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Visible light induced photocatalytic degradation of methylene blue using undoped Ag_2CrO_4

S.R.Patil[2], Sanjay R.Thakare[1]*, M.D.Choudari[2]
[1]Department of Chemistry, Science College, Congress Nagar, Nagpur - 400 012, (INDIA)
[2]Department of Applied Chemistry, B D College of Engineering, Seagram, Dist Wardha - 442 102, (INDIA)
E-mail: sanjaythakare@yahoo.co.uk; patil_subhashchandra@yahoo.co.in

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ABSTRACT

The photocatalytic degradation of methylene blue has been investigated in aqueous suspensions of silver chromate prepared by three different methods under variety of conditions which is essential from an application point of view. The degradation was monitored by measuring the change in substrate concentration as a function of irradiation time employing UV spectroscopic analysis. The degradation methylene blue was studied using different parameters such as type of photocatalyst, catalyst concentration and substrate concentration. The degradation rate was found to be strongly influenced by all above parameter. The photocatalyst AgC-US preparaed by ultrasonic method was found to be more efficient as compared with AgC-SS and AgC-RF.

KEYWORDS

Photocatalysis;
Methylene blue;
Silver chromate;
Dye;
Kinetics.

INTRODUCTION

Water is a basic requirement for all living organisms. Population increase and industrialization led to water pollution. One of the pollutants of water is the dye effluents from various textile industries. A substantial amount of dyestuff is lost during the dyeing process in the textile industry, which possess a major problem for the industry as well as a threat to the environment[1,2]. Decoulourization of dye effluents has therefore acquired increasing attention. During the past decades, photocatalytic processes involving $Ti0_2$ semiconductor particles under UV light illumination have been shown to be potentially advantageous and useful in the treatment of wastewater pollutants.

There are several studies related to the use of semiconductors in the photo mineralization of photo stable dyes[3-11]. The mechanism constituting heterogeneous photocatalytic oxidation processes has been discussed extensively in the literature[12,13]. Briefly, when a semiconductor such as $Ti0_2$ 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 (e_{cb}^-) leaving behind an electron vacancy or "hole" in the valence band (h_{vb}^+). If charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with sorbed species. Specially, h_{vb}^+ hole may react with surface-bound H_20 or OH^- to produce the hydroxyl radical ($OH^{.}$) and e_{cb}^- picked up by oxygen to generate superoxide radical anion ($O_2^{-\cdot}$) as indicated in eqs.1-3. It has been suggested that the hydroxyl radicals $(OH^{\cdot})$ and superoxide radical anions $(O_2^{\cdot -})$ are the primary oxidizing species in the photocatalytic oxidation processes. These oxidative reactions would result in the bleaching of the methylene blue.

$$\mathbf{TiO_2 + h\nu \rightarrow e_{cb}^- + h_{vb}^+} \tag{1}$$

$$\mathbf{O_2 + e_{cb}^- \rightarrow O_2^-} \tag{2}$$

$$\mathbf{H_2O + h_{vb}^+ \rightarrow OH^{\cdot} + H^+} \tag{3}$$

Earlier studies[3-11] have shown heterogeneous photocatalytic oxidation processes can be used for removing colouring material from dye effluent in the presence of light. But for the activation of TiO_2, UV light is required which hinder practical application. Ag_2CrO_4 have orthorhombic structure with 1.75 eV band gap and have a good photocatalytic activity than P25 Degussa. Ag_2CrO_4 is non toxic, quite stable in aqueous medium and activate under visible light are the advantages over TiO_2. Hence in the present study we use Ag_2CrO_4 prepared by different methods to understand more about photocatalytic processes. Methylene blue has been selected a refractory model compound in this oxidation process. Methylene blue is a basic dye extensively used for dying and printing cotton, silk etc. It is also used as a medicinal dye because of its antiseptic properties.

EXPERIMENTAL DETAILS

The photochemical degradation of methylene blue (s d fine-chem) was studied in presence of Ag_2CrO_4 prepared by different methods viz. ultrasonic, Reflux, Solid State reaction methods by using stoichiometric amount of $AgNO_3$ (s d fine-chem) and K_2CrO_4 (s d fine-chem). The water employed in all the studies was double distilled water. The samples prepared by ultrasonic, Reflux, Solid State reaction method was denoted as AgC-US, AgC-RF, and AgC-SS here after. The detail about its photophysical properties are described elsewhere. The pH of the resultant mixture was measured by using digital pH meter (systronics Model 335) and was found to be 5.6. The Photolysis of aqueous solution of methylene blue for 2, 4, 6 ppm and 100, 200, 300 mg of Ag_2CrO_4 prepared by different methods was carried out in a circular glass reactor (designed and fabricated in our laboratory). Tungsten lamp (40W/230V/36D, Phillips, Essential) was used as a visible light source. During the photolysis experiment air was bubbled in a solution continuously as a source of oxygen. Aliquots of the reaction mixture were withdrawn and suspensions were filtered through 0.2 μm millipore discs prior to a quantitative determination of methylene blue spectrophotometrically using UV-Visible spectrophotometer (ShimadzuUV-1800).

The mineralization of methylene blue was monitored by measuring the absorption intensity as a function of irradiation time whereas the degradation was monitored by measuring the absorbance on UV-Visible spectrophotometer (ShimadzuUV-1800). The absorption maxima of the methylene blue have been found to be 663 nm. Therefore, the degradation of the methylene blue was followed at the wavelength as a function of irradiation time with appropriate dilution. For each experiment, the degradation rate for the mineralization and decomposition of the model pollutants was calculated from the initial slope obtained by linear regression from a plot of the natural logarithm of absorbance of the methylene blue as a function of irradiation time, i.e. first order degradation kinetics. It was calculated in terms of mol $L^{-1}min^{-1}$.

RESULTS AND DISCUSSION

Photocatalysis is a powerful advanced oxidation process having many advantages over the other oxidation methods. Figure 1 shows the change in absorption intensity on irradiation of an aqueous solution of methylene blue in the presence of Ag_2CrO_4 prepared by different methods.

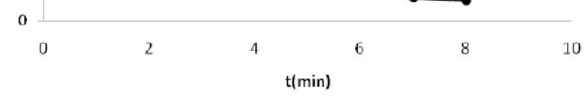

Figure 1 : Change in absoption intensity as a fuction of iradaition time for aqueous solution of methylene blue in present of different silver chromate. Experimental conditions: Concentration of methylene blue (2ppm), Volume 100ml, pH=5.6, Catalyst (200mg)

It was observed that the degradation of methylene blue is more for AgC-US, AgC-RF as compared with AgC-SS. The degradation curves can be fitted reasonably well by an exponential decay curve suggesting first order kinetics. For each experiment, the rate constant was calculated from the plot of natural logarithm of absorption intensity and dye concentration as a function of irradiation time. The degradation rate for the mineralization and decomposition was calculated using the formula given below,

$$-dk[A]/dt = kc^n$$

Where A=Absorbance, k= rate constant, c= concentration of MB, n=Order of reaction.

Blank experiments were carried out by irradiating aqueous solution of methylene blue in absence of photocatalyst, where no observable loss of methylene blue.

Silver chromate is known to be the semiconductor with the high photocatalytic activity is non-toxic, relatively inexpensive and stable in aqueous solution. Certain reviews have been written, regarding the mechanistic and kinetic details as well as the influence of experimental parameters. It has been demonstrated that degradation by photocatalysis can be more efficient than by other wet-oxidation techniques. We have tested the photocatalytic activity of three different photocatalysts prepared by different methods on the degradation kinetics of methylene blue. Figure 2 shows the degradation rate for the decomposition of methylene blue in the presence of different types of photocatalysts viz AgC-US, AgC-RF, and AgC-SS.

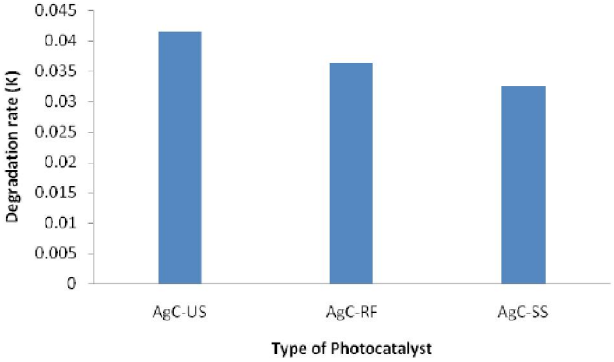

Figure 2 : Comparison of degradation rate for the mineralisation and decomposition of methylene blue in present of different silver chromate. Experimental conditions: Concentration of methylene blue (2ppm), Volume 100ml, pH=5.6, Catalyst (200mg)

It has been observed that the degradation of methylene blue proceeds much more rapidly in the presence of AgC-US, AgC-RF as compared with AgC-SS. This inferred that the catalyst prepared by ultrasonic method is more active than the other two catalysts. The differences in the photocatalytic activity of AgC-RF, AgC-SS and AgC-US are likely to be due to differences in the BET-surface, impurities, lattice mismatches or density of hydroxyl groups on the catalyst's surface since they will affect the adsorption behavior of a pollutant or intermediate molecule and recombination rate of electron-hole pairs.

In all the following experiments, AgC-US was used as a photocatalyst since this material exhibited the highest overall activity for the degradation of methylene blue.

It is important from a mechanistic and application point of view to study the dependence of photocatalytic reaction rate on the substrate concentration. Hence the effect of substrate concentration on the degradation of methylene blue was studied at different concentrations such as 2, 4 and 6 ppm. Figure 3 shows the degradation rate and decomposition of methylene blue as a function of substrate concentration employing Ag_2CrO_4 as photocatalyst prepared by different methods.

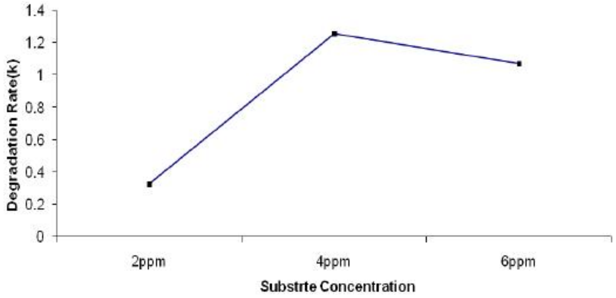

Figure 3 : Influence of sustrate concentration on the degradation rate for the mineralisation and decomposition of methylene blue in present of AgC-US Experimental conditions: Volume 100ml, pH=5.6, Catalyst (200mg)

It is interesting to note that for methylene blue, the degradation rate increases with the increase in substrate concentration from 2 to 4 ppm and further increase in substrate concentration led to decrease in degradation rate.

The effect of substrate concentration on the degradation rate for the decomposition and mineralization of methylene blue was studied, as it is important from both the mechanistic and application point of view. As oxidation proceeds, less and less of the surface of the Ag_2CrO_4 particle is covered as the pollutant is decomposed. Our results on the effect of the initial concentration on the degradation rate of methylene blue indicate that the degradation rate decreases with the increase in substrate concentration from 4 to 6ppm. This may be due to the fact that as the initial concentrations of the dye increases, the colour of the irradiating mixture becomes more and more intense which prevents the penetration of light to the surface of the catalyst. Hence, the generations of relative amount of $OH^\cdot$ and $O_2^{\cdot-}$ on the surface of the catalyst do not increase as the intensity of light, illumination time and concentration of the catalyst are constant. Conversely, their concentrations will decrease with increase in concentration of the dye as the light photons are largely absorbed and prevented from reaching the catalyst surface by the dye molecules. Consequently, the degradation efficiency of the dye decreases as the dye concentration increases.

The effect of catalyst concentration on the degradation of methylene blue was investigated by employing different concentrations of Ag_2CrO_4 varying from 100, 200 and 300 mg L^{-1} shown in figure 4.

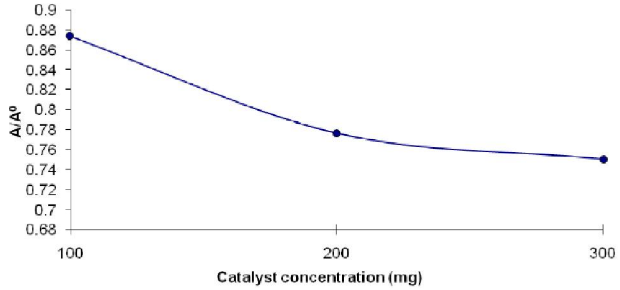

Figure 4 : Influence of catalyst concentration on the degradation rate for the mineralisation and decomposition of methylene blue in present of AgC-US as a photocatalyst. Experimental conditions: Concentration of methylene blue (2ppm), Volume 100ml, pH=5.6.

The degradation rate for the mineralization and decomposition of methylene blue under investigation was found to decrease with the increase in catalyst concentration and remain almost constant above certain level. This can be explaining as fallows, as amount of catalyst is increased, the substrate molecules available are not sufficient. As the number of Ag_2CrO_4 particles increases, i.e. although more area is available, for constant initial concentration of dye, the number of substrate molecules present in the solution is the same. Hence additional catalyst powder is not involved in catalyst activity and the rate does not increase with an increase in the amount of catalyst beyond certain limit. The results are in agreement with a number of studies reported earlier[14].

CONCLUSION

Ag_2CrO_4 as photocatalyst can efficiently catalyze the photomineralization of textile dye like methylene blue in the presence of visible light and oxygen. The degradation rate decreases with the increase in substrate concentration from 2 to 4ppm for AgC-US. The photocatalyst AgC-RF and AgC-US showed superior photocatalytic activity as compared with AgC-SS for the degradation of methylene blue under investigation. The observations of these investigations clearly demonstrate the importance of choosing the optimum degradation parameters to obtain a high degradation rate, which is essential for any practical application of photocatalytic oxidation processes. The best degradation condition depends strongly on the nature of pollutant. The investigations were conducted at the laboratory scale in order to determine the optimal degradation condition and further studies are required.

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