

## REMOVAL OF HEAVY METAL IONS FROM AQUEOUS SOLUTION BY NANO GRAPHENE OXIDE

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**Abstract.** The study's objective is to produce and evaluate Nano Graphene Oxide (GO) before using it for batch adsorption to remove heavy metals (vanadium  $V^{+5}$ , nickel  $Ni^{+2}$ , and cadmium  $Cd^{+2}$ ) ions from aqueous solutions polluted with these metals, which were used to imitate the contaminating elements found in the liquid industrial wastewater of the Doura oil refinery in Baghdad, Iraq. This study used a modified Hummers method to synthesize. The main constituents in preparation GO were graphite powder (40-100 micron),  $H_2SO_4$  acid, and  $KMnO_4$  powder. The GO structure synthesized and optical properties were investigated by FTIR, UV-vis, XRD, Raman spectroscopy, SEM, and EDX. The effects of various parameters were investigated to obtain the most efficient removal of  $V^{+5}$ ,  $Ni^{+2}$ , and  $Cd^{+2}$ , where pH of the acidic function is 7–8. The agitation speed was 375 RPM, with 150 minutes of equilibrium time for all metal ions. The removal efficiency is inversely associated with the temperature, where the highest removal is at 20 °C and the lowest at 50 °C. For  $Cd^{+2}$  and  $Ni^{+2}$ , the appropriate amount of GO was 0.5 g, while for  $V^{+5}$ , it was 0.6 g.

**Keywords:** removal heavy metal, nano graphene oxide, modified Hummers method, batch adsorption, refinery wastewater.

### 1. Introduction

The expansion and development of many contemporary industries have resulted in pollution of the air, soil, and water. Water pollution is of special concern since it has become a worldwide issue, with emerging countries bearing a disproportionately large burden as a result of their development drive.<sup>1</sup> Water pollution can take on a variety of forms, including toxicity caused by inorganic wastes, pesticides, or detergents, as well as pollution caused by food enrichment, thermal pollution, and contamination with oil materials from extraction residues, oil refineries, and other industrial wastewater sources.<sup>2</sup> Heavy

metals such as lead, cadmium, nickel, vanadium, and iron are present in most Iraqi crude oil types, and oil refinery wastes including these heavy metals are one of the most serious pollutants that must be addressed because of the severe impact that their accumulation has on human and animal health, as well as plant.<sup>3</sup>

Among all the previous techniques and methods used to treat heavy metal-contaminated wastewater, adsorption is considered one of the most important of these technologies due to its high efficiency in this field and the simplicity of the technology used for this purpose compared to other methods, as well as its reasonable economic cost. The adsorbent in most typical adsorption systems is Nanomaterials because of their unique properties, such as a high specific surface area, a large number of binding sites for the adsorbates to be adsorbed, numerous functional groups, and an appropriate pore size, which are considered desirable adsorbents for the treatment of wastewater contaminated with heavy metals.<sup>4,5</sup>

Porous materials reported and effectively employed to remove metal ions include activated carbons, activated carbon textiles, SBA-15, aerogels, carbon xerogels, and metal-organic frameworks (MOFs). However, many strategies for synthesizing and developing novel solids continue to be researched within the domain of adsorbent nanomaterials. A suitable substance for metal ion adsorption that has been examined recently is graphene oxide (GO), which is defined by the presence of the characteristic groups  $-C=O$  and  $-C-OH$  in its basal plane and  $-COOH$  at its edge.<sup>6</sup>

Graphene is a well-known monolayer-structured two-dimensional carbonaceous substance. Due to its exceptional features, including ultrahigh specific surface area, high mechanical strength, electrical and thermal conductivity, and chemical stability, graphene has become a hotspot for study in material science and engineering and other related domains. Graphene oxide (GO) is the most significant graphene derivative since it serves as a precursor for the fabrication of a variety of graphene-based products through an in situ or ex-situ technique. GO is often produced by an oxidative exfoliation of natural graphite using the famous Hummers process.<sup>7,8</sup> During GO preparation, many oxygenous groups such as carbon-

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yl, carboxyl, epoxy, and hydroxyl are introduced onto the aromatic ring, consequently making GO highly hydrophilic. As a result, GO disperses readily in water, forming a stable hydrosol. To start, the oxygenous groups and  $\pi$  electrons give GO a high capacity for adsorption of a wide variety of inorganic and organic pollutants. Additionally, because of the large specific surface area of graphene, the framework of GO makes it a perfect substrate for high-efficiency adsorbents.<sup>8</sup>

In this research, the synthesis, characterization, and adsorption capacity of Nano graphene oxide were prepared by modifying the Hummers method to ensure that this GO was synthesized by various techniques such as Fourier-transform infrared spectra analyzer (FTIR). A UV-spectrometer (UV-Vis) was utilized to gauge the optical ingestion properties of GO. the X-ray diffraction (XRD). Raman spectroscopy was also used. Scanning electron micrographs (SEM) were used to analyze microscopic morphologies on GO. Energy dispersive X-ray (EDX) was to determine the weight percentage of each element in the prepared GO. Then, GO was used to investigate the adsorption capacity from aqueous solutions of  $V^{+5}$ ,  $Ni^{+2}$ , and  $Cd^{+2}$  ions simulation found in industrial wastewater of Al-Doura refinery/Iraq, as well as the effect of the adsorbent and various parameters such as pH, temperature, adsorbent concentration, the agitation Time and, agitation speed (RPM) on the adsorption process's removal efficiency.

## 2. Experimental

### 2.1. Materials

Natural Graphite powder 40-100 micron, 99% purity, Glentham Life Sciences Ltd Co. Hydrochloric acid (35-38% concentration). Sulphuric acid (98% concentration). Hydrogen peroxide (30% concentration). Potassium permanganate powder and Deionized water (DI water).

### 2.2. Preparation of Nano Graphene Oxide GO

Nano-graphene oxide GO was synthesized using a modified Hummers method.<sup>9</sup> Graphite powder (1.0 g) and concentrated  $H_2SO_4$  (24 mL) stirred with (200 RPM) were placed in an ice bath, followed by a slow addition of  $KMnO_4$  (3.3 g) to maintain the temperature in the combination below 10 °C. After that, the reaction system was put in a 40 °C Paraffin-oil bath and vigorously agitated (300 RPM) for about half an hour. After that, 50 mL DI water was added to the solution and mixed at 95 °C for another 15 min. Dropwise, added 5 mL  $H_2O_2$  and then 150 mL DI water. The color of the solution has changed

from dark brown to yellow-brown, indicating that the graphite has oxidized. The suspension was filtered and washed with (150 mL) of 1:9 HCl aqueous solution to remove metal ions. The leftover acid or metal kinds were then flushed off with 1 liter of water. The GO dispersion that resulted was placed in 300 mL of water and ultrasonicated for 30 minutes at a frequency of 40 kHz. The GO dispersion was then centrifuged for 1 hour at 5000 rpm to remove any remaining particles that had not been exfoliated. Finally, the resulting material was dried at 60 °C for 24 hours to get Nano Graphene Oxide.

### 2.3. Characterization

The structure of materials was assessed using a Fourier-transform infrared spectrometer to analyze the morphology of GO (FTIR; Thermo Scientific inc., NICOLET iS10, Boston, MA, USA), A UV-VIS (UV-VIS; Hitachi inc., U-3900-Japan) spectrometer was used to measure the optical absorption characteristics of GO, X-ray diffraction (XRD; Rigaku inc., Ultima IV), Raman spectra (NT-MDTNTEGRA Spectra) with a 514 nm laser beam, Scanning electron micrographs SEM (Gemini SEM 500, ZEISS, Germany) functioning at 30 kV voltage at photomicrographs were obtained at multiple magnifications and were used to determine the microstructures of GO, Energy dispersive spectrometer EDX (EDX 2768; Broker, Germany) was used to detect the existed chemical elements in GO.

### 2.4. Samples obtained for the study

In 2021, samples were obtained from discharged industrial wastewater at the Al-Doura refinery in Baghdad, Iraq. by immersing a clean and sterile one-liter beaker in the refinery's wastewater collecting basin, taking the sample, and carefully capping it.

### 2.5. Laboratory Examinations of Heavy Metals for Collected Samples

The concentrations of heavy metals were assessed using the technique described in the literature.<sup>10</sup> 40 mL of wastewater samples were collected from the refineries and centrifuged at a speed of 6000 rpm for 1 h to remove any suspended contaminants or organic matter. The supernatant was taken from the test tube; 8 mL was withdrawn using a glass pipette, and 4 mL of concentrated nitric acid ( $HNO_3$ ) was added and warmed on a hot plate. Before drying, the same amount of nitric acid was added, and the heating procedure was repeated until a precipitate appeared in the beaker. Following that, deionized water was added to the precipitate to bring the level to 40 mL. Filtration of the solution was accomplished by the use of filtration paper and a vacuum filtration system. Finally, the

samples were analyzed using an atomic absorption spectrophotometer (AAS) to determine the concentrations of heavy metals in them and to compare them to previously generated calibration curves for each element. Vanadium, cadmium, and nickel concentrations were determined in all analyzed samples.

## 2.6. Stock Solution Preparation

Prepared stock solutions by dissolving estimated quantities of vanadium, nickel, and cadmium salts in one liter of deionized water to create a storage solution containing 1000 mg/L of vanadium, nickel, and cadmium salts, respectively. The dissolving procedure was carried out at a laboratory temperature of 25 °C and utilized a hotplate magnetic stirrer for 20 minutes to achieve optimal mixing. When creating the solutions for the future tests, the stock solution was diluted to the needed concentrations.

## 2.7. Calibration Curves of Heavy Metals Studied

Calibration curves for vanadium, nickel, and cadmium metals were created using particular concentrations of these salts and analyzed using an AAS apparatus that depends on the absorbance principle for each element at a given length. The calibration curve is used to determine the concentrations of metal ions during the adsorption process, with the residual concentration after treatment approximated using the device's absorbance. For vanadium, nickel, and cadmium ions, calibration curves were produced at wavelengths of 306.6, 351.5, and 326.1 nm, respectively.

## 2.8. Batch Adsorption Experiments

Adsorption tests were conducted using simulated solutions generated by diluting the stock solution to the

desired concentration in a water bath shaker using deionized water. 500 mg of GO had been added to 100 mL of an aqueous solution containing heavy metals with 1000 ppm concentration of (Vanadium, Nickel, and Cadmium) were put in 150 mL glass flasks and firmly wrapped with aluminum foil to prevent spilling during the shaking procedure. The solution's acidic function was regulated using 0.1M hydrochloric acid and 0.1M sodium hydroxide solutions. Additionally, the prescribed quantities of adsorbent GO were added to the heavy metals aqueous solution. After preparing the samples in the flasks, installing them in the shaker, and configuring the shaker's temperature, the treatment procedure starts by changing the agitation speed and continuing until the designated time expires. Conditions employed for the acidic function were (2-8), agitation speed (75-375) RPM, (0.01-1) g of GO, contact time (10-180) minutes, and temperature (20-50) °C, respectively. After the time has expired, the shaker is turned off, the flasks are removed, and the samples are filtered using Filter Paper. after the adsorbent material has been separated from the solution, The AAS device is used to determine the concentration of residual heavy metals and the percentage of removal (%R), as well as the capacity of the adsorbent for batch adsorption ( $q$ ), using Eqs. (1) and (2), respectively.

$$\%R = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

$$q = \frac{V}{m} \times (C_i - C_f) \quad (2)$$

Where  $R$  denotes the percentage of heavy metal ions removed,  $q$  denotes the adsorption capacity of adsorbent media ( $mg/g$ ),  $C_i$  and  $C_f$  denote the initial and final concentrations of heavy metal ions, respectively ( $mg/l$ ),  $m$  denotes the mass of adsorbent used for adsorption ( $g$ ), and  $V$  denotes the volume of solution ( $l$ ).

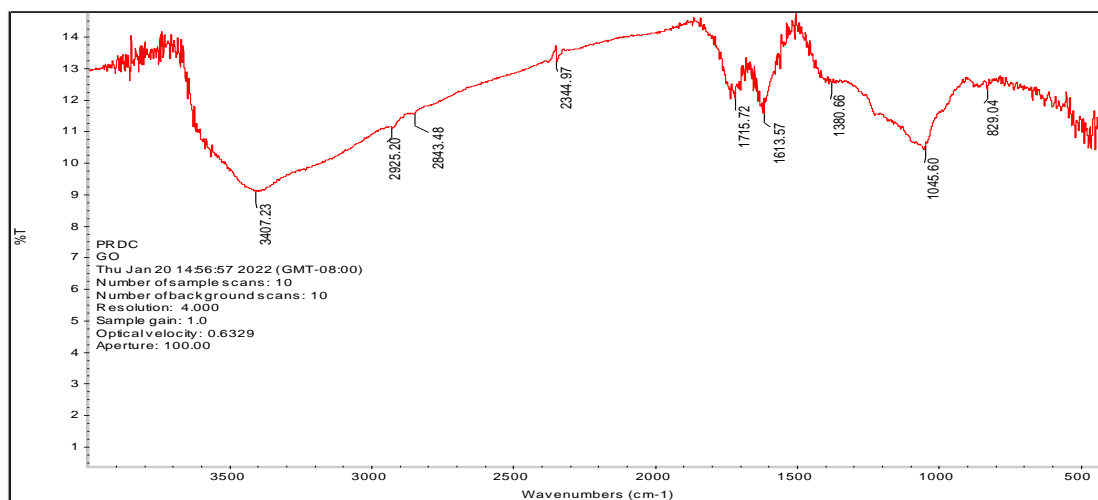


Fig. 1. FTIR-spectra of GO

### 3. Results and Discussion

#### Characterization

The FTIR of GO Fig. 1 shows peaks corresponding to oxygen-containing functional groups, showing that GO was produced. The prominent peak between  $3403.27$  and  $2925.2\text{ cm}^{-1}$  is due to hydroxyl O–H stretching. The absorption peak at  $2344.97\text{ cm}^{-1}$  is due to the C=O bond, whereas the absorption peak at  $1715.72\text{ cm}^{-1}$  is due to carboxylic and/or carbonyl moiety functional groups stretching.  $1613.57\text{ cm}^{-1}$  represents the aromatic bond group—observed absorption peaks C–O at  $1380.66$  and  $1045.60\text{ cm}^{-1}$ . The presence of active oxygen-containing

groups C–O and C=O indicated that graphite had been oxidized to GO.<sup>11,12</sup>

UV-vis diffuse reflectance spectra for GO Fig. 2 were used to examine its optical absorption properties. The maximum absorbance  $\lambda_{\text{max}}$  of nano-graphene oxide is  $0.197\text{ Abs}$  at  $286.5\text{ nm}$ . That is caused by the aromatic C=C bond transitions and a shoulder at around  $305\text{ nm}$  and  $0.084\text{ Abs}$ . The aromatic C=O bond transitions are responsible for this, which supports the existence of oxygen.<sup>13</sup>

The Raman spectrum of GO in Fig. 4 shows firm peaks at  $1342$  and  $1598\text{ cm}^{-1}$ , respectively. As a result, the 'D' (band of disorder) and 'G' (in-phase vibration) bands are identical.<sup>16</sup> The GO Id/I<sub>g</sub> ratio of  $0.84$  suggests that carbon networks include  $\text{sp}^2$  domains and that flaws and edges have been significantly decreased.

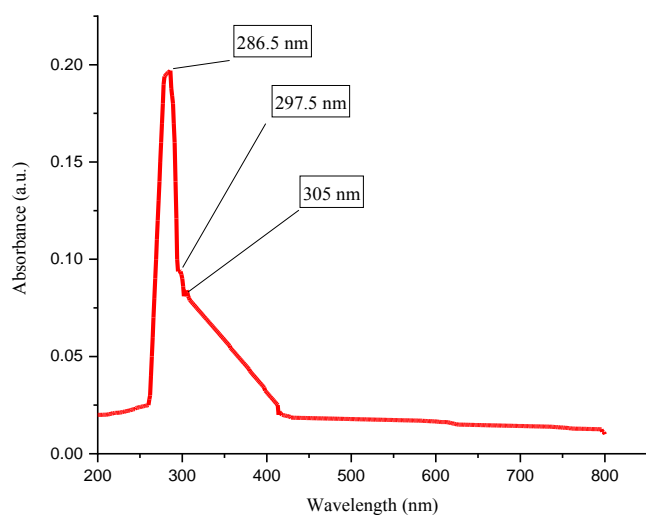


Fig. 2. UV-vis spectrum of GO

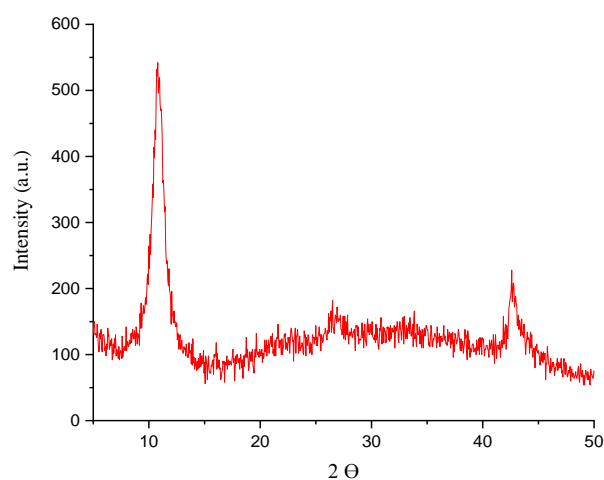


Fig. 3. X-ray diffraction of GO

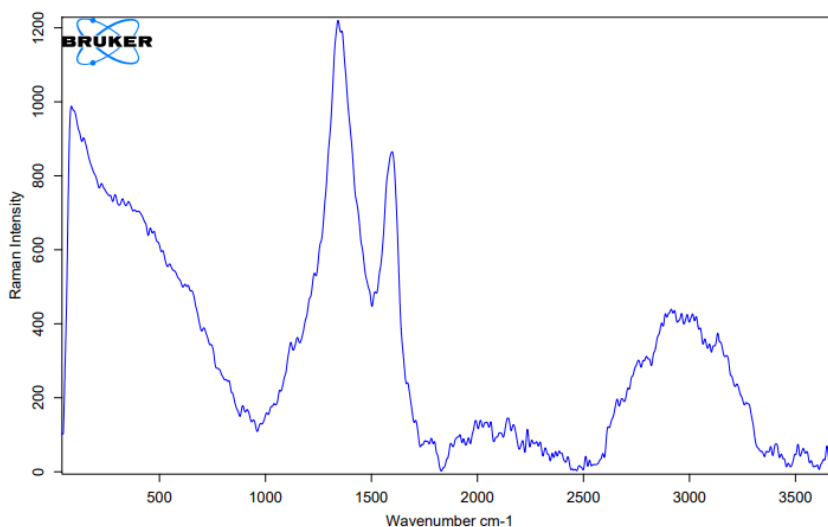


Fig. 4. The Raman spectrum

XRD analysis was used to demonstrate the effective production of GO at the peak of  $2\theta$  range of 10-12 degrees<sup>14</sup> and to discover the crystalline characteristics of GO. XRD is conducted using a wavelength of 1.54 Å and a range of  $2\theta$  angles between 5 and 60 degrees. The whole results are in Fig. 3. GO exhibited a very significant peak at  $2\theta = 0.92$  degrees.<sup>15</sup>

SEM was used to perform thorough morphological examinations, where the graphite oxidation rate is indicated by its crystallization. Fig. 5 shows the SEM images

of GO. The photos show GO is composed of randomly aggregated and thin folded sheets with surface creases and folds. Similar picture types have been reported before in the literature.<sup>17,18</sup>

EDX determines the elements' weight percentage in the prepared GO. Table. 1 shows that GO contains 39.5% of carbon, 53.8% of oxygen, 6.6% of sulfur, and 0.1% of chlorine. Fig. 6 shows a significant carbon peak. However, GO nanoparticles contain a lot of oxygen.<sup>19</sup>

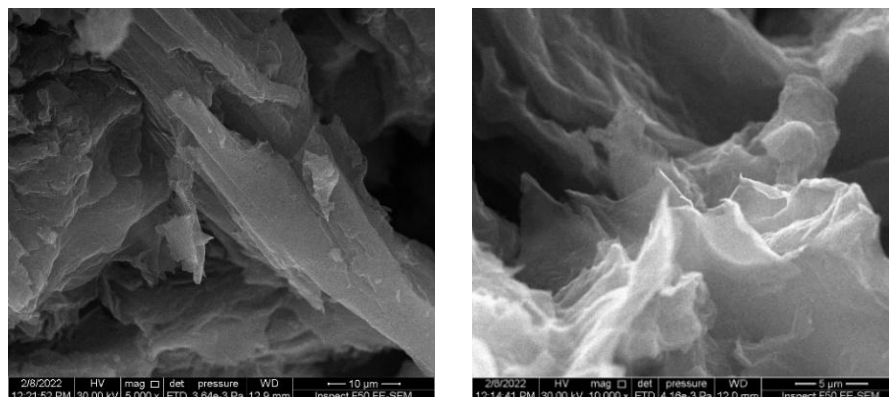


Fig. 5. Scanning electron micrographs of GO

Table 1. Energy-dispersive spectrometer analysis of GO

Element	Atomic %	Atomic % Error	Weight %	Weight % Error
C	47.9	0.7	39.5	0.6
O	49.1	0.9	53.8	1.0
S	3.0	0.2	6.6	0.3
Cl	0.0	0.0	0.1	0.1

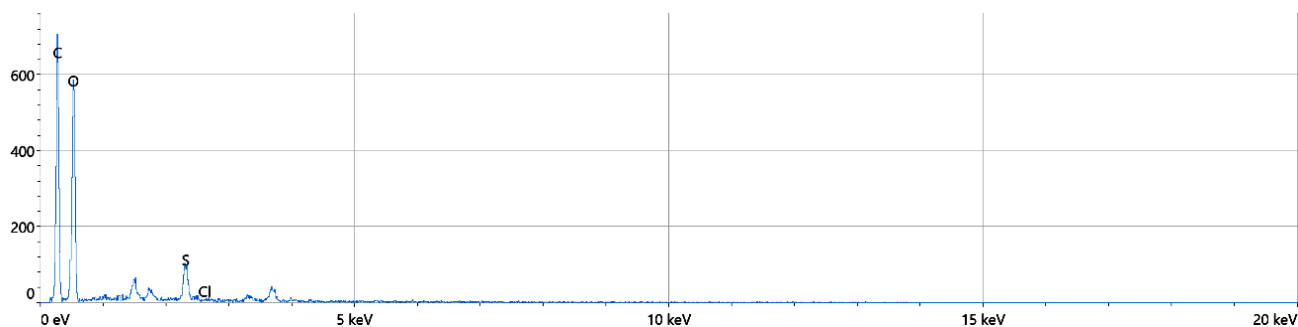


Fig. 6. Energy-dispersive spectrometer EDX of GO

## Adsorption performance

### 3.1. Effect of Acidic Function (pH)

The effect of the acidic function (pH) on the removal of heavy metal ions (Vanadium, Nickel, and Cadmium) from a simulated aqueous solution using Nano

graphene oxide was investigated over a pH range of (1-8). At the same time, the rest of the parameters was maintained under optimal operating conditions (Time  $t=120$  min, Temp  $T=25$  °C, RPM=200, 500 mg of GO). Adsorption of divalent metal ions Nickel ( $Ni^{2+}$ ) and Cadmium ( $Cd^{2+}$ ) rises rapidly at pH 5–6, the adsorption of  $Ni^{2+}$  and  $Cd^{2+}$  (>85%) increases due to the negative surface charge

of GO, and the electrostatic interactions between metal ions and GO nano-sheets grow stronger. The maximum adsorption for  $\text{Ni}^{2+}$  at pH 7 and  $\text{Cd}^{2+}$  at pH 8, where the sorption capacity was (0.426 and 0.833 mol/L) for  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  respectively. The adsorption of vanadium ions ( $\text{V}^{5+}$ ) increased significantly (>75 %), when pH was raised from 3 to 4, because of the interaction between a metal ion and an oxygen group on the GO surface. The highest adsorption occurs at pH 7, where the sorption capacity for  $\text{V}^{5+}$  was 0.949 mol/L. This conclusion might be because at lower acidic function values, heavy metal ion adsorption diminishes owing to competition between positive hydrogen ions ( $\text{H}^+$ ) and metal ions for adsorption sites which increases as the pH value decreases. However, as the pH value increases, the concentration of positive hydrogen ions ( $\text{H}^+$ ) decreases due to an increase in the concentration of negative hydroxide ions ( $\text{OH}^-$ ), reducing competition, and thus the adsorption of V, Ni, and Cd ions will increase<sup>20</sup>.

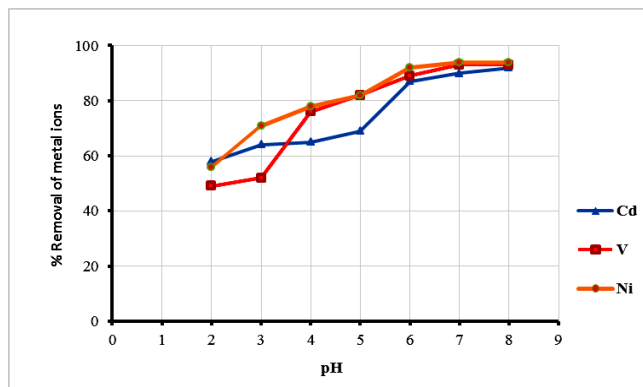


Fig. 7. Effect of acidic function (pH) on % removal of metal ions using GO

### 3.2. Effect of Contact Time (t)

The contact time is a crucial aspect to consider when planning adsorption tests. Vanadium, nickel, and cadmium adsorption studies were done using GO with the time ranging from 10 to 180 min, with the rest of the variables set at the optimal values (pH=7.5, T=25 °C, RPM=200, 500 mg of GO). To examine how much treatment efficiency was affected by the contact time, the time necessary for the system to attain equilibrium is known, and any time afterward is deemed useless. According to practical experiments, the proportion of heavy metals removed by GO increases as the contact duration increases, and the best processing efficiency is achieved at 150 minutes. However, when the contact time is increased beyond two and a half hours, the removal efficiency does not change and remains constant for all metals and adsorbed materials, as illustrated in Fig 8. where the sorption capacity for  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{V}^{5+}$  was (0.426, 0.833, and 0.949 mol/L) respectively.

Increasing the contact time of the ions in contact with the adsorption medium increases the likelihood that those ions will reach the effective sites on the adsorbent's surface, resulting in the adsorption of a more significant number of ions. As a consequence, their number in the solution decreases, increasing the removal efficiency.<sup>21</sup> The three initial rapid uptakes, slow uptakes, and equilibrium stages of the adsorption process were observed. The availability of many vacant sites on the sorbents causes the fast ion adsorption and disparities in ion concentrations on the surface and the soluble bulk during the first uptake phase, resulting in a maximum adsorption rate. The number of unoccupied sites decreases, the adsorption rate decreases, and the process eventually finds equilibrium.

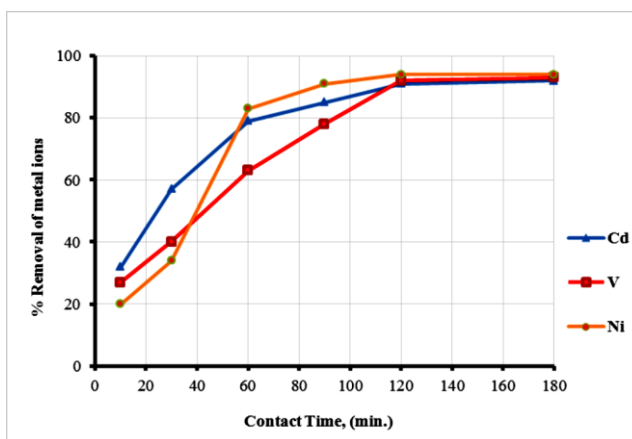


Fig. 8. Effect of contact time on % removal of metal ions using GO

### 3.3. Effect of Agitation Speed (As)

By maintaining the other operational variables at their optimal levels (pH=7.5, t=120 min, T=25 °C, 500 mg of GO), the nature of the relationship between the percentage of removal for Vanadium, Nickel, and Cadmium on the one hand, and the speed of agitation between (75 and 375 RPM) on the other hand was examined by employing GO, as shown in Fig 9. It's also worth noting that the removal of Vanadium and Cadmium rises dramatically from (225 RPM), but the adsorption of Nickel increases at (200 RPM).  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{V}^{5+}$  had sorption capacities of (0.435, 0.842, and 0.98 mol/L, respectively). The removal efficiency after reaching (375 RPM) stays steady and unchanged.

The higher diffusivity of heavy metal ions in the solution may be ascribed to the increased agitation speed, which in turn will enhance the possibility of vanadium, nickel, and cadmium ions reaching the active sites on the surface of GO, increasing the percentage of adsorp-

tion.<sup>22,23</sup> Alternatively, increasing the agitation speed may cause the boundary layers formed around the adsorbent molecules to be destroyed, increasing the number of heavy metal ions arriving at the active sites on the surface subject to adsorption, as well as their number in the solution will increase, and the treatment efficiency will increase.<sup>24</sup>

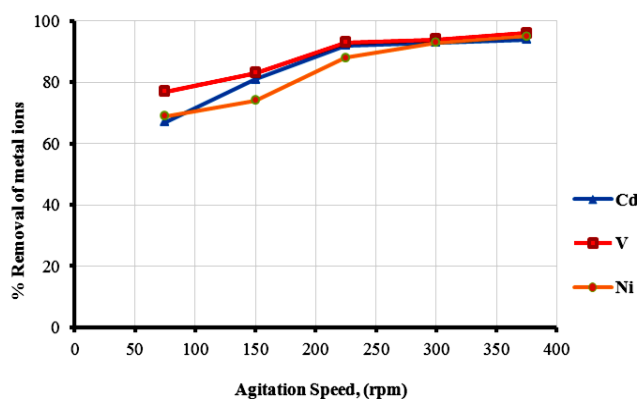


Fig. 9. Effect of agitation speed on % removal of metal ions using GO

### 3.4. Effect of Temperature (T)

The temperature influence on the effectiveness of removing vanadium, nickel, and cadmium using GO in a batch mode adsorption unit is shown in Fig. 10 at their optimal levels (pH=7.5, t=120 min, RPM=200, 500 mg of GO). The maximal removal is accomplished at the lower temperature, indicating an inverse connection between temperature and reduction efficiency for all heavy metals tested and all adsorbents utilized, as seen in the figures above.

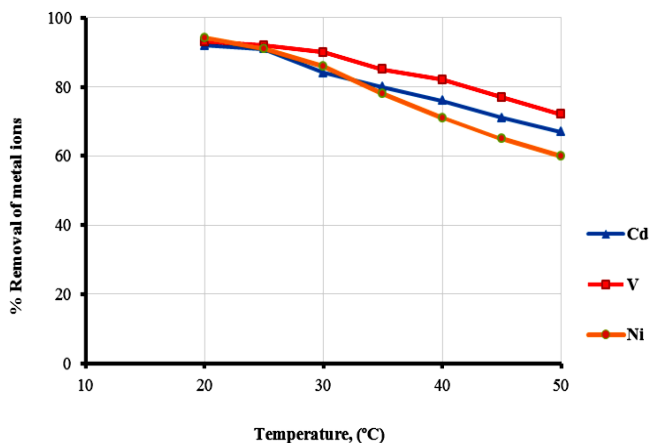


Fig. 10. Effect of temperature on % removal of metal ions using GO

This means that the adsorption process is exothermic, meaning that as the temperature rises, the bonds connecting the functional groups present in the active sites spread across the surface of GO with vanadium, nickel, and cadmium ions break down, allowing the material to be released and returned to the solution, lowering the removal efficiency.<sup>25</sup> The highest removal of metal ions occurred at 20 °C, after which the adsorption declined steadily with increasing temperature until it reached the lowest value.

### 3.5. Effect of Adsorbent Media Amount (m)

The effect of the adsorbent amount GO on the efficiency of heavy metal ion adsorption in aqueous solutions simulating the industrial wastewater of Iraqi petroleum refineries was investigated using different quantities of the adsorbent material ranging within 0.01–1 g, while the rest of the variables was kept at their optimum values (pH=7.5, t=120 min, T=25 °C, RPM=200). This research discovered that adding 0.4 g of GO to solutions polluted with vanadium, nickel, and cadmium enhanced the removal percentage by approximately equal rates. However, after adding more than 0.6 g of GO, the metal ions removal did not change. This result is due to the active sites on the adsorbent surface that are accessible for heavy metal ion adsorption, which is significant in GO. When more adsorbent is used, the mass of the central adsorbent desorption rises, increasing the surface area and hence the number of effective sites.<sup>26</sup> As a result, the likelihood of heavy metal ion adsorption increases, as does the adsorption efficiency, as shown in Fig. 11.

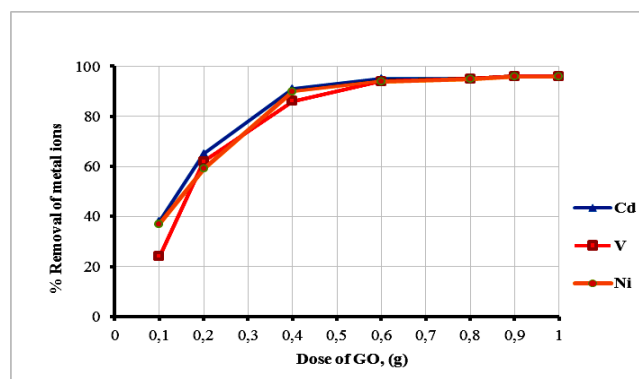


Fig. 11. Effect of GO dose on % removal of metal ions using GO

## 4. Conclusions

The purpose of this work was to synthesize and analyze Nano graphene oxide and then utilizes it to remove metal ions from an aqueous solution. The adsorption tech-



nology, which employs adsorption materials as GO, has shown excellent efficacy in cleaning liquid wastewaters from Iraqi petroleum refineries, particularly heavy metals, which are the principal contaminants in petroleum wastewaters and include vanadium, nickel, and cadmium. One of the most effective adsorption materials is GO.

A modified Hummers method was successfully used to prepare GO. FTIR spectroscopy, UV spectroscopy, XRD analysis, Raman spectroscopy, SEM, and the surface area with porosity were used to characterize GO. The presence of numerous unique functional oxygen groups in the FTIR spectrum of GO, such as O–H, C=O, and C–O, further supports the oxidation of graphite to GO. The ultraviolet-visible photoluminescence spectrum of GO shows a broad emission band with a visible maximum at 286.5 nm. The XRD big peak at  $2\theta = 10.92^\circ$  suggests the GO formation. The Raman spectrum first-order scattering from the E<sub>2g</sub> phonon, which is coupled to sp<sup>2</sup> carbon bonding and structural defects, causes the 'D' and 'G' bands to strong peaks at 1342 and 1598 cm<sup>-1</sup>. As seen in the SEM image, the prepared GO contains thin folded sheets with surface creases and folds sheet-like structures. EDX analysis indicated that 39.5 %wt. C, 53.8 %wt. O, 6.6 %wt. S, and 0.1 %wt. Cl was present in GO, respectively. The average pore size was 3.718 nm, with a surface area of 989.76 m<sup>2</sup> g<sup>-1</sup> and a total pore volume of 1.62 cm<sup>3</sup> g<sup>-1</sup>.

For batch adsorption, the findings indicated that the following operating circumstances resulted in the maximum removal efficiency for V<sup>+5</sup> and Ni<sup>+2</sup> at pH=7, Cadmium Cd<sup>+2</sup> at pH=8, and the agitation speed of 375 RPM for all metal ions. For all metal ions, the equilibrium time was 150 minutes. All metal ions removal efficiency was inverse with temperature, with the best removal efficiency at 20 °C and the lowest at 50 °C. The optimal quantity of GO was 0.5 g for Cd<sup>+2</sup> and Ni<sup>+2</sup> and 0.6 g for V<sup>+5</sup>.

## References

- [1] Breida, M.; Younsi, S.A.; Ouammou, M.; Bouhria, M.; Hafsi, M. Pollution of Water Sources from Agricultural and Industrial Effluents: Special Attention to NO<sub>3</sub><sup>-</sup>, Cr(VI), and Cu(II). In *Water Chemistry*; Eyvaz, M.; Yüksel, E.; Eds. *IntechOpen*, 2020. <https://doi.org/10.5772/intechopen.86921>
- [2] Phan, T.A.; Dang, K.H.; Dinh, L.N. Synthesis and Preparation of Hydrophobic CNTs-Coated Melamine Formaldehyde Foam by Green and Simple Method for Efficient Oil/Water Separation. *Chem. Chem. Technol.* **2020**, *14*, 531–537. <https://doi.org/10.23939/chcht14.04.531>
- [3] Allafta, H.; Opp, C. Spatio-Temporal Variability and Pollution Sources Identification of the Surface Sediments of Shatt Al-Arab River, Southern Iraq. *Sci Rep* **2020**, *10*, 6979. <https://doi.org/10.1038/s41598-020-63893-w>
- [4] Skiba, M.; Pivovarov, A.; Vorobyova, V. The Plasma-Induced Formation of PVP-Coated Silver Nanoparticles and Usage in Water Purification. *Chem. Chem. Technol.* **2020**, *14*, 47–54. <https://doi.org/10.23939/chcht14.01.047>
- [5] Dzyazko, Y.; Ponomarova, L.; Volfkovich, Y.; Tsirina, V.; Sosenkin, V.; Nikolska, N.; Belyakov, V. Influence of Zirconium Hydrophosphate Nanoparticles on Porous Structure and Sorption Capacity of the Composites Based on Ion Exchange Resin. *Chem. Chem. Technol.* **2016**, *10*, 329–335. <https://doi.org/10.23939/chcht10.03.329>
- [6] Kong, Q.; Preis, S.; Li, L.; Luo, P.; Wei, C.; Li, Z.; Hu, Y.; Wei, C. Relations between Metal Ion Characteristics and Adsorption Performance of Graphene Oxide: A Comprehensive Experimental and Theoretical Study. *Sep. Purif. Technol.* **2020**, *232*, 115956. <https://doi.org/10.1016/j.seppur.2019.115956>
- [7] Hummers, W.S.; Offeman, R.E. Preparation of Graphitic Oxide. *J. Am. Chem. Soc.* **1958**, *80*, 1339–1339. <https://doi.org/10.1021/ja01539a017>
- [8] Bulin, C.; Ma, Z.; Guo, T.; Li, B.; Zhang, Y.; Zhang, B.; Xing, R.; Ge, X. Magnetic Graphene Oxide Nanocomposite: One-Pot Preparation, Adsorption Performance and Mechanism for Aqueous Mn(□) and Zn(□). *J Phys Chem Solids* **2021**, *156*, 110130. <https://doi.org/10.1016/j.jpcs.2021.110130>
- [9] Chen, J.; Yao, B.; Li, C.; Shi, G. An Improved Hummers Method for Eco-Friendly Synthesis of Graphene Oxide. *Carbon*. **2013**, *64*, 225–229. <https://doi.org/10.1016/j.carbon.2013.07.055>
- [10] Ali, G.A.A.; Ibrahim, S.A.; Abbas, M.N. Catalytic Adsorptive of Nickel Metal from Iraqi Crude Oil Using Non-Conventional Catalysts. *Innov. Infrastruct. Solut.* **2021**, *6*, 7. <https://doi.org/10.1007/s41062-020-00368-x>
- [11] Tiwari, S.K.; Huczko, A.; Oraon, R.; De Adhikari, A.; Nayak, G.C. Facile Electrochemical Synthesis of Few Layered Graphene from Discharged Battery Electrode and Its Application for Energy Storage. *Arab. J. Chem.* **2017**, *10*, 556–565. <https://doi.org/10.1016/j.arabjc.2015.08.016>
- [12] Tiwari, S.K.; Huczko, A.; Oraon, R.; De Adhikari, A.; Nayak, G.C. A Time Efficient Reduction Strategy for Bulk Production of Reduced Graphene Oxide Using Selenium Powder as a Reducing Agent. *J Mater Sci.* **2016**, *51*, 6156–6165. <https://doi.org/10.1007/s10853-016-9903-x>
- [13] Eigler, S. Graphite Sulphate – A Precursor to Graphene. *Chem-Comm* **2015**, *51*, 3162–3165. <https://doi.org/10.1039/C4CC09381J>
- [14] Türkaslan, S.S.; Ugur, Ş.S.; Türkaslan, B.E.; Fantuzzi, N. Evaluating the X-Ray-Shielding Performance of Graphene-Oxide-Coated Nanocomposite Fabric. *Materials* **2022**, *15*, 1441. <https://doi.org/10.3390/ma15041441>
- [15] Gascho, J.L.S.; Costa, S.F.; Recco, A.A.C.; Pezzin, S.H. Graphene Oxide Films Obtained by Vacuum Filtration: X-Ray Diffraction Evidence of Crystalline Reorganization. *J. Nanomater.* **2019**, *2019*, 5963148. <https://doi.org/10.1155/2019/5963148>
- [16] Muzyka, R.; Drewniak, S.; Pustelny, T.; Chrubasik, M.; Gryglewicz, G. Characterization of Graphite Oxide and Reduced Graphene Oxide Obtained from Different Graphite Precursors and Oxidized by Different Methods Using Raman Spectroscopy. *Materials* **2018**, *11*, 1050. <https://doi.org/10.3390/ma11071050>
- [17] Li, H.; Wei, Z. Impacts of Modified Graphite Oxide on Crystallization, Thermal and Mechanical Properties of Polybutylene Terephthalate. *Polymers* **2021**, *13*, 2431. <https://doi.org/10.3390/polym13152431>
- [18] Chuah, R.; Gopinath, S.C.B.; Anbu, P.; Salimi, M.N.; Yaakub, A.R.W.; Lakshmi Priya, T. Synthesis and Characterization of Reduced Graphene Oxide Using the Aqueous Extract of *Eclipta prostrata*. *3 Biotech.* **2020**, *10*, 364. <https://doi.org/10.1007/s13205-020-02365-4>
- [19] Chintalapudi, K.; Rao Pannem, R.M. Strength Properties of Graphene Oxide Cement Composites. *Materials Today: Proceedings* **2021**, *45*, 3971–3975. <https://doi.org/10.1016/j.matpr.2020.08.369>



- [20] Cruz-Lopes, L.P.; Macena, M.; Esteves, B.; Guiné, R.P.F. Ideal pH for the Adsorption of Metal Ions  $\text{Cr}^{6+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$  in Aqueous Solution with Different Adsorbent Materials. *Open Agric.* **2021**, *6*, 115–123. <https://doi.org/10.1515/opag-2021-0225>
- [21] Parastar, M.; Sheshmani, S.; Shokrollahzadeh, S. Cross-Linked Chitosan into Graphene Oxide-Iron(III) Oxide Hydroxide as Nano-Biosorbent for Pd(II) and Cd(II) Removal. *Int. J. Biol. Macromol.* **2021**, *166*, 229–237. <https://doi.org/10.1016/j.ijbiomac.2020.10.160>
- [22] Alalwan, H.A.; Kadhom, M.A.; Alminshid, A.H. Removal of Heavy Metals from Wastewater Using Agricultural Byproducts. *J WATER SUPPLY RES T.* **2020**, *69*, 99–112. <https://doi.org/10.2166/aqua.2020.133>
- [23] Anirudhan, T.S.; Sreekumari, S.S. Adsorptive Removal of Heavy Metal Ions from Industrial Effluents Using Activated Carbon Derived from Waste Coconut Buttons. *J Environ Sci* **2011**, *23*, 1989–1998. [https://doi.org/10.1016/S1001-0742\(10\)60515-3](https://doi.org/10.1016/S1001-0742(10)60515-3)
- [24] Mustapha, S.; Ndamitso, M.M.; Abdulkareem, A.S.; Tijani, J.O.; Mohammed, A.K.; Shuaib, D.T. Potential of Using Kaolin as a Natural Adsorbent for the Removal of Pollutants from Tannery Wastewater. *Heliyon* **2019**, *5*, e02923. <https://doi.org/10.1016/j.heliyon.2019.e02923>
- [25] Soliman, N.K.; Moustafa, A.F. Industrial Solid Waste for Heavy Metals Adsorption Features and Challenges; a Review. *J. Mater. Res. Technol.* **2020**, *9*, 10235–10253. <https://doi.org/10.1016/j.jmrt.2020.07.045>
- [26] Vilardi, G.; Di Palma, L.; Verdone, N. Heavy Metals Adsorption by Banana Peels Micro-Powder: Equilibrium Modeling by Non-Linear Models. *Chin. J. Chem. Eng.* **2018**, *26*, 455–464. <https://doi.org/10.1016/j.cjche.2017.06.026>

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## ВИДАЛЕННЯ ІОНІВ ВАЖКИХ МЕТАЛІВ З ВОДНОГО РОЗЧИНУ НАНООКСИДОМ ГРАФЕНУ

**Анотація.** Метою дослідження є отримання та характеристика нанооксиду графену (ОГ) перед використанням його для періодичної адсорбції для вилучення іонів важких металів (ванадію  $\text{V}^{5+}$ , нікелю  $\text{Ni}^{2+}$  та кадмію  $\text{Cd}^{2+}$ ) з водних розчинів, забруднених цими металами, які були використані для імітації забруднюючих елементів, знайдених у рідких промислових стічних водах нафтопереробного заводу Доура в Багдаді, Ірак. У цьому дослідженні для синтезу використовували модифікований метод Гаммерса. Основними компонентами для приготування ОГ були порошок графіту (40-100 мкм), кислота  $\text{H}_2\text{SO}_4$  і порошок  $\text{KMnO}_4$ . Структуру синтезованого ОГ та його оптичні властивості досліджували методами ІЧ-спектроскопії з перетворенням Фур'є, оптичної, Раман-, енергодисперсійної рентгенівської спектроскопії, рентгеноструктурного аналізу та СЕМ. Було досліджено вплив різних параметрів для отримання найефективнішого вилучення  $\text{V}^{5+}$ ,  $\text{Ni}^{2+}$  і  $\text{Cd}^{2+}$  за рН 7-8. Швидкість перемішування становила 375 об/хв, час встановлення рівноваги для всіх іонів металів - 150 хвилин. Ефективність вилучення обернено пропорційна до температури, при цьому найбільше вилучення відбувається за 20 °С, а найменше - за 50 °С. Для  $\text{Cd}^{2+}$  і  $\text{Ni}^{2+}$  потрібна кількість ОГ становила 0,5 г, тоді як для  $\text{V}^{5+}$  - 0,6 г.

**Ключові слова:** вилучення важких металів, нанооксид графену, модифікований метод Хаммерса, періодична адсорбція, стічні води нафтопереробного заводу.