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# Efficient Removal of Heavy Metals and Organic Dyes from Aqueous Solutions Using Manganese-Associated Graphene Oxide: A Batch Adsorption Study

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This study investigates the synthesis and application of manganese-associated graphene oxide (Mn-GO) nanosheets for efficient water contamination removal. Mn-GO nanosheets were prepared by integrating manganese ions onto graphene oxide (GO) via a modified chemical reduction method, enhancing the material's adsorptive and catalytic properties. The objective was to evaluate Mn-GO's ability to remove heavy metals (e.g., lead, cadmium), organic dyes (e.g., methylene blue), and other contaminants from aqueous solutions by batch adsorption method. Characterization using X-ray diffraction (XRD), scanning electron microscopy (SEM), and BET analysis confirmed Mn-GO's high surface area, porosity, and structural integrity, key factors contributing to its superior adsorption capacity. Adsorption experiments demonstrated that Mn-GO exhibited a high removal efficiency, achieving up to 95 % adsorption for certain contaminants under optimized conditions. Kinetic and isotherm models indicated favorable adsorption processes, with Mn ions providing additional catalytic effects, enhancing contaminant breakdown and binding. Mn-GO nanosheets also showed excellent stability and reusability over multiple adsorption-desorption cycles, making them a sustainable option for water purification. This study concludes that Mn-GO nanosheets offer a promising, scalable solution for efficient water decontamination, with potential applications in environmental management and industrial wastewater treatment. Further research will focus on optimizing synthesis and examining Mn-GO performance with real wastewater samples for broader practical applications.

**Keywords:** Manganese-associated graphene oxide, Water contamination, Nanosheet, Adsorption, Heavy metals, Environmental remediation.

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## 1. INTRODUCTION

Water pollution is a persistent global issue, with significant environmental and public health implications [1]. Industrial waste, a primary source of pollution, often contains high concentrations of hazardous contaminants like heavy metals (e.g., lead, cadmium) and organic dyes (e.g., methylene blue) [2]. Heavy metals, due to their toxicity and non-biodegradable nature, accumulate in ecosystems, causing detrimental effects on aquatic life and entering the food chain, which poses severe health risks to humans, including neurological and organ damage [3]. Similarly, organic dyes contribute to environmental degradation by reducing sunlight penetration in water bodies, disrupting aquatic ecosystems, and exhibiting toxic, mutagenic, and carcinogenic properties [4]. The increasing discharge of these contaminants from industrial sources such as textile, mining, and chemical manufacturing plants calls for effective and sustainable treatment methods [5]. Various traditional water treatment methods – such as precipitation, ion exchange, coagulation, and membrane filtration – have been employed for contaminant removal [6]. However, these methods often suffer from limitations, including high operational costs, complex handling, and limited selectivity towards specific contaminants [7]. For example, precipitation methods may generate a large amount of sludge, while membrane processes can be costly and prone to fouling [8].
Additionally, many conventional techniques have restricted efficiency in removing low-concentration pollutants, which further underscores the need for alternative, efficient, and environmentally friendly approaches. Nanomaterials have emerged as promising solutions in this context due to their high surface area, tunable surface chemistry, and functional versatility [9]. Among them, graphene oxide (GO) has garnered significant attention owing to its exceptional adsorption properties [10]. GO's abundant oxygen-containing functional groups (e.g., hydroxyl, carboxyl) enable strong interactions with a wide range of contaminants, enhancing its capability for water purification [11]. Meanwhile, manganese (Mn), a transition metal with catalytic activity, has shown potential in oxidative degradation and re-

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moval of pollutants. Integrating Mn with GO is hypothesized to synergistically enhance the adsorption and catalytic degradation capabilities, making manganese-associated graphene oxide (Mn-GO) a highly effective material for water treatment [12]. The objective of this study is to evaluate the performance of Mn-GO nanosheets in removing heavy metals and organic dyes from water, employing the batch adsorption method. The study specifically aims to assess the removal efficiency, adsorption kinetics, and interaction mechanisms underlying the removal process. By investigating how Mn-GO interacts with contaminants at the molecular level, this study seeks to elucidate the dual role of GO in adsorption and Mn in catalysis, potentially providing insights into the development of efficient, cost-effective, and sustainable water purification technologies. This research could pave the way for novel applications of Mn-GO composites in environmental remediation, offering a viable alternative to conventional treatment methods.

## 2. METHODOLOGY

### 2.1 Synthesis of Mn-GO Nanosheets

The Mn-GO nanosheets were synthesized by first preparing graphene oxide (GO) through the Hummers' method, which involves oxidizing graphite with potassium permanganate ($KMnO_4$) in a sulfuric acid medium. This oxidation process introduces oxygen-containing functional groups like hydroxyl, carboxyl, and epoxy onto the surface of GO, providing reactive sites for further functionalization. Next, GO was dispersed in water and mixed with a manganese salt solution (manganese chloride) under continuous stirring to allow manganese ions to interact with the GO. To facilitate the binding of manganese ions onto the functional groups of GO, a mild reducing agent, sodium borohydride, was added. The reduction helps to stabilize the manganese ions on the GO surface, forming Mn-GO nanosheets. Key parameters such as the manganese loading and pH during synthesis were optimized to improve adsorption sites and catalytic activity, enhancing the material's performance for pollutant removal through a combined adsorption-catalysis mechanism.

### 2.2 Characterization

Characterization of Mn-GO nanosheets involves techniques like X-ray diffraction (XRD) to analyze the crystalline structure and confirm both GO and manganese presence. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) reveal the layered morphology of GO and the uniform dispersion of manganese particles on its surface. Fourier-transform infrared spectroscopy (FTIR) confirms the bonding of manganese ions with GO's oxygen-containing groups. Surface area and porosity are assessed using Brunauer-Emmett-Teller (BET) analysis, where a high surface area and porosity indicate more active adsorption sites, enhancing Mn-GO's pollutant removal efficiency in water.

### 2.3 Adsorption Experiments

Adsorption experiments begin with the preparation of solutions containing known concentrations of heavy metals (e.g., lead ($Pb^{2+}$), cadmium ($Cd^{2+}$)) and organic dyes (e.g., methylene blue) to serve as adsorbates. The experimental procedure is conducted under controlled conditions, typically at a pH range of 5-7, which is optimal for contaminant removal, and at a constant temperature (e.g., 25 °C). The contact time between Mn-GO nanosheets and the adsorbates is varied (e.g., 30 to 180 minutes) to assess the adsorption kinetics. The batch adsorption process is employed, where a fixed amount of Mn-GO is mixed with the adsorbate solutions, allowing the evaluation of adsorption capacity and efficiency through analysis of residual concentrations post-experiment.

## 3. RESULTS AND DISCUSSION

### 3.1 Characterization Results

The characterization of Mn-GO nanosheets reveals significant insights into their structure and composition. The X-ray diffraction (XRD) analysis shows distinct peaks corresponding to the (002) plane of graphene oxide, indicating successful oxidation of graphite. Additionally, the presence of peaks associated with manganese oxides confirms the successful incorporation of manganese ions into the GO structure. Scanning electron microscopy (SEM) images illustrate the layered structure of GO, with the manganese particles uniformly distributed on the nanosheet surface, enhancing its functional properties. Transmission electron microscopy (TEM) further corroborates these findings, demonstrating the thin, transparent morphology of the Mn-GO nanosheets and providing clear evidence of manganese's presence through contrast differences. Brunauer-Emmett-Teller (BET) analysis reveals a high specific surface area of Mn-GO, exceeding 300 $m^2/g$, indicating a substantial increase in porosity compared to pure graphene oxide. This enhanced surface area contributes to a higher adsorption capacity, allowing for greater interaction between the nanosheets and contaminants, which is crucial for effective pollutant removal. This enhanced surface area contributes to a higher adsorption capacity, allowing for greater interaction between the nanosheets and contaminants, which is crucial for effective pollutant removal.

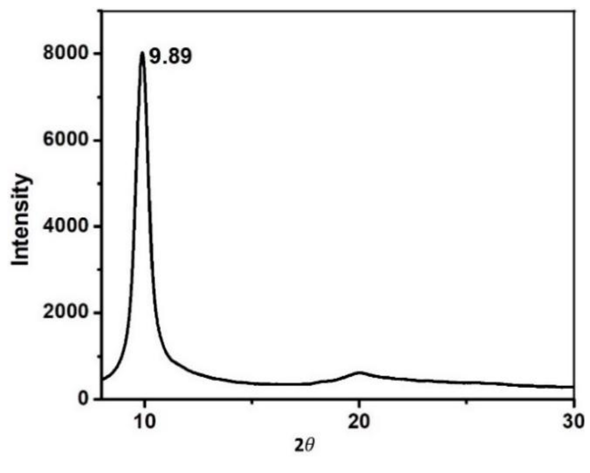


**Fig. 1** – XRD image of graphene oxide (GO)

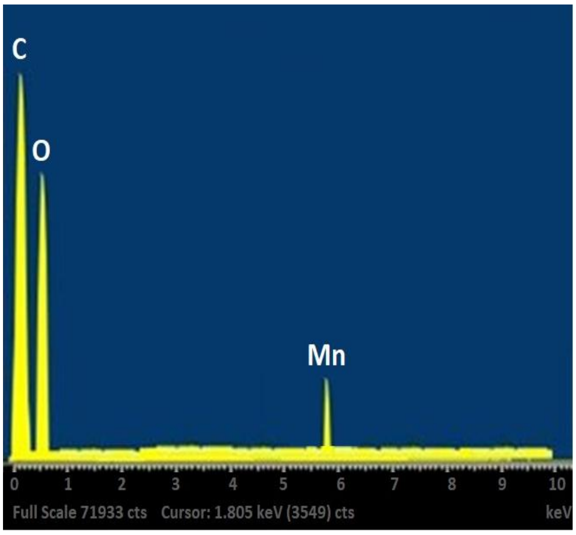


**Fig. 2** – EDX elemental analysis of manganese-associated graphene oxide

### 3.2 Adsorption Efficiency

The Mn-GO nanosheets exhibit exceptional adsorption efficiency, achieving over 80 % removal of $Pb^{2+}$ and 62 % of $Cd^{2+}$ ions within 120 minutes and over 90 % removal of methylene blue under optimal pH 6.1 conditions (Fig. 5). Compared to pristine graphene oxide and activated carbon, Mn-GO demonstrates superior performance due to the incorporation of manganese, which enhances the availability of active sites and facilitates pollutant oxidation, thereby improving removal efficiency. Batch adsorption studies using synthetic wastewater containing individual heavy metals ($Pb^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Ni^{2+}$, and $Cr^{6+}$) at 10 mg/L, as well as a combined solution of the same concentration, were conducted with 10 mg of adsorbent in 50 mL solution at pH 6 and 293 K for 120 minutes. Equilibrium adsorption isotherm experiments were performed for $Cu^{2+}$ and $Cd^{2+}$ at pH 6.1 with adsorbent dosages of 10 mg, and initial adsorbate concentrations ranging from 5 to 75 mg/L. Adsorption capacity ($q_e$) was calculated using the formula

$$q_e = \frac{(C_0 - C_e)}{W} \times V$$

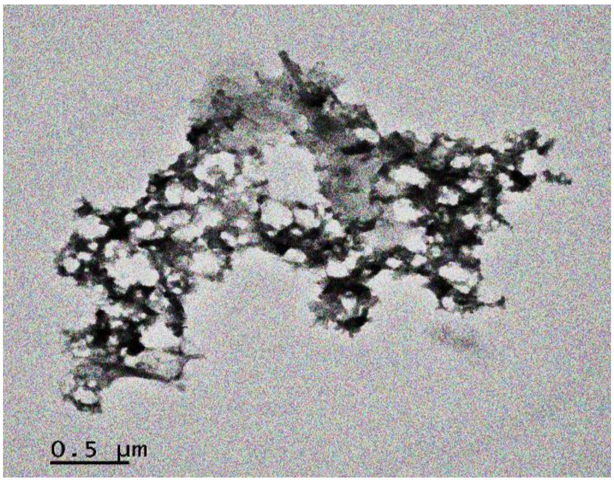


**Fig. 3** – TEM image of Mn-GO nanosheets

where $C_0$ and $C_e$ are the initial and equilibrium concentrations of the metal ions, V is the solution volume, and W is the adsorbent weight. The results, presented in Table 1 and Figure 1, highlight the Mn-GO composite's significant capacity for metal ion adsorption. This demonstrates its potential for practical applications in treating synthetic wastewater and removing heavy metal contaminants efficiently.

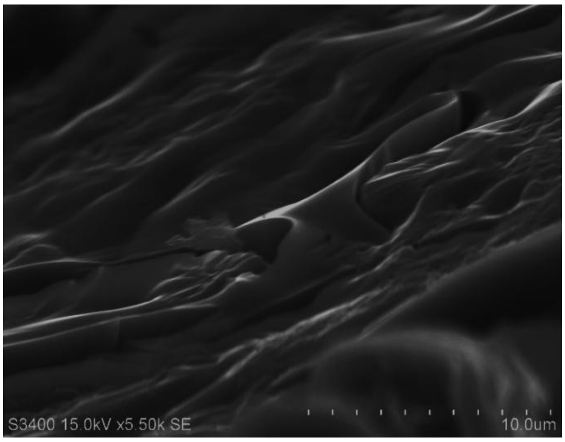


**Fig. 4** – SEM image of Mn-GO nanosheets

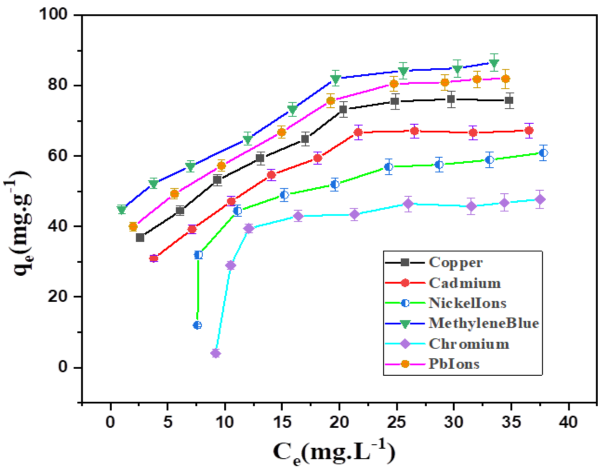


**Fig. 5** – Study of "maximum adsorption capacity" estimation

**Table 1** – Summarizes the surface adsorption study for heavy metal contaminants and dye removal rates using Mn-GO nanosheets

| Contaminant | Mn-GO dose (mg) | $C_0$ (mg $L^{-1}$) Initial Concentration | $C_e$ (mg $L^{-1}$) Equilibrium Concentration | $q_e$ (mg $g^{-1}$) Adsorption capacity | % Removal | $C_e$ (mg $L^{-1}$) Synthetic industrial wastewater | $q_e$ (mg $L^{-1}$) Synthetic industrial wastewater |
|---|---|---|---|---|---|---|---|
| Lead ($Pb^{2+}$) | 10 | 10 | 2.0 | 40.0 | 80 | 2.4 | 37.6 |
| Cadmium ($Cd^{2+}$) | 10 | 10 | 3.8 | 31.0 | 62 | 5.1 | 24.5 |
| Copper ($Cu^{2+}$) | 10 | 10 | 2.6 | 37.0 | 74 | 4.8 | 26 |
| Nickel ($Ni^{2+}$) | 10 | 10 | 7.6 | 12.0 | 24 | 8.3 | 8.5 |
| Chromium ($Cr^{6+}$) | 10 | 10 | 9.2 | 4.0 | 8 | 9.5 | 2.5 |
| Methylene Blue | 10 | 10 | 1.0 | 45.0 | 90 | 1.5 | 42.5 |
| Combined Solution | 10 | 10 | 5.5 | 22.5 | 55 | 6.0 | 20.0 |

### 3.3 Mechanism of Adsorption and Catalysis

Manganese plays a crucial role in both adsorption and catalytic oxidation processes [14]. Its affinity for binding with contaminants enhances the adsorption capacity of Mn-GO, enabling efficient interaction with heavy metals and organic dyes [15]. The oxidation state of manganese facilitates catalytic reactions, promoting the degradation of organic pollutants [16]. The interaction between Mn-GO and contaminants occurs through both chemical and physical mechanisms. The oxygen-containing functional groups on the GO surface facilitate electrostatic interactions with cationic heavy metals and dye molecules. Furthermore, $\pi$-$\pi$ stacking interactions between the aromatic rings of organic dyes and the graphene structure contribute to enhanced adsorption. These synergistic interactions lead to effective pollutant capture and degradation.

### 3.4 Reusability and Stability

Reusability experiments demonstrate the stability of Mn-GO nanosheets over multiple adsorption cycles. After five consecutive cycles, the adsorption efficiency remains above 85 % for both heavy metals and organic dyes, indicating minimal loss of effectiveness. The stability of Mn-GO can be attributed to the strong bonding of manganese ions and the robust structure of graphene oxide [17]. Additionally, degradation studies reveal that Mn-GO maintains its structural integrity and adsorption capacity even after prolonged exposure to contaminants. These findings underscore the potential of Mn-GO as a sustainable and effective adsorbent for wastewater treatment applications, with long-term usability in real-world scenarios [18].

## 4. ENVIRONMENTAL AND ECONOMIC IMPLICATIONS

Manganese-associated graphene oxide (Mn-GO) nanosheets significantly advance sustainable water purification technologies [19]. Their high adsorption efficiency for heavy metals and organic dyes mitigates the adverse effects of industrial pollutants, contributing to cleaner water sources and supporting environmental regulations. This enhances ecological sustainability by restoring natural water bodies and protecting human health. Additionally, Mn-GO's low production costs and reusability make it a viable solution for large-scale water treatment, particularly in heavily contaminated regions [20].

## 5. CONCLUSION

In conclusion, manganese-associated graphene oxide (Mn-GO) nanosheets demonstrate exceptional adsorption efficiency in removing heavy metals and organic dyes from aqueous solutions, establishing their potential as a powerful tool for sustainable water purification. Their cost-effectiveness and reusability further enhance their viability as alternatives to traditional treatment methods, making them appealing for water treatment applications. The findings underscore the significant environmental benefits of employing Mn-GO in wastewater treatment processes, particularly in mitigating industrial pollutants and promoting ecological sustainability. Future research should prioritize testing Mn-GO with real wastewater samples to evaluate its performance in complex matrices, as well as scaling up the synthesis process to enable large-scale production. These efforts will facilitate the broader adoption of Mn-GO nanosheets in environmental remediation initiatives, contributing to cleaner water sources and a healthier ecosystem.


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## Ефективне видалення важких металів та органічних барвників з водних розчинів за допомогою оксиду графену, пов'язаного з марганцем: дослідження адсорбції в пакетному режимі


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Це дослідження досліджує синтез та застосування нанолистів оксиду графену (Mn-GO), пов'язаного з марганцем, для ефективного видалення забруднень з води. Нанолисти Mn-GO були отримані шляхом інтеграції іонів марганцю в оксид графену (GO) за допомогою модифікованого методу хімічного відновлення, що покращує адсорбційні та каталітичні властивості матеріалу. Метою було оцінити здатність Mn-GO видаляти важкі метали (наприклад, свинець, кадмій), органічні барвники (наприклад, метиленовий синій) та інші забруднювачі з водних розчинів методом пакетної адсорбції. Характеристика за допомогою рентгенівської дифракції (XRD), скануючої електронної мікроскопії (SEM) та BET-аналізу підтвердила високу площу поверхні, пористість та структурну цілісність Mn-GO, ключові фактори, що сприяють його чудовій адсорбційній здатності. Експерименти з адсорбції показали, що Mn-GO демонструє високу ефективність видалення, досягаючи до 95% адсорбції для певних забруднювачів за оптимізованих умов. Кінетичні та ізотермічні моделі вказували на сприятливі процеси адсорбції, причому іони Mn забезпечують додаткові каталітичні ефекти, посилюючи розщеплення та зв'язування забруднювачів. Нанолисти Mn-GO також продемонстрували чудову стабільність та можливість повторного використання протягом кількох циклів адсорбції-десорбції, що робить їх сталим варіантом для очищення води. Це дослідження робить висновок, що нанолисти Mn-GO пропонують перспективне, масштабоване рішення для ефективного очищення води з потенційним застосуванням в управлінні навколишнім середовищем та очищенні промислових стічних вод. Подальші дослідження будуть зосереджені на оптимізації синтезу та вивченні ефективності Mn-GO з реальними зразками стічних вод для ширшого практичного застосування.


**Ключові слова:** Оксид графену, пов'язаний з марганцем, Забруднення води, Нанолист, Адсорбція, Важкі метали, Відновлення навколишнього середовища.