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Removal of Methylene Blue in aqueous system using Copped based sandwich compound

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Abstract

We have prepared the copper based sandwich compound by graphene oxide which is further used as catalyst for removal of dye. It removed the dye in less time without using any specific reaction condition. Surface morphology of catalyst was characterized by FT-IR and SEM. The recycling test was also performed with catalyst up to 5 cycles.

Keywords: Sandwich compound, methylene blue, grapheme oxide, parameters.

Introduction

In several facets of the textile manufacturing industry, dyes are crucial. However, the dyes lack biodegradability and are frequently discharged into aquatic environments.[14] The majority of dyes contain harmful and cancer-causing qualities that can harm ecosystems and human health.[10] Because of their complex aromatic structures, dyes are resistant to natural degradation processes.[19] As a result, many treatment techniques have been employed to eliminate dyes. The adsorption process is the most often utilized method because low-cost adsorbents with large adsorption capabilities are readily available.[8] Owing to its ease of usage, the photo-catalysis process is another widely utilized approach.[5]

In the photo-oxidation of dye pollution, superoxide and hydroxyl radicals are commonly recognized as reactive oxygen species (ROS).[9] The removal of dyes in both reactions is largely reliant on the material's surface area.[18] The chemical process seems to be better because it is easy to use, inexpensive and produces large quantities.[6] To be more precise, there are three main steps in the process of preparing rGO using this method. The first step involves oxidizing graphite to produce graphite oxide which gives the graphene layers surface oxygen functionalities. Graphite oxide may disperse in polar solvents and may form stable dispersions due to the oxygenated functionalities (epoxides, hydroxyls and carboxyls) on its surface. Graphite oxide is then exfoliated by mechanical stirring or sonication to yield graphene oxide (GO) with one or more layers.

Finally, the surface oxygen functions are eliminated, reducing GO to rGO.[2] Traditionally, carbon-based materials have been used in adsorption reactions to remove both organic and inorganic pollutants.[20,21] Activated carbon is among the most widely used adsorbents.[7] rGO has been used in dye adsorption applications more and more recently.[4,12] Because some graphitic domain defects and residual surface oxygen functions exist, rGO is considered effective for the adsorptive removal of dyes.[1] Generally speaking, rGO interacts with dyes by p–p interaction, electrostatic interaction, hydrophobic association and structural conjugation. Many different dyes can adsorb on rGO.[13]

Large surface area and high porosity rGO are desirable for increasing the dye adsorption capacity; this can be accomplished by regulating the GO precursor's quality and the reduction technique employed.[22] The photocatalytic degradation of dyes is currently used to exploit the technological benefits of photocatalysis. When a photocatalyst's band gap is less than or equal to the energy of light absorbed, electrons are often activated and produce holes and electrons. The photogenerated electron–hole pairs then use the surrounding oxygen and water molecules to make reactive oxygen species (ROS), which degrade the dye molecules.[11]

In this study, we are reporting the graphene oxide based sandwich compound for removal of methylene blue dye. The removal process was further optimized with various parameters like effect of contact time, catalyst loading and dye concentration.

Material and Methods

We used all chemicals without further purification in our research and all were of reagent grade. CDH provided the methylene blue, graphite powder, citric acid and copper nitrate. Using a Scanning electron microscope, the products' morphology and structure were ascertained. With a Nicolet FT-170SX spectrometer, Fourier transforms infrared (FT-IR) spectra were recorded using KBr pellets in the 4000 – 400 cm^{-1} range. A UV-2450 ultraviolet–visible spectrophotometer was used to measure ultraviolet–visible (UV–vis) spectroscopy in ethanol dispersion.

Preparation of Graphene oxide: We synthesized GO using an altered version of Hummer's method. Conc. H_2SO_4 (20 ml) was added to a beaker placed into an ice bath and 1 g of graphite powder was then stirred into the beaker. The mixture was then swirled for two to three minutes. Next, 25 grams of potassium permanganate were added and it was stirred for an additional three minutes. Finally, 0.5 grams of sodium nitrate were added. The produced mixture was agitated for about two and a half hours, until it became greenish-black and became slightly thick. Distilled water was added to the prepared reaction mixture gradually after it had been submerged in a water bath that had been heated to 35 °C. For three hours, the finished mixture was swirled and maintained at 80 °C.

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As the reaction proceeds, the reaction mixture begins to take on a little yellowish tinge. After treating the produced final combination with forty milliliters of H_2O_2, Whatmann filter paper was used to filter the obtained mixture. After filtering, the material was mixed with distilled water and sonicated for an hour. The graphene oxide solution was then centrifuged at a speed between 2000 and 5000 rpm. Graphene oxide was finally obtained by drying and finely powdering the precipitate.

Preparation of copper oxide decorated graphene oxide (rGO–CuO): 200 milliliters of distilled water are put in a beaker along with one gram of graphene oxide. After that, the mixture is sonicated for 10 minutes. In a different beaker, 400 mg of CuO was added to 100 ml of distilled water and the mixture was sonicated for 10 minutes.

Subsequently, 50 mg of $NaBH_4$ was added to the sonicated copper oxide solution together with a sonicated graphene oxide combination. For four hours, the resulting reaction mixture was left to be stirred. Following that, it was filtered, repeatedly cleaned with ethanol and dried at 60 to 80^0C for 8 to 10 hours to obtain copper-decorated reduced graphene oxide.

Preparation of sandwich compound: Prepared rGO-CuO was divided into two equal part. One part (0.35 gram in 50 ml water) was treated with 0.2 gram citric acid and allowed to sonication for 30 minutes. After that, other part of rGO-CuO (0.35 gram) was added in it and allowed to sonicate further for 30 minutes at room temperature. The prepared mixture was filtered and dried in oven for 4 hrs.

Catalytic performance of prepared sandwich compound in reduction of Methylene Blue: Prepared sandwich material was added in reaction mixture of dye (100 ppm) and water (10 ml) and stirred at room temperature, after that $NaBH_4$ (10 mg) was added in it. The progress of reduction of dye was checked by UV – visible spectrometry.

Characterization: The FTIR and SEM were used to determine the surface shape and structure. The morphology of the generated material was measured using field emission scanning electron microscopy. For the measurements, the Nova Nano FE-SEM 450 was utilized, which has a resolution of up to 1.6 nm at 1 kv.

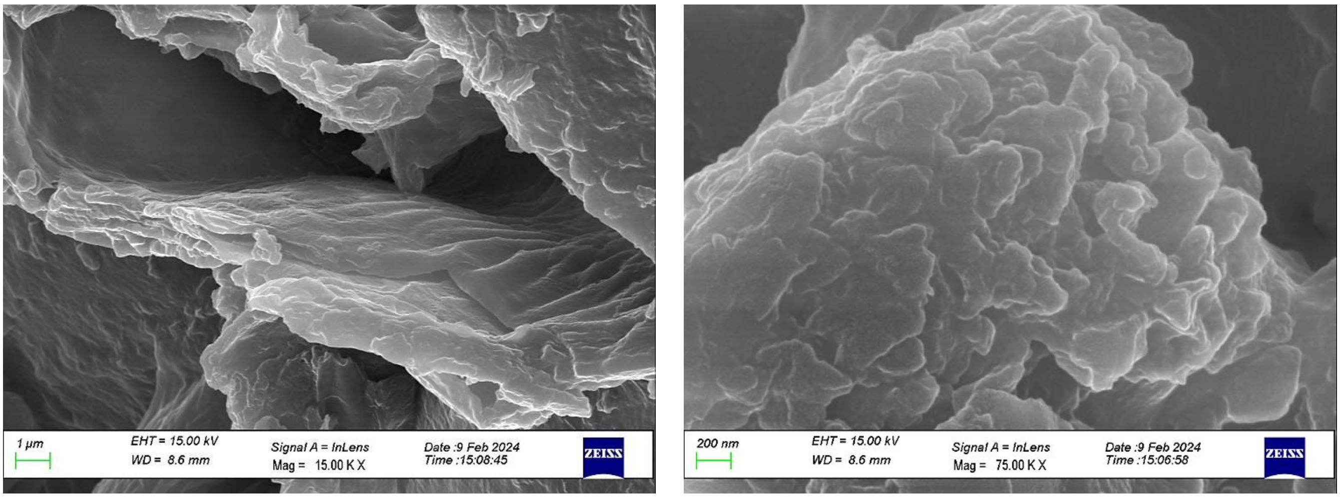
Additionally, produced materials were studied using FT-IR using a Perkin Elmer instrument to analyze and view the peaks of various functional groups. The LAMBDA 750 UV-visible spectrophotometer (Perkin Elmer) was utilized to measure the remaining concentrations of dye and nitroaromatics in catalytic reduction experiments.

Results and Discussion

FE-SEM and EDS: As shown in figure 1, synthesized material appeared as layered structured, which is prepared by GO doped CuO material and appeared as sandwich structure. The difference in morphology of material can be affected by type of reactant, attractive forces, kinetic energy and energy aspects during synthesis of composite.

Catalytic activity of Sandwich compound in removal of Methylene Blue dye: Prepared sandwich compound was used for removal of methylene blue dye with optimized reaction conditions. The best optimized reaction condition was found out by using different solvent systems with different catalyst quantity.

Methylene blue was treated with different parameters like catalyst loading, different $NaBH_4$ quantity. As shown in table 1, 10 mg of catalyst with 10 mg of $NaBH_4$ reduced the dye in 120 minutes, while 38 mg of $NaBH_4$ reduced the dye in 70 minutes. As the catalyst loading increases, the reduction time for dye decreases (entries 4-9). We also vary the quantity of methylene blue with different catalyst loading and $NaBH_4$ quantity.



(a) (b)

Figure 1: SEM images of sandwich compound

Table 1
Removal of Methylene blue with 100 ppm quantity using different parameters.

Reagent	Catalyst	$NaBH_4$	Time (Minutes)
Methylene blue	10 mg	10 mg	120
Methylene blue	10 mg	19 mg	100
Methylene blue	10 mg	38 mg	70
Methylene blue	20 mg	10 mg	90
Methylene blue	20 mg	19 mg	60
Methylene blue	20 mg	38 mg	45
Methylene blue	30 mg	10 mg	100
Methylene blue	30 mg	19 mg	60
Methylene blue	30 mg	38 mg	40

Table 2
Removal of Methylene blue with 250 ppm quantity using different parameters.

Reagent	Catalyst	$NaBH_4$	Time
Methylene blue	10 mg	10 mg	160
Methylene blue	10 mg	19 mg	130
Methylene blue	10 mg	38 mg	110
Methylene blue	20 mg	10 mg	120
Methylene blue	20 mg	19 mg	100
Methylene blue	20 mg	38 mg	90
Methylene blue	30 mg	10 mg	100
Methylene blue	30 mg	19 mg	70
Methylene blue	30 mg	38 mg	60

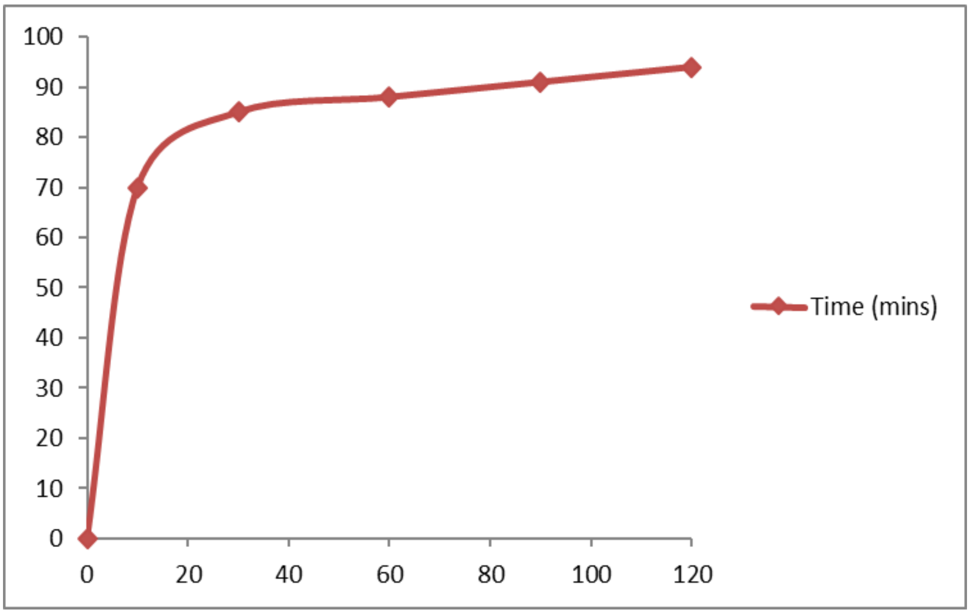


Figure 2: Effect of contact time on removal of dye
(catalyst = 0.010 g, dye volume = 10 mL, dye concentration = 100 ppm)

The increased quantity (250 ppm) of methylene blue also required high time for reduction than less quantity (100 ppm) of methylene blue. As shown in table 2, catalyst loading with more $NaBH_4$ quantity required less time compared to catalyst loading with less $NaBH_4$ quantity (Table 2, entry 9 and 1).

Effect of Contact time on removal of dye: Fig. 2 illustrates how contact time affects removal of methylene blue. The findings demonstrate that the adsorption process took 120 minutes to attain equilibrium and that the amount of dye removed increased as contact time increased. Over 72% of the dye was quickly removed by catalyst during the first 12 minutes of contact. After the 12-minute mark, the changes in the percentage of adsorption grew more gradual and the equilibrium reached in 100 minutes. The high clearance rate at the beginning of the contact time was caused in part by the huge surface area that was accessible for the dye's adsorption during that early stage. But as the few available surface sites become harder to fill because of the repulsive forces between the solute molecules on the solid and bulk phases, the adsorbent's capacity gradually decreased over time.

Effect of Dye Concentration on removal of dye: As shown in figure 3, as concentration of dye increases, the % removal of dye decreases. This result was observed after 120 minutes with 10 mg of $NaBH_4$ quantity and 10 mg of catalyst. The growing number of dye molecules could eventually no longer be accommodated by the saturated adsorption sites.[17]

Additionally, the photocatalytic dye degradation reaction's ability to produce ROS was constrained.[3] According to the Beer-Lambert equation, when the initial dye concentration increased, the photocatalytic degradation rate decreased due to the shorter path length of photons entering the solution.[15]

Effect of catalyst loading on removal of dye: Figure 4 illustrates how catalyst loading affects the elimination of methylene blue. The removal time reduces in tandem with an increase in catalyst loading. As the amount of catalyst increased, so did the photocatalyst's total surface area. The dye adsorption process was subsequently enhanced by the subsequent increase in accessible adsorption sites.[16]

In addition, there were more catalyst particles which improved the rate at which reactive oxygen species (ROS) was formed in order to break down dye molecules and improved photon absorption for the creation of electrons and holes.

Recycling of Catalyst: The recycling test of catalyst was performed up to 5 cycles. Initially, it removed the dye without significant less. In 3rd cycle, recovered catalyst required more time for complete removal of dye, it may be due to catalyst leaching. In the last cycle, catalyst required 200 minutes for complete removal of dye.

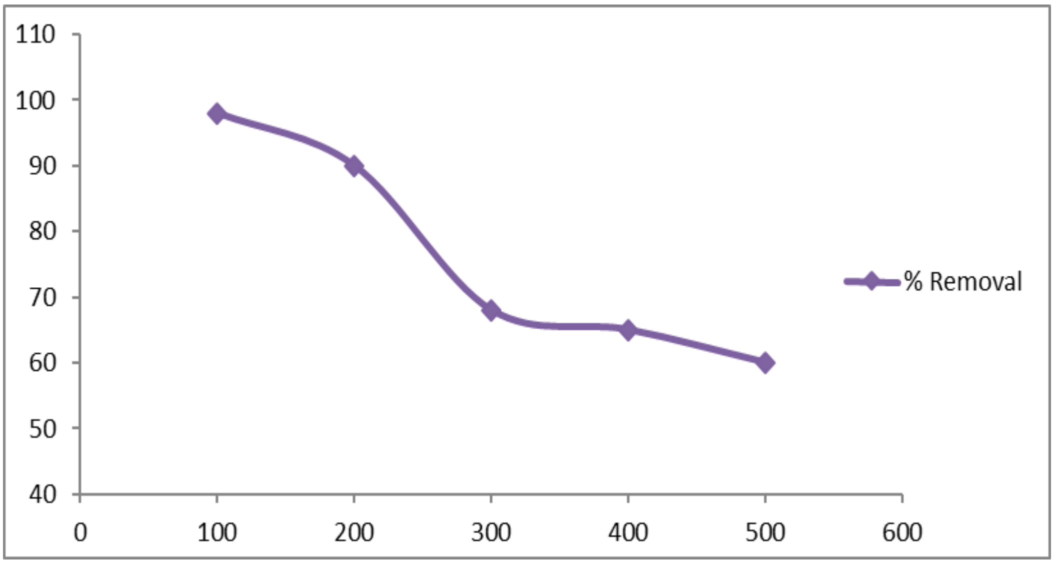


Figure 3: Effect of Dye concentration on removal of dye
(catalyst = 0.010 g, dye volume = 10 mL, contact time = 120 min)

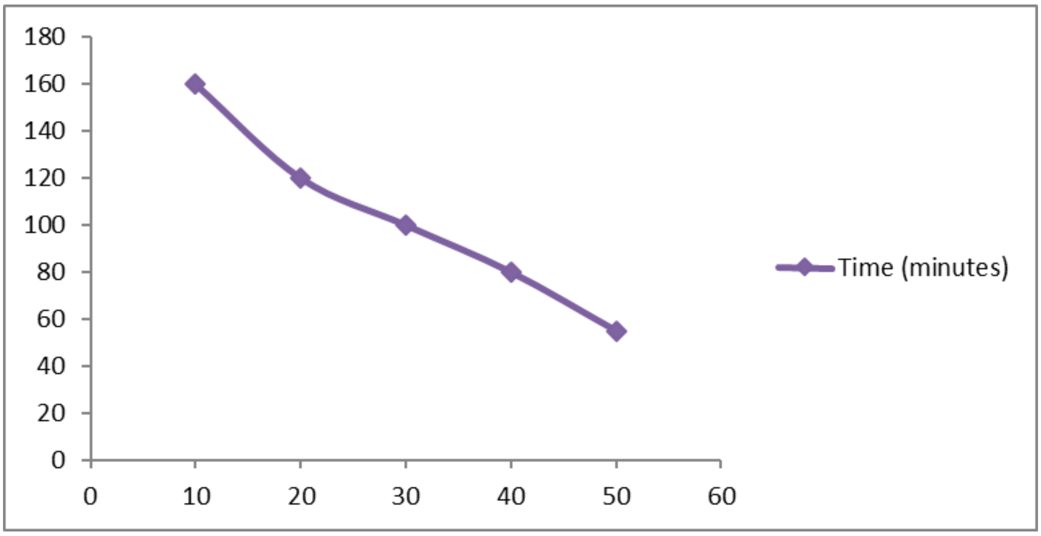


Figure 4: Effect of catalyst loading on removal of dye (dye volume = 10 mL, dye concentration = 100 ppm)

Conclusion

Copper based sandwich compound was developed by grapheme oxide which was further used for the removal of methylene blue dye. Various parameters like catalyst loading, effect of contact time, have been used to optimize the removal process of methylene blue dye. 10 mg of catalyst was enough to remove the methylene blue dye from aqueous solution. $NaBH_4$ also used for removal of methylene blue dye.

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