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Removal of Organic Dyes Using Gd_2ZnMnO_6/ZnO Ceramic Nanocomposites as a Photocatalysts

Masoud Kouchakzadeh[1], Amin Honarbakhsh[1,2]*, Seyed Mojtaba Movahedifar[1,2], Rahele Zhiani[2], Farhad Hajian[1], Seyed Mohsen Sadeghzadeh [2,3,4]

1- Department of Civil Engineering, Neyshabur Branch, Islamic Azad University, Neyshabur, Iran
2- New materials Technology and Processing Reserearch Center, Neyshabur Branch, Islamic Azad University, Iran
3-Department of chemistry, Neyshabur Branch, Islamic Azad University, Iran
4-Advanced Research Center for Chemistry, Biochemistry and Nanomaterial; Neyshabur Branch, Islamic Azad University, Iran

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Abstract
The photocatalytic degradation of organic dye residues offers a promising and eco-friendly solution to challenges that endanger living organisms. A highly efficient fibrous nanocatalyst was carefully fabricated, designed, and utilized to remove acid black 1, acid blue 92, acid brown 214, and acid violet 7 [Wastewater colors]. The findings indicated that the amount of Gd_2ZnMnO_6/ZnO quantum dots affects the degradation efficiency. Integrating quantum dots into the photocatalyst structure boosts light absorption, accelerates electron transfer rates, and enhances charge transfer efficiency. The catalyst's performance was assessed by considering various catalyst components for the removal of organic wastes. The study proposed rational procedures based on the interaction between Gd_2ZnMnO_6 and ZnO nanoparticles within the catalyst, which can be reused and recovered for at least 10 cycles without significant loss of reactivity.

Keywords
Organic wastes; Ceramic; Nanocatalyst; Green chemistry; Photocatalyst.

1.INTRODUCTION

The quality of surface water has a significant impact on both environment and ecosystems [1]. As the development progresses and human population grows, challenges related to waste management, environmental protection, providing safe drinking water, and pollution control have intensified [2]. In both developing and developed countries, water pollution levels are continuously rising [3]. Dyes, being among the most persistent and toxic pollutants, have garnered considerable attention for their removal [4]. For example, eosin, a water-soluble xanthene dye, is widely used in pharmaceuticals, food, and cosmetics. High concentrations of this dye can lead to various allergic reactions, carcinogenic effects, and thyroid issues. It is noteworthy that extensive research has been carried on the degradation of Acid Violet 7 and Acid Black 1 [5]. These organic pollutants, characterized by N–N bonds linked to complex aromatic structures and sulfonic acid, are highly resistant and more genotoxic than other polluting colors. The dyeing, printing, and textile industries are the primary sources of color pollutants in sewage due to the substantial water consumption involved [6]. The discharge of untreated industrial wastewater into aquatic ecosystems poses a global threat to water resources. Advanced oxidation processes (AOPs) are recognized as the most effective method for eliminating persistent organic contaminants [7]. AOPs are distinguished by their ability to generate oxidant species, such as hydroxyl radicals, which are highly effective at degrading organic compounds due to their strong oxidation potential of 2.8 V.

In this study, Gd_2ZnMnO_6 was investigated as one of the key compounds [8]. The synthesis approach, along with the size and morphology, significantly influences the physical and chemical properties of nanoparticles [9-12]. The sol-gel auto-ignition method is favored for synthesizing nanoparticles due to its advantages, including high product

* Corresponding author:
A. Honarbakhsh; E-mail: amin_honarbakhsh@yahoo.com

homogeneity, low calcination temperature, and easy modification of components [13-16]. This method has proven to be a practical, convenient, and cost-effective way to produce ceramics and nanocomposites. A heterojunction structure in photocatalysis refers to a photocatalyst made up of two or more different semiconducting materials with varying band gaps [17-20]. The interface created at the junction between these materials allows holes to move across it and photoexcited electrons [21, 22]. This photocatalyst design enables the transfer of electrons between semiconductors with varying energy levels, allowing for effective electron-hole pair separation and enhancing the overall performance of the photocatalyst [23, 24].

This study investigated the impact of using saffron as a green fuel in the synthesis of Gd_2ZnMnO_6/ZnO, demonstrating that the resulting nanocomposites can serve as effective nanocatalysts for the removal of organic dyes. The prepared catalyst's various physical and chemical properties were thoroughly examined and subsequently applied to the removal of wastewater colors.

2.EXPERIMENTAL

2.1.Fabrication of Gd_2ZnMnO_6/ZnO

A specific amount of saffron (2.6 mg) was added to a mixture containing $Gd(NO_3)_3$ (3.6 mmol), $Zn(NO_3)_2$ (3.6 mmol), and $Mn(NO_3)_2{\cdot}6H_2O$ (3.6 mmol). The mixture was incubated in an aerobic chamber at 58°C for 45 min. After incubation, the Gd_2ZnMnO_6/ZnO was centrifuged for 12 minutes and then eluted with 45% acetone in H_2O (1:1 volume equivalent) [25].

2.2.Photocatalytic Measurement

Wastewater color was added in a Pyrex glass container at room temperature. Approximately Gd_2ZnMnO_6/ZnO (7 mg) was dispersed in 25 mL of the pollutant solution, which was continuously stirred magnetically while being exposed to air bubbles.

3. RESULTS AND DISCUSSION

The efficiency of binary Gd_2ZnMnO_6/ZnO nanocomposites in photodegrading four toxic contaminants under different light sources was analyzed. Figure 1 presents a comparative study of these organic dyes using the Gd_2ZnMnO_6/ZnO under UV light exposure. The UV-induced reaction of Gd_2ZnMnO_6/ZnO was conducted for 9 minutes, resulting in an 88% decolorization of acid black 1. As shown in Figure 1a, the photodegradation rate for acid brown 214 reached approximately 97%. Additionally, the presence of acid violet 7 and acid blue 92 in the photocatalytic process yielded decolorization percentages of 95% and 93%, respectively. The photocatalytic performance was also assessed under visible light irradiation, as depicted in Figure 1b. Under these conditions, the degradation efficiency for acid black 1 was 79%, while the photocatalytic yields for acid brown 214, acid blue 92, and acid violet 7 were 85%, 83%, and 80%, respectively.

Degradation tests were conducted in the presence of EDTA and benzoic acid to determine the most effective species in the degradation of toxic dyes. As shown in Figure 2, the efficiency of industrial wastewater removal increased when EDTA was present, indicating that it acts as an H^+ scavenger. However, a significant reduction in dye degradation was observed when benzoic acid was used, suggesting that •OH radicals are the most effective species in removing organic substances and neutralizing toxins.

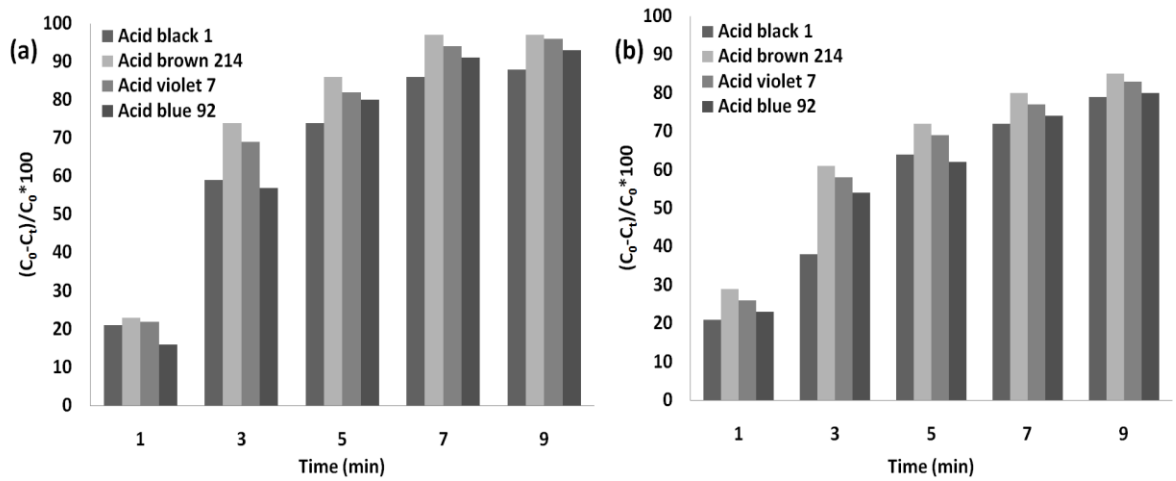

Fig.1. Photocatalysis performance of Gd_2ZnMnO_6/ZnO for the removal of wastewater colors under (a) UV and (b) visible light.

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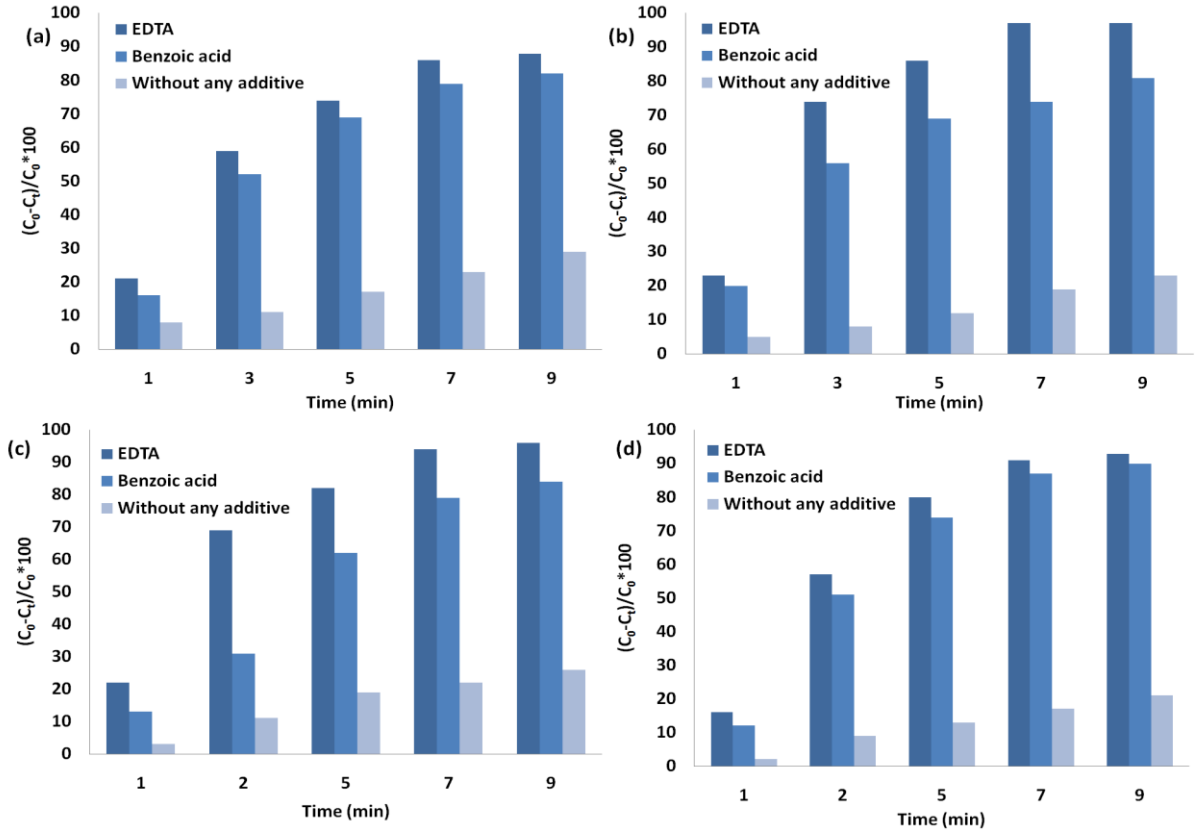

Fig.2. The influence of time on the removal of acid black 1 (a), acid brown 214 (b), acid violet 7 (c), and acid blue 92 (d) under UV light.

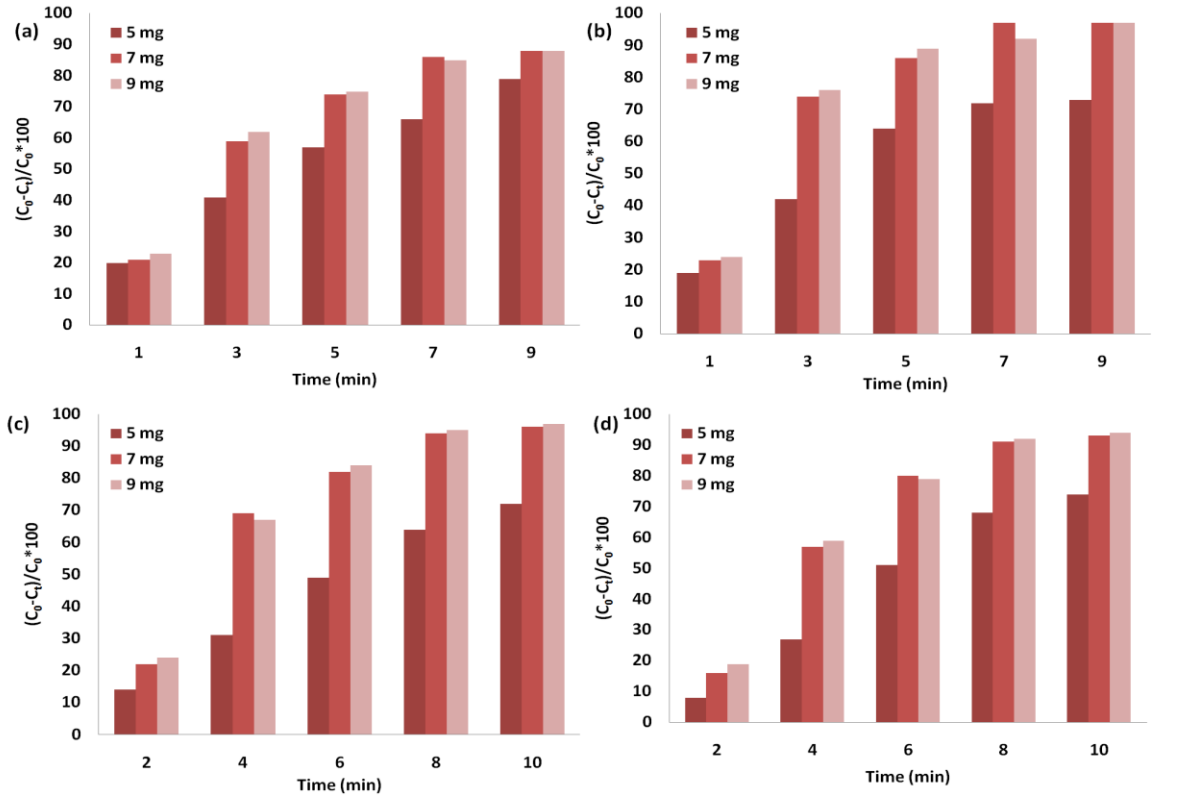

Fig.3.The impact of Gd_2ZnMnO_6/ZnO dosage on the removal of acid black 1 (a), acid brown 214 (b), acid violet 7 (c), and acid blue 92 (d).

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We investigated the effect of Gd_2ZnMnO_6/ZnO dosage on degradation yield. As illustrated in Figure 3, the photodegradation performance improved as the amount of Gd_2ZnMnO_6/ZnO increased from 5 mg to 7 mg. With a dosage of 7 mg, the photocatalytic activity achieved degradation rates of 88%, 97%, 96%, and 93% for acid black 1, acid blue 92, acid violet 7, and acid brown 214, respectively. Increasing the catalyst dosage enhanced the surface area of Gd_2ZnMnO_6/ZnO, leading to better dye absorption on the Gd_2ZnMnO_6/ZnO surface. However, the photocatalytic activity declined at a dosage of 7 mg due to the increased thickness of the Gd_2ZnMnO_6/ZnO. Consequently, the optimal Gd_2ZnMnO_6/ZnO dosage was determined to be 5 mg of the Gd_2ZnMnO_6/ZnO. Blank experiments were conducted to assess the removal of wastewater colors under UV and visible light without any catalyst. The degradation percentages for acid black 1, acid blue 92, acid violet 7, and acid brown 214 were 4%, 5%, 4%, and 6% under UV light, and 1%, 3%, 3%, and 2% under visible light.

Figure 4 illustrates the photodegradation analysis conducted to evaluate the effect of pH on the photodegradation efficiency of Gd_2ZnMnO_6/ZnO. Three separate experiments were performed using wastewater colors to determine the optimal pH for photocatalytic activity, with pH=11 identified as the most favorable condition. To further examine the alkaline environment, a pH range of 9-13 was tested, confirming that pH=11 yielded the best results. It was observed that altering the pH above or below this value did not enhance photocatalytic activity. Specifically, when the pH was controlled at 2, 7, and 11, the degradation yields were 81%, 37%, and 88%, respectively. The findings indicate that an alkaline medium significantly improves the photocatalytic performance, with pH=11 leading to the optimal activity of Gd_2ZnMnO_6/ZnO nanoparticles. In alkaline conditions, the surface of Gd_2ZnMnO_6/ZnO exhibited more effective sites and a higher density of •OH radicals. Consequently, increasing the pH of the toxic dye solutions resulted in enhanced photocatalytic degradation activity.

The reusability of Gd_2ZnMnO_6/ZnO in the removal of polluting colors was investigated. After each run, the Gd_2ZnMnO_6/ZnO catalyst was separated, washed with distilled ethanol, and reused. Impressively, Gd_2ZnMnO_6/ZnO maintained its efficiency even after 10 consecutive runs, as shown in Figure 5. To confirm the stability of the catalyst, the recovered Gd_2ZnMnO_6/ZnO was analyzed using XRD and TEM (Figure 6). The XRD and TEM spectra revealed no significant changes in the catalyst's structure before and after the 10 cycles, indicating its robustness. Additionally, Figure 7 illustrates the structures of wastewater colors. The comparison includes water containing effluent both after 10 minutes and before irradiation. The data demonstrates the catalyst's effectiveness in degrading the dyes and its ability to be reused without loss of activity.

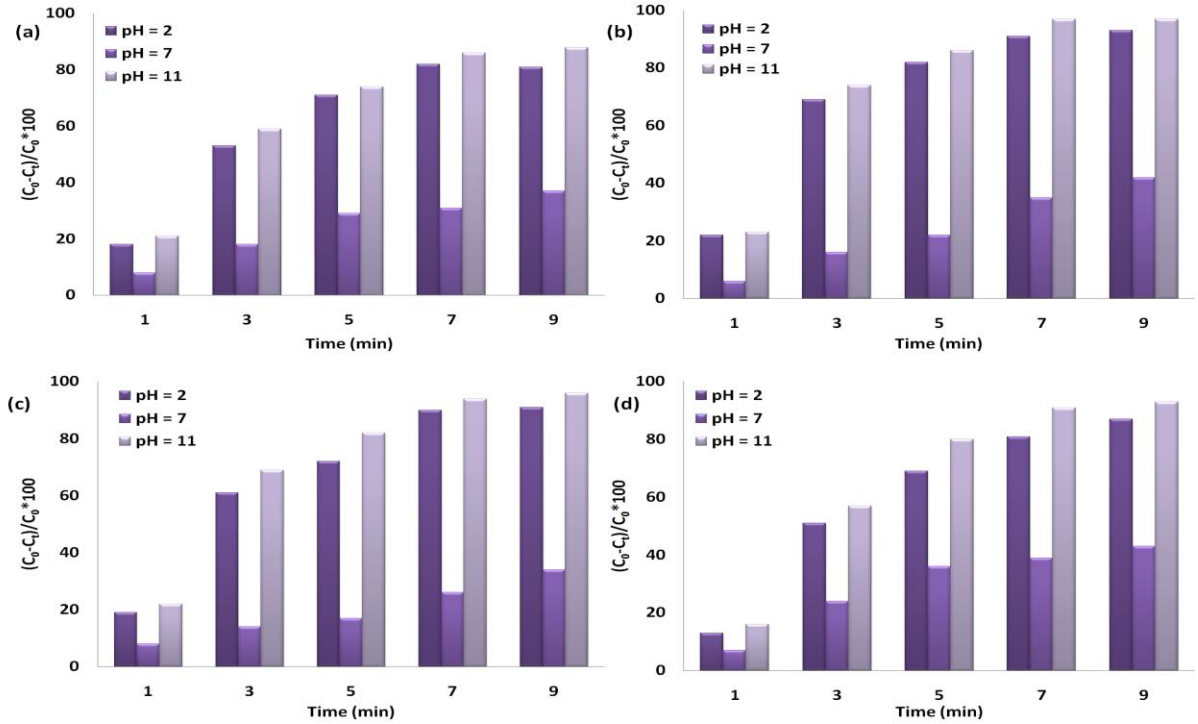

Fig.4. Influence of pH on the removal of acid black 1 (a), acid brown 214 (b), acid violet 7 (c), and acid blue 92 (d) under UV light.

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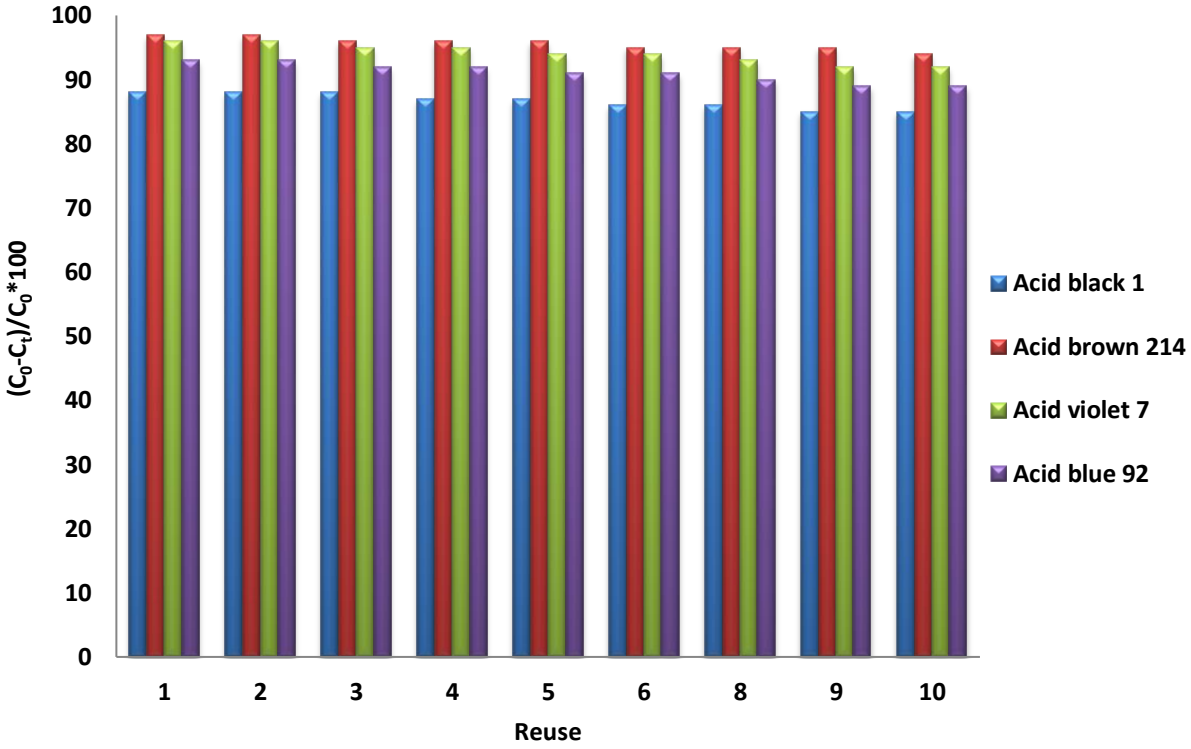

Fig.5.The reusability of Gd_2ZnMnO_6/ZnO to degradation of effluent.

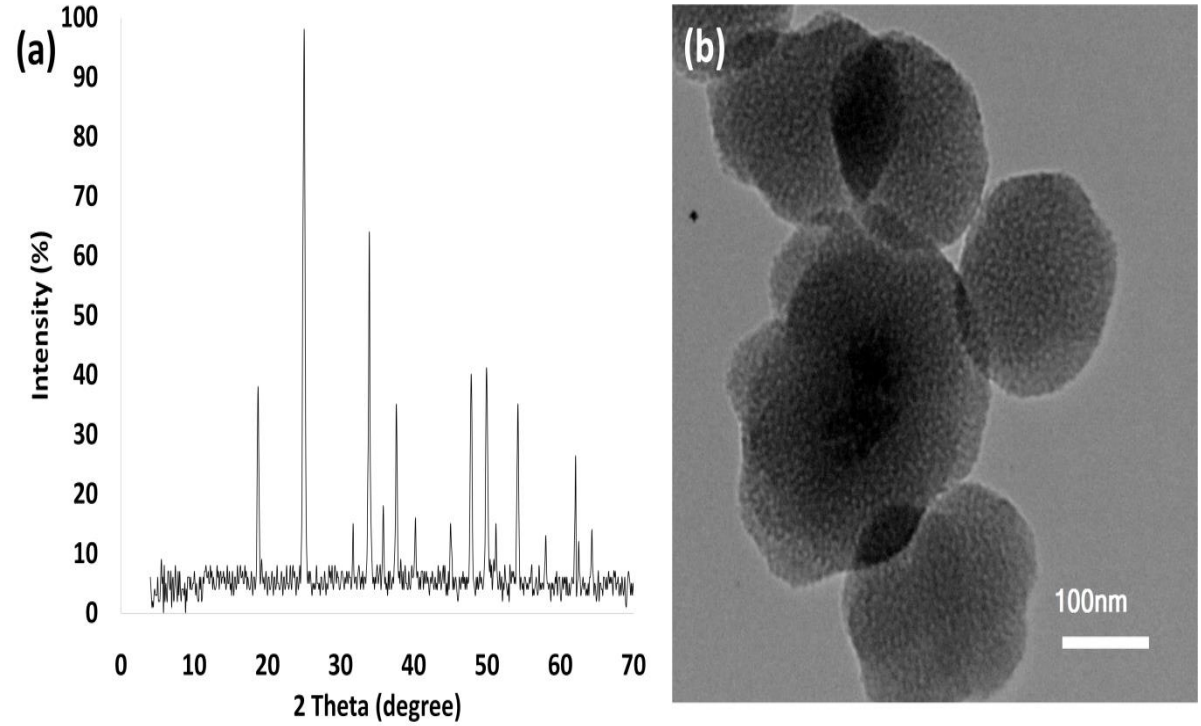

Fig.6.XRD (a), and TEM (b) of the recovered Gd_2ZnMnO_6/ZnO after the tenth run for degradation of effluent.

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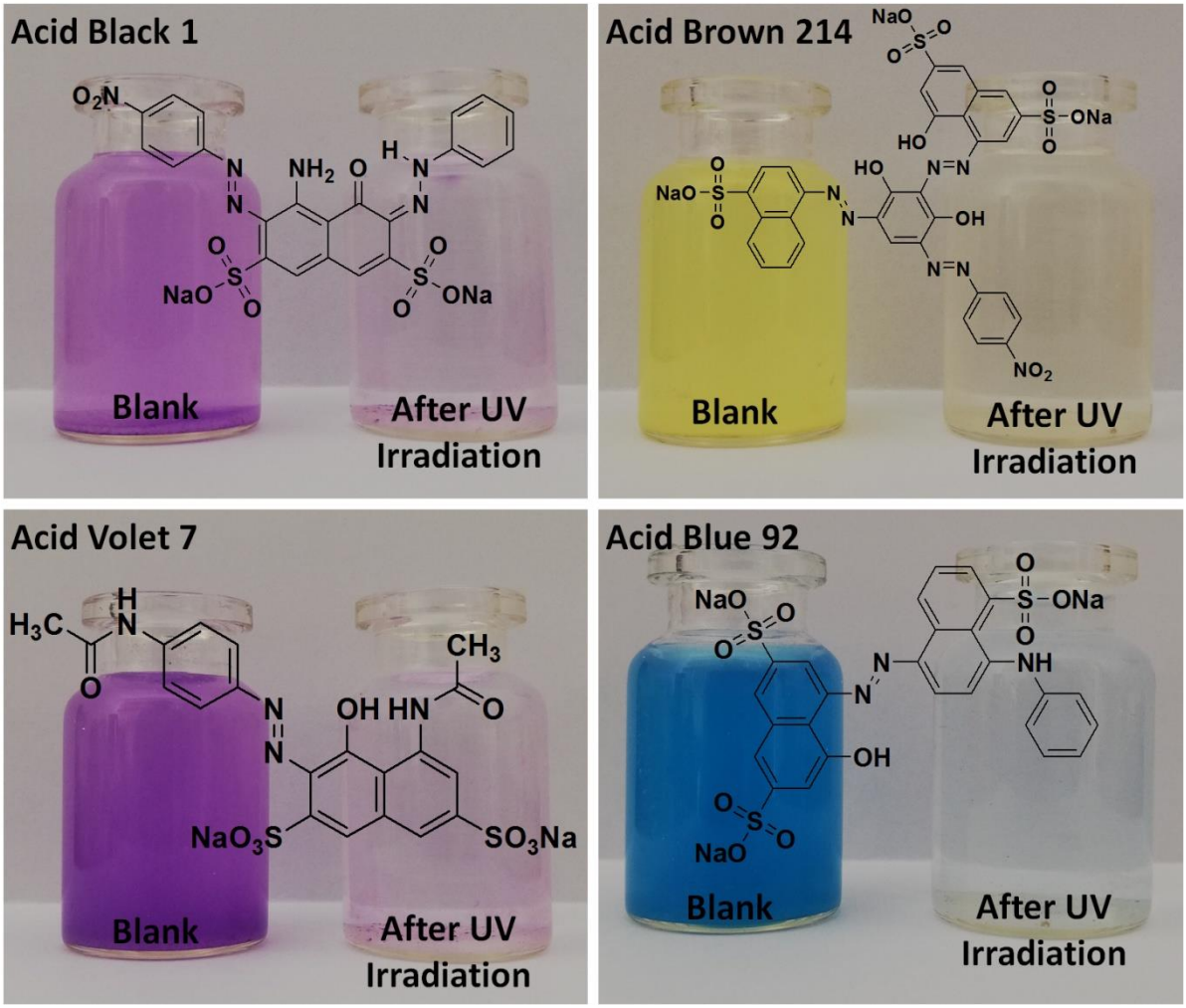

Fig.7.The formula of dyes and its solution after UV irradiation.

4.CONCLUSIONS

This study demonstrates that Gd_2ZnMnO_6/ZnO quantum dots hold significant potential for the photodegradation of polluting colors. The Gd_2ZnMnO_6/ZnO was thoughtfully fabricated, applied, and designed for the degradation of wastewater colors. A series of physicochemical analyses were performed to assess the morphology, textural, and mesoporosity properties of Gd_2ZnMnO_6/ZnO. The photodegradation efficiency of the Gd_2ZnMnO_6/ZnO was compared under UV and visible light, showcasing their effectiveness. The study highlights the potential of the newly developed Gd_2ZnMnO_6/ZnO as a highly productive semiconductor for environmental cleanup. Notably, Gd_2ZnMnO_6/ZnO maintained over 88% of its activity after ten consecutive cycles, demonstrating its strong reusability and stability.

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حذف رنگ های آلی با استفاده از نانوکامپوزیت های سرامیکی Gd_2ZnMnO_6/ZnO به عنوان فتوکاتالیست

مسعود کوچک زاده[۱]، امین هنربخش[۱و۲*]، سیدمجتبی موحدی فر[۲و۱]،راحله ژیانی[۲]، فرهاد حاجیان[۱]، سید محسن صادق زاده[۲و۳و۴]

۱- گروه مهندسی عمران، واحد نیشابور، دانشگاه آزاد اسلامی، نیشابور، ایران

۲- مرکز تحقیقات فناوری و فرآوری مواد نوین، دانشگاه آزاد اسلامی، واحد نیشابور، ایران

۳- گروه شیمی، واحد نیشابور، دانشگاه آزاد اسلامی، ایران

۴- مرکز تحقیقات پیشرفته شیمی، بیوشیمی و نانومواد، واحد نیشابور، دانشگاه آزاد اسلامی، ایران

* E-mail: amin_honarbakhsh@yahoo.com

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چکیده

تخریب فتوکاتالیستی بقایای رنگ آلی راه حلی امیدوارکننده و سازگار با محیط زیست برای چالش هایی است که موجودات زنده را به خطر می اندازد. یک نانوکاتالیست فیبری بسیار کارآمد برای حذف اسید سیاه ۱، آبی اسیدی ۹۲، قهوه ای اسیدی ۲۱۴ و بنفش اسیدی ۷ [رنگ های فاضلاب] به دقت ساخته، طراحی و مورد استفاده قرار گرفت. یافته‌ها نشان داد که مقدار نقاط کوانتومی Gd_2ZnMnO_6/ZnO بر راندمان تخریب تأثیر می‌گذارد. ادغام نقاط کوانتومی در ساختار فتوکاتالیست، جذب نور را افزایش می‌دهد، سرعت انتقال الکترون را تسریع می‌کند و راندمان انتقال بار را افزایش می‌دهد. عملکرد کاتالیزور با در نظر گرفتن اجزای مختلف کاتالیزور برای حذف ضایعات آلی ارزیابی شد. این مطالعه رویه‌های منطقی را بر اساس برهمکنش بین نانوذرات Gd_2ZnMnO_6 و ZnO در داخل کاتالیزور پیشنهاد کرد که می‌توان آنها را برای حداقل ۱۰ چرخه بدون از دست دادن قابل توجه واکنش‌پذیری مجدداً استفاده و بازیابی کرد.

کلید واژه ها

ضایعات آلی، سرامیک، نانوکاتالیست، شیمی سبز، فوتوکاتالیست.

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