Preparation Nanocomposite CuO-Attapulgite, Used as Catalyst in Photo Degradation of Methyl Orange

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ABSTRACT

The purpose of this paper was analyzing the chemical degradation of Methyl Orange in water via “Photo-Fenton reaction. CuO - Attapulgite nano particles have been used as coating in an internal dike surface of the reactor. The degradation of MO dye has been predestined to be discovered by the catalytic work of CuO- Attapulgite synthesized surface in a turnout of hydrogen peroxide and UV light. Nanoparticles have been described by SEM, EDX, AFM and XRD. MO dye solution with 5 ppm initial concentration was decreased by 100% under the condition of (2.5ml H2O2), (temperature =25°C), (pH= 7) within (3 min). The remaining was observed in the solution via high-performance-liquid chromatography (HPLC). Each overhead state was calculated to reach an optimum working condition for the method (photo - Fenton). The Methyl orange degradation method has pursued first - order reaction basics. Photo - Fenton method caused a more effective oxidation average. The photo - Fenton”degradation was found to be an efficient and economical method via making higher proportion of mineralization and degradation in short time radiation.

Keywords: Kinetics, Photocatalytic Degradation, Methyl Orange Dye, Nano Technique.

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Received: 11 December 2017
Accepted: 25 March 2018

1. INTRODUCTION

Nano volume materials have shown unique medicinal, electronic, catalytic, optical and magnetic properties as well as the commercial and classical materials (Devi, Singh, 2014). The main characteristic of using metal oxides as a catalyst has been their low metal leaching through the catalytic reaction so averting the secondary metal contamination for the treated wastewater (Ameta et al., 2014). Metal oxide nanoparticles (NPs) have been receiving big attention for their possible implementations in nano-devices, optoelectronics, nanosensors, nano-electronics, catalysis, and information storage. Among several metal oxide NPs, CuO has attracted special interest because it has been the simplest organ in the family of copper complexes, and contains a sum of helpful physical properties like spin dynamics, high temperature superconductivity, and electron correlation effects (Ahamed et al., 2014). CuO nanoparticles have been increasingly applied in several enforcements like in batteries, catalysis, heat transfer fluids, gas sensors, and solar energy (Filipič, Cvelbar, 2012). CuO crystalline frames take possession of a tight band gap, giving helpful photovoltaic and photocatalytic properties (Li et al., 2011). Attapulgite body has been usually termned a series stratum. It is a unique metal structure that shows bands of alumino-silicate coats to be attached at their brinks. Attapulgite crystals are of needle shaped(circular) sort, rather than flake or - flat like, that have high surface area shown in figure (1) (Al-Sharify, Abdalla, 2012).

Usually, dyeing process uses big amounts of water for dyeing, washing and fixing processes (Naser, 2017), which fetches pollution along that harms human health and the environment (Ahu, et al., 1978; Srivastava, et al., 2004; Zanoni et al., 2014). Each year, it has been estimated that 12% of the synthetic texture dyes like methyl orange (MO), indigo red, methylene blue (MB), Rhoda mine B and eriochrome Black-T (EBT), get absent during the industry and processing, and 20% of these wasted dyes enter into the circumference through effluents derived from the treatment process of the industrial wastewaters. The problem of using synthetic dyes use and eliminating dyes from wastewater has been serious and challenging, since the generality of dyes and their degradation products may be toxic and carcinogenic to mammals (Hsiao, et al., 2014; Zhang, 2014). Methyl orange (MO) has been the most exemplary of all anionic azo dyes, which is not decomposed under the ambient conditions, and is generally resistant to the
classic biological pretreatment." The conventional physicochemical techniques, like reverse osmosis, adsorption, and coagulation, have been the most frequently developed to remove MO from the aqueous solutions. These processes can merely accumulate MO, and cannot transform the dye to harmless complexes (Jo, Selvam, 2015; Kumar, et al., 2013; Chamjangali, et al., 2015; Zhu, et al., 2012; Tripathy, et al., 2014).

"Amono-azo" dye methyl orange (MO) "(p-dimethyl amino-azo benzene sulfonic acid)", (MO) supplied via Merckco, having molecular weight of 327.33 and molecular structure of C14H14N3NaO3S, was used as the adsorbate in this work. Methyl orange was chosen as a sample of the series from popular azo dyes largely applied in the industry, its formula has been shown in Figure (2) (Samarghandi et al., 2009).

Advanced oxidation processes (AOPs) like photocatalytic process have become one of the most promising technologies for waste management, especially for the decomposition of the organic pollutants like dyes. The photocatalytic action of a process can be improved by a combination of heterogeneous catalyst and photolysis irradiation, thus, more hydroxyl radicals have been created. Several kinds of the heterogeneous catalysts have been widely investigated for a photocatalytic degradation of organic dyes like metal oxides heterogeneous catalyst which play an important role in catalytic reactions, and they additionally have been used in several applicable areas in physics, chemistry and materials science (Farzaneh, 2011). Fenton process has been well studied lately for its prospective applications in the unmanageable wastewater remediation (Feng and Le-Cheng, 2004). The aim of this work was using the industrial pollutants such as Methyl orange dye and designing photo-reactor system, where, a nano-catalyst such as Copper Oxide - Attapulgite composite was used. The technology of AFM, X-Ray, SEM, EDXA and HPLC was used to determine the structure of nanoparticles, and prove the degradation of dyes. The final conditions including time, pH, Temperature, H2O2 concentration, and the initial pollutant concentration, to reach the highest percentage of pollutant degradation were identified.

2. MATERIALS AND METHODS:

2.1. Materials:
Methyl Orange as used in this study, shown in Table (1), was obtained from Merck com. On the other hand, H2O2 (30%), Cu(NO3)2·3H2O, H2SO4, KMnO4, Na2CO3 and H2C2O4 were obtained from Sigma com. The predation was achieved using double distilled water. The Attapulgite clay used in present study was supplied from Geological Survey in Ministry of Industrial mineral, Baghdad, Iraq.

2.2. Preparation of Catalyst:
The preparation of CuO - Attapulgite nanocomposite was done in the following steps: an aqueous dispersion of Attapulgite clay was prepared by adding 2g attapulgite clay to 100 mL H2O under vigorous stirring for 3 h at 25°C. Sodium carbonate was added 4.8g slowly as a powder to a vigorously stirred solution of copper nitrate for 3h such that a molar ratio of 1:1 for [Na+] / [Cu+] was established. 100mL solution of the second step was added drop by drop to the dispersion of attapulgite clay prepared in the first step under vigorous stirring. The suspension was stirred for 3h followed by ageing at 100°C in an autoclave for 48h, and finally 200 mL solution containing CuO – Attapulgite nanocomposite was obtained for the coating of the CuO - Attapulgite nanocomposite on the stainless steel plate substrate. The photo-reactor was made of stainless steel pipe with the length of 15cm and the diameter of 4 cm, as shown in Figure (3).

2.3. Preparation of Dye Sample:
Standard stock solutions of 100 mg/L of Methyl Orange were prepared by diluting the corresponding mass of MO in de-ionized water, and then protected from light. A different initial concentration of MO was prepared by further diluting the standard stock solutions.

3. RESULTS AND DISCUSSION:

3.1. Characterization of the Catalyst:
3.1.1. XRD:
X-ray diffraction was used to analyze CuO- Attapulgite nanocomposite, and the result has been shown in Fig. (4). The particle sizes were calculated by Deby-Sherrer formula as given below (14):
The estimated particle size of the (Copper Oxide - Attapulgite composite) was (33.35) nm. The peaks’ position in the samples indicated the monoclinic structure and single phase, which was in agreements with those reported in JCPDS file (NO.48-1548). The existence of the sharp peaks in XRD samples and particle size of less than (100) nm referred to the Nanocrystalline nature of the surface.

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]  

(1)

Figure 4: XRD for: CuO-Attapulgite nanocomposite

3.1.2. AFM Analysis:
Atomic force microscope was used to investigate CuO-Attapulgite nanoparticles. AFM analysis represented data in three dimensions, so that it was possible to measure the height of the nanoparticles quantitatively. The average diameter was 42.53 nm for CuO-Attapulgite composite as shown in figure (5).

Figure 5: AFM of CuO-Attapulgite Nano composite

Figure 6: Scanning Electron Microscope (SEM) of CuO-Attapulgite nano composite

Energy Dispersive X-ray Analysis (EDXA)
EDXA was used to determine the crystallization of particles, and represented the presence of elements and their percentage in nature. Figure (7) shows the EDX result of a copper product, it could be concluded that the sample was composed mainly of copper.
3.2. Degradation of Methyl Orange:

Figure (8) shows the calibration curve for MO which was determined in λ max= 462.6 nm that obeyed the (Lambert beer’s law) at specific concentrations prepared for each compound. After that, the absorption was recorded, and a calibration curve was plotted between the adsorption and concentration, the best line between the points was drawn.

HPLC Chromatographic Analysis

The photo- Fenton degradation process was also observed by HPLC chromatogram for methyl orange degradation. Figure (9) explains the HPLC chromatogram and displays the absorbance peak of methyl orange dye degradation. After the irradiation, the ferocity of this peak was decreased with the irradiation time gradually.

To study the effect of initial dye concentration on the degradation efficiency, the experiments were carried out by using different initial concentration (5-20) ppm at temperature of 298.15K, pH= 7, and in presence of (15.3*10^-4 M H_2O_2 + catalyst+ 6W UV), Figure (10) shows that the higher initial dye concentration after 3 min led to 99.5% percentage, while 5ppm M.O concentration after 3 min reached to 100%. This phenomenon might be due to the fact that the number of dye molecules was increased, but the number of OH was still constant. On the other hand, with the increase in initial concentration of the dye, more dye molecules were adsorbed onto the surface of the catalyst, leading to a decrease in the oxidation process.

Figure (11) shows that in the absence of H_2O_2, with the catalyst at temperature of 298.15K, pH= 7, the degradation of 5 ppm M.O dye after 140 min was 99.3% and for 20 ppm dye, it was 97%. This indicated that H_2O_2 was important in diluting the concentration of dye but was not important in high murexide concentration.

Figure (12) indicates the effect of H_2O_2 concentration on the M.O dye degradation at the temperature of 298.15K, pH= 7, and [catalyst+ 6W UV], 5 ppm of M.O dye degradation was 99.1%, in case the concentration of H_2O_2 was 3.2*10^-4M while the degradation percentage was 99.5% in case of using 15.3*10^-4M H_2O_2 for high M.O dye concentration (20 ppm). The low H_2O_2 concentration (3.2*10^-4M) led the degradation percentage reach 98.4%. It was clear that 6.4*10^-4M H2O2 was
suitable to reach the degradation percentage ranging (98.7-99.6) % for M.O concentration of 5,10,15,20 ppm.

Figure 12: Variation of R% with H2O2 Concentration for Different M.O Concentration in Presence of UV-Light and Catalyst at 298.15K and pH=7

The effect of temperature on the degradation of M.O dye was investigated in three different temperatures (298.15, 308.15, 318.15) K in the following condition of pH=7, with different initial concentration of (5,10,15,20) ppm of M.O. The results in Figure (13) showed that, the removal percentage of (5,10,15,20) ppm increased when the temperature increased.

Figure 13: %R against Temperature for Different M.O Dye Concentration after 140 Minutes

The degradation of M.O dye by Fenton was a first order reaction. This was determined from the slope of the linear plot of logarithmic remaining M.O concentration versus the treatment time of t as shown in the following Figure (14).

Figure 14: The Relation between –log C and Time (min) at Temperature 298.15K

4. CONCLUSION:

CuO-Attapulgite nanocomposite as a heterogeneous Photo-Fenton catalyst in the presence of UV light and H2O2 was used for the degradation of Methyl Orange dye. Using optimal conditions (pH=7, 2*10^-3 M H2O2, and 6W UV), 100% degradation of Methyl Orange dye could be achieved in 3 minutes. The CuO-Attapulgite plated catalyst film could be applied for the treatment of wastewater in an inserted system consisting of a biological reactor and a photochemical reactor.

REFERENCES