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ROLE OF LITHIUM COPPER MOLYBDATE AS PHOTOCATALYST FOR THE DEGRADATION OF INDIGO CARMINE DYE: AN ECOFRIENDLY APPROACH

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ABSTRACT

$Li_2CuMo_2O_8$ was used as photocatalyst for the degradation of indigo carmine dye. It was synthesized by solid state reaction between Li_2CO_3, CuO and MoO_3. The effect of variation of different parameters, i.e., pH, amount of semiconductor, concentration of dye and light intensity was also investigated. Maximum (92%) degradation of indigo carmine was observed. The formation of the inorganic products, NO_3^- and SO_4^{2-} and the evolution CO_2 revealed continuous mineralization of indigo carmine dye during the photocatalytic process. Quality parameters of dye solution before and after degradation were also determined. The rate of photodegradation of indigo carmine dye followed pseudo-first order kinetics. A tentative mechanism has been proposed.

Key words: Indigo carmine, Lithium copper molybdate, Chemical oxygen demand, Degradation, Mineralization, Ecofriendly.

INTRODUCTION

Dye effluents from textile, paper, chemical, and pulp industries are becoming a serious environmental problem because of their toxicity, unacceptable colour, high chemical oxygen demand content and biological degradation.[1] The presence of dye in water is not only aesthetically displeasing, but also affects water transparency, which results in the reduction of sunlight penetration, gas solubility and the photosynthetic reaction.[2] Therefore, many physical, chemical, and biological methods have been employed for the treatment of dye effluents from industries.[3] Major limitations of these methods are the operating cost, generation of byproducts and the process of regeneration of the starting compounds which are difficult.[4]

Therefore in the last decade, attention has been focused on treatment technologies that lead to complete destruction of the dye molecule. Among these treatments advanced oxidation processes (AOPs) have emerged as powerful remediation treatments to destroy refractory pollutants in water.[5] Among the various advanced oxidation process (AOPs) heterogeneous photocatalysis on metal oxide semiconductor particles has been found to be very effective for removing the organic pollutants from waste water.[6] .

Gondal and Sayeed[7] used ZnO semiconductor as a photocatalyst for the removal of phenol from water while Zhang et al.[8] synthesized TiO_2-graphene (TiO_2-GR) nanocomposites for gas-phase degradation

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of benzene and volatile aromatic pollutants in air. Mahyar et al.[9] reported the photodegradation of new fuchsin and amarnath using SiO_2-TiO_2 nanoparticle. Lin et al.[10] synthesized polyaniline (PANI)/TiO_2 nanocomposites for degradation of methyl orange. Zhang et al.[11] synthesized SnO_2/α-Fe_2O_3 semiconductor for the degradation of methylene blue. Li et al.[12] have prepared In_2O_3 for photodegradation of perfluorooctanoic acid (PFOA).

TiO_2/ZrO_2/SnO_2 nanocomposite was studied for photodegradation of rhodamine B dye by Lu et al.[13] Yadini et al.[14] reported photocatalytic degradation of fenamiphos organophosphorus pesticide using slurry and supported TiO_2. Yang et al.[15] have studied the photodegradation of methyl orange dye using $BaFeO_3$ photocatalyst. Huang et al.[16] synthesized $LaVO_4$/TiO_2 nanocrystals for decomposition of benzene. Chen et al.[17] used $SrTiO_3$ for NO degradation under UV light irradiation while Huang et al.[18] reported photodegradation of isopropanol by utilizing silver vanadate photocatalyst. Sadiq and Nesaraj[19] have carried out photodegradation of methyl orange and rhodamine B dye using NiO-Co_3O_4 nano-ceramic composite. A variety of semiconductor such as TiO_2, SiO_2-TiO_2, WO_3, ZnO, ZnS, etc. have been used for photocatalytic degradation of organic pollutants.

In the present work, $Li_2CuMo_2O_8$ was used as photocatalyst for photodegradation of indigo carmine dye. Indigo carmine dye, which is an anionic dye, is usually used in the textile, food and cosmetic industries. Indigo carmine is regarded as a highly toxic dye that may lead to tumours at the site of application, cause skin cancer or eye irritation and permanent injury to cornea.[20-22] The effect of various parameters such as pH, concentration of dye, amount of semiconductor and light intensity were studied.

EXPERIMENTAL

Indigo carmine (IC), 3,3'-Dioxo-2,2'-bis-indolyden-5,5'-disulfonic acid disodium salt, lithium carbonate, cupric oxide, molybdenum oxide, polyvinyl acetate, acetone $K_2Cr_2O_7$, $HgSO_4$, Ag_2SO_4, $Na_2S_2O_3$. $5H_2O$ were employed in the present study. Indigo carmine was used as a model system to investigate the photcatalytic activity of synthesized $Li_2CuMo_2O_8$. Its molecular formula is $C_{16}H_8N_2Na_2O_8S_2$ and molar mass 466.36 g/mol. 1.0 x 10^{-3} solution of IC (0.046 g IC in 100 mL water) was prepared with doubly distilled water and stored as a stock solution. The photocatalytic degradation of IC was observed by taking dye solution of 3.8 x 10^{-5} M and 0.10 g of $Li_2CuMo_2O_8$ at pH 9.5. Irradiation was carried out keeping the whole assembly exposed to a 200 W tungsten lamp (light intensity = 50.0 $mWcm^{-2}$). The intensity of light was measured with the help of a solarimeter (SM CEL 201). The pH of the solution was measured by the digital pH meter (Systronics Model 335). The desired pH of solution was adjusted by the addition of previously standardized 0.1 N sulphuric acid and 0.1 N sodium hydroxide solutions. The absorbance (A) was measured by a spectrophotometer (Systronics Model 106). Some water quality parameters like pH, conductivity, salanity, TDS (Total dissolved solids), and DO (Dissolved oxygen), were determined with the help of water analyzer (Systronic Water Analyzer Model 371). Structure of indigo carmine is given in Fig. 1.

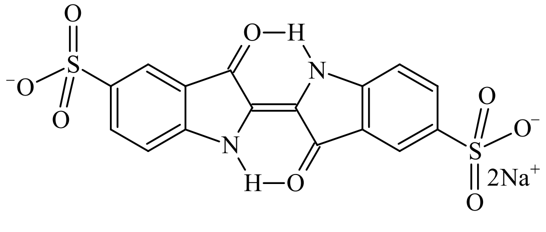

Fig. 1: Structure of Indigo carmine

Synthesis of semiconductor

A quaternary oxide was prepared by method of solid state reaction. Stoichiometric amounts of Li_2CO_3, CuO and MoO_3 were mixed and ground in an agate motor using acetone for homogeneity. 5% solution of polyvinyl acetate in acetone was added as a binder.

Calcination of semiconductor

The sample was kept in electric muffle furnace at 300^0C for 3 hrs to evaporate the binder. Then, the sample was calcined in furnance at 650^0C for 30 hrs. Then, the mixture was ground with a pestle in a mortar.

Photocatalytic degradation of indogo carmine

The photocatalytic degradation of indigo carmine dye using nanosized $Li_2CuMo_2O_8$ photocatalyst under visible light was investigated. The concentration of dye (in the form of absorbance) during photocatalytic degradation was measured at 640 nm (λ_{max}). A 200 W tungsten lamp was used as the visible light source. The progress of the photocatalytic reaction was observed by taking absorbance at regular time intervals. The change in absorbance versus irradiation time was measured. A typical run is presented in Fig. 2. It was observed that the absorbance (A) of indigo carmine solution decreased in presence of the photocatalyst and light. The plot of log A versus time was linear and hence, this reaction follows pseudo-first order kinetics. The rate constant (k) for this reaction was determined from the expression k = 2.303 x slope and it was 6.21×10^{-4} sec^{-1} under optimum conditions. The plot of a typical run is presented in Fig. 2.

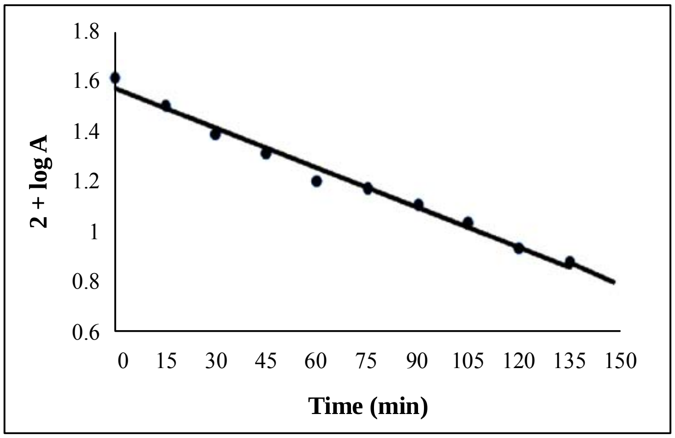

Fig. 2: A typical run

RESULTS AND DISCUSSION

Effect of pH

The effect of pH on photocatalytic degradation was investigated in the range 5.0- 10.0. The results are reported in Table 1.

It has been observed that the rate of photocatalytic degradation of indigo carmine increases as pH was increased and it attained optimum value at pH 9.5. On further increasing pH, the rate of the reaction was decreased. This behavior may be explained on the basis that as pH was increased, there is greater probability for the formation of oxygen anion radicals ($O_2^{-\bullet}$), which are produced from the reaction between O_2 molecule and electron (e^-) of the semiconductor. With the formation of more oxygen anion radicals, the rate of photocatalytic degradation of the dye increases. Above pH 9.5, a decrease in the rate of photocatalytic degradation of the dye was observed, which may be due to the fact that anionic form of indigo carmine is faces repulsion from the negatively charged semiconductor surface due to absorption of OH^- ions.

Table 1: Effect of pH

[Indigo carmine] = 3.8 × 10^{-5} M Light intensity = 50.0 mW cm^{-2}
Lithium copper molybdate = 0.10 g

pH	Rate constant (k) × 10^4 (sec^{-1})
5.0	1.53
5.5	2.51
6.0	3.21
6.5	3.52
7.0	4.20
7.5	4.78
8.0	5.23
8.5	5.48
9.0	5.92
9.5	**6.21**
10.0	5.09

Effect of Concentration of Indigo Carmine

The concentration of dye was varied from 3.4 x 10^{-5} to 4.3 x 10^{-5} M. The result are reported in Table 2.

Table 2: Effect of dye concentration

pH = 9.5 Light intensity = 50.0 mW cm^{-2}
Lithium copper molybdate = 0.10 g

[Indigo carmine] × 10^5 M	Rate Constant (k) × 10^4 (sec^{-1})
3.4	1.54
3.5	2.33
3.6	3.67
3.7	4.02
3.8	**6.21**
3.9	5.56
4.0	5.06
4.1	4.21
4.2	3.96
4.3	3.36

It has been observed that the rate of photocatalytic degradation increases with increasing the concentration of the dye up to 3.8 x 10^{-5} M. This may be due to the fact that as the concentration of the indigo carmine was increased, more dye molecules were available for excitation and consecutive reaction. Hence, an increased rate was observed. The rate of photocatalytic degradation was found to decrease with further increase in the concentration of dye. This may be attributed to the fact that the dye started acting as a filter for the incident light and it does not permit the desired light intensity to reach the photocatalyst surface in a limited time domain; thus, decreasing the rate of photocatalytic degradation of indigo carmine.

Effect of the amount of photocatalyst

The effect of the amount of photocatalyst is also likely to affect the process of dye degradation and therefore, different amounts of photocatalyst were used. The result are reported in Table 3.

Table 3: Effect of Lithium Copper Molybdate

pH = 9.5 Light intensity = 50.0 mW cm^{-2}
[Indigo carmine] = 3.8 × 10^{-5} M

Lithium copper molybdate (g)	Rate constant (k) × 10^4 (sec^{-1})
0.02	2.53
0.04	3.83
0.06	4.88
0.08	5.52
0.10	**6.21**
0.12	6.18
0.14	6.18
0.16	6.17

The rate of reaction was found to increase on increasing the amount of semiconductor, lithium copper molybdate. The rate of degradation reached to its optimum value at 0.10 g of the photocatalyst. Beyond 0.10 g, the rate of reaction becomes almost constant. This may be explained on the basis that as the amount of semiconductor was increased, the exposed surface area of the semiconductor also increases. However, after a particular value (0.10 g), an increase in the amount of semiconductor will only increase the thickness of layer of the semiconductor and not its exposed surface area. Therefore, a saturation like behavior (almost constant rate) was observed.

Effect of Light Intensity

The effect of the variation of the light intensity on the rate was also investigated and the result are reported in Table 4.

The results indicate that photocatalytic degradation of indigo carmine was enhanced with the increase in intensity of light, because an increase in the light intensity will increase the number of photons striking per unit area per unit time on the surface of photocatalyst. There was a slight decrease in the rate of reaction as the intensity of light was increased beyond 50.0 mW cm^{-2}. This may be due to some side reactions or thermal effects.

Table 4: Effect of light intenstiy

pH = 10 Lithium copper molybdate = 0.10 g

[Indigo carmine] = 3.8×10^{-5} M

Light intensity (mW cm^{-2})	Rate constant (k) × 10^4 (sec^{-1})
20.0	2.98
30.0	3.39
40.0	4.41
50.0	**6.21**
60.0	4.69
70.0	4.60

Determination of water quality parameters

Quality of water before and after photocatalytic degradation has been tested by measuring some parameters and results are summarized in Table 5.

Table 5: Water quality parameters

Parameter	Before photocatalytic degradation	After photocatalytic degradation
pH	9.5	7.8
Conductivity (µS)	271	372
TDS (ppm)	222	330
Salinity (ppt)	0.42	0.51
DO (ppm)	13.3	19.7
COD (mg/L)	40	20

pH: pH of sample represents the extent of its pollution by acidic and alkaline wastes. All chemical and biological reactions directly depend upon the pH of medium. pH of indigo carmine is in basic range before the degradation but after the photocatalytic degradation of the dye, pH reaches to near neutral range. It is clear that photocatalytic treatment affects the pH and makes it more desirable. pH of dye solution is not in permissible limit and therefore, it is not useful for irrigation and drinking purpose according to WHO standard, whereas pH of photocatalytically treated water by $Li_2CuMo_2O_8$ is suitable for animal and aquatic biota. This result indicates that pH value of sample was in alkaline range but within the ISI permissible limits.

Conductivity: Conductivity, as summation parameter is a measure of the level of ion concentration of a solution. It is directly proportional to contents of its dissolved mineral matter. Consequently, it is an index of the salt load in waste water or the impurity of water. Conductivity is only a quantitative measurement. Only ionizable material will contribute to conductivity. Conductivity was found to be increased in treated water. Slight decrease in pH and increase in conductivity also confirms the mineralization of dye into CO_2 and inorganic ions such as NO_3^-, SO_4^{2-} etc.

Total dissolved solid (TDS) and salinity: Dissolved solids refer to any minerals, salts, metal cations, or anions dissolved in water. This includes anything present in water other than pure water molecules and suspended solids. In general, high TDS result in an undesirable taste, which could be salty, bitter or metallic. It could also give gastrointestinal irritation. TDS value of indigo carmine increased from 222 ppm to 330 ppm due to mineralization of dye molecules.

Dissolved oxygen (DO): Dissolved oxygen indicates physical and biological activity in water. The minimum standard limit is 5 ppm. Oxygen can serve as electron sink to trap the excited conduction band electron from reactive oxygen species. DO is proposed to be responsible for cleavage of aromatic ring of dye molecule. Value of DO for indigo carmine dye solution increased from 13.3 to 19.7 ppm.

Chemical oxygen demand (COD): The chemical oxygen demand is widely used as an effective data to measure the organic strength of wastewater. This allows the measurement of waste in terms of the total quantity of oxygen required for the oxidation of organic matter to CO_2 and water. The COD of the dye solution before and after the treatment was estimated. The reduction in COD values of the treated dye solution indicates the mineralization of dye molecules along with colour removal.

Mechanism

On the basis of experimental observations, a tentative mechanism for photocatalytic degradation of malachite green may be proposed as:

$$^1IC_0 \longrightarrow {}^1IC_1$$

$$^1IC_1 \xrightarrow{ISC} {}^3IC_1$$

$$SC \xrightarrow{h\nu} e^- (CB) + h^+ (VB)$$

$$e^- + O_2 \longrightarrow O_2^{-\bullet}$$

$$O_2^{-\bullet} + {}^3IC_1 \longrightarrow \text{Leuco IC}$$

$$\text{Leuco IC} \longrightarrow \text{Products}$$

Indigo carmine absorbs radiations of desired wavelength and it is excited to its first excited singlet state. Further, it undergoes intersystem crossing (ISC) to give its more stable triplet state. Along with this, the semiconducting lithium copper molybdate (SC) also utilizes this energy to excite its electron from valence band to the conduction band. This electron will be abstracted by oxygen molecule (dissolved oxygen) generating superoxide anion radical ($O_2^{-\bullet}$). This anion radical will reduce indigo carmine dye to its leuco form, which may ultimately degrade to products. It was confirmed that this degradation proceeds through reduction and not oxidation as the rate of degradation was not affected appreciably in presence of hydroxyl radical scavenger (2-propanol). The presence NO_3^- and SO_4^{2-} ions were confirmed by their usual chemical tests. Carbon dioxide and water were the major products of degradation.

CONCLUSION

In the present study, the efficiency of photocatalytic degradation of indigo carmine dye solution using $Li_2CuMo_2O_8$ in presence of UV-light has been studied. The effects of pH, concentration of dye, amount of semiconductor, and light intensity have been investigated. The experimental result demonstrated that the optimal catalyst was 0.10 g with indigo carmine dye concentration of 3.8 x 10^{-5} M at 9.5 pH. 92% degradation has been achieved. This study highlights that the $Li_2CuMo_2O_8$ can be used as the photocatalyst for degradation of indigo carmine dye.

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