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RESEARCH ARTICLE

Catalytic Activity of CuO-bentonite Bead for the Removal of Methylene Blue by Fenton like Process

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ABSTRACT: Non-biodegradable dyes, potentially contaminate the water and poses serious risk to the environment. So their removal requires alarming attention. The formation of CuO-bentonite bead and their dye removal application is the main focus of the current investigation. X-ray diffraction spectroscopy (XRD), Field emission scanning electron microscopy (FESEM), and Energy dispersive X-ray spectroscopy (EDS) analysis were implemented to evaluate the crystalline structure and morphology of the prepared sample. The catalytic activity of the CuO-bentonite bead was studied against the dye methylene blue (MB) by an advanced oxidation process like Fenton. The experimental data shows a maximum 94.08 % of the dye removal capacity of the beads in just 20 minutes. Further, for the detail dye removal study optimum environments such as initial MB concentration, pH range, and oxidant dosage were altered during the reaction. Additionally, the CuO-bentonite bead showed 89.03 % dye removal even after five reuse cycles; which exhibits the heightened stability and robustness of the CuO-bentonite bead as a catalyst. Therefore, this simply prepared CuO-bentonite bead revealed a new approach to wastewater treatment.

Keywords: Catalysis, CuO-bentonite bead, Fenton process, MB removal.

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1. INTRODUCTION

A rising development in an industrial sector becomes a reason behind the damage to the ecosystem; while water contributes as a chief part of this ecosystem [1]. The more and more number of industries, especially textile industries produce highly toxic carcinogenic products such as dye contaminants [2, 3].

MB is a typical toxic dye contaminant that released into the natural water resources that cause water pollution. The cationic dye MB is also known as Swiss Blue or Methylthioninium chloride. The widespread applications of MB captures the textile industry; but their highly toxic, non-biodegradable, and carcinogenic nature substantiates the MB as a representative contaminant of the industrial wastewater. This water pollution contaminates the potable drinking water and cause several hazardous effect on human health [4,5]. Hence, it is necessary to remove this contaminant from water.

Several actively discovered techniques such as adsorption, reduction, flocculation, reverse osmosis, coagulation, Fenton, etc. processes were used to resist the risk of water pollution [6–10]. Among them, the Fenton is the strong advanced oxidation process (AOPs) that catches huge attention due to their simple, low cost, and rapid operating system. The hydroxyl radical is a key free radical molecule of the AOPs. The hydroxyl radical generation ability of the catalyst and the hydrogen peroxide (H_2O_2) is majorly preferred in the Fenton reaction [11]. The contaminant removal capacity of the oxidizing agent hydrogen peroxide (H_2O_2) was studied by Henry J. H. Fenton in 1894; they oxidize the tartaric acid in the presence of H_2O_2 and salt Fe

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(II) [12]. Many other research teams also reveal their result of the Fenton process. As per the above discussion the H_2O_2 and the catalyst are the foremost supports of the Fenton process.

Clay minerals are abundant, economical and having remarkable textural properties, they have been recognized as good adsorbent [13]. Hence they can be used as a catalyst in the field of catalysis. Bentonite clay is a natural resource containing montmorillonite or smectite group. These smectite group containing bentonite clay possess anionic surface which facilities the adsorption and removal of the cationic dye [14]. Furthermore, copper oxide (CuO) is added into the bentonite clay. These copper oxide bentonite clay reacts with oxidant H_2O_2 and enhances the rate of Fenton reaction by generating the hydroxyl radical [15].

This current context reported a simple preparation method of Copper oxide bentonite composite bead **(**Cuo-bentonite beads). XRD, FESEM, and EDS analysis was aimed to establish the crystalline nature, morphology, and elemental composition of the sample. The catalytic activity of the as-fabricated catalyst was investigated for the degradation of cationic dye MB. The effect of optimal experimental parameters including initial MB concentration, pH, and oxidant dosage was also studied. The recycle study of the catalyst entitles its robustness and constancy.

2. EXPERIMENTAL DETAILS

2.1. Materials

Copper chloride dihydrate (99%, $CuCl_2.2H_2O$) obtained from LOBA CHEMIE were used. The commercial bentonite clay was employed for the formation of the beads. At last for dough preparation NaOH solution were prepared by using 98%, sodium hydroxide pellets from Fisher scientific.

2.2. Copper oxide bentonite composite bead preparation

Initially, 1 g of copper chloride and 6 g of bentonite clay powder and grind it in a Morten piston for proper mixing. Afterwards 1 M NaOH was added in a dropwise manner in this mixed powder to make an appropriate dough. Further, weigh 2 g weight from this dough and prepare the beads. At last, calcinated these beads at 500 °C for 2 hours (Scheme 1) and then store them for future use.

2.3. Characterizations

X-ray diffraction (XRD) spectroscopy was utilized to determine the crystalline structure of the sample. The field emission scanning electron microscopy (FESEM) was performed to scrutinize the surface morphology of the sample. The energy dispersive spectroscopy (EDS) analysis was used for elemental composition.

2.4. Fenton process

Fenton is an advanced oxidation process carried out under ambient temperature. To run the experiment, 2 g Cuo-bentonite bead and 1 ml H_2O_2 (30%) were added into 0.1 mM of the MB solution. This reaction mixture was continuously stirred on the shaker. After each 5-minute contact time; 2 ml aliquot from the reaction mixture was collected. Further, the absorbance of this collected aliquot was read off by a UV-visible spectrophotometer at 664 nm [16] to calculate the MB removal percentage.

3. RESULTS AND DISCUSSION

3.1. Characterizations

Figure 1 exhibits typical XRD pattern of CuO-bentonite bead. The 2θ degree region from 10 to 80 °C was used to perform the X-ray diffraction spectroscopy of CuO-bentonite bead. As observed from the XRD pattern, the main diffraction peak at (37.6) resembles to CuO [17-19]. This outcomes recommends the successful incorporation of the CuO into a CuO- bentonite bead.

Fig. 2 (a) and (b) presents the scanning electron microscopy (SEM) images of CuO-bentonite bead captured at 50 µm and 10 µm displaying the surface morphological structure. The SEM investigation confirms smooth and fluffy appearance of the CuO-bentonite bead. Fig. 2 (a) represents the agglomeration of the smaller particles at 50 µm; while Fig. 2 (b) specifies the smooth surface of the CuO-bentonite bead with different morphological structures.

Scheme 1: Preparation of CuO-Bentonite beads.

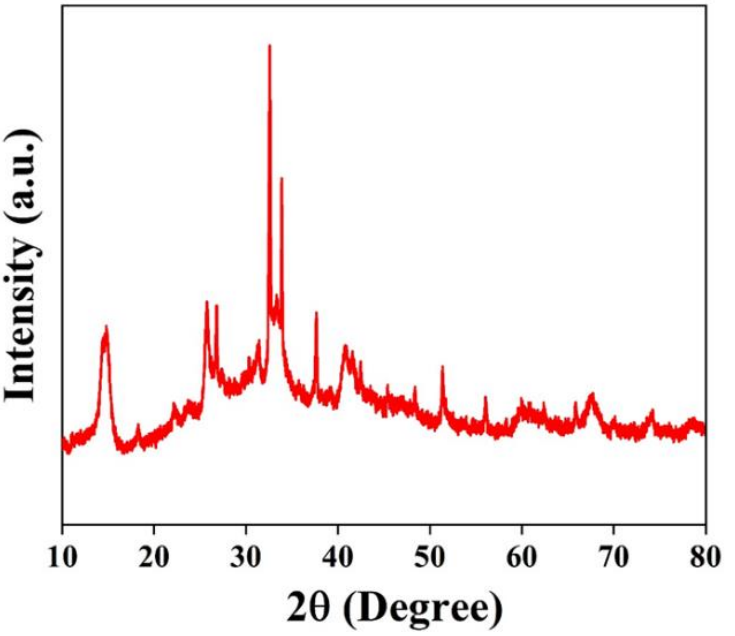


Fig. 1. XRD spectra of CuO-bentonite bead.

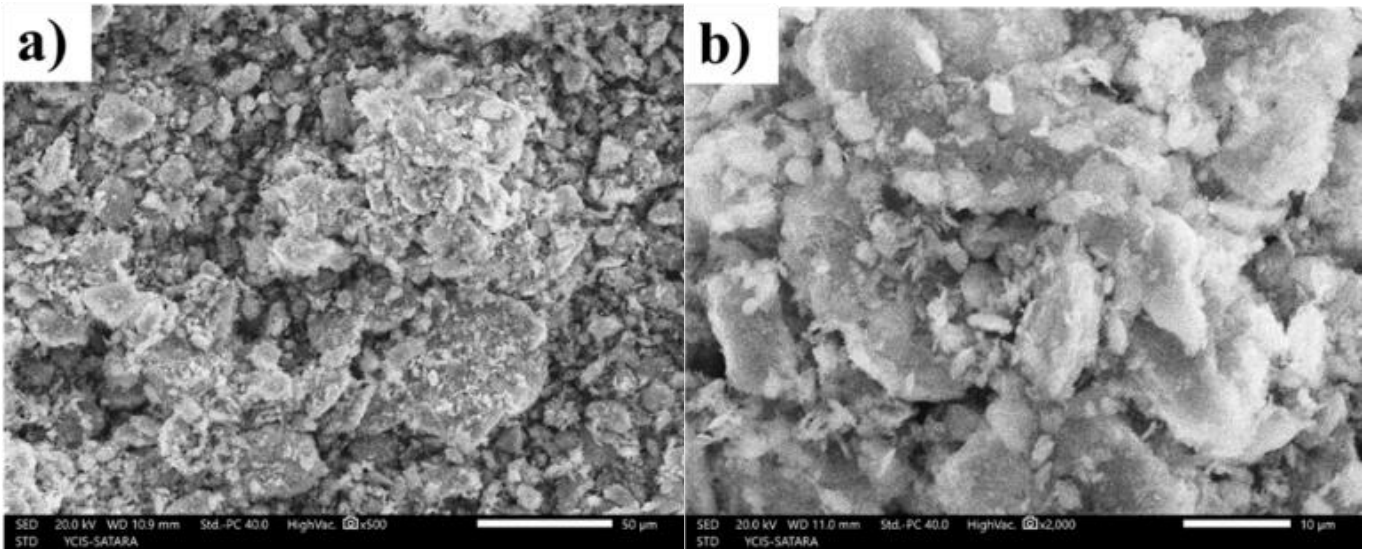
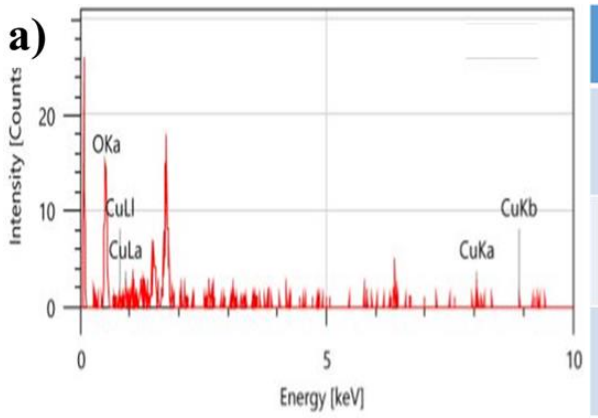


Fig. 2. SEM images of CuO-bentonite bead at a) High and b) Low magnification.

Energy dispersive X-ray spectroscopy (EDS) investigation further confirms the evidence revealed in X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses. The EDS spectrum (Fig 3 (a)) and its quantitative analysis (Fig 3 (b)) confirm the presence of copper (Cu) and oxygen (O) in the prepared bead. This corroborates the structural and compositional details identified in the XRD and SEM analyses, providing a comprehensive understanding of the bead's composition.

3.2. Catalytic Removal of Methylene Blue (MB) Dye

The catalytic dye removal capacity of the CuO-bentonite bead was investigated using methylene blue (MB) as a model dye pollutant. Fig. 4 (a) and (b) illustrate the spectral and color changes that occurred during the Fenton reaction. The results demonstrate that the CuO-bentonite bead is highly effective in removing MB, achieving over 90% removal in just 20 minutes. This significant removal rate highlights the potential of the CuO-bentonite bead as a powerful catalyst for dye degradation in wastewater treatment applications. The rapid and efficient reduction of MB indicates that the bead could be utilized in practical environmental remediation scenarios, offering a promising solution for reducing dye pollutants in water systems.



b) Element	Mass (%)	Atom (%)
O	86.84	96.33
Cu	13.16	3.67
Total	100	100

Fig. 3. (a) EDS spectrum, and b) Quantitative table analysis of CuO-Bentonite bead.

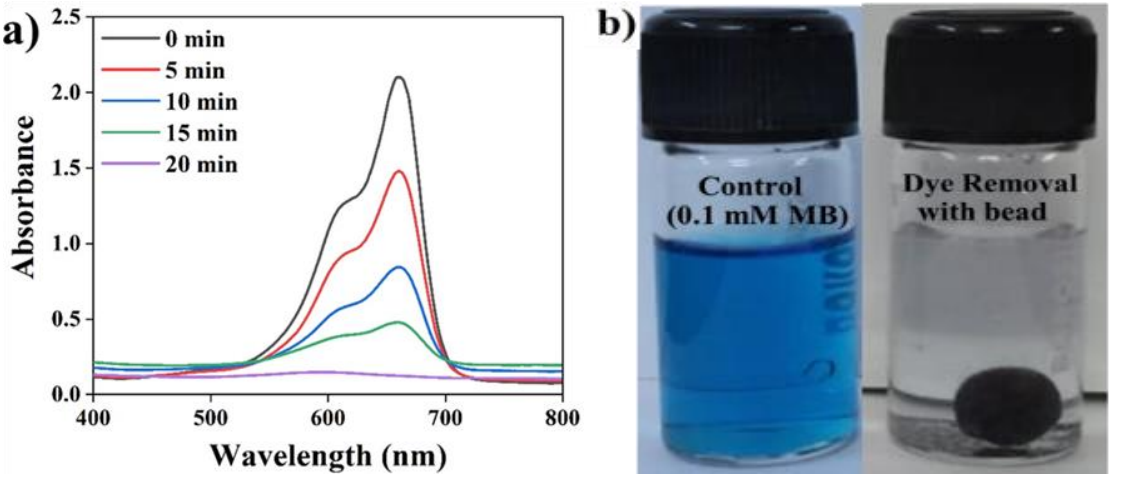


Fig. 4. (a) Spectral, and b) Color changes during Fenton process.

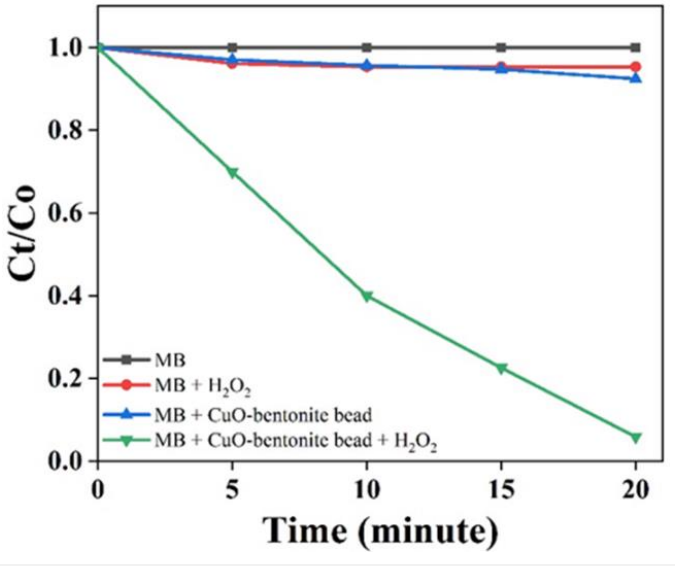


Fig. 5. Catalytic removal of MB as a function of as a function of irradiation time under varied experimental parameters, MB, MB + H_2O_2, MB + CuO-bentonite bead, and MB + CuO-bentonite bead + H_2O_2).

Furthermore, the Fenton activity of the CuO-bentonite bead was tested under various experimental conditions, as presented in Fig. 5. The experiments were designed to compare the effectiveness of different combinations: MB alone, MB with hydrogen peroxide (H_2O_2), and MB with the CuO-bentonite bead. Under these conditions, no significant change in the methylene blue (MB) removal capacity was observed. This suggests that neither H_2O_2 nor the CuO-bentonite bead alone was sufficient to significantly degrade MB.

However, a marked improvement in the MB removal capacity was observed during the Fenton reaction, which involved the combined use of MB, the CuO-bentonite bead, and H_2O_2. This specific combination significantly increased the rate of reaction, resulting in the removal of 94.08% of MB within just 20 minutes. The enhanced removal efficiency can be attributed to the Fenton reaction mechanism, where H_2O_2 is catalytically decomposed by the CuO present in the bead to produce hydroxyl radicals (•OH). These radicals are highly reactive and capable of rapidly breaking down the MB dye molecules.

This outcome highlights the crucial role of the CuO-bentonite bead in facilitating the Fenton reaction, leading to a substantial increase in the degradation rate of MB. The CuO-bentonite bead acts as an effective catalyst, significantly boosting the generation of hydroxyl radicals, which in turn accelerates the oxidation and breakdown of the dye. Therefore, the combination of CuO-bentonite bead and H_2O_2 proves to be a highly efficient method for the catalytic removal of dye pollutants, demonstrating its potential for practical applications in wastewater treatment.

3.4. Influence of initial MB concentration on the MB removal

The initial concentration of methylene blue (MB) is a crucial parameter that significantly influences the dye removal efficiency of the CuO-bentonite bead. To investigate this, a fixed amount of the catalyst (CuO-bentonite bead) and hydrogen peroxide (H_2O_2) was tested against varying MB concentrations of 0.05 mM, 0.1 mM, 0.15 mM, and 0.2 mM. The study found that as the initial MB concentration increased, the dye removal efficiency of the CuO-bentonite bead decreased, as demonstrated in Fig. 6.

At an initial MB concentration of 0.05 mM, the CuO-bentonite bead achieved a removal efficiency of 95.09%. However, when the initial concentration was increased to 0.2 mM, the removal efficiency dropped significantly to 80.08%. This decline can be attributed to the availability of active sites on the catalyst's surface. At lower dye concentrations, more active sites on the catalyst are accessible for the adsorption and breakdown of the dye molecules. This leads to higher removal efficiency as there is less competition for the active sites.

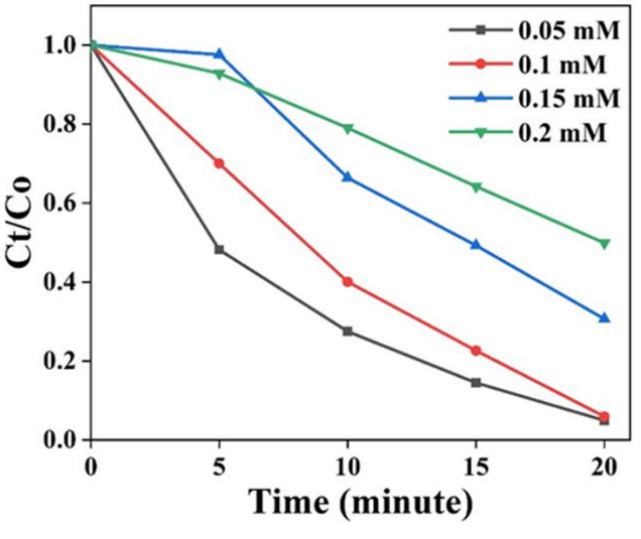


Fig. 6. Influence of the initial MB concentration on the MB removal.

In contrast, at higher dye concentrations, the surface of the catalyst becomes saturated with MB molecules, leading to multilayer adsorption. This excessive adsorption creates a barrier that hinders direct contact between the catalyst and the hydroxyl radicals generated during the Fenton reaction. Consequently, the efficiency of the catalytic process diminishes as the active sites are blocked and less effective in facilitating the reaction. This phenomenon ultimately inhibits the overall dye removal efficiency.

Similar observations have been reported by other research teams when studying the effects of varying initial dye concentrations [5, 17, 20, 21]. These findings highlight the importance of optimizing the initial dye concentration to maximize the efficiency of the CuO-bentonite bead in removing dye pollutants from wastewater. Understanding these dynamics is essential for the practical application of this catalyst in environmental remediation processes.

3.4. Influence of pH of the solution on the MB removal

Fig. 7 illustrates the impact of the initial pH of the solution on the methylene blue (MB) removal capacity of the CuO-bentonite bead. In this study, the pH range was varied from 3 to 9, while keeping other parameters constant: 0.1 mM of MB, 10 mM of H_2O_2, and 2 g of CuO-bentonite bead. The results indicate that the MB removal efficiency improves significantly with increasing pH.

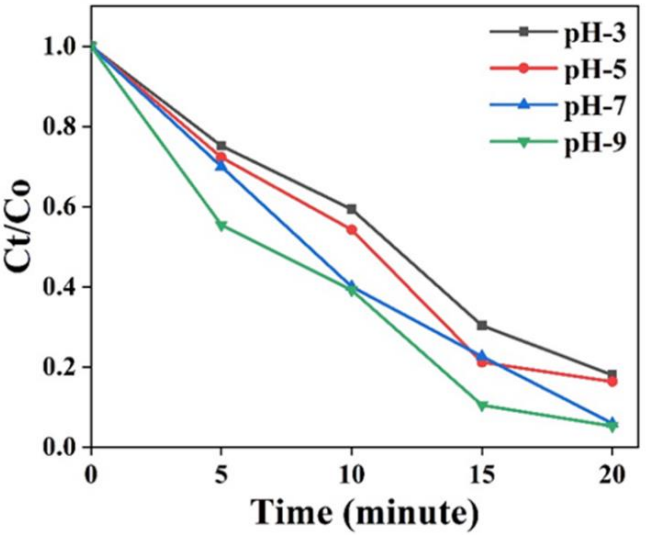


Fig. 7. Influence of solution's pH on the MB removal.

At a lower pH of 3, the removal efficiency was 86.87%. However, at a higher pH of 9, the removal efficiency increased to 96% within just 20 minutes. This enhancement at higher pH levels can be attributed to several factors. Under alkaline conditions, the cationic dye MB dissociates to form positive ions. These ions react with the negatively charged surface of the CuO-bentonite catalyst, resulting in electrostatic interactions that enhance the adsorption and removal of the dye.

Additionally, higher pH levels promote the production of hydroxyl radicals, which are crucial for the Fenton reaction. The increased generation of these radicals further accelerates the degradation of MB, thereby improving the overall dye removal efficiency. This dual mechanism of enhanced electrostatic interaction and elevated hydroxyl radical production under alkaline conditions explains the superior performance of the CuO-bentonite bead at higher pH levels.

Comparable results regarding the effect of pH variation on dye removal efficiency have been documented by other researchers [5, 14, 22-26]. These studies consistently show that optimizing the pH is critical for maximizing the efficacy of catalytic materials in dye degradation processes. Understanding the influence of pH helps in tailoring the conditions for optimal performance of the CuO-bentonite bead, making it a more effective solution for wastewater treatment applications.

3.4. Influence of oxidant dosage on the MB removal

The methylene blue (MB) removal capability of CuO-bentonite beads is significantly influenced by the dosage of the oxidant, hydrogen peroxide (H_2O_2). In this study, the amount of H_2O_2 was varied from 5 mM to 20 mM, and the results are presented in Fig. 8. The findings indicate that less than 70% of MB was removed with a 5 mM H_2O_2 dose even after 20 minutes. However, when the H_2O_2 dose was increased to 10 mM, the removal efficiency dramatically improved, reaching up to 90.08%. Beyond this point, increasing the H_2O_2 dosage to between 15 mM and 20 mM did not result in significant further improvements in removal efficiency.

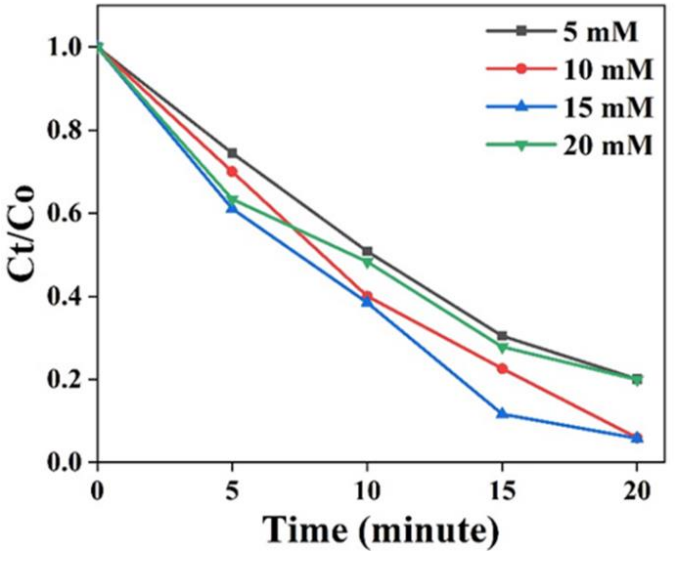


Fig. 8. Influence of solution's pH on the MB removal.

The enhanced MB removal capacity observed up to the optimal H_2O_2 dose (10 mM) is attributed to the sufficient availability of hydroxyl radicals (•OH). These radicals are highly reactive and play a crucial role in breaking down the dye molecules, thus improving the removal efficiency [22-25]. However, beyond the optimal concentration, the excess H_2O_2 acts as a scavenger for hydroxyl radicals, reducing their availability for the Fenton reaction. This phenomenon restricts the MB removal efficiency because the excess H_2O_2 begins to inhibit the catalytic process instead of enhancing it.

Similar findings were reported by Nadeem and his research team, who varied the oxidant dose from 9.8 mM to 47 mM and observed its effect on the degradation of reactive synozol red dye [27]. They also noted that the dye degradation was most efficient at an optimal H_2O_2 concentration, beyond which the removal efficiency declined. This is consistent with the current study's observation that there is a threshold level of oxidant dosage that maximizes dye removal efficiency, and exceeding this level can be counterproductive.

These results highlight the importance of optimizing the oxidant dosage to achieve maximum efficiency in dye removal processes. Understanding the precise relationship between H_2O_2 dosage and MB removal efficiency is essential for the effective application of CuO-bentonite beads in wastewater treatment. It ensures that the catalytic activity is maintained at an optimal level, avoiding the adverse effects of excess oxidant [18, 20, 21].

3.5. Reuse of the catalyst

The practical usability and durability of CuO-bentonite beads were evaluated through multiple reuse cycles. In this study, the CuO-bentonite beads were subjected to up to five consecutive cycles under optimized reaction conditions to assess their reusability. After each cycle, the beads were removed from the reaction mixture, thoroughly washed, and dried to prepare them for the next use. The results of this reusability study are illustrated in Fig. 9.

In the first cycle, the CuO-bentonite beads demonstrated a high MB removal efficiency of 94.08%. However, a gradual decrease in efficiency was observed over subsequent cycles. Specifically, the removal efficiency dropped to 92.67% in the second cycle, 91.44% in the third cycle, 90.89% in the fourth cycle, and 89.03% in the fifth cycle. Although there was a slight reduction in efficiency with each reuse, the beads maintained a relatively high level of performance throughout all five cycles.

This slight decline in MB removal efficiency over successive cycles can be attributed to several factors. Over time, the active sites on the surface of the beads may become partially blocked or less accessible due to the accumulation of reaction by-products or the gradual wear and tear of the material. Additionally, the repeated washing and drying processes could potentially cause minor physical or chemical changes in the beads, slightly affecting their catalytic activity.

Despite the observed decrease in efficiency, the results suggest that CuO-bentonite beads retain a substantial portion

of their dye removal capability even after multiple uses. This indicates that they have good practical usability and durability, making them a viable option for repeated applications in wastewater treatment. The ability to reuse the beads multiple times without significant loss of efficiency contributes to their cost-effectiveness and sustainability as a treatment solution [28]. The study demonstrates that CuO-bentonite beads can effectively remove methylene blue over several reuse cycles, with only a marginal decrease in performance. This reusability enhances their practicality for long-term use in environmental remediation, providing a reliable and efficient method for dye pollutant removal from wastewater [29, 30].

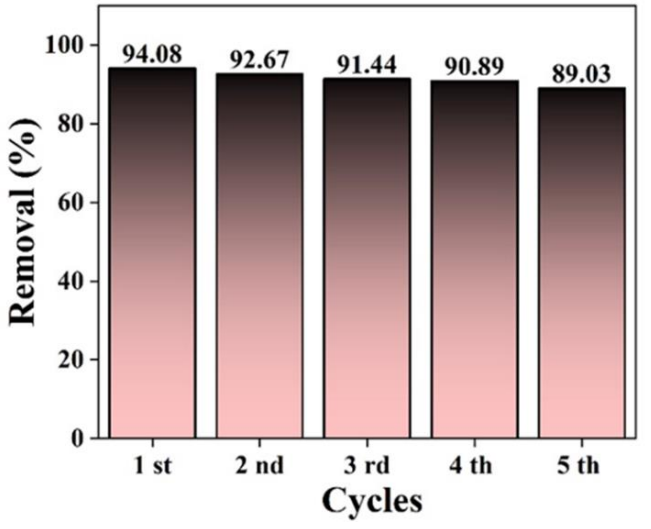


Fig. 9. Reuse capacity of CuO-bentonite bead by Fenton process.

4. CONCLUSION

This research work reported very simple and quick methods for the formation of CuO-bentonite beads. The successful synthesis and formation of these beads were confirmed through various analytical techniques, including X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and energy dispersive X-ray spectroscopy (EDS). These studies provided detailed insights into the structural and compositional characteristics of the CuO-bentonite beads. The catalytic activity of the CuO-bentonite beads was evaluated through dye removal experiments using methylene blue (MB) as a model pollutant. The beads demonstrated high efficiency in removing MB from wastewater under various optimal conditions. Specifically, the study found that the CuO-bentonite beads could remove up to 94.08% of the dye when operating under the following constant parameters: an initial dye concentration of 0.1 mM, an initial pH of 7, an H_2O_2 dose of 5 mM, and an adsorbent dose of 2 g. The high removal efficiency achieved by the CuO-bentonite beads underscores their excellent catalytic and adsorption capabilities. These results indicate that the beads can effectively facilitate the breakdown and removal of dye pollutants from wastewater. The simplicity and effectiveness of the preparation method, combined with the beads' robust performance, suggest that CuO-bentonite beads are a promising alternative for wastewater treatment applications. Furthermore, the reusability tests highlighted the durability and practical usability of the CuO-bentonite beads, showing only a slight decrease in efficiency over multiple reuse cycles. This aspect enhances their viability as a cost-effective and sustainable solution for environmental remediation. Overall, the study demonstrates that CuO-bentonite beads have significant potential for use in wastewater treatment due to their high dye removal efficiency, ease of preparation, and reusability. These attributes make them a viable and efficient alternative for addressing dye pollution in industrial and environmental settings.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests.

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