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Abstract: Irregular removal methods of industrial waste have caused water source problems due to toxic materials such as heavy metals. These heavy metals are carcinogenic and pose serious health risks, which may accumulate in human bodies via water sources. Therefore, it is important to treat heavy metals in contaminated water before consuming them. Out of these heavy metals, manganese has proven to be a difficult heavy metal to remove from water due to its complex chemistry. According to the World Health Organization (WHO), the maximum permissible manganese concentration in drinking water is 0.05 mg l-1. Therefore, it is vital to find a solution for the removal of excess manganese from drinking water. This study focuses on removing manganese from a material synthesized by coating MnO_2 on graphene oxide quantum dots (GOQD). The prepared material was characterized by RAMAN Spectroscopy. The RAMAN spectra revealed bands around 580 cm⁻¹ and 630 cm⁻¹ which proves the presence of MnO₂. Adsorption studies were analyzed using Atomic Absorption Spectroscopy. Adsorption studies concluded that 0.6 mg l-1 of initial concentration, pH of 8.0, and dosage value of 1.0×10^4 mg l⁻¹ were the optimum conditions for maximum adsorption.

Keywords: Adsorption; Graphene oxide; Heavy metals; Manganese; Quantum dots

Introduction

Removal of heavy metals from water sources is very vital since the water quality of drinking water depends on the number of heavy metals and concentrations present in water and several parameters that govern it al., (Tobiason 2016). The et conventional methods for heavy metal removal include chemical precipitation, membrane filtration, adsorption, ultrafiltration, ion exchange, etc.

Chemical precipitation requires many chemicals and further treatment to deal with sludge, although it is the most widely used for its simplicity (Zhao et al., 2016). Due to the cost-effectiveness nature and reliability

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Dr.E.G. W Gunawardana, B.Sc. (Perad), M.Sc., Ph.D. (Tokyo, Japan), Chemist (Chief Scientist c/u), JRDC Email: wasanagun@gmail.com adsorption is widely used for the removal of these pollutants and heavy metals.

Because traditional water treatment processes are frequently inefficient in removing undesirable metal pollutants from water resources, membrane filtration systems combined with a variety of graphene-based nanomaterials have been developed in recent years for effective heavy metal removal.

By functionalizing graphene with oxygen-containing functional groups such as hydroxyl, carboxyl, carbonyl, and epoxide, the hydrophilicity of graphene can be increased. These functional groups are able to interact with heavy metal through electrostatic ions interactions (Nasrollahzadeh et al., 2021). Although many methods for the removal of heavy metals in wastewater can be formulated, the ideal treatment should be not only suitable, appropriate and practical to the actual situation, but also able to meet the maximum contaminant level standards of the country's Health established (World Organization, 2011). Advanced materials that combine mechanical robustness with fast permeation are crucial to applications such as water purification, ions selectivity, and graphene oxide quantum dots offer a promising opportunity for the fabrication of that because of their unique morphology, oxidizable surface, and electrical conductivity (Shukla et al., 2018). Here the material is synthesized to achieve an effective removal of Mn by a green

approach. Mn is a transition metal that can be found in both surface and underground water (Khadse et al., 2015). In surface water, Mn can undergo many oxidation cycles; in underground water, it can be present as Mn (II). Therefore, removing manganese (Mn) has become a tedious process. Problems occur when dissolved Mn (II) is converted to insoluble forms, Mn (III) and Mn (IV)(Sun et al., 2021). As a result, black-brown turbidity will be visible in the water sources contaminated by Mn.

Removal of manganese from water can be achieved using many physical, chemical, and biological processes as shown in figure 1 (Bhol et al., 2021).





The critical first step would be the identification of the source water including the form of Mn with other parameters such as concentration, pH, hardness, alkalinity, organic carbon, etc. Then it is important to distinguish between dissolved and particulate forms to select the relevant treatment processes (Yan et

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al., 2014). Particulate Mn can be removed by the particle separation method. Dissolved Mn can be directly removed by physical/chemical processes. Also dissolved Mn (II) can be oxidized to insoluble forms of Mn (II) or Mn (IV) to remove in the form of a particle.

Using equation (1) extent of Mn (II) removal can be calculated as a percentage.

Percentage removal of Mn(II)
=
$$\left(\frac{C_i - C_f}{C_i}\right) \times 100\%$$
 (1)

Where C_i is the initial concentration and C_f is the final concentration of adsorbate.

According to equation (2) amount of adsorbate in mg, adsorbed by 1 g of adsorbent can be calculated. C_i is the initial concentration and C_f is the final concentration (in mg L⁻¹) of adsorbate and m is the amount of adsorbent in the system (in g L⁻¹).

Amount adsorbed =
$$\left(\frac{C_i - C_f}{m}\right)$$
 (2)

Kinetic studies are conducted to understand the mechanism of an adsorption process and to better understand the details of the performance. In the adsorption reaction models, the adsorption process is considered a reaction between the adsorbent and the adsorbate. The basic differential equation related to the first-order kinetics model is given below.

$$\frac{\mathrm{d}q\mathrm{t}}{\mathrm{d}\mathrm{t}} = \mathrm{k_1}(\mathrm{q_e} - \mathrm{q_t}) \text{ (3)}$$

In equation (3) qt is the adsorption capacity at time t, q_e is the equilibrium adsorption capacity and k_1 is the pseudo-first-order rate constant. Here, it is assumed that adsorbate concentration remains constant throughout the reaction while sites that are available for adsorption will decrease. This can only be applied to the adsorption process's initial time stage. The main driving force of this adsorption process is the available active sites.

By applying boundary conditions t=0, $q_t=0$, and t=t, $q_t=q_t$ to the above equation we can obtain equation (4).

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$
 (4)

In this model, it is assumed that two different active sites are involved in the adsorption process of a single adsorbate particle. Differential equations related to that can be shown as below (equation (5)).

$$\frac{\mathrm{dqt}}{\mathrm{dt}} = \mathrm{k}_2(\mathrm{q}_\mathrm{e} - \mathrm{q}_\mathrm{t}) \text{ (5)}$$

Here qt is the adsorption capacity at time t, q_e is the equilibrium adsorption capacity and k_2 is the pseudo-second-order rate constant. Integrating the above linear form can be obtained as below.

By applying boundary conditions t=0, $q_t=0$ and t=t, $q_t=q_t$ to the above equation

$$\frac{\mathsf{t}}{\mathsf{q}_{\mathsf{t}}} = \frac{1}{\mathsf{k}_2 \mathsf{q}_{\mathsf{e}}} + \frac{1}{\mathsf{q}_{\mathsf{t}}} \mathsf{t}$$

This model had been widely used in describing the adsorption of metal ions. By using the kinetic parameters, the behavior of the adsorption process can be identified and it can be improved accordingly.

Materials and Methods

The improved hummers method (Marcano et al., 2010) was used for the synthesis of graphene oxide from local graphite.

A modified oxidative cutting method was used for the synthesis of graphene oxide quantum dots.

Synthesis of MnO₂-coated GOQD

Graphene oxide quantum dots and MnCl₂.4H₂O were dispersed in isopropyl alcohol at suitable temperatures with ultrasonication. KMnO₄ dissolved in deionized water was added rapidly into the above solution. The resulting boiling mixture was washed several times using deionized water. Finally, the product dried was at room temperature for 2 days.

Adsorption batch studies

The optimum conditions required for the highest adsorption were determined by varying pH, dosage, and initial concentration of the solution. MnCl₂.4H₂O was used for the preparation of Mn (II) solutions. Experiments were done in triplicates. Final concentrations were determined using an atomic absorption spectrophotometer. During the process volume of the solutions was kept constant at (10.00 ± 0.05) cm³.

Results and discussion

Synthesized materials



Figure 2- Graphene oxide

Figure 2 shows the final product of graphene oxide obtained using the improved hummers method.



Figure 3- GOQD under normal light and under UV light

Figure 3 depicts the observation that occurred when GOQD is exposed to a trans UV illuminator emitting light blue.



Figure 4- GOQD-MnO₂

Figure 4 shows the final product which is used for the removal of manganese in an aqueous medium.

Characterization



Figure 5- FTIR spectrum of graphene oxide

A JASCO FT/IR-6700 spectrometer was used to obtain the 500-4000 cm⁻¹ FTIR spectrum. Spectroscopy measurement was obtained at room temperature. Figure 5 shows the FTIR spectrum of graphene oxide where bands at 3280 cm⁻¹ (O-H vibrations),1718 stretching cm-1 (C=O stretching vibrations),1616 cm⁻ $^{1}(C=C)$ aromatic stretching vibrations),1365 cm⁻¹(C-OH stretching vibrations),1225 cm⁻¹(C-O-C stretching vibrations) which aids the oxidation of graphite to graphene oxide.



Figure 6- Raman spectrum of graphene oxide

The Raman spectrum for prepared graphene oxide was obtained by Renishaw inVia InSpect confocal Raman microscope by a laser edge of 514 nm (1 % of power) at static mode. Figure 6 shows bands at 1350 cm⁻¹ correspond to the D band which is due to the breathing modes of sp² atoms in the ring.

The band at 1575 cm⁻¹ corresponds to the G band which is due to the E_2g phonon of the sp² carbon atoms. D band is an indication of defects that can be due to the defects such as grain boundaries and vacancies.



Figure 7- Raman spectrum of GOQD-MnO2

Figure 7 shows strong bands at 590 cm⁻¹ and 646 cm⁻¹ are due to

symmetrical Mn-O vibrations. This confirms the formation of MnO_2 on graphene oxide quantum dots.



distribution of GOQD

According to figure 8, it was observed that 5% of particles were less than 10 nm and 32.5 % of particles were less than 20 nm and quantum dots were formed under these conditions.

Batch studies



Figure 9- Graph of removal (%) vs dose

According to figure 9 highest removal of 69.5% was observed with a GOQD-MnO₂ dose of 0.01 g cm⁻³. With increasing doses, more adsorption sites are being added to the system. Initially, this results in

an increased removal. It was observed that the percentage removal (%) increased with the increasing amount of pH values.



Figure 10- Graph of removal (%) vs pH

According to figure 10, it was percentage observed that the removal (%) increased with an increasing amount of pH values. The pH of the solution has a huge effect on the adsorbent surface properties. optimum pН where The the maximum adsorption occurs is pH= 8.0. This can be explained by the change in the surface functionalities in the fabricated GOOD-MnO₂. When the pH of the solution is very low there is a higher degree of H⁺ present in the system. Due to that H⁺ will compete with the metal ions to form electrostatic interactions with the oxygen functionalities present in the GOQD-MnO₂. Therefore, the adsorption will be very lower compared to the higher pH values. But when it comes to the higher pH values oxygenated functional groups will be easily protonated, leading to electrostatic better interactions between the metal and the oxygen functionalities, eventually leading to a higher degree of adsorption.



Figure 11- Graph of removal (%) vs concentration

Figure 11 shows the removal (%) vs initial concentration. The highest removal of 70.5% was observed with a GOQD-MnO₂ concentration of 0.01 g cm⁻³. Here the pH of the system was maintained at 8.0 while maintaining the dosage of 0.01 g cm⁻³.

Table 1 shows the results obtained from kinetics studies. Higher R² values were obtained for both the pseudo-first-order and pseudosecond-order kinetics.

Table 1: R² values and rate constant values obtained for kinetic studies

| Pseudo 1st order | | Pseudo 2nd order | |
|------------------|----------------------------------|------------------|----------|
| R ² | k1(min- | R ² | k2(mg-1 |
| value | ¹) x10 ⁻³ | value | g min-1) |
| 0.9889 | 4.755 | 0.9998 | 1.592 |



Figure 12- Graph of $ln(q_e-q_t)$ vs time



Figure 13- Graph of (t/q_t) vs time

According to figure 12 and figure 13 (pseudo-order plots) for both cases, a higher R^2 value was observed. But for the case of the first 60 minutes adsorption follows first-order kinetics while for the latter part adsorption follows second-order kinetics. Therefore, we can say that the adsorption occurs through a combination of pseudo first and second-order mechanisms.

Conclusion

GOQD-MnO₂ is an excellent adsorbent for Mn (II). Under optimum conditions, removal of over 85% can be obtained. The optimum conditions for adsorption are 0.6 mg l^{-1} of initial concentration, pH of 8.0, and dosage value of $1.0 \times$ 10⁴ mg l⁻¹. From the kinetic analysis, it was found that for the case of the initial hour adsorption follows firstorder kinetics while for the later stages of the process adsorption follows second-order kinetics.

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