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Process intensified removal of methyl violet 2B using modified cavity-bubbles oxidation reactor

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ABSTRACT

An intensified method for treatment of wastewater containing a commercial dye (Methyl Violet 2B (MV 2B)) has been studied with novel approaches based on UV-air bubble induced oxidation. A modified reactor containing small glass balls was used for this purpose. The impact of the operating parameters such as initial concentration and pH as well as the effect of loadings of various catalysts likeTiO_2, MnO_2, ZnO etc. on the extent of removal of MV 2B dye have been investigated. So as to maximize the efficacy of removal of the dye, the reactor used in the author's earlier work was modified by incorporating ultraviolet light source in the system. The removal of Methyl Violet (2B) was found to be maximum (96.8%) with the loading of a mixture of TiO_2 and MnO_2 catalysts. Also, the effect of various metal oxide catalysts on the removal of methyl violet 2B has been observed in the order of $TiO_2 > MnO_2 > ZnO$. Overall, the present investigation established that hybrid processes with the use of optimized loading of catalysts have promising future and can be successfully applied for the removal of toxic dyes from aqueous solution with intensification benefits.

1. Introduction

The production of toxic waste is increasing day by day as textile and other industries are growing remarkably. The impact of this toxic waste on the environment is quite quick and treacherous. Especially, dyes and pigments which play a vital role in the textile and dyeing industry and create a tremendous amount of toxic waste [1]. It has been observed that more than ten thousand dyes are currently utilized in the textile industry [2]. The discharge of such harmful dyes into the atmosphere creates severe environmental damage. The dyes have strong, complex and penetrative color with high mineralization demand. Also, azo dyes and subsequently their resulting products cause the serious carcinogenic effect to the environment [1]. The main purpose of the treatment of wastewater is to allow sewage and industrial effluents disposed of without causing unacceptable damage to the human and aquatic life, health or to the natural environment. Thus, there is a need to develop a sustainable process intensification technology which will treat the wastewater produced by industry before its disposal into the water bodies. Several efforts have been dedicated to develop the intensified process technologies those are ready to minimize the dangerous effects caused by industrial activities.

Various processes have been developed to treat the textile wastewater containing dyes which include membrane technology, activated carbon adsorption, chemical precipitation and biological treatment. However, these methods, singularly, are not efficient because of the high salt contents resulting from reactive dying [3] and there are chances of generation of the secondary waste. The biological process is ineffective for the treatment of these dyes because of the requirement of large carbon footprint, less flexibility in the operation with other processes and more time requirement. The other process such as adsorption, electrocoagulation and flocculation [4] used for the treatment of wastewater containing dyes are not effective as they produce secondary waste in the form of solid. Thus, it is important to build up critical systems with intensified techniques leading to complete removal of these dyes from the effluents without generation of the secondary waste.

Advanced oxidation processes (AOP) produce hydroxyl radicals and could be one of the intensified processes to degrade MV 2B. These OH radicals are produced either by using chemical oxidants such as O_3, H_2O_2 etc. or by adding the external energy such as ultrasound or ultraviolet irradiations with or without the use of catalysts. [5–15]. However, it has been observed that the approach of a combination of

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different AOPs is more competent for wastewater treatment than that of individual AOP due to considerably higher energy efficiencies [15–20].

In the present work, cavity-bubbles induced oxidation reactor with glass balls has been used in combination with ultraviolet irradiation. The working principle of this reactor is similar to the hydrodynamic cavitation where cavities are generated based on the orifice and venturi. In this work, two mechanisms have been explained which are responsible for the degradation. Use of glass balls and passage for high-velocity air through interstitial areas are creating similar conditions to the cavitation. In the first mechanism, when the high-velocity liquid fall on the surface of the glass balls continuously, it might create sufficient shear effects where the conditions of high local temperature and pressure could be developed resulting in the generation of oxidizing radicals. In another mechanism, when air passes through the glass balls, it induces liquid jets, which distribute into many smaller bubbles. The bubble contains some amount vapor and when the inner wall tension reaches a maximum limit, the bigger bubbles break instantly leading to the formation of oxidizing agents. However, UV light is used for the direct oxidation of the dye and also driven for the photo-excitation of the semiconductor [21,22]. The general mechanism of the formation of oxidizing radicals and their interaction with UV light is as follows:

$$H_2O + \text{cavity-bubble collapse} \rightarrow H^+ + OH^* \quad (1)$$

$$H_2O + \text{cavity-bubble collapse} \rightarrow \tfrac{1}{2} H_2 + \tfrac{1}{2} H_2O_2^* \quad (2)$$

$$OH^* + \text{Dye} \rightarrow \text{Degradation of the dye} \quad (3)$$

The present work is an extension of the work by Mahale D et al. [23] who investigated the degradation of MV 2B dye from aqueous solutions using air bubble-induced oxidation using glass balls. It was reported that the removal efficiency of MV 2B from wastewater can be enhanced in presence of various process intensifying additives using air bubble oxidation. However, in the present work, authors have intensified the process by modifying the equipment. The equipment now operates in a continuous mode and introduces UV light inside the reactor. The objective of the present work was to investigate the effectiveness of cavity-bubbles induced reactor by introducing the UV light and also to intensify the operation by investigating the effect of catalyst and additives to achieve maximum degradation of a basic dye MV 2B.

MV 2B has been used as a model pollutant for the destruction with the help of modified cavity-bubbles induced oxidation with UV irradiation. It is a basic dye with highly brilliant color and intensity and widely used in textiles as a purple dye and in paint and ink as a deep violet. It was also reported that the MV 2B affects the bacterial growth and reaction of photosynthesis by the aquatic plant. MV 2B which can cause irritation of eyes and skin damages. The harmful properties of the MV 2B dye may cause damage to human and aquatic life. Therefore complete removal of MV 2B dye from industrial effluents before disposing into the river is necessary [24,25].

2. Materials and methods

2.1. Materials

Methyl Violet 2B (crystal structure) is also called Gentine violet B, methylrosanilinium, basic violet 3. Methyl Violet is an organic compound containing methyl groups. The molecular structure of methyl violet 2B has been shown in Fig. 1. The required concentration of aqueous solution of Methyl Violet 2B was made by using demineralized water. Titanium Dioxide (TiO_2), Manganese Oxide (MnO_2) and Zinc Oxide (ZnO) were purchased (all of AR Grade) from Merck Specialties Pvt. Ltd., Mumbai, India. TiO_2 (fine powder with nano-size range) used in the present work was a combined of anatase and rutile form. The characterization of titanium dioxide powder with SEM images was reported in the earlier work [26].

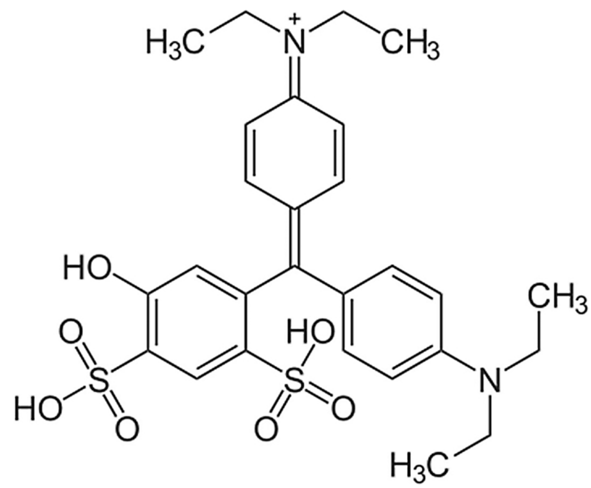

Fig. 1. Chemical Structure of Methyl Violet 2B.

2.2. Equipments and procedure

In the author's earlier study [23], the maximum degradation of 73.1% of 20 ppm Patent blue V solution was obtained using cavity-bubbles induced oxidation without adding any catalyst for reaction time of 180 min in batch mode. However, our main objective is to reduce the reaction time and to achieve the maximum efficacy of removal of the dye. To reduce the reaction time, it is important to introduce maximum amount of energy which generates more amount of oxidizing radicals in the solution. Thus, authors modified the earlier cavity-bubbles induced oxidation reactor with the addition of UV source. Also, this technique can be useful for the effluent treatment of any industry if it can be operated at a larger volume. But the limitation of the reactor is the size of the reactor; as to induce cavities in the solution thus, it requires certain jet flows inside the reactor. Authors made an attempt to suppress the above limitation by carrying out experiments in a continuous mode. The detailed schematic representation of UV-air bubble oxidation reactor has been depicted in Fig. 2. An ultraviolet lamp was introduced in the central compartment of the reactor and −submerged pump was used to operate the reactor in a continuous mode. The rest of the assembly was kept same as per the previous work [23].

The effect of process intensifying additives with the range of 0.2–1% (w/v) loading has been investigated. 10 ml of the samples were withdrawn from the solution after regular interval of 20 min. Before analysis, the samples were filtered using Whatman's filter paper (0.1 μm) for removal of solid particles. To check the reproducibility, all the experimentally obtained results were checked repeatedly and average values within 2% error bar have been reported in the discussion. The samples for treated and untreated solutions were determined for degradation under a UV–VIS spectrophotometer (Chemito Spectra scan UV 2600 double beam) at a wavelength, $\lambda = 675$ nm.

Adsorption studies of MV 2B on catalyst surface of metal oxides were also investigated as a preliminary study. In the experimental run, the catalyst of TiO_2, ZnO, and MnO_2 has been used with 100 ml of the dye solution and the mixture was kept for 24 h in a dark room. It has been observed the change in the dye concentration on the catalyst surface was 4%, 3% and 2% for the catalyst of TiO_2, ZnO, and MnO_2, respectively. Thus, based on the result of adsorption studies, error bars have also been shown to depict the variation, which was within 2% of the reported average value.

3. Results and discussions

3.1. Effect of initial dye concentration

The effect of initial concentration of MV 2B on the extent of

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