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Degradation of brilliant green dye using combined treatment strategies based on different irradiations

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ABSTRACT

The present study is based on the use of combination strategies based on sonolysis, photolysis, and microwave applied for wastewater treatment. Brilliant green (BG) dye has been considered as the model pollutant. The operating parameters viz. initial concentration of dye and pH of the solution were optimized for the individual effect of sonolysis, photolysis and microwave. The optimized initial concentration of dye pollutant as 20 ppm and pH of 6.0 was found to be same for all the individual approaches. It has been observed that the first order kinetic rate constant was the maximum for individual microwave (6.1×10^{-2} min^{-1}) and also operation was effective in terms of the energy requirement (maximum degradation efficiency as 2.8×10^{-8} g/J). The percentage degradation was found to be the maximum for the sequential operation of microwave followed by sonolysis (93.2%) compared to the combination of sonolysis and photolysis (84.5%), and sequential operation of sonolysis followed by microwave (80.6%). The effectiveness of combination and sequential approaches was analyzed based on the kinetic rate constant, percentage degradation, time required for degradation, and energy requirement. The obtained results in the present study indicate that the sequential operation of microwave followed by sonolysis was the most effective approach as compared to the other approaches. A continuous process has been also developed based on the sequential effect and the percentage degradation was found to be same for batch and continuous mode of operation.

1. Introduction

More than 10,000 different dyes and pigments are used in industries and its worldwide annual consumption is 7×10^5 tonnes [1]. These industries are considered as the one of the largest water consuming and are known to have maximum contribution to the wastewater that can contaminate the natural streams. Untreated dye remains in the environment for an extended period of time due to the high stability to light and temperature. The presence of low concentrations of dyes in effluent streams has acute or chronic effect on the organisms and thus on the activity of aquatic life. The biological activity present in the environment is insufficient to treat these dyes as well as the possible intermediate complexes and hence there is a significant risk to the food chain [2].

Chemical oxidation is most commonly used for decolorization of low concentrations of dye pollutants. Oxidants used for the treatment includes chlorine, hydrogen peroxide, ozone and chlorine dioxide. Chlorine (as sodium hypochlorite) has been used for the bleaching of textile wastewater [3]. Water soluble dyes can be easily bleached by chlorination but the insoluble dyes resist decolorization process. The treatment based on the adsorption on activated carbon has limitation of lower applicability, low efficiency and transfer of dyes from the liquid to the solid phase causing secondary pollution [3,4].

Considering the limitations of these process, interest into alternative treatment techniques such as advanced oxidation processes (AOPs) or sonochemical reactors based on cavitation effects developed with processes being operated alone or in combination with the other AOPs such as photolysis and Fenton chemistry. The phenomena of cavitation can be defined as the nucleation, growth and collapse of bubble/cavities in liquid, releasing large magnitude of energy. The collapse of the bubbles induces conditions of high temperature and pressures also releasing free radicals [3]. The sonochemically induced reactions can occur inside the cavity (pyrolysis mechanism), at the interface of gas–liquid and/or in the bulk of the solution. Generation of free radicals, hot spots and intense turbulence are favorable for the treatment of dye pollutants by oxidation. The formation of hydroxyl radicals (during bubble collapse, the hydroxyl radicals are formed due to the thermal

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decomposition of water molecule) and its subsequent attack on dye molecules can be controlling mechanism for the degradation of dye pollutants [2,3]. Cavitation alone may not produce enough hydroxyl radicals for the complete and efficient treatment of the dye pollutant and this effect can be further intensified in presence of additives such Fe metal, Fenton's reagent and hydrogen peroxide [3]. The use of additives can also pose additional disadvantages such as separation of additive, disposal of secondary waste and enhanced cost of processing. The combination of sonolysis with other oxidation processes viz. microwave irradiation and photolysis can also be an important approach and can give synergistic effects. Microwave irradiation passes through the walls of the vessel directly into the bulk of reaction mixture and these interactions produce three specific effects viz. (a) thermal (b) specific excitation and (c) non-thermal. The thermal and specific excitation effects are useful for generation of 'hydroxyl radicals'. Non-thermal effects are the electrostatic polar effects arising from the dipole–dipole type of interaction of polar molecules and changes in the electric fields. These effects improve the collision efficiency by mutual orientation of polar molecules involved in the process [5]. Microwave has limitation of localized heating in certain zones of the reactor. Another method commonly practiced in wastewater treatment is photolysis which is also based on the mechanism of 'hydroxyl radical' formation. When UV light is exposed to the aqueous solution, the positive holes (h^+) and electrons (e^-) are generated which can trap the pollutant on the actives (positive) holes. The limitation of photolysis is that photo-induced holes can recombine before they trap the pollutant and hence give low quantum efficiency [6]. Photolysis alone results in low degradation rate and long reaction time, which can make the process uneconomical. In order to overcome the limitations of the individual processes, the combination of these techniques can be effectively harnessed for the treatment of wastewater. The combination of sonolysis and photolysis (sonophotolysis) may improve the process efficiency compared to the individual effect [7]. The combination of microwave with ultrasound technique can also improve the process chemistry and reduce the process time significantly as compared to the individual operations [8]. Development of this combination of ultrasound and microwave is mainly affected by the problems related to the material of construction. The presence of metal in microwave cavity produces electric arc and hence it is difficult to use a simultaneous operation of microwave and ultrasound. Separate sequential effect of sonolysis and microwave can solve the problem of metal arc issue but may not be that effective. The present work investigates the efficiency of combined approaches based on sonolysis, photolysis and microwave for treatment of brilliant green containing wastewater. To the best of our knowledge, this is first depiction of combined approaches based on sonolysis and microwave for removal of dyestuff industry waste.

Brilliant green dye (BG) is commonly used in the paper industry and the requirement per ton of paper is 0.8–1.0 kg of BG. Besides paper industry, BG is commonly used in textiles, rubber and plastic industries and generates large amounts of effluents. BG is a toxic recalcitrant compound and it has mutagenic and carcinogenic effects affecting both aquatic life and humans [1]. There have been some earlier reports of application of cavitational reactors for the treatment of BG such as combination of cavitation and oxidizing agents (H_2O_2, $Na_2S_2O_8$ and NaOCl) [2], combination of ethanol, isobutanol, and 2-propanol with sonolysis [9], sonocatalysis involving polyacrylic acid hydrogel [10], and sonophotocatalytic treatment [7–11]. There have also been some literature reports based on the use of microwave (catalyst as $CoFe_2O_4$) [12], microwave assisted photocatalytic degradation [13] and photocatalytic oxidation (catalyst as TiO_2) [6].

The present work deals with investigation of degradation of BG dye using the individual effect of sonolysis, photolysis and microwave irradiation. Process parameters such as initial concentration of dye pollutant and pH were optimized for each approach. The degradation study also investigated the combined effects of sonophotolysis and sequential operation of microwave and sonolysis. The effectiveness of each approach has been analyzed based on the first order kinetic rate constant, percentage degradation, time required for degradation and energy required for the degradation. Continuous approach has been developed based on the optimized parameters of the batch process, which should introduce confidence for application of treatment schemes at large scale of operations.

2. Materials and methods

2.1. Materials

Brilliant green (BG) (also known as Malachite green, $C_{27}H_{33}N_2HO_4S$, C.I. number 42040) dye was obtained locally from Dyestuff Technology Department of the Institute of Chemical Technology, Mumbai. The stock solution of BG dye was prepared in distilled water, obtained from distilled water plant procured from Millipore. For adjusting the pH of BG dye solution, H_2SO_4 and NaOH solution has been used. Titanium dioxide (+50 mesh size, GR grade Merck) has been used for photocatalysis experiment. These chemicals were obtained from M/s Newneeta Chemicals, Pune, India. All the chemicals were used as received from the suppliers.

2.2. Experimental setup

The ultrasonic irradiations have been achieved using a simple ultrasonic horn, with tip diameter as 2 cm, operating frequency of 20 kHz and fixed power dissipation as 120 W. Ultrasonic horn was procured from M/s Dakshin, Mumbai. The actual power dissipation was 39 W (based on calorimetric measurement) which indicates an energy efficiency of 32.5%. The horn was introduced in a glass reactor (OD 83 mm and height 115 mm) of 500 ml capacity. Horn position was kept at the centre of the reactor and the tip was immersed to a depth of 1 cm. In the case of continuous ultrasound operation, peristaltic pump (Make: Miclins, Model No: VSP 50) was used for maintaining liquid level in the reactor. The inlet from feed tank was passed through the glass reactor equipped with ultrasonic horn using a peristaltic pump such that the horn tip was always immersed in the liquid.

A domestic microwave oven (LG Make, Model 1947C) with rated power of 160 W was used for introducing the microwave irradiations. The temperature of the reactor was recorded using infrared thermometer (Mextech, Model: DT – 8811). The calorimetric measurement revealed that the exact power dissipation was 108 W which indicates around 68% energy efficiency. In the case of continuous mode of operation, microwave oven has been modified for introducing the input and output lines. In order to avoid the microwave leakage, the drilled part of the oven was properly sealed. The beaker is kept at the centre location for maximum absorption of energy. Two peristaltic pumps were used for introducing and removing the solution from the reactor. The reaction mixture was exposed for various time intervals under microwave and ultrasound for the sequential mode of operation.

The experiments related photolysis and photocatalytic oxidation were performed using two UV tubes (Philips make with capacity of 11 W). The typical spectrum pattern of UV tube in terms of wavelength was observed to be in the range 350–450 nm with a prominent peak at 365 nm. The tubes were placed on two adjacent sides of the reactor and covered with black paper in order to avoid the diffusion of radiations from the assembly. Magnetic stirrer was used for the uniform distribution of catalyst and to avoid the