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Removal of Ni ions from aqueous solutions using melamine-modified nano graphene oxide adsorbent

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Abstract

Heavy metal pollution is a serious environmental issue that poses significant risks to both human health and the environment. When heavy metals enter the human body through food consumption, they can harm various organs, including the cardiovascular system, lungs, liver, and kidneys, leading to potentially severe health effects. Industrial sewage contains heavy metals such as nickel, lead, copper, zinc, and cadmium. In the present research, melamine-modified nanographene oxide was used to remove Nickel from sewage. For this, the field emission microscope (FESEM), the Tensor Fourier transform infrared spectroscopy (FTIR) and the X-ray diffraction (XRD) were employed. We investigated the effects of pH (2-7), concentration (5-200) mg/g, absorbent dose (0.01-0.06) g, temperature (15-50) °C and Contact time (15 to 150) minutes on the adsorption process. To determine the adsorption mechanism, thermodynamics, pseudo first and second-order kinetics, and Freundlich and Langmuir adsorption isotherms on the adsorption process were performed. Nickel concentration was measured by atomic absorption spectrometry. The results showed that the adsorption rate is consistent with the Freundlich isotherm model and the pseudo-second-order kinetic equation. Thermodynamic studies also showed that the adsorption process is associated with increasing irregularities and is endothermic. The highest absorption rate at a concentration of 200 mg /l, and the highest percentage of removal occurs in 150 minutes, which is equal to 1915.75 mg/g and 99.825%, respectively. Based on the results, melamine-modified nanographene oxide can be used as a suitable adsorbent to remove nickel from aqueous environments due to its high adsorption capacity and convenient and cost-effective performance.

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Introduction

The discharge of heavy metal ions into the environment has become a global problem due to widespread industrialization and improper disposal of waste. Because heavy metals are not biodegradable, they accumulate in living organisms (Nujić MH-S et al.,2019). Industrial wastewater is the main source of pollution of aquatic environments, because of organic compounds, pathogens, and heavy metals. The importance of heavy metals is due to their resistance and toxic compounds so that even at low concentrations, they are toxic and dangerous (Turtureanu et al.,2008). These metals also have a cumulative property in the body of organisms and are not degradable, which leads to health and environmental problems (Zazouli and Yousefi,2008). The pollution caused by these pollutants is cumulative in plants and animals, associated with health effects for the people that consume these products (Zafarzadeh et al.,2015). If these metals enter the human body in high amount, they will disrupt the enzymes and damage the nervous system, digestive system, and kidneys. They may also cause mental retardation and cancer (Salvato et al.,2003). Nickel is a dangerous heavy metal and is present in aqueous media in the form of divalent ions and causes cancer and fetal malformations (Ghasemi et al.,2013). Nickel is produced by metal plating, paint and painting industries, nickel battery manufacturing, and steel industries (Quintelas et al.,2009). The United States Environmental Protection Agency has set the maximum permissible concentration of nickel in drinking water at 0.1 mg/L, and the World Health Organization has set the permissible level of nickel in drinking water at 5 mg/L (Mukherjee,1998). Graphene oxide is produced by oxidation of graphite powder with strong oxidizers. The surface layers of graphene oxide is polar, due to the presence of oxidized functional groups that increase its strength in an aqueous environment and cause immobilization of materials such as drugs, inorganic nanoparticles and biomolecules, and metals (Cao et al.,2010). Many methods can be used to remove heavy metals from water. These methods are adsorption, chemical precipitation, ion exchange, filtration, membrane separation, and reverse osmosis (Leyva Ramos et al.,1995; Mohan et al.,2006). Among the mentioned methods, adsorption has been welcomed due to simplicity and low cost, high efficiency, compatibility, and greater availability of other adsorbents (El-Sadaawy and Abdelwahab,2014). Graphene oxide has been chosen to remove heavy metals instead of graphene because graphene oxide works more quickly and efficiently with other composites due to other functional group presence. The produced graphene oxide is prepared using the improved Hummers method because graphene oxide's chemical performance can be one of the highest for removal of heavy metals (Zhao et al.,2011). The carboxylic acid group is highly polar and contains a partial negative charge, to which ions with a positive charge such as nickel are highly adsorbed. Graphene oxide also has a very high mass to surface ratio that is highly efficient at adsorbing nickel (Fan et al.,2017). Graphene oxide is relatively inexpensive to manufacture and does not require advanced equipment. Its chemical composition is mostly carbon, which is an abundant element, so there is no concern about its deficiency (Mohammadnia et al.,2017)

Nujić and Habuda-Stanić (2019) studied removing toxic metal ions in drinking water by graphene oxide nanocomposites. The results showed that graphene oxide and its composites can effectively remove heavy metal ions from water (Nujić MH-S et al.,2019). White (2015) used graphene oxide to adsorb nickel, and measured concentrations and pH parameters. The results showed that the amount of nickel adsorption for one g of graphene oxide reached 365.9 mg (White,2015).

The purpose of this study was to effectively adsorb heavy metal nickel using melamine-modified nanographene oxide for the first time as an efficient adsorbent. The effects of adsorbent amount, initial concentration of heavy metal nickel, pH, time, and temperature on the adsorption rate were examined. Thermodynamic and kinetic models, Freundlich and Langmuir

adsorption isotherms were performed to investigate the adsorption isotherm. Considering that adsorption is an easy, low-cost, fast method, graphene oxide, due to its structure being full of OH groups with a negative charge, provides a suitable adsorbent that can bond with metal ions and remove them from the environment. Also, due to amine groups with negative charge melamine adsorbs metal cations and can be employed as an adsorbent modifier. The results of this study can help treat aquatic environments polluted with heavy metals.

Materials and Methods

Materials

Ni $(NO3)_2$ was used to prepare nickel-containing solutions and 0.1 Hcl and NaOH solutions purchased from German Merck company were used to adjust the pH. Double ionized distilled water was used to dilute the solutions. Graphene was also purchased from Merck Germany.

The instruments used for testing were: pH meter model AZ 8653 made in Taiwan to check the pH, digital scale model (Bands Bs-3003) with accuracy of 0.001 for weighing, shaker incubator model Ikaks model (4000 IC) made in Germany, to mix adsorbents and solvent pollutants, and a US-made (Hermle Z300) centrifuge at 4000 rpm to separate suspended particles from the solution, and a British-made Uniam919 flame atomic absorption device (AAS).

Preparation of Modified Nano Graphene Oxide Adsorbent

Graphene nanostructure synthesis was performed by Hummer method. A mixture of 360 mL of sulfuric acid, 40 mL of phosphoric acid, and 4 g of graphite was prepared and stirred slowly. Gradually, 18 g of potassium permanganate was added to the reaction mixture. Once the reaction temperature reached approximately 35–40 °C, the container was transferred to an oil bath set at 50 °C and stirred for 12 hours, then allowed to cool to room temperature. Under a fume hood, the reaction mixture was transferred to a beaker containing 3 mL of hydrogen peroxide and 400 mL of ice water to quench the remaining potassium permanganate. The resulting solid was separated by centrifugation and washed with 200 mL of water. After centrifugation, the solid was washed again with 200 mL of ethanol and twice with 200 mL of 30% hydrochloric acid to remove residual metal ions and acids. The material was dried by freeze-drying and then placed in a vacuum oven at 50 °C overnight to remove residual moisture, resulting in the production of graphene oxide (Gharebiglou et al.,2016). To enhance the efficiency of the graphene oxide, it was mechanically converted into nano-graphene oxide. Melamine (2,4,6-triamino-1,3,5-triazine) was used as a co-precipitating agent to modify the nano-graphene oxide.

Preparation of Standard Ni Solution

First, a stock solution of 1000 mg/L nickel was prepared by dissolving 3.1196 g of nickel nitrate $[Ni(NO_3)_2]$ in a 1000 mL volumetric flask. The calculated amount of nickel nitrate was weighed using a balance with an accuracy of 0.001 g and transferred to the flask, then diluted to volume with deionized distilled water. This stock solution was used to prepare nickel solutions with concentrations of 5, 10, 20, 50, 100, and 200 mg/L. All adsorption experiments were conducted in a batch (discontinuous) system and repeated twice for accuracy.

General Procedure for Ni Adsorption Experiment by Nano Graphene Axide Adsorbent in Discontinuous System

According to the literature and research done on heavy metal absorption, five parameters including temperature, contact time, adsorbent dose, initial concentration and pH have important role in the removal of pollutants. Experiments in the range of pH (3-8), temperature (15-50 °C), Ni concentration (5-200) mg/g, adsorbent (0.01-0.06) g and contact time (15 to 150 min) were performed. The effect of each parameter on the removal of heavy metals was investigated by graphene oxide nano-adsorbent. One parameter was considered

variable at each stage and the others were considered constant. Experiments were performed in a discontinuous system and repeated twice. Initial conditions for each parameter were considered pH= 6, initial metal concentration of 20 mg/l, contact time of 60 min, adsorbent dose of 0.01 g and temperature of 22 °C. First, the desired volume was taken from the stock solution, diluted to 100 mL with deionized distilled water in a volumetric flask, and then transferred to a 250 mL beaker. The pH was adjusted using a pH meter. The required amount of adsorbent was weighed using an analytical balance and transferred to a 250 mL Erlenmeyer flask. The prepared solution was added to the flask, which was then placed on a shaker set to 120 rpm for a specified time and temperature. After shaking, the mixture was transferred to 50 mL Falcon tubes and centrifuged at 3000 rpm for 5 minutes. The supernatant was filtered through Whatman No. 42 filter paper, and 1 mL of 32% nitric acid was added to prevent the precipitation of metal ions. The samples were then stored in a refrigerator until analysis. The final concentration of the solution was determined using Atomic Absorption Spectroscopy (AAS). Data analysis, including removal efficiency, adsorption capacity, kinetics, thermodynamics, and adsorption isotherms, was performed using Microsoft Excel (version 2013) and SPSS software.

Calculation of the Adsorption Percentage and Adsorption Capacity of Ni:

The removal percentage is obtained by the adsorbent in each experiment using equation (1).

equation (1): $$A = \frac{(Ci-Ce)}{Ci} \times 100$$

In this equation, Ci, Ce and A are the initial metal concentration in mg/l, the final metal concentration in mg/l and the removal percentage, respectively.

The amount of adsorption or equilibrium adsorption capacity is calculated from equation (2).

equation (2): $$q_e = \frac{(Ci - Ce)}{M} \times V$$

In this equation:

M: mass of adsorbent (g). V:sample volume and q_e: equilibrium adsorption capacity in mg/g, that is, the amount of mg of metal adsorbed per g of adsorbent (Rezaei,2016).

Nickel Adsorption Isotherms

The adsorption isotherm is a key parameter in designing adsorption systems, describing the relationship between the concentration of the adsorbate and the adsorption capacity of the adsorbent. In this study, the Langmuir and Freundlich isotherm models were applied to investigate the equilibrium distribution of the adsorbate between the solid and liquid phases. The Langmuir isotherm assumes that adsorption occurs on a homogeneous surface with uniform energy sites, forming a monolayer coverage. In contrast, the Freundlich isotherm describes adsorption on heterogeneous surfaces with a non-uniform distribution of adsorption heat (Fan et al., 2017).

Langmuir Adsorption Isotherm

The Langmuir isotherm is based on the assumption of monolayer adsorption on a homogeneous surface, where all adsorption sites have equal energy and affinity for the adsorbate (Jamali et al.,2015).The final absorption capacity is obtained from Equations (3 and 4).

Equation (3): $$qe = \frac{q_{max} \times Ceb}{1+Ceb}$$

Equation (4): $$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}}$$

In the above equations:

Ce: final equilibrium metal concentration,

Qe: equilibrium adsorption capacity equal to mg of adsorbed metal per g of adsorbent,

b: Langmuir adsorption equilibrium constant, and qmax: maximum equilibrium absorption capacity (Rezaei,2016)

One of the features of the Langmuir equation is the dimensionless parameter R_L separation coefficient. With this parameter, the type of process and the adsorption state can be determined using Equation 5:

Equation (5): $$R_L = \frac{1}{1+bc_0}$$

In the above equation, c is the initial concentration before adsorption.
When $R_L>1$, $R_L=1$, $R_L=0$ and $0<R_L<1$, the adsorption is undesirable, linear, irreversible and desirable (Mahvi and Heibati,2011).

Freundlich Isotherm

The Freundlich isotherm is based on multilayer adsorption on a heterogeneous surface, and its linear form is expressed as follows:

Equation (6): $\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$

K_f: Freundlich isotherm constant
n: Adsorption intensity
Ce: Final equilibrium metal concentration (mg/l)
qe: amount of metal adsorbed on g of adsorbent in equilibrium (mg/g).
The values of n and K_f are obtained by the slope and y-intercept of the linear diagram of ln Ce against ln qe, respectively. In this model, n values of less than 1 represent a weak adsorption and a value between 1 to 10 is desirable (Iram et al.,2010).

Nickel Adsorption Kinetics
Kinetics is necessary to collect data on parameters affecting the reaction rate as well as to determine the mechanisms controlling the adsorption process such as adsorption on the chemical reaction and the mechanism of diffusion on the kinetics evaluation. The pseudo-first order kinetic model is for diffusion from a single layer based on solid capacity, and the pseudo-second order kinetic model shows that the chemical adsorption is a deceleration step and it is a surface adsorption controller based on the solid phase adsorption (Wang,2012). The linear form of the pseudo-first order kinetic model is as follows:
Equation (7): $\ln(qe-qt)=\ln qe - k\,t$
Equation (8):

$$\log(q_e - q_t) = \log q_e - \frac{k}{2.303} t$$

q_e: the amount of metal adsorbed on the adsorbent in equilibrium in mg/g
qt: the amount of metal absorbed per unit time in mg/g
K: the equilibrium constant of first order kinetic speed in min.
The linear form of the pseudo-second order kinetic model is as follows:
Equation (9): $\frac{t}{q(t)} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}$
q_e: the amount of metal absorbed in equilibrium,
q(t): the amount of metal absorbed at time t,
K_2: the equilibrium constant of the pseudo-second order kinetic speed in g/ mg per min (Yakout and Elsherif,2010).

Thermodynamic Parameter
To study the thermodynamic processes, the adsorption process of three main parameters of Gibbs free energy (kJ/mol) as ΔG_0, enthalpy change (kJ/mol) as ΔH_0 and entropy change (kJ/mol.K) as ΔS_0 are required. These can be calculated using Equations 10 and 11.
Equation (10): $\Delta G_0 = - R_T \, Ln.k_0$
Equation (11): $\Delta G_0 = \Delta H_0 - T\Delta S_0$
Equation (12): $\ln k_0 = \frac{(\Delta s°)}{R} - \frac{(\Delta H°)}{RT}$
T: System temperature in units of Kelvin
R: General gas constant J (mol.K), 8.314
K_0: equilibrium constant
The value of k can be determined by tracing the line of diagram as ln (qe/Ce) versus qe.
In addition, ΔS and ΔH_0 are determined by the y-intercept and the slope of the L/K_0 regression corresponding to 1/T (Kakavandi et al.,2013).

Results and Discussion
Adsorbent Properties
X-Ray Diffraction (XRD) Analysis
Japan's XRD, Ultima IV Model was used to investigate the crystalline structure of graphene oxide nano-adsorbent. The spectra in the range of 5 to 15 and 25 to 35 indicate the crystalline and non-amorphous adsorbent structure, respectively. Figure (1) shows the XRD image of the adsorbent.

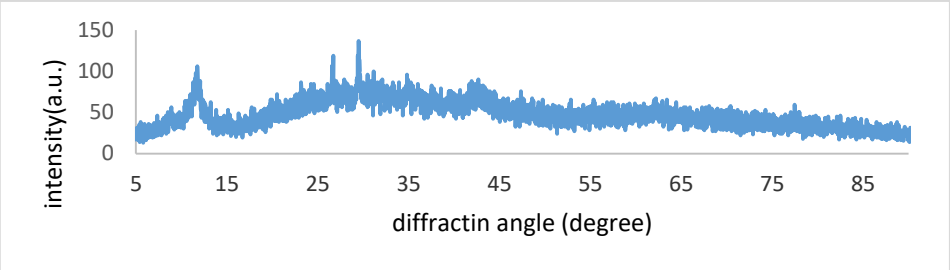
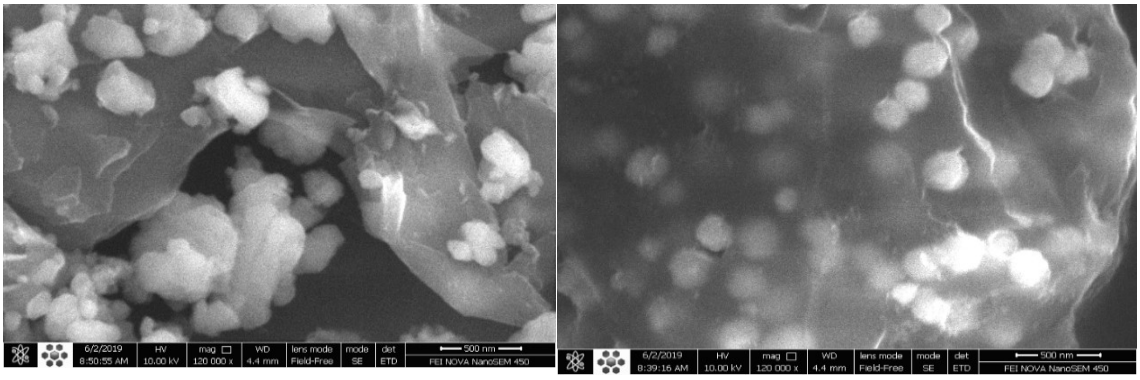


Figure 1. X-ray diffraction analysis (XRD) of modified nano graphene oxide

FE SEM

Figure (2) shows (FE-SEM) images before and after the absorption of nano graphene oxide. The porous structure indicates the high adsorption property of this adsorbent.



b a

Figure 2. FE-SEM (a) Graphene oxide nanoparticles prior to adsorption. (B) Graphene oxide nanoparticles after adsorption

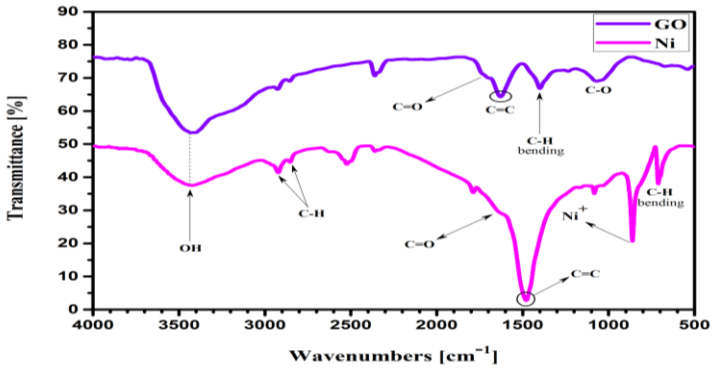


Figure 3. The FTIR spectra before and after the absorption of Ni.

FTIR

As shown in the spectra image, the hydroxyl or amino, carbonyl as well as carbon-carbon double bonds groups show good adsorbent conditions for the Ni adsorption.

Measurement of Effective Parameters in Removal of Heavy Metals by Graphene Oxide Nano Adsorbent

Effect of Initial pH on Ni

To evaluate the effect of pH, the experiment was performed at an initial concentration of 20 mg /L nickel, an adsorbent of 0.01 g, a temperature of 22° C, a contact time of 60 minutes and a pH range of 3 to 8. According to Figure (4), from pH 3 to 6, the percentage of removal and adsorption capacity had an increasing trend and was upward, but from pH 6 to 8 it was decreasing.Statistical analysis using one-way ANOVA showed

that different pH levels have a significant effect on removal percentage and adsorption capacity ($p < 0.05$). Duncan test showed no significant difference in adsorption capacity at pH 6 and 7. Finally, pH = 6 was selected as optimal.

The pH of the solution affects the adsorption of metals. This parameter can change the adsorbent and adsorbed properties or affect the adsorbent load in the adsorption process and thus its effect on the adsorption process's efficiency (Balati et al.,2014). By increasing pH, the amount of absorption increases reaching a maximum at pH=7. By increasing pH, the amount of absorption increases and its maximum value is at pH=7.

White (2015) evaluated the effects of graphene oxide on removing nickel ions from sewage and found that pH had a main effect on adsorption, and at pH=2 the adsorption was lowest and gradually increased. The maximum adsorption rate was recorded at pH = 6, which again increased, in accordance with the present study (White,2015).

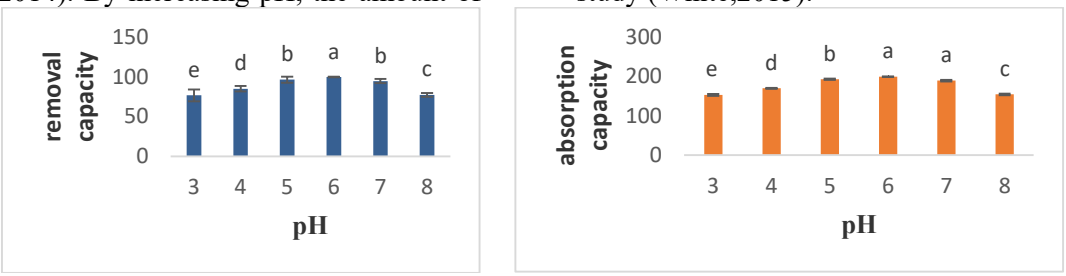


Figure 4. Effect of pH changes on percentage of Ni Removal and adsorption capacity (initial concentration: 20 mg/l, contact time: 60 min, adsorbent dose: 0.01 g and temperature of 22°C). (Different letters indicate the significance of differences)

Effect of Adsorbent Dose on Ni

To investigate the effect of adsorbent on adsorption of Ni metal ions, the experiment was performed at pH=6, initial concentration of 20 mg/l, contact time of 60 min and temperature of at 22°C and in the range of 0.01 to 0.06 g adsorbent dose. As shown in Figure (5), as the adsorbent amount increased, the adsorption capacity of nano graphene oxide for Ni adsorption decreased. The removal percentage increased up to 0.02 being at its highest in 0.02 g, after which it decreased. Analysis by one-way ANOVA showed that different amounts of graphene oxide nanoparticles had a significant effect on the rate of removal and adsorption capacity of Ni ($p<0.05$). Duncan test showed that there was no significant difference among the adsorbent doses 0.01 and 0.02 and 0.03. Considering the cost of preparing the adsorbent, the dose 0.01 g was selected as optimum.

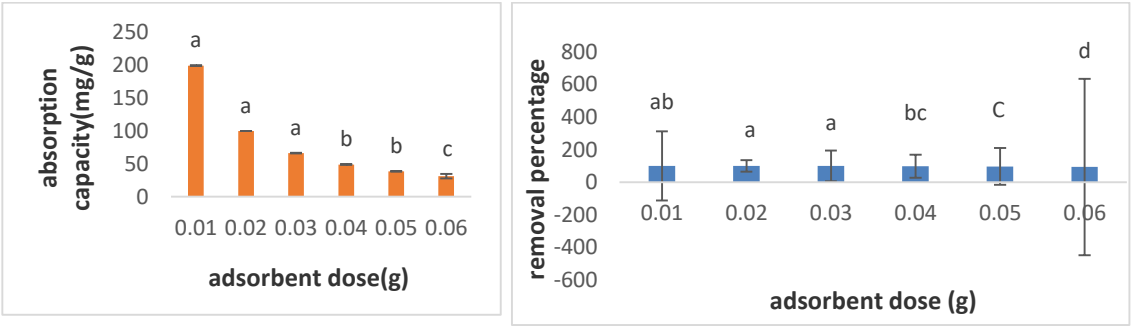


Figure 5. Effect of adsorbent dose on percentage of Ni removal and adsorption capacity (initial concentration: 20 mg/l, contact time: 60 min.pH:6 and temperature of 22 °C)

As the amount of adsorbent increased, the adsorption capacity decreased, but the removal percentage increased initially with increasing adsorbent but then decreased. As

a result, the removal percentage decreased as the adsorbent increased a lot. Naghizadeh et al. (2015) examined the removal of lead and chromium by graphene nanoparticles. It was observed that the adsorption capacity decreased with increasing adsorbent dosage, with the optimal amount for maximum adsorption capacity being 0.01 g. However, the removal percentage increased as the adsorbent dose increased from 0.01 to 0.03 g/L. Beyond this point, the removal percentage began to decrease with further increases in adsorbent dose. These findings are consistent with the results of the present study (Naghizadeh and momeni,2015).

Effect of Initial Concentration on Ni

Experiments were performed at pH=6, contact time of 60 min, temperature of 22 °C and 0.01 g adsorbent dose in the concentration range of 5 to 200 mg/l. According to Figure (6), with increasing initial concentration, the removal percentage decreases and the adsorption capacity increases. Analysis by one-way Anova showed that initial concentration had a significant effect on the removal percentage and adsorption capacity of Ni. Duncan's test showed that the removal percentages of 5, 10 and 20 mg / l were not significantly different. A concentration of 20 mg was selected as the optimal concentration.

As the initial concentration increases, the removal percentage decreases but the adsorption capacity increases. Barati et al. (2017) studied the effect of initial concentration by adsorption method on removing lead using graphene. They observed that the removal percentage decreased with increasing metal concentration consistent with the results of the current study (barati et al.,2017).

Effect of Contact Time on Ni

The effect of contact time in the range of 20 to 150 minutes at pH 6, initial concentration of 20 mg / l nickel, adsorption rate of 0.01 g and temperature of 22 ° C was investigated. As shown in Figure (7), it was found that with increasing time, removal percentage and adsorption capacity increased. Analysis by one-way ANOVA test showed that time has a significant effect on the removal rate and adsorption capacity of nickel ($p < 0.05$). There was no main difference between 60 and 150 times. The 60 minutes was selected as the optimal time.

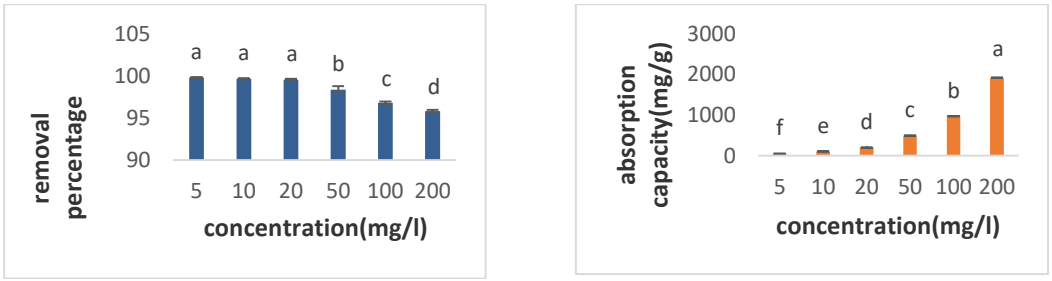


Figure 6. Effect of concentration changes on percentage of Ni removal and adsorption capacity (pH:6, contact time: 60 min, adsorbent dose: 0.01 g and temperature of 22 °C).

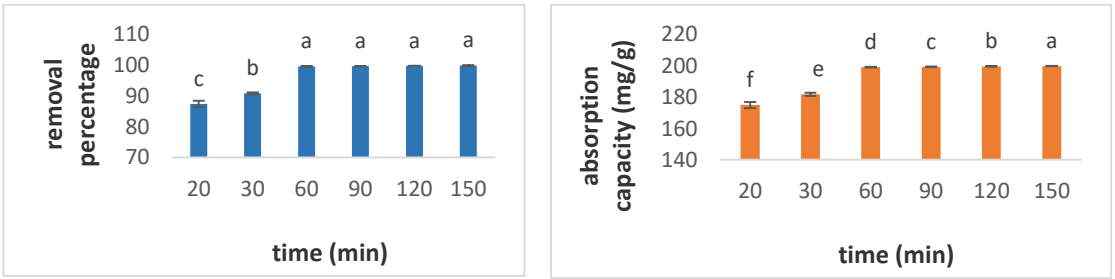


Figure 7. Effect of time changes on percentage of Ni removal and adsorption capacity (initial concentration: 20 mg/l, pH=6, adsorbent dose: 0.01 g and temperature of 22 °C).

As contact time increases, both the removal percentage and adsorption capacity increase. However, no significant difference was observed between 60 and 150 minutes, so 60 minutes was selected as the optimal contact time. Davarpanah et al. (2014) investigated the effect of contact time on nickel removal using graphene-based adsorbents. They found that maximum adsorption occurred at 60 minutes, and the adsorption process followed pseudo-second-order kinetics, which is consistent with the findings of the present study (Davarpanah et al.,2014).

Effect of Temperature Changes on Ni

To investigate the effects of temperature on the rate of Ni adsorption, an experiment was performed at pH=6 with an initial concentration of 20 mg, adsorbent dose of 0.01 g for 60 min in the temperature range of 15-50 °C. As shown in Figure (8), it was found that with increasing temperature, removal percentage and adsorption capacity increased. The analysis by one-way ANOVA showed that different values of temperature have a significant effect on the removal rate and adsorption capacity of nickel ($p < 0.05$). According to Duncan's test for the percentage of nickel removal, it was found that there is no significant difference between 22 and 50° C. The temperature of 22°C was selected as the optimal temperature. As the temperature increased, the removal percentage and adsorption capacity increased as well. According to the results, there was no significant difference between 22 and 50°C and ambient temperature of 22°C was selected as the optimal temperature. Akbari et al. (2015) removed lead by halloysite nanotubes nanocomposite/graphene oxide, and by examining the temperature in the range of 18-30 °C, they found that the optimal temperature for lead removal by adsorbent is the temperature of the environment, which is consistent with the results of the present study (Akbari et al.,2015).

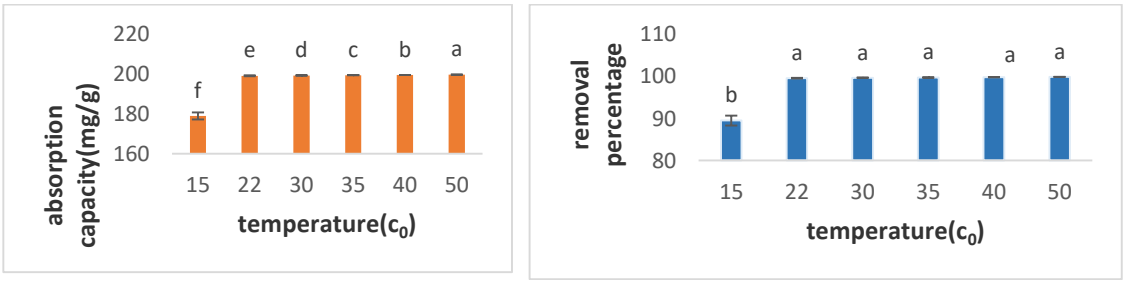


Figure 8. Effect of temperature changes on percentage of Ni removal and adsorption capacity (initial concentration: 20 mg/l, contact time: 60 min, adsorbent dose: 0.01 g and pH;6).

Determination of Adsorption Isotherm Model

The required parameters of each model are given in Table (1). According to Figures (9) and (10), it was found that Freundlich model R_2 = 0.995 compared to Langmuir R_2 = 0.8665 can better describe the adsorption of nickel ions by the adsorbent and also according to the amount obtained The valuof 1.91681 indicates the superiority of the Freundlich model, as it falls between 1 and 10, which is considered desirable. The RL value is between 0 and 1, confirming the favorability of the adsorption process. The Freundlich model effectively describes the heterogeneity of the adsorbent surface. Therefore, it can be concluded that nickel adsorption onto graphene oxide nanoparticles occurs through multilayer adsorption.

Table 1. Langmuir and Freundlich isotherm model parameters

model	R_L	n	K_f (I/mg)	qmax (mg/g)	B (i/mg)	R^2
Langmuir	0.21875	-	-	2000	0.714286	0.8665
Freundlich	-	1.91681	581.8426	-	-	0.995

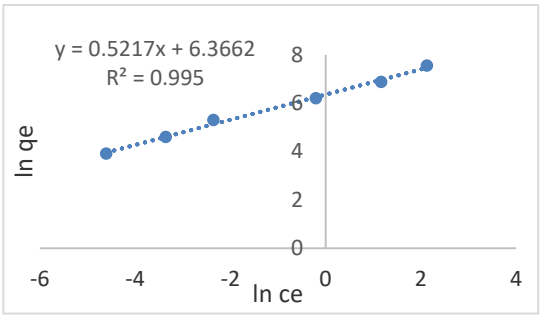


Figure 9. Freundlich isotherm curve

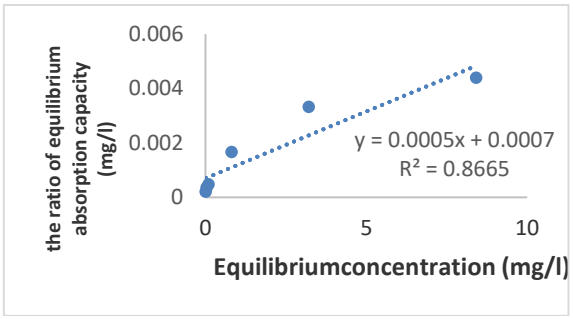


Figure 10. Langmuir isothermal curve of Ni

Evaluation of Adsorption Kinetics

According to Figures (11) and (12) and Table (2) we found that pseudo-second coefficient of determination is higher. As a result, pseudo-second-order model, better reflects the process of absorption of nickel.

Table 2. Parameters used in the Ni kinetic model

kinetic models	K_2	K_1	R^2
pseudo-first order	-	0/0269	0/3084
pseudo-second order	0/001656	-	0/9997

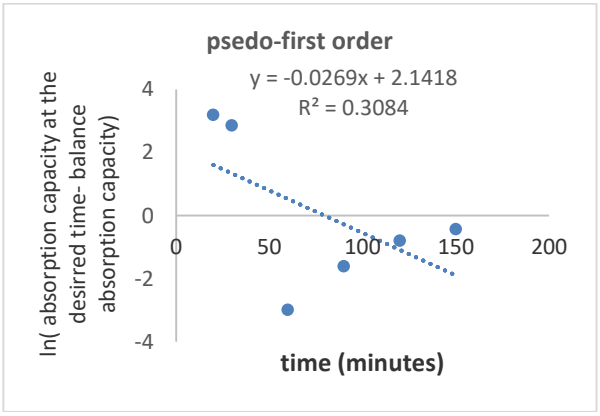


Figure 11. The pseudo-first-order kinetic model

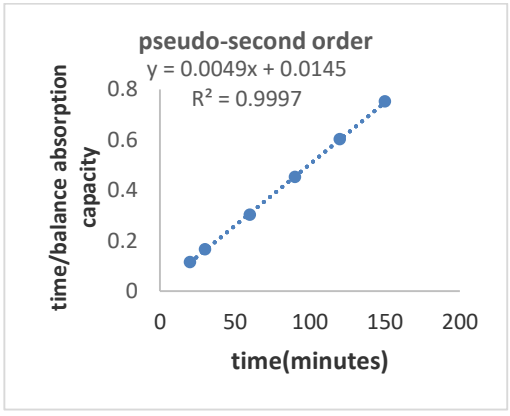


Figure 12. The pseudo-second -order kinetic model

Determination of Thermodynamic Parameters of Adsorption

To study the thermodynamics of the adsorption process, the parameters ΔS, ΔG, and ΔH must be calculated. ΔH is determined from the slope, and ΔS is obtained from the intercept of the plot of ln k versus 1/T, while ΔG is calculated using the Van 't Hoff equation. Table 3 presents the calculated values of these parameters. As shown in Figure 13 and Table 3, the positive value of ΔH indicates that the adsorption process is endothermic. The positive ΔS suggests an increase in disorder during the reaction, and the negative ΔG at higher temperatures indicates that the reaction becomes spontaneous as temperature rises. Notably, ΔG is positive at 15 °C, meaning the reaction is non-spontaneous at this temperature, but it becomes negative and spontaneous at higher temperatures. Overall, thermodynamic analysis demonstrates that the adsorption reaction is spontaneous and endothermic, with increasing randomness as temperature increases.

Table 3. Thermodynamic Parameters of Adsorption by Ni

Thermodynamic parameters	ΔH(kjmol^{-1})	ΔG(kjmol^{-1})	T(k)	T(c)	ΔS(j mol^{-1}k^{-1})
	75580	2048/5	288	15	266/18
		-5761/52	295	22	
		-6515/79	303	30	
		-6991/03	308	35	
		-7789/23	313	40	
		-8638/66	323	50	

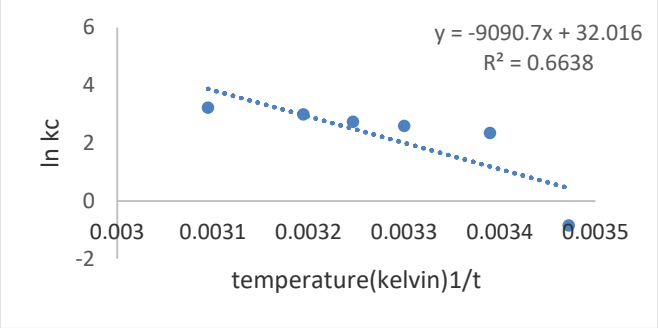


Figure 13. lnkd thermodynamics in terms of 1/ T for Ni adsorption on modified nano graphene oxide Adsorbent

Conclusion

The parameters of pH, adsorbent dosage, contact time, temperature, and initial nickel concentration in the batch system had a statistically significant effect on the adsorption process ($p < 0.05$). The maximum adsorption capacity of nickel by melamine-modified nano-graphene oxide was achieved under the following conditions: pH = 6, contact time of 60 minutes, ambient temperature of 22 °C, adsorbent dosage of 0.01 g, and an initial nickel concentration of 200 mg/L, resulting in an adsorption capacity of 1915.75 mg/g. Equilibrium studies indicated that the Freundlich isotherm model provided a better fit to the experimental data, suggesting multilayer adsorption on a heterogeneous surface. Regarding adsorption kinetics, the pseudo-second-order model showed a stronger correlation with the experimental results, implying that chemisorption is the rate-limiting step. Thermodynamic analysis revealed that the adsorption process was spontaneous (negative ΔG), endothermic (positive ΔH), and accompanied by an increase in randomness (positive ΔS). The high adsorption capacity was attributed to the large surface area and pore volume of the adsorbent. Additionally, the presence of functional groups such as epoxy and hydroxyl on the graphene oxide surface enhanced its hydrophilicity, making it effective for removing metal ions from aqueous solutions. The findings of this study confirm that melamine-modified graphene oxide is a highly effective adsorbent for the removal of nickel from water, and the incorporation of melamine significantly enhanced both the adsorption capacity and efficiency of the material.

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Conflict of Interest disclosure

The authors declare that they have no conflict of interest

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