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Use mix of Chitosan-Graphene oxide nanoparticle to reduce Cadmium from aqueous solution

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ABSTRACT

The current study aims to evaluate the adsorption of Cadmium element in aqueous solution by using a nano-material consisting of a mixture of reduced graphene oxide and nano-chitosan, which was prepared in a 1:1 ratio. And an X-ray diffraction device for studying the crystal structure of nanomaterials.

The results showed that the percentage of element removal increases with increasing concentration of the nanomaterial and under constant conditions of temperature and pH, and the percentage of removal was studied in three time replicates (24,48,96 hours).

Keywords: Chitosan-Graphene oxide, nanoparticle, Cadmium, aqueous solution.

1.Introduction

Pollution of the environment is currently one of the most critical difficulties that the world is experiencing, and as a result, people from all over the world are becoming increasingly interested in the topic. It is a consequence of inflation in the agricultural and industrial sectors, in addition to the massive growth in the total number of people living on the globe [1]. Heavy metals are regarded as one of the most harmful pollutants that can be found in nature. Heavy metals can be broken down into several categories, including elements that are essential for the survival of living organisms such as copper, chromium, zinc, and iron that are needed by organisms in low concentrations but toxic at high concentrations; elements that are harmful in high concentrations such as lead, mercury, and cadmium; and excess elements that are not required by the organism in any concentrations, such as cadmi [10]

Cadmium is released into the environment by natural processes such as volcanic eruptions, weathering, and river transport, as well as by human activities such as mining, smelting, tobacco smoking, municipal waste burning, and the production of ingots, batteries, and dyes . Cadmium is also released into the environment by natural processes such as volcanic eruptions, weathering, and river transport [21]. The most common sources of exposure to cadmium are inhalation of cigarette smoke and consumption of contaminated food and water, according to the Environmental Protection Agency. Skin absorption is quite unusual [14].

2.Materials & methods

The nanomaterial was prepared by mixing (reduced graphene oxide and nano-chitosan) in a ratio of 1:1.

2.1. Diagnostics of the nanomaterial (reduced graphene oxide and nano-chitosan)

The nanomaterial(reduced graphene oxide and nano-chitosan) was diagnosed using different techniques such as (SEM),(AFM),(XRD),(FT-IR).

2.2. Preparation of heavy metal (Cadmium) solutions

The heavy metal chloride stock solution was made by dissolving small volumes of Cadmium chloride in deionized water, followed by further diluting the solution with deionized water a concentration of 1000 mg/mL The solutions were maintained in sterile flasks until they were needed. In accordance with the dilution equation, the requisite concentrations of heavy metals were prepared using the following formula $N1V1 = N2V2$ [4].

2.3.The experiment of removing heavy metals (Cadmium) with nanomaterial's

It was prepared in 250 ml flasks, in which heavy metal chlorides (Cadmium) were added at the concentrations (100 ,200 ,300 Ppm) one by one, and then the volume was increased to 100 ml and the pH was adjusted to 6. It was then diluted to 100 ml and the pH was adjusted to 6.

For each concentration, the solutions were divided into 10ml tubes and labeled. The nanomaterial was introduced to the tubes in three different concentrations (0.5, 1, and 1.5 mg/ml), each of which was added singly to the tubes. Three replicates were created for each weight of the nanomaterial.

2.4. statistical analysis

The findings were put through a statistical examination with the NOVA-TWO Way program, and tables and figures were created with the Excel software.

3.Results and Discussion

3.1.Scanning electron microscopy of the nanomaterial (graphene oxide and nano-chitosan)

Scanning electron microscopy was utilized to do a cursory analysis of the nanomaterial samples (reduced graphene oxide and nano-chitosan), focusing on their size and shape, respectively.

demonstrated that the sheets of the nanomaterial are essentially wrinkled flakes, as well as individual flakes that have an excellent lamellar structure . In addition to this, the nanomaterial possesses a surface that is uniformly smooth and exhibits a typical wrinkled structure It was shown that the nanoparticles were of sizes between 10 - 80 nanometers.

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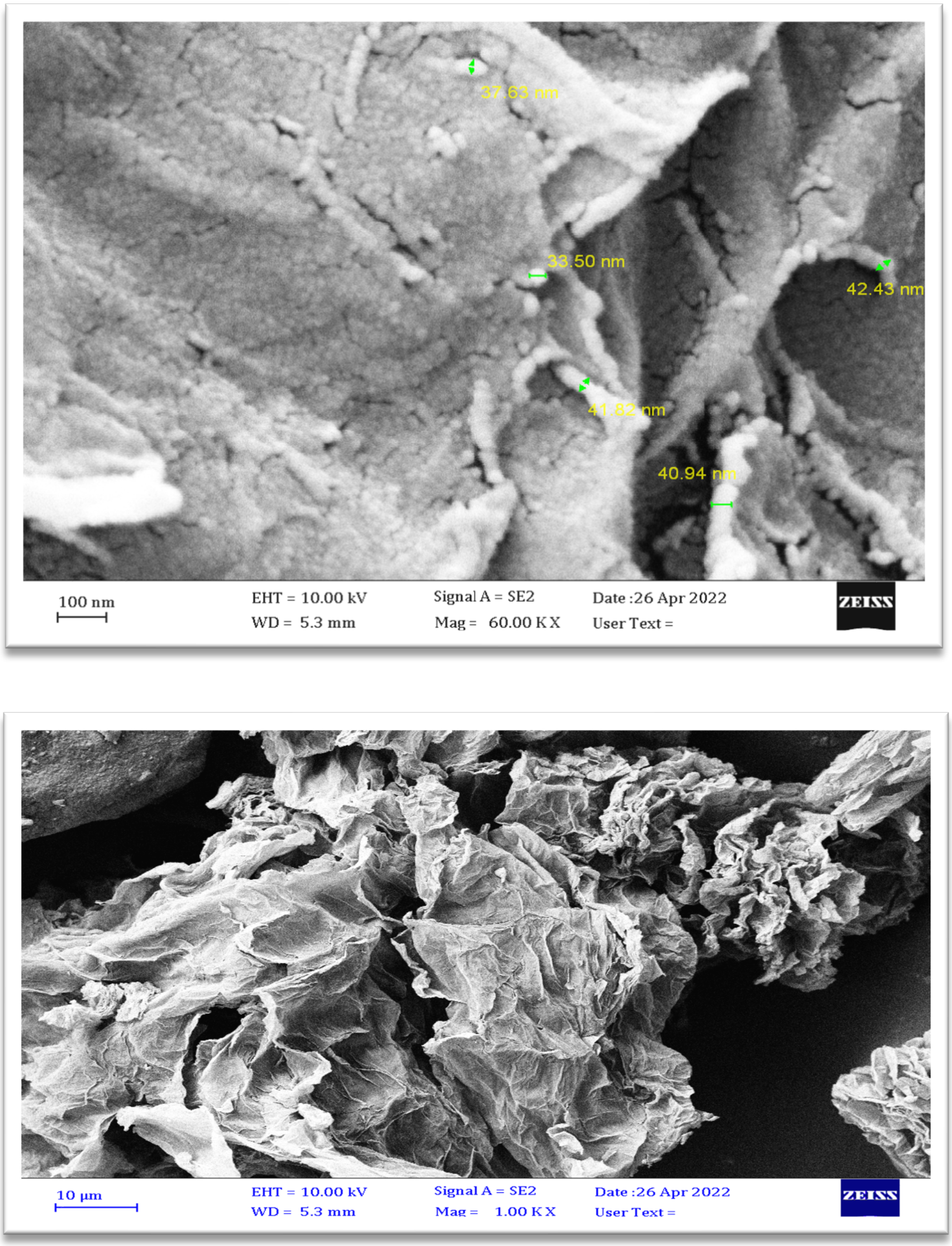


Figure(1) Micrographs with a device (SEM) of nanoparticles (reduced graphene oxide and nano-chitosan)

3.2. Atomic force microscopy (AFM)

An image of the nanomaterial particles (reduced carbon dioxide and nano-chitosan) was created with the assistance of the AFM instrument, from which information regarding the particles' average diameter and roughness was derived. The average size of the nanomaterial was 24.22 nm.

The extraordinary resolution of the atomic force microscope allows accurate three-dimensional visualization of molecular structures, as well as atomic scale strategies.

AFM sample preparation procedures are straightforward, since samples can be displayed under quasi-physiological conditions.

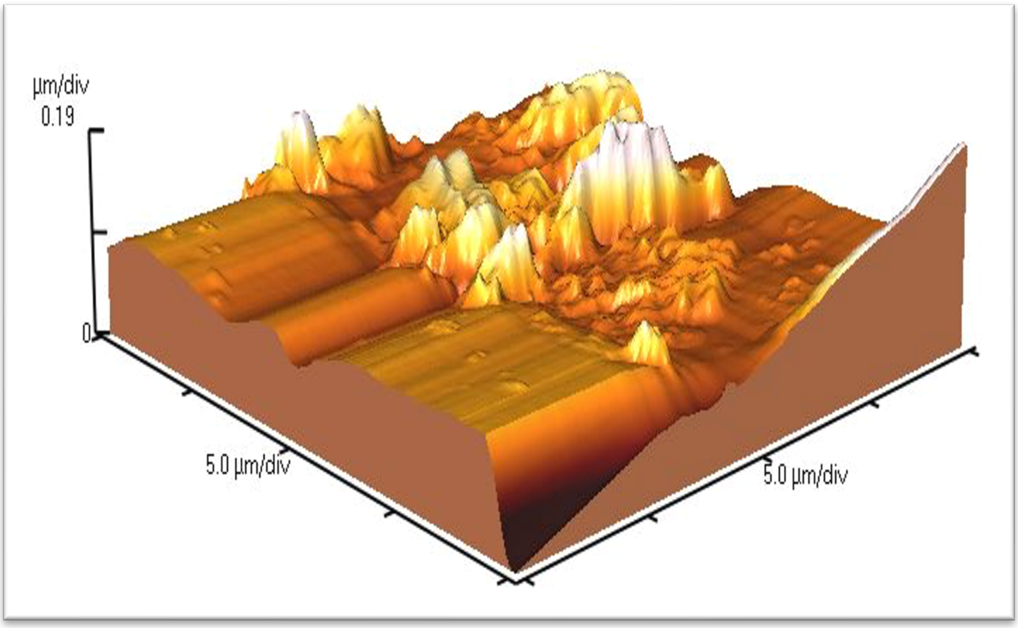


Figure (2) Atomic force microscopy analysis of the nanomaterial (reduced graphene oxide and nano-chitosan)

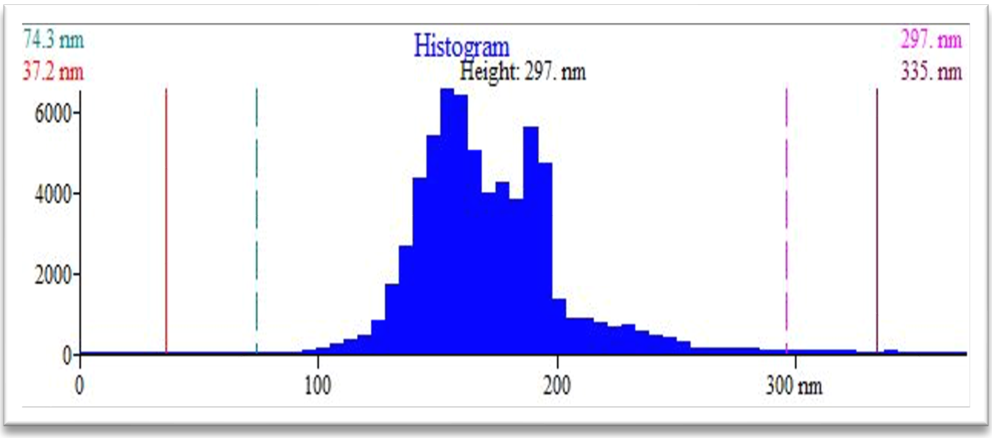


Figure (3) Atomic force microscopy analysis of the nanomaterial (reduced graphene oxide and nano-chitosan)

3.3. Infrared spectroscopy (FT-IR) analysis of the nanomaterial (reduced graphene oxide and chitosan)

The structural investigation of the nanomaterial (reduced graphene oxide and nano-chitosan) was carried out using FT-IR, the wave number ranging between 500-4000. Infrared spectroscopy is used to detect functional groups in compounds and to assess the interaction between atoms.

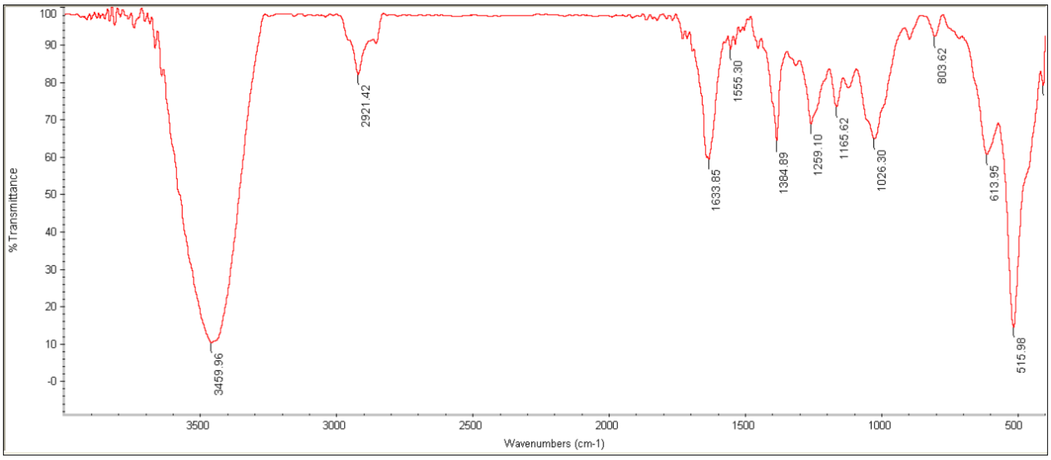
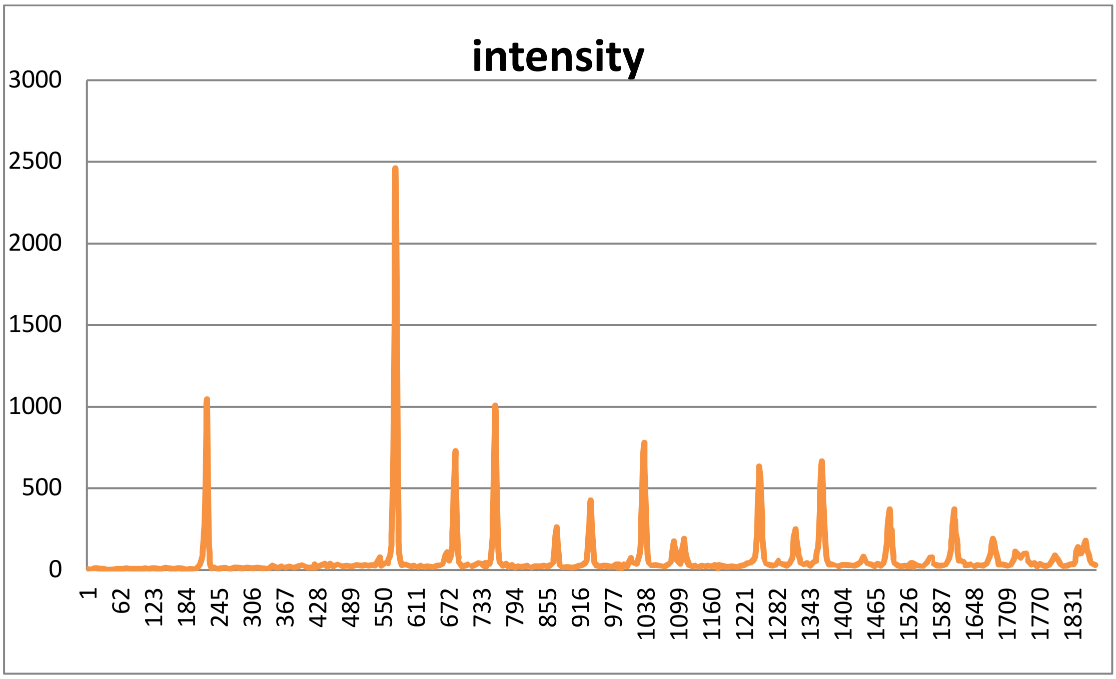


Figure (4) Examination of the nanomaterial (reduced graphene oxide and nano-chitosan)

3.4. X-ray diffraction analysis of nanomaterial (reduced graphene oxide and chitosan)

An X-ray diffraction apparatus was utilized in order to investigate the crystalline structure of the nanomaterial, which consisted of (reduced graphene oxide and nano-chitosan).

The analysis revealed that the nanomaterial (reduced graphene oxide and nano-chitosan) exhibited the appearance of three prominent peaks of high intensity at angles (13.92,27.92,35.32) degrees, corresponding to the crystalline levels (760,575,225), and the predominant trend of the compound was at (13.92). (575).



Figure(5) Represents pattern (XRD) for chips of nanomaterial (reduced graphene oxide and chitosan)

3.5.The ability of the nanomaterial (graphene oxide and nano-chitosan) to remove heavy metal (Cadmium) from their solutions.

At the current study, nanomaterials (reduced graphene oxide and nano-chitosan) were utilized in concentrations of (0.25, 0.5, 0.75 mg/l) and heavy elements (Cadmium) in concentrations (0.05, 0.1, 0.15 mg/l) were chosen because of their high density and the fact that they are harmful to all ecosystems [16].

3.5.1. Cadmium (Cd) removed in 24h

The results of the statistical analysis showed the ability of the nanomaterial (graphene oxide and chitosan) at all concentrations (0.25, 0.5, 0.75 mg/l) to remove the cadmium element at its concentrations (0.05, 0.1, 0.15 mg/l), where the highest removal percentage was recorded at a concentration of 0.75 mg/l of the nanomaterial and at a concentration of 0.15 mg/l of the cadmium percentage of 46.29%, while the lowest removal was at a concentration of 0.75 mg/l of nanomaterials and at a concentration of 0.1 mg/l of cadmium with a percentage of 18.90%.

Significant differences were found between the concentrations of nanomaterial and heavy metals. As shown in Table (1) and Figure (6)

Table (1) concentration of Cadmium after treatment with (rGO-ChNP) in 24h.

Con. Nanomaterials / Con. Heavy metals	0.25 mg/l	0.50 mg/l	0.75 mg/l	Total	Control
	D.O (Removal %)	D.O (Removal %)	D.O (Removal %)		
0.5 mg/	**39.507** (35.64%)	**33.797** (44.95%)	**38.060** (38.00%)	**37.121**	61.389
1.0 mg/l	**57.252** (39.92%)	**65.305** (31.47%)	**72.039** (24.40%)	**64.865**	95.289
1.5 mg/l	**80.581** (44.32%)	**80.468** (44.40%)	**77.723** (46.29%)	**79.591**	144.718
Total	**59.113**	**59.857**	**62.607**	**60.526**	
LSD Con. Heavy metals= 0.089		**LSD Con. Nano= 0.089**		**LSD Interaction= 0.153**	

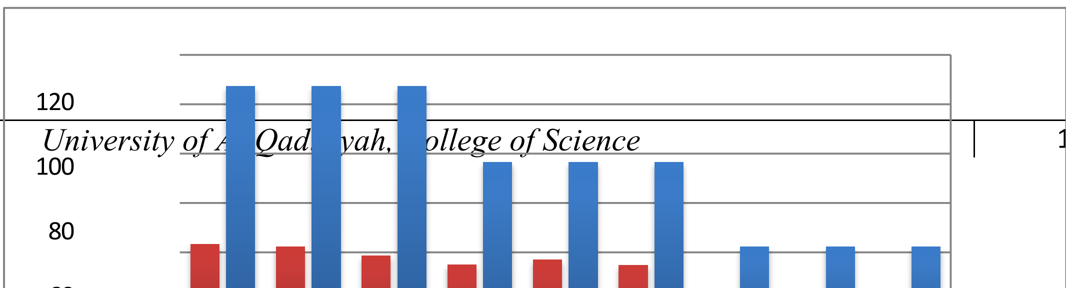


Figure (6) concentrations of Cadmium before and after treatment with rGO-ChNP in 24h

3.5.2. Cadmium (Cd) removed in 48h

The results of the statistical analysis showed the ability of the nanomaterial (graphene oxide and chitosan) at all concentrations (0.25, 0.5, 0.75 mg/l) to remove the cadmium element at its concentrations (0.05, 0.1, 0.15 mg/l), where the highest removal percentage was recorded at a concentration of 0.25 mg/l of the nanomaterial and at a concentration of 0.15 mg/l of the cadmium percentage of 44.42%, while the lowest removal was at a concentration of 0.75 mg/l of nanomaterials and at a concentration of 0.1 mg/l of cadmium with a percentage of 32.88%.

Significant differences were found between the concentrations of nanomaterial and heavy metals. As shown in Table (2) and Figure (7)

Table (2) concentration of Cadmium after treatment with (rGO-ChNP) in 48h.

Con. Nanomaterials / Con. Heavy metals	0.25 mg/l	0.50 mg/l	0.75 mg/l	Total	Control
	D.O (Removal %)	D.O (Removal %)	D.O (Removal %)		
0.5 mg/	**34.350** (44.05%)	**36.986** (39.75%)	**38.652** (37.04%)	**36.663**	61.389
1.0 mg/l	**53.723** (43.62%)	**58.160** (38.96%)	**63.963** (32.87%)	**58.615**	95.289
1.5 mg/l	**80.431** (44.42%)	**89.976** (37.83%)	**81.450** (43.72%)	**83.952**	144.718
Total	**56.168**	**61.707**	**61.355**	**59.743**	

LSD Con. Heavy metals= 0.336	**LSD Con. Nano= 0.336**	**LSD Interaction= 0.582**

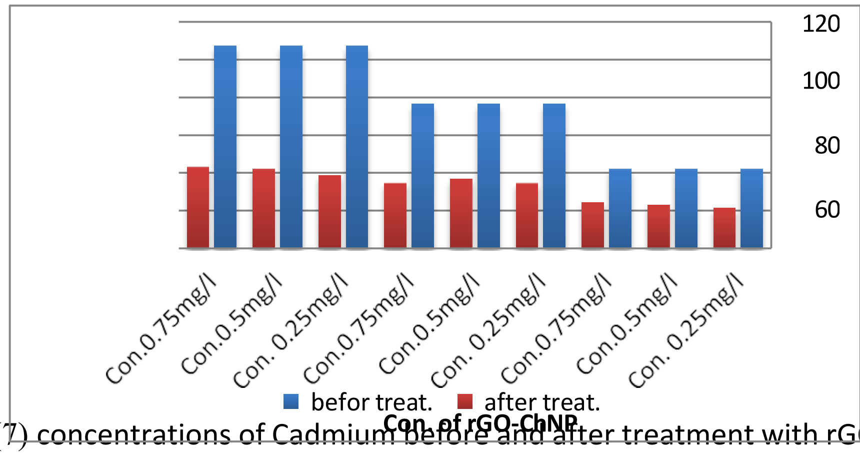


Figure (7) concentrations of Cadmium before and after treatment with rGO-ChNP in 48h

3.5.3. Cadmium (Cd) removed in 96h

The results of the statistical analysis showed the ability of the nanomaterial (graphene oxide and chitosan) at all concentrations (0.25, 0.5, 0.75 mg/l) to remove the cadmium element at its concentrations (0.05, 0.1, 0.15 mg/l), where the highest removal percentage was recorded at a concentration of 0.75 mg/l of the nanomaterial and at a concentration of 0.05 mg/l of the cadmium percentage of 55.17%, while the lowest removal was at a concentration of 0.25 mg/l of nanomaterials and at a concentration of 0.1 mg/l of cadmium with a percentage of 29.61%.

Significant differences were found between the concentrations of nanomaterial and heavy metals shown in Table (3) and Figure (8)

Table (3) concentration of Cadmium after treatment with (rGO-ChNP) in 96h.

Con. Nanomaterials / Con. Heavy metals	0.25 mg/l D.O (Removal %)	0.50 mg/l D.O (Removal %)	0.75 mg/l D.O (Removal %)	Total	Control
0.5 mg/	**36.181** (41.06%)	**29.905** (51.29%)	**27.521** (55.17%)	**31.202**	61.389
1.0 mg/l	**67.073** (29.61%)	**63.173** (33.70%)	**63.347** (33.52%)	**64.531**	95.289
1.5 mg/l	**79.231** (45.25%)	**74.613** (48.44%)	**80.036** (44.70%)	**77.960**	144.718
Total	**60.828**	**55.897**	**56.968**	**57.898**	
LSD Con. Heavy metals= 0.063		**LSD Con. Nano= 0.063**		**LSD Interaction= 0.108**	

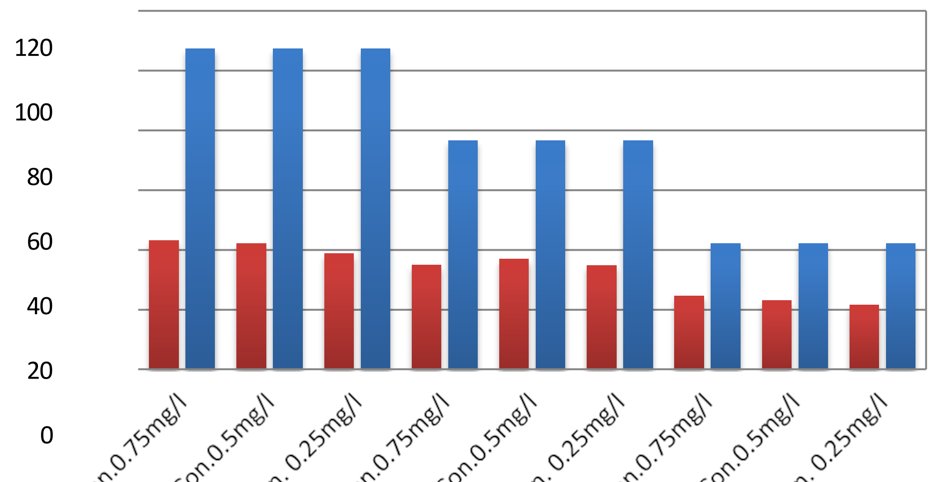


Figure (8) concentrations of Cadmium before and after treatment with rGO-ChNP in 96h

The results of the statistical analysis revealed that increasing the concentration of the nano-material (reduced graphene oxide and nano-chitosan) would lead to an increase in the percentage of elimination. It will cadmium to an increase in its surface area and thus its adsorption capacity becomes large [19]. these results are consistent with [5, 8, 9, 18].

According to the findings of the present investigation, the level of adsorption that was found to be optimal was achieved at a concentration of 200ppm of the elements cadmium. This indicates that the fraction of the heavy element that is removed rises even at low concentrations of the element , These results are consistent with [7], In this research, nano-copper oxide, or CuO, was utilized to remove nickel ions from an aqueous solution. However, there was only one concentration of the nanomaterial, whereas there were three distinct concentrations of the heavy element ion (0.1, 0.2, and 0.3). Results The higher the concentration of primary metal ions, the lower the proportion of nickel ions that are removed from the solution. The findings of this investigation are in line with the findings of the current study, in which we make the observation that an obvious adsorption efficiency may be seen at the initial concentration of heavy metals.

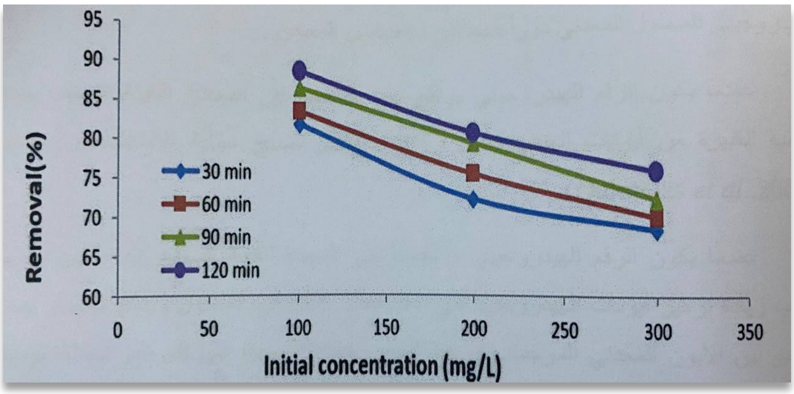


Figure (9) It shows the relationship between the initial concentration of nickel ion (100,200,300 mg/ml) on the percentage of its removal at different contact times [7].

Also, the results of the current study are consistent with the study that was done by [3], where they used in their study different concentrations of heavy metal ions (copper, cadmium, and nickel) to study the variation in the removal efficiency with different initial concentrations, and it was noted that the removal percentage did not change significantly. The reason for this is that the nanomaterial has sufficient sites for the initial concentration range, but as the concentration of the adsorbent material increases, the concentration sites in the nanomaterial will not be sufficient as a result of the accumulation of this concentration, which results in a clear depletion in the removal efficiency ratio, and also at a low concentration of the heavy element can be removed. The production of an ionic layer over the adsorbed surface, which makes the process of bonding with the nanomaterial easier; however, when there is a large concentration of the heavy element, the formation of this layer over the adsorbed surface is hampered [11, 17].

According to the findings, the capacity of the nanomaterial to absorb heavy elements from its solutions is at its highest when the pH is equal to 6. This makes sense given that the pH of the mineral solution plays a key part in the process of mineral adsorption.

Because of the high concentration of hydroxyl ions (-OH), heavy metals will precipitate at a pH that is high and moving toward basic; as a result, it will be unable to absorb the metals [15].

Due to an increase in the concentration of hydrogen ions that are present in the solution when the pH is low, the adsorbing surface has a positive total charge. This is because (OH) is being replaced by hydrogen ions. Therefore, a process of competition takes place between the positively charged metal ion and the positively charged hydrogen ions for the bonding active sites, and as a result, the hydrogen ions bind to these sites while the free metal ions continue to stay in solution [2].

In the current investigation, a pH of 6 was used since this is the ideal value for the mechanism by which elements are absorbed (cadmium). The findings of the present investigation are in agreement with those of [6, 12].

[3] employed nano-copper oxide to remove copper, nickel, and cadmium ions from the water. They discovered that pH 6 resulted in the highest removal percentage, and the findings of their study corresponded with the findings of the current study.

The exposure time is one of the very important factors in the process of removing or absorbing the nanomaterial of the heavy metals used in the study (cadmium), and the reason for this is that the increase in the exposure time led to making the surface area of the nanomaterial (Reduced graphene oxide and nano-chitosan) are available for more time and thus will lead to a high efficiency of adsorption, and the percentage of heavy metal removal depends on the abundance of the number of binding sites on the surface of the adsorbent, which increases with increasing time [13, 17].

The results of the current study agree with the study [7], where they used nano-copper oxide in their study to remove nickel ions from their solutions, as they used different times in their study (30, 60, 90,120 minutes). The results showed that the percentage of removal increases with the increase of nickel ions.

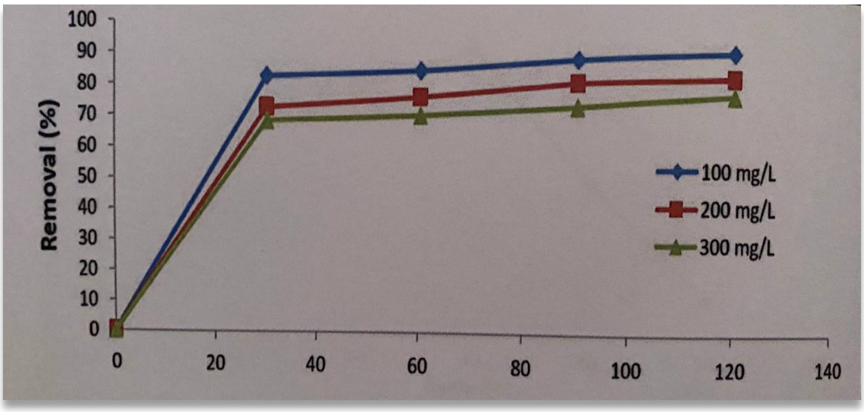


Figure (10) Shows the effect of contact time on the percentage of nickel ions removal using copper oxide CuO nanoparticles with different initial concentrations [7].

However, the results of the current study contradict the study [9], where this study indicated that the increase in time does not increase the removal rate of heavy metals except slightly, as this study showed that the removal of heavy metals increases first and then becomes constant. Initially, there were a large number of vacant sites available for removal, after some time it was difficult to occupy these sites due to the repulsive force between the ions adsorbed on the solid in the solution as the adsorption sites become saturated.

Temperature is an important factor and has a significant impact in the current study, and the temperature used in the current study is 30 degrees Celsius, which is the optimum temperature for this study, according to a study [20].

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