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VISIBLE LIGHT ASSISTED PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE USING TITANIUM DIOXIDE PILLARED SILVER-MONTMORILLONITE COMPOSITE IN WATER

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Abstract: Water is an easy solvent, enabling most of the pollutants to dissolve in it easily and contaminate it. Now a days industrial wastes mainly organic wastes are the main sources of water pollution. Among the advanced oxidation processes, photocatalysis by semiconducting materials has become a leading technology in the field of environmental cleaning. In the present study a naturally occurring smectite clay, montmorillonite is modified with Ag(I) and TiO_2. The performance of the material was tested in degradation of methylene blue under visible light irradiation. Dose variation, concentration variation and effect of time of the degradation reactions are done in the study. The catalyst was characterized by FTIR spectra and BET surface area analysis. Due to the excellent sedimentation property after reaction the clay can be easily recovered and reused.

Keywords: montmorillonite; TiO_2; silver; methylene blue

1. Introduction:

The ideal heterogeneous catalysts are expected to be cheap, obtainable for wide pH vary, in addition as have high chemical action activity and stability. At present, the catalyst supports embrace organic and inorganic materials. Among these supports, clays have been reportable to be smart candidates as catalyst supports because they're natural, abundant, efficient, environmentally benign in addition as their distinctive properties and structures [1]. Cation-doped pillared clays have attracted nice interest in academia and trade. Researchers in many teams have found that the chemical action performance of pillared clays is greatly enhanced by doping a little quantity of transition metal ions. For loading transition metal ions into pillared clays a Na^+ or K^+-exchanged clay is used as the starting material for the preparation of PILCs. A rigid microporous system forms after calcination at >400°C. The calcined PILCs are then changed with resolution containing the desired cations. By the process of calcination, because the pillaring precursors are reborn to rigid chemical compound pillars, protons are released. This method for Al-PILC is expressed as

$$2[Al_{13}O_4(OH)_{24}]^{7+} \xrightarrow{\qquad} 13Al_2O_3 + 14H^+ + 17H_2O$$

The liberated protons, with a charge and tiny volume, supposedly migrate into the salt layers, and are hardly accessible to succeeding cation-exchange processes [2, 3].

TiO_2, ZnO, Fe_2O_3, CdS, ZnS are semiconductors which can act as photocatalysts. Among all these, titania (TiO_2) is the most widely used semiconductor material owing to its nontoxicity, superior photoreactivity, long-run stability, and low worth. The photocatalytic activity of TiO_2 depends on numerous parameters, including impurities, extent, crystallinity, and density of surface radical teams. Generally, TiO_2 might be used as a photocatalyst in each anatase and rutile crystal structures. Anatase section includes an abundant higher activity than rutile [4, 5]. Irradiating the surface of a semiconductor with photons of energy up to or bigger than the band gap of the semiconductor, from the valence band Associate in promoting an electron to the conductivity band by making a hole, h^+ within the valence band. The ensuing photogenerated species h^+ and e^- will oxidize and scale back different species by completely different mechanistic pathways. In a semiconductor photocatalyst the photogenerated holes, h^+ should be highly oxidizing in nature to produce hydroxyl radicals. Whereas, the photogenerated electrons, e^- should be able to produce superoxides from the oxygen [6]. It is also important that the semiconductor does not undergo decomposition (photocorrosion) like Zn^{2+} in ZnO and Cd^{2+} in CdS by the formation of holes. So,the element should have more than one stable valence in the semiconductor. Furthermore, a semiconductor must have a suitable band gap and must be nontoxic and cheap [7-9].

About 15% of the full world production of dyes is lost throughout the coloring method and are discharged in the textile effluents [10]. The discharge of these coloured waste waters within the system may be a dramatic supply of non-aesthetic pollution, eutrophication and perturbations within the aquatic life [11]. Many of these dyes are very toxic and even carcinogenic and this posses a serious hazard to aquatic living organisms. Cationic dyes are known to be more toxic than anionic dyes [12]. Colored effluents decrease the transparency, influence chemical change activity, and lift the chemical oxygen demand, which hinders microbic activities of submerged organisms. Dyes cannot be simply removed by typical waste matter treatment processes due to their advanced structure and artificial origin, though most dyes break down with time and exposure to daylight, water, soap, and oxidizing agents. Treatment of waste matter containing dyes has been an important and difficult space of analysis [13].

In this work, heterogeneous catalyst TiO_2-Ag-montmorillonite was prepared and employed for the photocatalytic degradation of methylene blue (MB) dye under visible light irradiation. The effects of operating parameters such as initial concentration, catalyst dosage and irradiaton time on the degradation of MB were investigated systematically.

2. Materials and methods:

2.1. Materials:

Starting materials for the preparation of composites were TiO_2 and the fine fraction of montmorillonite. silver nitrate was used for ion exchange in clay minerals. Dye degradation was performed with methylene blue. All the chemicals were of analytical grade and were used without any further purification. $AgNO_3$, TiO_2, MB were purchased from Merck Chemicals, USA. Deionized water (conductivity < 0.15 $mScm^{-1}$) was used throughout the experiments.

2.2. Preparation of the catalyst:

One gram of clay was left to swell in 100 mL of distilled water for 1 day. The next day, 1 mmol of Ag(I) nitrate were added to the clay swollen in distilled water, the volume of the medium was brought up to 500 mL by the addition of distilled water, and the suspension was left to stand in a hot air thermostat at 35^0C for 2 days. The precipitate obtained was next washed 3 times in distilled water, centrifuged and dried at 65^0C. The composite was calcined at 500^0C for 3 hours and then grinded, for 30 minutes in an agate mortar with Calcined TiO_2 to get a powdered mixture consisting of 20% exchanged transition metal-clay and 80% TiO_2 [14].

2.3. Preparation of dye solution:

A stock solution of the dye Methylene Blue (MB) of concentration 1.0×10^{-4} M (= 31.985 mg L^{-1}) was prepared by dissolving an accurately weighed amount in double distilled water. The stock solution was appropriately diluted to obtain experimental dye solutions of concentrations 1.0×10^{-5} (= 3.1985 mg L^{-1}) and 5.0×10^{-5} M(= 15.9925 mg L^{-1}) and 5.0×10^{-6} M(= 1.59925 mg L^{-1}).

2.4. Photocatalytic reactions:

The photocatalytic reactor consisted of a stainless steel chamber fitted with a 300 W tungsten lamp (Philips 38941-1; PS 25, Frost-6100) as the visible-light source, equipped with a wavelength filter ($\lambda > 400$ nm) at the bottom. The degradation experiments of the dye were carried out at 30^0C and the reaction mixture was taken in a double walled beaker with continuous circulation of running water in the outer jacket ensuring constant temperature of the reaction mixture. In all the degradation experiments, the reactants were vigorously stirred for 30 min in the dark to establish an adsorption/desorption equilibrium between the catalyst and the dye, followed by exposure to visible-light irradiation. 10 ml aliquots were taken out at 15 min intervals and centrifuged to remove solid catalyst particles and the centrifugate was analyzed for the unconverted dye using a Shimadzu UV-1800 spectrophotometer at a λ_{max} of 664 nm. The reaction blank was carried out with the same procedure without adding the catalyst. Catalyst loadings of 0.02,0.04,0.06,0.08,0.1 and 0.12 g in 200 mL dye solution were used to investigate the effects of the same on methylene blue photo-degradation at pH 6.5 and a dye concentration of 1.0×10^{-5} M (= 3.198 mg L^{-1}). The photocatalytic conversion of the dye was done at three different concentrations of 5.0×10^{-6}, 1.0×10^{-5} and 5.0×10^{-5} M with a catalyst loading of 0.1 g in 200mL and pH 6.5.

2.5. Characterisation of the prepared catalyst:

The catalyst were characterized by Fourier Transform Infrared spectroscopy (FT-IR) measurements which was carried out with Shimadzu FT-IR 3000 spectrometer (resolution 4 cm^{-1}), the sample was pressed into KBr discs with a weight ratio of sample to KBr of 1 : 100. The surface area of the catalysts were determined by BET Adsorption isotherm method (Micromeritics Tristar Surface area and Porosity Analyzer).

3. Results and discussions:

3.1. Characterization of the catalysts:

3.1.1. FT-IR study:

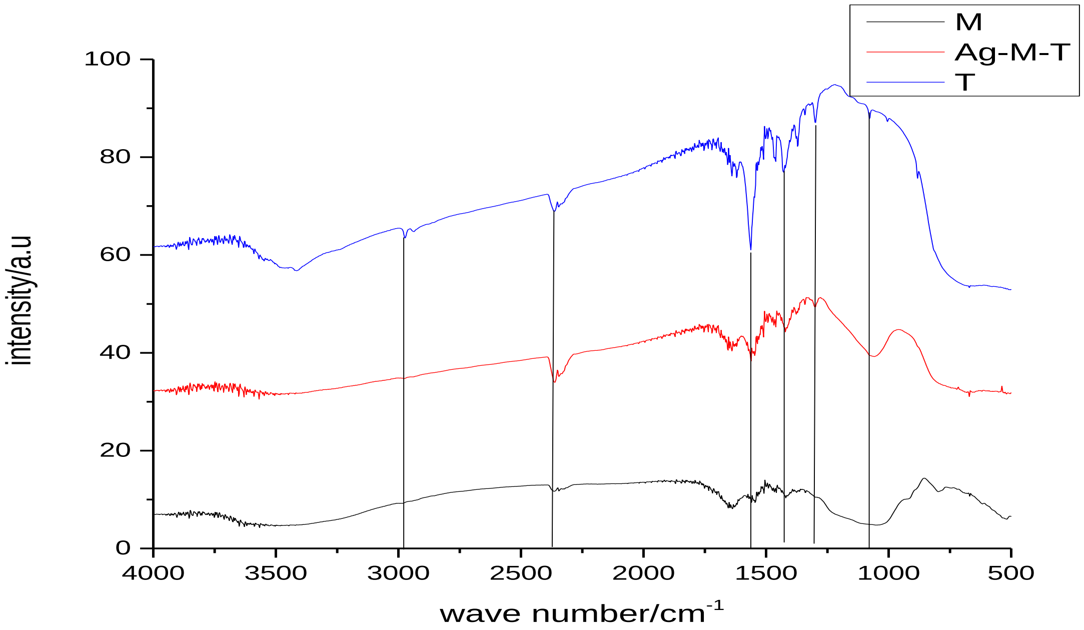

Figure 1: comparative FTIR plots of calcined TiO_2(T), Silver-montmrillonite-TiO_2(Ag-M-T) and calcined raw montmorillonite(M).

The FT-IR is used to determine the various functional groups and changes occurs due to various metals doping. The peak at 3650cm-1 is due to the O-H stretching frequency and the peaks around 1505 and 1625 cm-1 is due to the bending vibrations of H-O-H . At 518cm-1 is due to the Si-OH bending. The parent clay showed strong absorption bands at 1072 cm-1(Si–O stretching), 1636 cm-1 (interlayer water deformation vibrations), 914 cm-1 (OH deformation frequency of AI–AI–OH structural moiety), 799 cm-1 (Si–O stretching of quartz and silica), 694 cm-1 (coupled Al–O and Si–O (out-of-plane)), 525 cm-1 (Si–O–Al (octahedral Al)), and 471 cm-1 (Si–O–Si bending vibrations). All these bands are in conformity with those reported in a wide spectrum of literature [15]. In the 2000–1700 cm1 range a complex envelope of bands is present for both materials: it can be assigned to the typical overtones of the SiO2-like matrix [16]. The typical peaks for Ag are found in the range of 500-700 cm-1. In silver montmorillonite titania composite the peaks of titania and montmorillonite are modified.

3.1.2. BET surface area study:

The surface areas of the catalysts were determined by BET adsorption isotherm method. For the determination of the surface area of the catalysts, the samples were first degassed under vacuum at 300^0C for 4hr. N_2 was used as the absorption gas. After cooling the sample, the surface areas were determined. The surface areas found were 34.398 and 22.45 m^2g^{-1} for Ag-mont-TiO_2 and original montmorillonite. Again, the pore radius of modified catalyst and the original one was found as 17.808 and 48.95 Å. The surface areas of the catalysts were found to increase and pore radius is decreased after modification. The increase in surface area and decrease in pore radius of the catalyst after metal impregnation and titania modification indicated the increase in catalytic activity of the same.

3.2. Photocatalytic degradation of Methylene Blue:

3.2.1. Blank Experiment:

Before we investigated the effectiveness of the prepared catalyst for photocatalytic degradation of MB, in water (0.5 g/L each), a set of blank experiments (i.e. without any catalysts) were carried out under the same conditions of temperature (room temperature), atmospheric pressure, and time interval. No measurable conversion could be observed in this case.

3.2.2. Effect of reaction time:

The reaction were carried out under photocatalytic reactor at room temperature, atmospheric pressure and under visible light irradiation, MB concentration of $1x10^{-5}$M and catalysts load of 0.5g/L at as prepared pH for 1.5h. The samples were taken out after irradiation of visible light at an interval of time of 15 min after half an hour dark reaction.

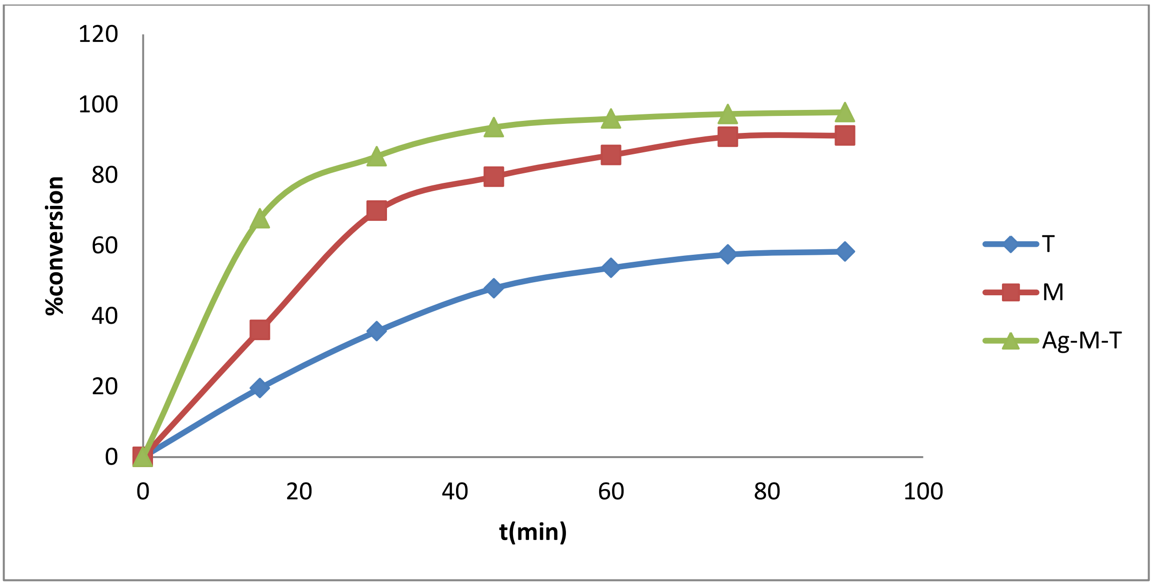

Figure 2: Effect of % Conversion with time for Titania(T), montmorillonite(M) and silver montmorillonite titania(Ag-M-T) catalysts.

It was found that with increase in time the % conversion of MB increases and gets a maximum value of 58.2738, 88.6792 and 97.8367 for TiO_2, montmorillonite and modified catalyst with silver respectively. After 80 min of irradiation time the conversion became stable. The degradation is shown in fig 2. With increase in reaction time the catalyst surface gets more and more exposure to photons and forms $OH^{\cdot}$ Radicals resulting in degradation of MB.

3.2.3. Effect of dye concentration on Methylene blue degradation:

For different MB concentrations of $5x10^{-5}$, 10^{-5} and $5x\ 10^{-6}$ M were studied for Ag-M-T loads of 0.5 gL^{-1}. The most efficient degradation occurs with $5x10^{-6}$M dye solution. The extent of decomposition of the dye was obtained from the ratio C_e/C_0, where C_e and C_0 are the absorbances at a particular time interval and at t = 0 respectively. As MB concentration increases degradation decreases. The chance of formation of $OH^{\cdot}$ radicals on the catalyst surface and $OH^{\cdot}$ radicals reacting with dye molecules verify the degradation rate. Because of the increase in initial dye concentrations, a lot of dye molecules are readily available for excitation and energy transfer. On the opposite hand, the decrease in degradation with the rise in dye concentration happens when the initial concentrations of the dye increase more, dye molecules are adsorbed on the surface of the catalyst and important quantity of visible light is absorbed by the dye molecules instead of the TiO_2 particles. Hence, the penetration of irradiations to the surface of the catalyst decreases. The active sites was occupied by dyes which decreases the generation of hydroxyl radicals. The adsorbate dye on the photocatalyst also inhibits the reaction of adsorbate molecules with the photo-induced positive holes or radicals, since there is no direct contact of the semiconductor with them. This reduces the path length of the photons getting into the solution [17].

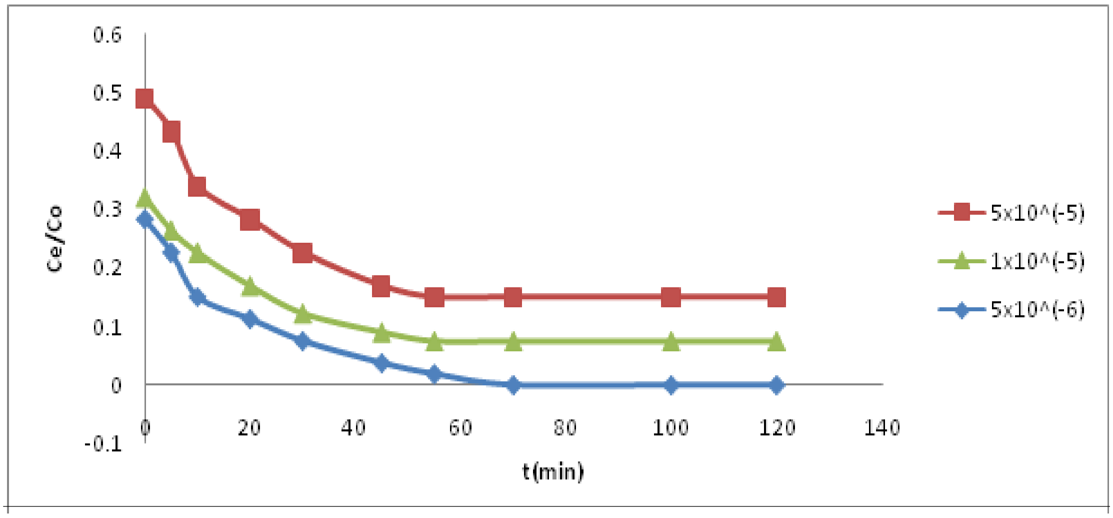

Figure 3: Effect of dye concentration on Methylene Blue degradation.

3.2.4. Effect of catalysts load on Methylene Blue degradation:

Different doses of catalysts were used to degrade MB under room temperature and one atmospheric presuure with a MB solution of 10^{-5}M at a pH 6.5. At all catalyst loadings upto 0.5 gL^{-1}, the photodegradation efficiencies were found to extend step by step with increasing doses of catalysts. The rise in catalyst loading is in the course of a rise within the variety of active sites on the photocatalyst surface, that successively redoubled the formation rate of hydroxyl radicals. Once the catalyst loading exceeded the limiting value, degradation rate decreases (i.e., at 0.6 gL^{-1}), because of the interception of light by the suspension. Aggregation of catalyst particles is predicted at high catalyst loading, inflicting a discount in surface active sites, increasing lightweight scattering and at last resulting in decrease within the passage of irradiation through the samples [18].

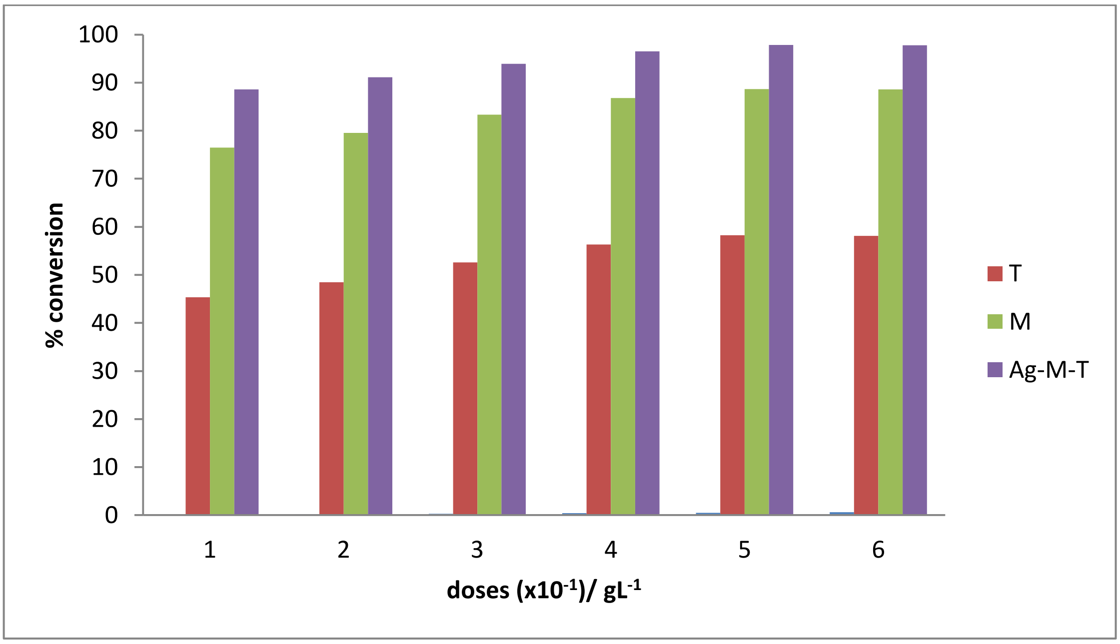

Figure 4: Effect of dose variation on Methylene Blue degradation for T,M and Ag-M-T.

3.3. Reaction study:

The products of the reaction were studied by GC-MS analysis (Perkin Elmer Precisely Clarus 600 C Mass Spectrometer). The products found were low molecular weight organic acids which are less harmful than the original dye, which could further be converted to CO_2 and H_2O.

4. Conclusions:

From the above discussions, it was concluded that silver impregnated montmorillonite supported titania was more efficient catalyst than that of raw montmorillonite or titania under visible light irradiations. As the reactions showed a high degradation of the dye, so this is very useful study for removal of dye in aqueous medium and the final products found were less harmful than the original one. So, titanium dioxide pillared silver-montmorillonite composite act as an active catalyst for removal of methylene blue dye at room temperature.

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