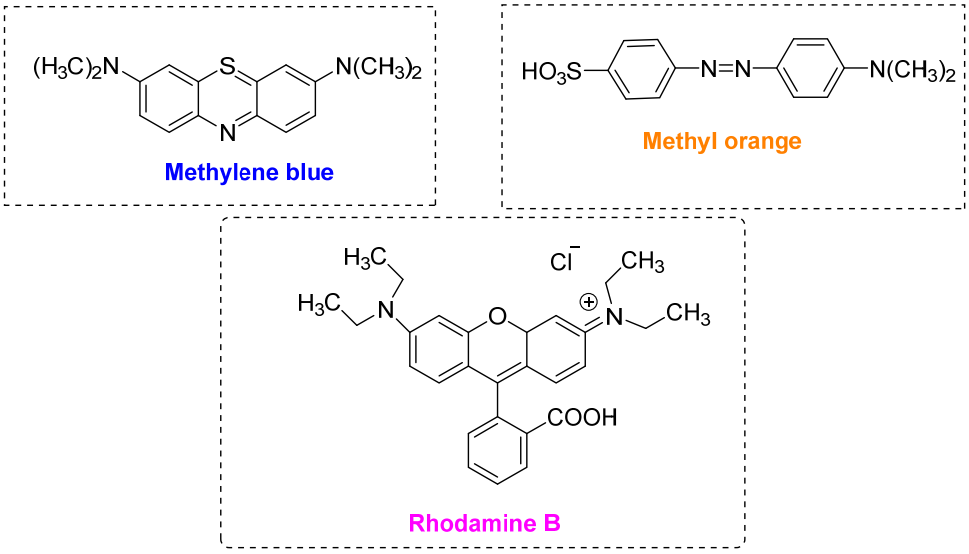
aquatic life. In addition, most of the dye even in low concentration can hamper the catalytic properties of suspended microorganisms in water.[1] Many dyes are really difficult to degrade due to their stable structure, and some of the representative dyes are shown in Scheme 1.



Scheme 1. Structure of methylene blue (MB), methyl orange (MO) and Rhodamine B (RhB)

Dyes are categorized based on their origin, chemical composition, and application. They may be natural or artificial according to their origin. The natural dyes are obtained from plants and animals. Artificial dyes are divided into two types, such as azo dye and non-azo dye. Azo dyes are again divided as vat, acidic, basic, reactive, and dispersed and sulfur dyes. The acidic, basic, and reactive dyes are generally ionic.[2] The classification of dye compounds is shown in Scheme 2.

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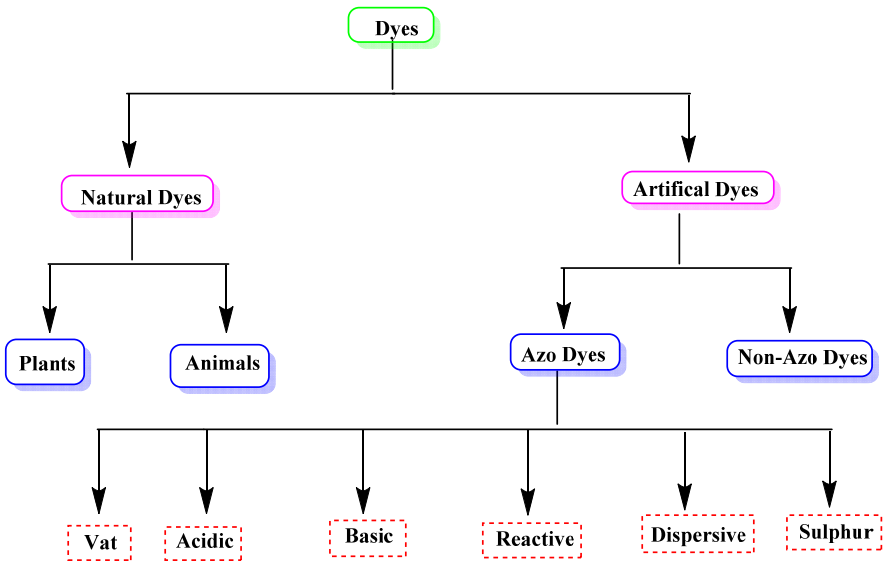

Scheme 2. Classification of dyes based on their origin and application.

Different processes such as physical, chemical, biological, etc. have been used to degrade the color dye from the wastewater. The molecules are separated via adsorption, ion-exchange, coagulation, and membrane processes. The adsorption process is mostly performed using activated carbon and biosorption methods. The activity of the adsorption process using activated carbon is found to be high, but the recycling of the catalysts are quite clumsy. The degradation of the organic pollutant can also be carried out via biodegradation, chemical oxidation, and advanced oxidation processes. These processes are found to be unsuitable to degrade the wastewater effectively. Each method has its own advantages and disadvantages. The activity of advance oxidation processes are very high due to the formation of highly reactive hydroxyl radicals in the reaction mixture. The various advanced oxidation processes are photolysis,

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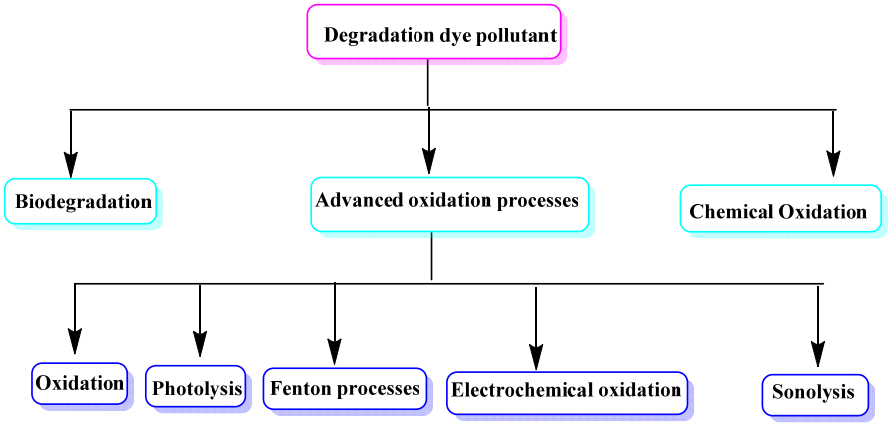
ozonation, sonolysis, and Fenton process.[3] The various process of dye removal or degradation processes is shown in Scheme 3.



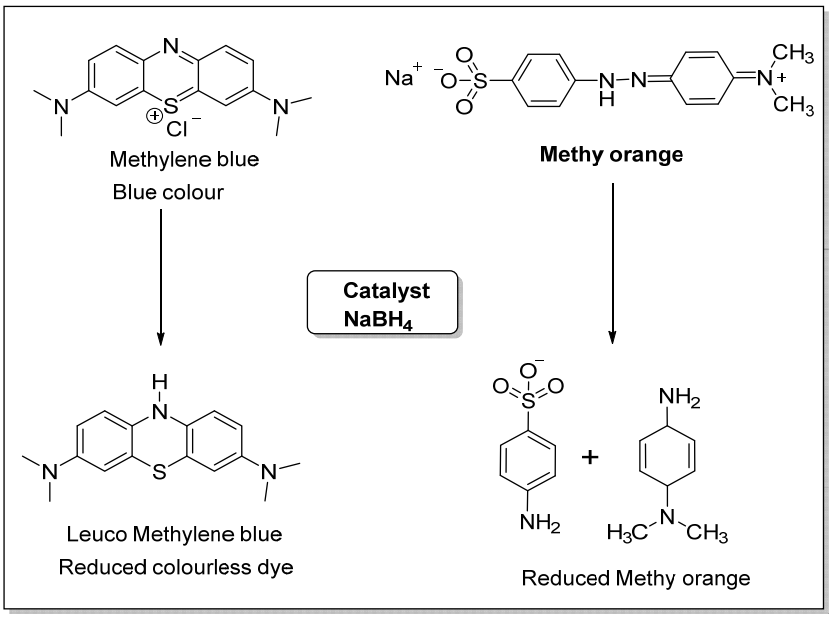
Scheme 3. Various processes for wastewater treatment.

Adsorption Method

Among different physicochemical processes, adsorption technology is considered to be one of the most effective methods for separation of dye molecule from wastewater. The adsorption process is very facile in case of supports like activated carbon, MWCNT, etc. Adsorption techniques are also considered as few conventional methods, and has high efficiency to separate the highly stable form of organic waste from water sources.[4] Marechal *et al.* demonstrated the possibility of decolorizing via ion exchange and adsorption process. Various factors are found to influence the adsorption of dye molecule and some of them are the particle size of the material, interaction with dye molecule, surface area, pH and temperature.[5]

Reduction of dye compounds

Dye molecules are reduced in the presence of metal catalyst using some reducing agent such as sodium borohydride, hydrazine, etc. The reduction of dye molecule do not take place in the presence of only reducing agent or catalyst. The presence of the catalyst and reducing agent is required for the reduction of dye. Different types of noble metal or metal oxides NPs were used to reduce the wastewater. However, the reduction of dye does not mean the complete mineralization into CO_2 and H_2O. In this process, it usually forms some byproduct during the reduction of methylene blue, and methyl orange is shown in Scheme 4.



Scheme 4. Formation byproduct in the reduction of dye.

Advanced Oxidation Process (AOP). AOPs are the processes in which hydroxyl radical generate during the reaction, and it catalyzes the reaction.

The formations of hydroxyl radical from hydrogen peroxide generally found to boost the reaction. The advanced oxidation processes are subdivided into various categories such as oxidation process, ozonization, Fenton process, photo Fenton process, etc. The hydroxyl radical is very reactive species, and has a very short lifetime. They react immediately with the organic substrate after its generation in the reaction mixture. Hao *et al*. reported that the stability of $OH^{\cdot}$ radical was very low and also suggested that the reaction is selective when the hydroxyl are generated via an in-situ process.[6]

Fenton Process. Fenton reagent, i.e. (H_2O_2 /Fe^{2+}) is an effective oxidation process among all the AOPs. The Fenton process is performed in a mixture of H_2O_2 and Fe^{2+} under pH conditions (acidic).[7] The reaction between H_2O_2 and Fe^{2+} generate highly reactive $OH^{\cdot}$ radical species. The OH·radical is considered as an excellent oxidizing agent in various reactions.[8] This process can be employed in the degradation of various pollutant like MB, MO, RhB, etc. and has gained huge attention in the wastewater treatment. Fenton process is also effective in the degradation of aromatic amines as well as for different organic substrate, surfactants, and pesticides.[9-11] The paint and textile industry also uses Fenton process in wastewater treatment. The main advantage associated with Fenton technique is that the waste management can be performed via $OH^{\cdot}$ radical without providing any energy.[12] H_2O_2 is considered as a green oxidant and has been used in large scale due to its low cost. The problem associated with the Fenton process is in the regeneration of the catalyst. In general, metal

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catalysts are usually dissolved in the presence of H_2O_2.[13] The generation of hydroxyl radical get enhanced when the reaction is irradiated by UV visible light.[14]

Photocatalytic Dye Degradation. Photocatalytic degradation of organic pollutants such as methylene blue has attracted the researcher due to its high efficiency. The degradation is generally performed using some of the semiconducting material such as TiO_2, ZnO, WO_3 etc.[15-17] The semiconducting material, i.e. TiO_2 possesses to be as an ideal catalyst in the various reactions owing to its ability to act as photocatalyst. The band gap of TiO_2 are high, and it only absorbs the UV light of the solar spectrum. Moreover, the recombination of electron and hole of TiO_2 during the photocatalytic decreases the activity. The growth of effective semiconductor such as TiO_2, CdS, ZnO, etc. are used to degrade the dyes with high effectiveness, but only in the UV-region. Therefore, various photocatalysts were designed to degrade the toxic dye pollutant from the water under visible light.

Heterogeneous photocatalysts are nowadays considered as one of the highly beneficial processes in wastewater management. Such catalysts have the tendency to absorbs the visible light from the solar spectrum generating the photogenerated pair of electron and hole for degradation of organic pollutants. TiO_2 in the degradation of dye pollutant are classified as (1) The color of the dye vanishes after photocatalytic oxidation, and it also get back via reduction process.[15] (2) The photodegradation process degrades complex stable dye molecule to CO_2 and water as the final

products. The vanishing of color cannot be considered as an indicator for the complete degradation of the dye molecule. The efficiency of photocatalytic degradation can also be accurately determined from total organic carbon (TOC) analysis.

Metal oxides in photocatalysis

The presence of structural defects in the semiconducting material increases the reactivity of the catalysts. The nanomaterial with high surface area enhances the activity in various organic reactions. In general, nanomaterial shows high catalytic activity in comparison to the bulk or pure metal.[19] Sakthivel *et al.* reported that among various photocatalysts, TiO_2, and ZnO are found to be suitable in wastewater treatment.[20] The most important criteria for good catalyst in the photochemical reaction are that it must have a suitable band gap, high surface area, and porous material, morphology, and must possess high stability and reusability. Khan *et al* reported that after excitation of metal oxide, the photoexcited electrons jump to the conduction band (CB) and create hole in valence band (VB) The photogenerated pairs (e^-/h^+) forming the highly active radicals such as hydroxyl, superoxide's, etc. participates in the degradation of organic pollutant, Scheme 5. The excited electron and hole then recombine and releases the energy gained from the excitation of the electron. This recombination of electron-hole pair in higher levels leads to an inefficient photocatalytic activity. Therefore, to reduce the electron-hole pair rate or to increase the exciton lifetime, modification of the semiconductor is essential methods to enhance the photocatalytic activity.

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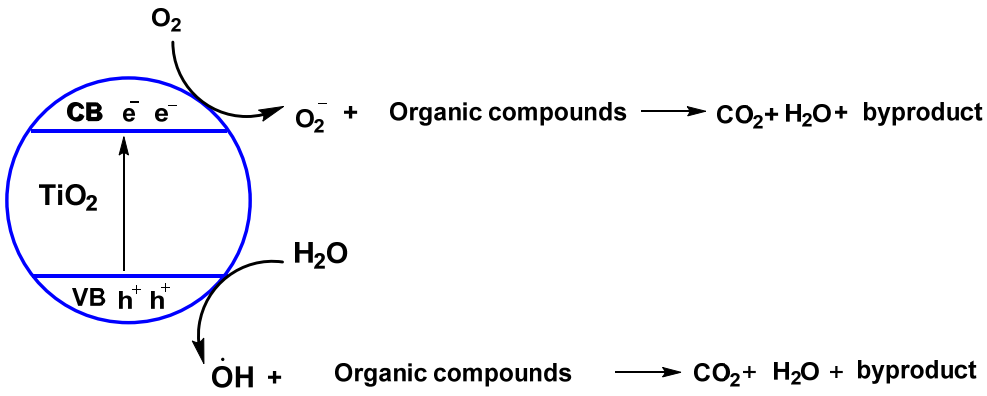

Scheme 5. A plausible mechanism of dye degradation under visible light using TiO_2.

Conclusion

Different types of dye degradation processes have been discussed, including their advantage and limitations. Among all the processes, photocatalytic degradation of dye pollutant was found to be an excellent way of mineralization into CO_2 and H_2O.

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