COMPOSITES OF CHITOSAN AND GRAPHENE OXIDE: EFFICACY IN CADMIUM

(Cd²⁺) REMOVAL FROM INDUSTRIAL EFFLUENT

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Abstract

This study evaluates the effectiveness of a Chitosan-Graphene Oxide (CGO) composite for the elimination of cadmium (Cd²⁺) ions from industrial wastewater. The CGO adsorbent was prepared via a modified Hummers method and was characterized through FTIR, XRD, and SEM techniques. Spectral analysis by FTIR demonstrated the presence of ionizable functional groups essential for adsorption, while XRD results indicated the existence of crystalline phases, including quartz, orthoclase, and aragonite. SEM imaging revealed a uniform dispersion of chitosan nanoparticles across graphene oxide sheets. The modifications notably improved the composite's surface area and increased the number of available active sites. Batch adsorption experiments were conducted to assess the influence of several factors, including contact time, pH, temperature, and adsorbent dosage, on the removal of Cd²⁺.The optimal conditions identified 120 minutes of contact time, 0.5 g of adsorbent, pH 10.0, and a temperature of 373 K yielded a maximum removal efficiency of 99.83%. Isotherm studies revealed that the process of adsorption conformed to Freundlich, Temkin, and Dubinin-Radushkevich models, indicating the formation of multiple adsorption layers on non-uniform surfaces. Kinetic analysis revealed that the Pseudo-second-order model provides the most accurate representation of the data. Additionally, intra-particle diffusion emerged as a contributing factor, although it was not identified as the only rate-limiting step. Thermodynamic evaluations revealed that the adsorption process demonstrated characteristics of spontaneity and endothermic behavior, accompanied by an increase in disorder at the solid-liquid interface. These findings position the CGO composite as a notably efficient, eco-friendly, and sustainable option for cadmium elimination from wastewater, highlighting its promising applications in industrial water treatment processes.

Keywords: Chitosan-Graphene Oxide Composite, Cadmium Removal, Industrial Wastewater Treatment, Adsorption Mechanism, Heavy Metal Remediation.

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INTRODUCTION

The environment is significantly affected by major industrial sources that produce heavy metals. The presence of these heavy metals in wastewater, resulting from numerous manufacturing processes, causes a global and authorized concern [1] inducing the decline of the surrounding environment, which creates a significant a danger to both the environment and human health and well-being [2]. Large amounts of wastewater with high concentrations of dangerous heavy metals are produced as a result of the increased use of metals and chemicals in industrial operations. This presence of such metals poses significant challenges for environmentally safe disposal due to their resistance to decomposition and long-lasting characteristics. Unlike organic pollutants, which are often prone to biological breakdown, heavy metal ions do not break down into benign substances over time [3].

Heavy metal ions are identified within the effluent discharges originating from various industrial operations, including mining activities, tanneries, electronics manufacturing, electroplating, petroleum refining, and petrochemical sectors [2]. These heavy metals in the waste water have been remedied using an array of remediation methods, which encompass photo-catalytic degradation, reactive decomposition, organic matter decomposition, combined chemo-biological treatment, current-driven chemical reaction, adsorption process, particle destabilization via chemicals, Suspended solids aggregation etc. [2]. However, adsorption technique has shown to be the most sustainable among the different cleanup methods available [2], [4]. This is due to the possibility of regeneration, sludge-free operation, and excellent recovery.

Water pollution, especially from heavy metal contamination, has become an urgent environmental issue with significant repercussions for both ecosystems and human health. Prolonged environmental contaminants known for their toxicity, bioaccumulation, and capacity to have detrimental effects on human health and the environment include heavy metals like cadmium (Cd), copper (Cu), mercury (Hg), and lead (Pb), they can accumulate in aquatic environments, thereby posing substantial risks to marine life and the safety of drinking water supplies. The release of industrial effluents, agricultural runoff, and inappropriate disposal of electronic trash are the main causes of the rising concentrations of heavy metals in wastewater [6], [7].

Heavy metal prevalence, including cadmium (Cd²⁺), in aquatic system represents a serious challenge to both environmental sustainability and public health [8]. Cadmium, a resistant-to-degradation and poisonous metal, is frequently discharged as a result of various industrial processes, including electroplating, battery manufacturing, mining, pigment production, and plastic fabrication [8]. At even low concentrations, cadmium poses significant risks to human health, leading to serious physiological and biochemical dysfunctions. These may include damage to the kidneys, skeletal disorders, and potential carcinogenic effects [9]. In response to these dangers, the World Health Organization (WHO) has set a maximum allowable limit of 0.003 mg/L for cadmium in drinking water. [10].

Conventional techniques for cadmium remediation from wastewater, including membrane filtration, ion exchange, chemical precipitation, and electrochemical treatment, usually face major obstacles.. These include high operational costs, incomplete removal efficacy, the generation of sludge, and complex technical requirements [11]. In contrast, adsorption has gained recognition for its cost-effectiveness, straightforward implementation, high efficiency, and the ability to regenerate materials [12].

A naturally occurring polymer derived from chitin, chitosan, has garnered attention as a reliable adsorbent due to its availability, biodegradability, non-toxic nature, and strong affinity for metal ions facilitated by its amine and hydroxyl groups. However, challenges such as its low surface area, mechanical fragility, and limited stability in acidic environments often restrict its effective standalone application [14]. In order to tackle these issues, scholars have looked into the application of composite materials that incorporate graphene oxide (GO). This two-dimensional carbon nanomaterial is

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renowned for its exceptional mechanical strength and surface area. Additionally, the material's rich array of numerous functional groups that contain oxygen, such as carboxyl and epoxy, and hydroxyl, significantly enhances its capacity to interact with metal ions [15].

Chitin ranks among the most The most extensively distributed biopolymers, following cellulose. This natural polysaccharide is primarily found in crustaceans, including crabs and shrimp, in addition to the cuticles of fungus cell walls and insects [16, [17]. When the French scientist Braconot first isolated chitin from a fungus in the 19th century, the history of chitosan began. Roget successfully produced chitosan in 1859 by employing potassium hydroxide to decylate chitin, and by 1950, its entire structure had been determined [18], [19]. Chitosan is extensively utilized in both with uses spanning medical and industrial sectors, thanks to its unique structure as a natural amino polysaccharide, which bestows it with versatile properties [20], [21].

Cellulose and chitin, serve essential safeguarding mechanisms in living organisms, respectively. Plants synthesize these materials for their biological functions. Structurally, cellulose and chitin exhibit notable similarities [22], [23]. A byproduct of chitin is chitosan. The distinction between the two polymers is based on the quantity of steel groups on the polymer chain. Chitin has all of its NH₂ groups acetylated, while chitosan's amine groups are amide-free. Traditionally, chitin and chitosan are thought to separate when 50% of amide groups are present [24], [25], and [26]. Beta chitin is sourced from diatoms and squid arms, while gamma chitin, which occurs in relatively minor quantities, is a hybrid of alpha and beta chitin [27], [28], [29].

Variations in the polymer's structure are attributed to different chain orientations, which significantly influence the material's characteristics. The presence of steel groups contributes to this variability, facilitating the formation of the polymer structure's hydroxyl groups and carbon-2 steel groups form both intra- and extra-chain hydrogen bonding. [30], [31]. Configuration allows for additional hydrogen bonding beyond the intra-chain bonds, contributing to enhanced structural integrity [32], [33]. Most naturally occurring polysaccharides exist in an alkaline form. Chitin does not dissolve in water and many organic solvents due to its lipophilicity; however, but dissolves in dilute acid solutions [34], [35], [36], [37].

Physical alterations to chitosan, including its transformation into fibers, films, membranes, hydrogels, and beads, significantly enhance its mechanical properties, surface area, and adsorption capacity [38], [39]. Furthermore, chemical modifications such as cross-linking and the grafting of other polymers or inorganic materials improve chitosan's solubility, stability, and adsorption characteristics [38], [40]. On the other hand, graphene is made up of a one-atom-thick sheet of carbon atoms arranged in a hexagonal (honeycomb), with a thickness of just one atom. It is the basic component of several carbon allotropes, such as fullerenes, graphite, and carbon nanotubes [41], [42], [43].

The material's structure is inherently unstable due to the arrangement of carbon layers that rest upon one another, with these layers bonded solely through van der Waals interactions [44], [45]. Lately, graphene has emerged as a viable option to traditional carbonaceous nanofillers in the development of composite materials that is polymeric. The incorporation of composite nanoparticles significantly enhances the mechanical, electrical, and thermal properties of polymers [47], [48], [49].

The anticipated increase in the application of nanoparticles in the development of modern materials is significant in the near future [49], [50], [51]. Graphene has the potential to subsitute metal conductors in electronic devices, given their remarkable properties. Furthermore, in recent years, it has garnered attention from researchers worldwide for its ability to adsorb heavy metal ions from water, attributable to its large surface area and capacity to be chemically modified with functional groups [52], [53], [54], [55]. The properties of graphene oxide can be adjusted by managing the level of oxidation, the concentration of functional groups, and the dimensions as well as morphology of the flakes. The synthesis of graphene oxide involves several key steps. Initially, biomass undergoes

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carbonization, which is achieved by thermally treating it in an inert gas environment to produce carbon material [56]. Subsequently, this carbonized biomass is processed using the Hummers method for oxidation [57]. During the oxidation phase, the carbonized biomass is combined with concentrated H_2SO_4 and H_3PO_4 solutions, to which potassium permanganate is introduced as a potent oxidizing agent. The mixture is then heated and stirred to promote the oxidation of the carbon material [57]. Following this process, water is added to dilute the mixture, and hydrogen peroxide is incorporated to decompose any remaining oxidizing agents [57].

The solution obtained undergoes a thorough filtration and washing process using water and hydrochloric acid to achieve a neutral pH [56]. Subsequently, the resulting product is dried, yielding graphene oxide. This method efficiently transforms biomass into high-quality graphene oxide by integrating the initial carbonization stage with the well-known Hummers oxidation process [57], [56]. The final graphene oxide product is well-suited for a variety of applications, thanks to its efficiency and high yield.

Oxygen is supplied by the various attachment present in the material, which enhance the bonding capacity with metals. Similarly, the NH₂ groups found in chitosan interact with metals, enabling their adsorption from contaminated effluents. However, the standalone use of graphene oxide and chitosan is associated with several limitations, such as low operational efficiency, stability issues, and aggregation tendencies. To address these challenges, researchers have conducted studies on the crosslinking and functionalization of chitosan with polar groups, including graphene oxide [58], [59].

The circulatory system serves as a primary pathway for exposure, with blood vessels identified as key organs affected by cadmium toxicity. Chronic inhalation of cadmium particles has been associated with abnormalities in pulmonary function, as well as chest radiographs indicative of emphysema. Studies indicate that cigarette smokers exhibit elevated cadmium concentrations in both blood and urine, while former smokers show intermediate levels, and non-smokers tend to have lower concentration [60] s.

In addition, elevated levels of chromium (VI) in the air can lead to irritation of the nasal lining and the development of ulcers. Common health issues observed in animals consuming Cr⁶⁺ compounds include gastrointestinal disorders, as well as anemia and reproductive impairments. Lead is recognized as a highly systemic toxin, impacting various organs [61].

Mercury is particularly concerning due to its low excretion rate after absorption with all forms posing significant health risks [60]. Furthermore, while certain essential elements like copper are necessary for biological functions, excessive exposure can lead to damage, resulting in a spectrum of injurious health effects and diseases in humans. For several elements, including chromium and copper, the margin between beneficial and harmful concentrations is notably narrow [62]. The chitosan-graphene oxide (CGO) composite serves as a multifunctional platform, effectively achieving high adsorption capacities for a range of heavy metals [63]. Nevertheless, the adsorption characteristics of CGO composites concerning cadmium ions remain a subject of ongoing research, particularly in relation to varying physicochemical parameters [64].

The current body of knowledge regarding the elimnimation of heavy metals from wastewater presents several notable gaps. There is an evident shortage of environmentally friendly and sustainable techniques, coupled with an underutilization of seafood waste for innovative applications [65], [66], [67], [68]. Chitosan, a biopolymer obtained from the exoskeletons of crustaceans, notably shrimps and crabs, has attracted significant interest due to its impressive adsorption properties [69], [70]. Its high surface area, reinforced by functional groups such as amino and hydroxyl, pictures the material as a potential candidate for the eliminating heavy metals from various environments [71]. Similarly, graphene oxide, a two-dimensional nanomaterial, has demonstrated outstanding adsorption capabilities, attributed to its extensive surface area and distinctive physicochemical characteristics

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[72]. Exploring the synergy between naturally derived chitosan and graphene oxide to create a composite material presents a compelling opportunity. The collaborative effects of these two substances may enhance their adsorption performance, offering a more effective and sustainable approach to heavy metal removal in wastewater treatment. This integration could significantly advance the creation of green technologies for heavy metal decontamination in wastewater applications [73].

Additionally, there is a limited understanding of the synergies within composite materials, challenges in scaling up advanced water treatment technologies, and a lack of comprehensive methodologies for the heavy metal removal process. Traditional methods employed for this purpose. Consequently, there is an increasing need for innovative and sustainable solutions to tackle the challenges posed by heavy metal contamination in our water resources

This research focuses on assessing the effectiveness of CGO composites in the elimination of cadmium from industrial wastewater. The adsorbent was created employing a modified Hummers method and was identified using spectroscopic and surface analyses. The adsorption process was examined through isotherm, kinetic, and thermodynamic models to give more insights in the mode of adsorption and spontaneity involved in Cd²⁺ removal. The results are anticipated to aid in the advancement of green and economical technologies for mitigating heavy metal pollution in wastewater treatment.

MATERIALS AND METHODS

Materials/Reagents

Present study was conducted using general laboratory glassware, all of which were thoroughly rinsed with distilled water prior to experimental procedures to ensure cleanliness and accuracy. Analytical-grade reagents were employed throughout the study unless otherwise specified. The key reagents used include KMnO₄, H₂SO₄, HCl, H₂O₂, H₃PO₄, and deionized water.

Method

Banana peels were employed to synthesize graphene oxide through the modified Hummers method, producing a high-quality, cost-effective, and eco-friendly form of graphene oxide.

Carbonization of Banana peels

The carbonization of the banana peels was achieved by weighing out batch quantities of the peel in grams. The sample was put in clean crucible and heated in an oven, in the absence of oxygen at 450-600°C for 5 hours [74], [75]. The equation for the process is shown below:

Banana peels 450-600^oC (5 hours) C + CO₂ (Carbonization)

Preparation of Graphene-oxide from Banana Peels

To obtain GO, was produced using a modified Hummers approach [76]. Carbonized banana peel powder (20g) was combined with a solution consisting of 60 mL of H_2SO_4 , 10g of P_2O_5 , and 10g of $K_2S_2O_8$, preheated to 80 °C. After cooling, the solution underwent filtration and was rinsed until the filtrate was free of any residual acid.

The resultant material was then dried at 80 °C for a duration of 24 hours. The dried product (20g) was gradually introduced to 460 mL of concentrated H_2SO_4 , below the temperature of 5 °C. Subsequently, 60g of KMnO₄ was added slowly, and the resultant suspension was stirred at 35 °C for 2 hours, achieving a yellowish-brown color. The mixture was then diluted with approximately 3L of deionized water and stirred for 15 minutes. To remove any excess KMnO₄, 50 mL of 30% H_2O_2 was incorporated. The solution was further washed with 5% HCl and deionized water until a neutral pH was reached. Finally, the obtained product was dried in an oven at 60 °C for 24 hours, which yielded GO.

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Preparation of Chitosan

Crab and clam shells intended for chitosan extraction were sourced from a seafood restaurant located in Uyo metropolis. The extraction process commenced with a preconditioning step, where the shells were immersed in a 0.05 M acetic acid solution for a duration of 24 hours. After soaking, the shells were treated to eliminate any residual moisture. Following the drying phase, demineralization of the shells was performed using a 0.68 M hydrochloric acid solution for 6 hrs. at ambient temperature. The resultant residue was further cleansed until achieving a pH level between 6.5 and 7.5 before proceeding with the drying process.

Subsequently, the demineralized shrimp and crab shells underwent deproteinization using a 0.62 M sodium hydroxide solution for 16 hrs. at ambient temperature. This solid was also thoroughly cleansed to achieve the working pH. The obtained substance was dried, ground, and sieved using a 150 μ m mesh. In the final stage, the chitin underwent deacetylation in a 25 M sodium hydroxide solution for 20 hrs. at a temperature of 30 °C. After which the chitosan was cleansed extensively until a pH between 6.5 and 7.5 was achieved.

Preparation of Chitosan/Graphene oxide (CS/GO) Composite

The procedure was conducted in accordance with the methodologies outlined in prior research [77]. To initiate, 0.25 g of synthesized graphene oxide powder was incorporated into 250 mL of distilled water. Following a 300-minute ultrasonic dispersion at 300W, a Go hydrosol (1.0 mg/mL) was successfully produced.

This hydrosol was then gradually added, dropwise, to 0.5 g of chitosan, resulting in a mixture that was adjusted to a paste-like consistency, ensuring complete wetting before drying. This dropwise addition was performed ten times to enhance the coating thickness of graphene oxide on chitosan. Finally, the mixture was dried to yield a dark brown graphene-chitosan adsorbent, which will be ground, weighed, and stored in an airtight container labeled as CGO.

Characterization of CS/GO Composite

The synthesized CS/GO will be characterized using the following characterization techniques:

Infrared Spectroscopy of CS/GO

To ascertain the functional groups and the bonding presence in sample, the sample was characterized using FTIR (Shimadzu-8400S). The wavelength of the measurement was set at $4000 - 500 \text{ cm}^{-1}$.

Morphology of CS/GO

The powdered sample was applied to the aluminum plate with silver ink and allowed to dry for several minutes prior to the imaging process. The images were captured at magnifications ranging from 5000X to 10000X. The types of rays released by the substance being analyzed serve as a fingerprint which gives information on the distribution on the elements in the sample. This technique is very efficient, less expensive and nondestructive to the sample surface during analysis.

Crystallinity of CS/GO

One of the essential aspects to examine regarding the crystallinity of the chitosan/graphene oxide composite (CS/GO) is through X-ray diffraction (XRD) with Diffractometer 6000, utilizing Cu K α radiation at a wavelength of 1.5406 Å.

Batch Adsorption Experiments

The study aimed at the removal of cadmium from industrial effluent, specifically sourced from Nigeria Brewery. A 100 mL sample of a solution with a known concentration of Cd²⁺ ions was prepared at an ambient temperature. For each experimental run, a precise weight of CGO was introduced into the

pot, which was then agitated on a mechanical shaker at a constant speed of 150 rpm for predetermined contact times. Following agitation, the mixture was filtered to set the metal ion aside. Cd²⁺ concentration was obtained using an Atomic Absorption Spectrophotometer. Mean values of triplicate experiments were reported for accuracy and reliability.

Effects of Contact Time

This study was carried out in alignment with prior studies conducted by [78]. 100ml of the brewery effluent was aliquoted into four separate 250 ml flasksand adjusted accordingly to pH 7.00 using O.1M NaOH and 0.1M HCl. 0.2g Chitosan- graphene oxide composite was added to the NBE. The blend was maintained in a shaker at 27±10°C (which is considered room temperature) and was set to vibrate at 115 rpm. The contact times for the four different conical flasks were established at 30, 60, 90, and 120 minutes. The Sample was then digested by addition of aqua- regia, before analysis using AAS.

Effect of pH

pH studies was investigated in accordance with the methodology outlined in [79]. A total of 100 ml of brewery wastewater was aliquoted into four different flasks. PH levels were subsequently adjusted to 2.0, 4.0, 7.0, 8.0, and 10.0. 0.2g of Chitosan- graphene oxide composite was added to the NBE. The blend was subsequently maintained in a shaker at 27±10°C (room temperature) and agitated at a 115 rpm for 120 minutes. The Sample was then digested by addition of aqua- regia, before analysis using AAS.

Effect of Adsorbent Dosage

The impact of adsorbent dosage was assessed following the methodology outlined in previous research [79]. A total of 100 ml of brewery wastewater was aliquoted into four distinct 250 ml flasks at an optimal pH of 7.0. Various dosages 0.1g, 0.2, 0.3, 0.4, and 0.5g of Chitosan- graphene oxide composite was added to the flask respectively. The blend was subsequently maintained in a shaker at 27±10°C (room temperature) and agitated at 115 rpm for 120 minutes. The Sample was then digested by addition of aqua-regia, before analysis using AAS.

Effect of Temperature

The impact of adsorbent dosage was assessed following the methodology outlined in previous research [79]. A total of 100 ml of brewery wastewater was aliquoted into four distinct 250 ml flasks and adjusted to an optimal pH of 7.0. Various dosage 0.1g, 0.2, 0.3, 0.4, and 0.5g of Chitosangraphene oxide composite was added to the flask respectively. The blend was subsequently maintained in a shaker at 27±10°C (room temperature) and agitated at 115 rpm for 120 minutes. The Sample was then digested by addition of aqua- regia, before analysis using AAS.

Adsorption Isotherm study of CGO

Equilibrium experiments were performed by exposing the adsorbents (CGO) to Solutions with differing initial Cd²⁺ ions concentrations. Each experiment utilized an adsorbent dosage of 0.2 g in 100 ml of Cd²⁺ ion solutions. A series of flasks containing these blends were agitated on a rotary shaker at a consistent 150 rpm. At specified time intervals between 30 and 120 minutes, samples were collected for measurement with AAS. Equilibrium concentrations of the metal ions (Ce) were subsequently quantified, and the adsorption capacity at equilibrium (qe) was determined by calculating the amount of metal ions adsorbed per unit weight of the adsorbent.

Adsorption Kinetics of CGO

CGO's kinetics tests were carried out with known initial concentrations of Cd²⁺. A dosage of 0.2g of the adsorbent (CGO) was employed in 100 cm³ of solution. The texts were carried out at 27±10 °C. Samples were agitated at 150 rpm on a rotary shaker, with samples being taken at 15, 30, 45, 60, 90, 105, 120, 135, and 150 minute intervals. The obtained samples were then filtered analyzed using an AAS.

Data Evaluation

Equation 1 was used to calculate the adsorbent's percentage removal of Cd²⁺ during the experiments.

$$\% \operatorname{Removal} = \left(\frac{C_{O} - C_{e}}{C_{O}}\right) \quad x \quad 100 \%$$
(1)

Equation 2 was used to determine the quantity of Cd^{2+} adsorbed per unit weight of adsorbent at equilibrium.

$$q_e = \left(\frac{C_0 - C_e}{m}\right) V \tag{2}$$

In Equations 1 and 2, Co and Ce stand for Cd^{2+} initial and final concentrations, respectively. The mass (g) of the used adsorbent is denoted by m, while V is the volume (L) of the experimental solution.

Characterization of CGO

4.1.1 FTIR Analysis of CGO

In furtherance of identifying the surface spots where adsorption has occurred, Fourier transformed infrared spectroscopy, or FTIR spectral analysis, offers details on the particular functional groups that may have taken part in the adsorption reaction [80]. Figure 1 displays the FTIR spectra of CGO, which were examined in the 4000–500 cm⁻¹ range.





The FTIR of CGO (Figure 1) displays all characteristics peaks such as non-intense peak at 2098.50 cm⁻¹ because of C-H vibration from alkanes and alkyls, peak at 1934.50 cm⁻¹ due to C=C Stretch, peak at 1785.40 cm⁻¹ as a result of C=O Stretch from acyl chlorides, prominent peak at 1440.20 cm⁻¹ because of C-H bend from alkanes and alkyls, peaks at 857.30 cm⁻¹ as a result of C-Cl stretch from alkyl halides and peak at 711.90 cm⁻¹ due to C-H bend from alkenes [81].

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Crystalline nature of CGO

The structural crystallinity of the produced CGO was confirmed by the associated XRD data in Figure 2



Figure 2: XRD pattern of CGO

The several strong and sharp diffraction peaks in CGO curve, at 20 The crystal planes identified in XRD were ascribed to aragonite, portlandite, quartz, orthoclase and carbonate-fluorapatite (NR) with the weight fraction (wt%) of 63(5) %, 10.9(14) %, 5.6(4) %, 18(5) % and 2(2) % respectively. The distinctive diffraction peaks observed in the XRD pattern served as proof for the successful preparation of CGO).

SEM Analysis

SEM analysis is frequently applied to study the surface properties and morphological traits of adsorbent materials. Figures 3, 4, and 5 display the images captured by scanning electron microscopy. Small irregular chitosan (CS) particles are approximately dispersed across the GO surface in the SEM image in Figure 3. The highly enlarged SEM image of CS/GO (Figures 4 and 5) showed a flat structure of carbon atoms in sp² hybridization form with irregular borders and a smooth surface. Bonding between GO and CS was demonstrated by the intimate attachment and good dispersion of CS with GO. Clusters of different nanoscale CS particles were extensively dispersed across the GO sheets' surface. This mechanism stopped GO buildup and enhanced the composites' surface availability for adsorption.



Figure 1: SEM micrograph of CGO @ Magnification 250×



Figure 4: SEM micrograph of CGO @ Magnification 500×



Figure 5: SEM micrograph of CGO @ Magnification 1000×

Equilibrium Studies

Effect of Contact Time

Using tCGO composite, the results shown in Figures 6(a) and (b) show how contact time affects the adsorption capacity and cadmium (Cd²⁺) ion removal efficiency. According to Figure 6(a), the proportion of Cd²⁺ ions removed rose steadily over the course of contact time, peaking at 120 minutes. This pattern suggests that in order to maximize the interplay between the adsorbate and the CGO adsorbent's active sites, adequate contact time is necessary. Similarly, Figure 6(b) shows a steady decrease in residual Cd²⁺ concentration, reflected by increasing adsorption capacity over time, which plateaus at equilibrium, indicating saturation of the available adsorption sites. This behavior aligns with previous findings that longer contact times enhance metal ion diffusion onto active surfaces of nanocomposites [82]. The efficient adsorption capacity observed could be due to the favourable surface area and functional group provision of the CGO material, which facilitates strong electrostatic interaction and complexation with Cd²⁺ ions [83]. Furthermore, the equilibrium achieved around 120 minutes supports the pseudo-second-order kinetics model reported in related studies, which describes chemisorption as the rate-limiting step [84]. Using the chitosan-graphene oxide (CGO) composite, the results shown in Figures 6(a) and (b) show how contact time affects the adsorption

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capacity and cadmium (Cd²⁺) ion removal efficiency. According to Figure 6(a), the proportion of Cd²⁺ ions removed rose steadily over the course of contact time, peaking at 120 minutes. This pattern suggests that in order to maximize the interplay between the adsorbate and the CGO adsorbent's active sites, adequate contact time is necessary. The fast sorption rate in the early phases suggests that the exterior surface of the CGO adsorbent had a large number of active sites, which led to the easy and immediate adsorption of the metal ions [86]. Due to the external surface being occupied, the Cd²⁺ ions diffused into the interior of the adsorbents, causing the slower rate in the later stages [87], [88], and [89].



Figure 6: (a): Plot illustrating the relationship between contact time and the % removal of Cd2+ ions. (b): Plot illustrating the relationship between contact duration and the adsorption capacity of Cd2+ ions

Effect of Adsorbent Dosage

The observed trends in Figures 7(a) and (b) highlight the influence of CGO adsorbent dosage on the adsorption capacity (qe) and percentage removal of Cd²⁺ ions from aqueous solution. As the adsorbent dosage increased from 0.2 g to 0.5 g, the percentage removal of Cd²⁺ increased significantly, while the adsorption capacity decreased. This inverse relationship is commonly observed in adsorption studies and can be attributed to the saturation of available adsorption sites. The increasing percentage removal with higher adsorbent dosage is due to the greater availability of active sites for metal ion binding, which enhances the probability of interaction between Cd²⁺ ions and the surface functional groups of CGO composites. However, the decline in adsorption capacity with increasing dosage is due to the lower metal ion-to-adsorbent ratio at higher dosages, which causes underutilization of available sites, leading to a dilution effect.

Furthermore, agglomeration of adsorbent particles at higher dosages may reduce the effective surface area and block some active sites, thereby lowering the efficiency per unit mass of adsorbent. These findings are consistent with the behavior of other chitosan-based adsorbents used for heavy metal removal in batch adsorption studies. The adsorption capacity of ions of Cd²⁺, metal ions decreased as the CGO dosage increases from 0.1g to 0.5g. While the percentage removal of ions of Cd, Cu, Pb, & Co metals increased as the CGO dosage increases from 0.1g to 0.5g. Similar trend was reported in literature by [89]. A potential reason for the decline in adsorption capacity as the adsorbent dose increases is the unsaturation of the CGO's adsorption sites during the adsorption process, this reduction could also result from active site overlap, which restricts the availability of all active sites

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throughout the adsorption process. However, the availability of additional adsorption sites and functional groups at larger dosages is primarily responsible for the increase in the percentage removal of the metal ions with an increase in adsorbent dose. Van Der Waals bonds, which are crucial for attaching metals to the adsorbent during the adsorption process, were formed in part by these functional groups [89].



Figure 7: (a): Plot illustrating the relationship between adsorption adsorbent dosages of Cd²⁺ ions (b): Plot illustrating the relationship between CGO dosage and percentage removal of Cd²⁺ ions

Effect of pH

The results depicted in Figures 8(a) and (b) illustrate the effect of pH on the adsorption capacity and percentage removal of Cd^{2+} ions using CGO composite. As pH increased from 2 to 10, a remarkable decrease in the equilibrium concentration of Cd^{2+} (Ce) was observed, which translated to increased adsorption capacity and removal efficiency, especially at higher pH levels. The lowest Ce value (0.306 mg/L) observed at pH 10 indicates optimal adsorption, corresponding to maximum cadmium removal. This trend can be attributed to the protonation and deprotonation behavior of the attached groups to the surface of CGO. At low pH, excess H⁺ ions compete with Cd^{2+} for the available binding sites, thereby reducing adsorption efficiency [78]. As the pH increases, surface attachments become deprotonated, Increasing the electrostatic interaction between the negatively charged adsorbent surface and Cd^{2+} ions [79]. However, adsorption slightly levels off or decreases beyond pH 10 due to the possible formation of insoluble cadmium hydroxide ($Cd(OH)_2$), which may not adsorb but instead precipitate out of solution [90].

Thus, pH 10 appears to be the optimal point for cadmium adsorption using CGO in this study. It can be observed from the Figures that the adsorption capacity and percentage removal of ions of Cd, Cu, Pb, & Co metals onto CGO adsorbent increased as the pH of the solution increased from 2 to 10. Similar trends have been observed by other workers [91]. The reason for this decrease in adsorption capacity and efficiency at lower pH and increase at higher pH is that at lower pH, the adsorbent's overall surface charge will be positive, which will prevent positively charged metal cations from approaching and thereby reduce metal ion binding on the adsorbent surface. Additionally, the adsorption capacity and percentage removal diminish at lower pH levels due to the H+ ions' efficient competition with the metal ions. Higher pH causes the adsorbent surface in the solution to become negatively charged, which promotes the uptake of additional metal ions because of the electrostatic forces that pull the positively charged metal ions to the negatively charged adsorbent surface [91].

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Figure 2: (a): Plot illustrating the relationship between pH and adsorption capacity of Cd²⁺ metal ions (b): Plot illustrating the relationship between pH and the percentage removal of Cd²⁺ metal ions

Effect of Temperature

The results depicted in Figures 9(a) and (b) show that increasing the temperature from 30 to 100 °C led to a notable decrease in the equilibrium concentration of Cd^{2+} ions in solution (Ce), resulting in higher adsorption capacity and increased percentage removal. At 30 °C, the Ce value was 0.507 mg/L, which dropped significantly to 0.12 mg/L at 100 °C, indicating enhanced adsorption at elevated temperatures. This trend infers Cd^{2+} ions' adsorption onto the CGO composite is endothermic in nature.

The increase in temperature likely enhances the mobility of Cd²⁺ ions and the active sites on the CGO surface, promoting greater interaction and stronger binding between the Cd²⁺ metal ions and CGO. This observation aligns with prior studies where higher temperatures increased the adsorption capacities of similar materials due to improved diffusion and interaction kinetics [92], [93]. It can be observed that the adsorption capacity and percentage removal increased as temperature increased from 30°C to 70°C.

Similar trends were observed by other researchers [92], [93]. An increase in temperature may accelerate the rate at which the adsorbate molecules diffuse through the external boundary layer and into the internal pores of the adsorbent particles, lowering the solution's viscosity and contributing to the increase in adsorption capacity and efficiency [92], [93]. The fact that adsorption efficiency and capacity rise with temperature suggests that the process is endothermic.

He ascribed this to the activation of the adsorption surface, the expansion of pore size, and the breakage of some internal bonds close to the adsorbents' edges, which resulted in an increase in the number of active sites.

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Figure 9: (a): Plot illustrating the relationship between temperature and the adsorption capacity of Cd²⁺ ions (b): Plot illustrating the relationship between temperature and the percentage removal of Cd²⁺ ions

Adsorption Kinetics

In contrast to the pseudo-second order kinetic model, which argues that the heavy metals are binding through chemical adsorption, the pseudo-first order kinetic model proposes that the heavy metals are binding by physical adsorption. The Webber-Morris plot, or intra-particle diffusion, provides insight into whether or not the adsorption rate is constrained by mass transfer (diffusion) within the pores [94], [95].

The pseudo-first-order and pseudo-second-order kinetics for the adsorption of Cd metal ions onto CGO adsorbent are shown in Figures 10(a) and (b). For the adsorption of Cd^{2+} ions onto CGO, the experimental and calculated qe values are 4.672 mgg-1 and 14.397 mgg-1, respectively, whereas the pseudo-first-order rate constant (K₁) value is 0.069 (mni⁻¹). Given the poor correlation coefficients (R²) for all metal adsorption, it is evident from Figure q0 (a) that the relationship between In (qe – qt) against t is non-linear. Additionally, as the estimated qe values were neither equal to nor substantially close to the experimental qe values, it was noted that they did not agree with the experimental qe. Therefore, pseudo-first-order model was not a good fit in representing the adsorption of Cd²⁺ metal ions onto CGO adsorbent.

Similar results were reported by [85]. The pseudo-second-order rate constant K₂ value is 0.0228 (mni⁻¹) while the experimental and calculated qe values are 4.672 mgg⁻¹, and 4.975 mgg⁻¹ respectively for the adsorption of Cd²⁺ unto CGO adsorbent. This result entail that there are good agreements between the calculated q_e values (q_{e(cal.)}) and the experimental q_e values (q_{e(exp.)}) also the highly linear plots with high values of correlation coefficient were also observed (Figure 10b) for the adsorption of Cd²⁺ metal ions onto CGO adsorbent. This outcome indicates that the computed qe values (qe (cal.)) and the experimental qe values (qe values (qe (cal.)) for the adsorption of Cd²⁺ metal ions onto CGO adsorbent. This outcome indicates that the computed qe values (qe (cal.)) and the experimental qe values (qe (cal.)) and the experimental qe values (qe (cal.)) coincide well. Additionally, Figure 10b shows extremely linear plots with high correlation coefficient values for the adsorption of Cd²⁺ metal ions onto CGO adsorbent.

They reported similar findings [85]. Thus, it is clear that the best-fit kinetic model for explaining the adsorption of Cd^{2+} metal ions onto CGO adsorbent is pseudo-second-order. Consequently, it was determined that chemisorption was a part of the adsorption process [94]. The Weber-Morris kinetic model plot for the adsorption of Cd^{2+} metal ions onto CGO adsorbent is shown in Figure 10(c). It is found that the intra-particle diffusion Weber-Morris constants, Ki and C, are 0.128 mg/gmin0.5 and 3.267 mg/g, respectively. Intra-particle diffusion is engaged in the adsorption process, as

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demonstrated by the linearity of the plots in Figure 10(c), which is implied by the correlation coefficient (R^2) values for the adsorption of Cd²⁺ metal ions onto CGO adsorbent [94]. The plots did not, however, cross the origin, suggesting that there were other factors influencing the rate besides intra-particle diffusion. This illustrates that the adsorption of Cd²⁺ metal ions onto CGO adsorbent is a multi-step process that includes both intra-particle diffusion (i.e., diffusion into the inside pores of CGO) and film diffusion (i.e., adsorption on the exterior surface of CGO) [85].





Adsorption Isotherms

The adsorption isotherm describes the equilibrium isotherm. It illustrates how different equilibrium concentrations of dye can be dispersed between the liquid and solid phases. The maximum adsorption capacity and correlation coefficients (or linear egression values) R2, which indicate the degree of efficiency, were used to assess the suitability of the four (4) isotherm models for describing the adsorption process. The Langmuir isotherm model plots for the adsorption of Cd metal ions onto CGO are displayed in Figure 11(a). Analysis has been done on the Langmuir model parameters and linear regression (R2) values. It is evident from the low linear regression R2 values that the Langmuir isotherm does not sufficiently represent the adsorption of Cd²⁺ metal ions onto CGO. These findings demonstrate how inadequate this model is to describe the adsorption processes.

The Freundlich isotherm model's linear plot of the Cd²⁺ metal ions onto CGO is displayed in Fig. 11(b). The analysis of the Freundlich model parameters is summarized and the plots and correlation coefficient values show that the experimental data fit the model well. Additionally, the Freundlich

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isotherm constant, n, (3.63), was found to be greater than 1 (n>1), indicating a physical process [93]. The linear form of the Temkin isotherm model for the adsorption of ions of Cd^{2+} metal ions onto CGO is plotted in Figure 11 (c). The high correlation coefficient values as can be seen in the plot in Figure 11 (c) indicate better linearity, which also reflects the Temkin model's suitability for explaining the adsorption processes. Other studies observed similar findings [93]. A strong interaction between the adsorbates and adsorbents is indicated by the experimental data, which also shows that the values of heat of adsorption B (17.9 Kjmol 1) for the adsorption of ions of Cd^{2+} metal ions onto CGO adsorbent were found to be greater than 8KJ/mol (B > 8KJ/mol). Chemical adsorption or process is one way to describe this process, which is indicated by the heat of adsorption, B [93].

Figure 11(d) displays the plot of In qs against ε^2 of the D-R isotherm model for the Cd²⁺ metal ions onto CGO. The highest adsorption capacity q_M_m for Cd²⁺ metal ions, one of the Dubinin-Radushkevich (D-R) isotherm parameters, has been determined to be 99.64 mgg-1. Better linearity is indicated by the high linear regression (R²) values shown in figure 11(d), demonstrating the suitability of the D-R model for describing the adsorption processes of Cd²⁺ metal ions onto CGO. The literature showed similar findings [96], [97].





Adsorption Thermodynamics

Figure 12 depicts the linear Van't Hoff equation plots for the adsorption of Cd²⁺ metal ions onto CGO. ΔH^0 (19791 KJ/mol) and ΔS^0 (81.35 (J/mol. K) values were obtained from the Van't Hoff plots and given as including the calculated ΔG^0 of values. At every temperature, negative values ΔG^{0}

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demonstrated the viability and spontaneous nature of Cd^{2+} metal ions on CGO. Additionally, it is evident that when the temperature rose, the values of ΔG for the adsorption of Cd^{2+} metal ions by CGO reduced. Positive ΔH^{0} values for the adsorption of Cd^{2+} metal ions onto CGO corroborated the endothermic nature of the adsorption processes [99], [98]. This suggests a faster and more spontaneous adsorption at the higher temperatures of the adsorption processes [98]. The fact that the adsorption capabilities increased as the temperature rose further supported the endothermic nature of the processes [98]. Increased randomization at the solid/solution interface and strong adsorbent affinity for the dyes were demonstrated by positive values of ΔS^{0} found for the adsorption of Cd^{2+} metal ions onto CGO [97].



Figure 12: Van't Hoff equation plots for the adsorption of Cd²⁺ metal ions onto CGO

CONCLUSION

Findings from the study showed that as the temperature rose, the adsorption capabilities increased, confirming the endothermic nature of the processes. Adsorption of Cd^{2+} metal ions onto CGO showed positive values of ΔS^0 , indicating excellent affinity of the adsorbents and increased randomization at the solid/solution interface. The greatest Cd^{2+} removal efficiency of 99.83% was attained under ideal removal circumstances, which included a contact period of 120 minutes, a pH of 10.0, a temperature of 373 K, and a 0.5 g adsorbent dosage. The Dubinin–Radushkevich, Freundlich, and Temkin isotherms provided the best description of the adsorption process, and the pseudo-second-order model was supported by the kinetic data, indicating chemisorption as the predominant mechanism. The spontaneity and endothermic character of the adsorption process were validated by thermodynamic analysis. All things considered, CGO composite offers a viable, economical, and environmentally acceptable adsorbent for the removal of Cd^{2+} metal ions from wastewater, with a great deal of promise for use in actual industrial effluent treatment systems.

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