

Adsorption Study of Ni (II) and Pb (II) by Silver oxide Nanoparticles

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ABSTRACT:

In the present work, silver oxide nanoparticles (Ag₂O-NPs) were used as an adsorption surface for removing nickel and lead ions from aqueous solutions, the surface properties were studied using various techniques like Fourier-transform infrared spectroscopy (FTIR) spectra shown the functional groups present in the synthesis silver oxides nanoparticles, X-ray diffraction (XRD) confirmed the crystalline nature of Ag₂O-NPs with a crystallite size 38.69 nm, field emission scanning electron microscopy (FE-SEM) images showed that the Ag₂O-NPs has spherical shape, and the presence of elemental silver signals of the silver oxide nanoparticles was confirmed by energy dispersive x-ray (EDX) analysis spectrum.

Adsorption experiments were carried out in order to determine the effect of contact time, adsorbent dose, and temperature on adsorption capacity, as well as to track the removal of Ni (II) and Pb(II) by Ag₂O nanoparticles. Experiments showed that 50 min was a good choice as the ideal contact time to remove Ni (II) and Pb(II) ions, the optimal quantity of adsorption is approximately 200 (mg/l), and the optimal temperature that can be used to remove Ni(II) and Pb(II) ions is 298K. The results showed that both Ag(I) and Ni(II) could be effectively removed from aqueous solutions.

Keywords: - Heavy metals, Adsorption, Nanomaterials, Silver oxide.

الخلاصة:- في البحث الحالي ، تم استخدام جزيئات أكسيد الفضة النانوية (Ag₂O-NPs) كسطح امتزاز لإزالة أيونات النيكل والرصاص من المحاليل المائية ، تمت دراسة خصائص السطح باستخدام تقنيات مختلفة مثل أطياف الأشعة تحت الحمراء (FTIR) التي أظهرت المجموعات الوظيفية الموجودة في تركيب جزيئات أكاسيد الفضة النانوية ، حيود الأشعة السينية (XRD) .) أكد الطبيعة البلورية لـ Ag₂O-NPs بحجم بلوري 38.69 نانومتر ، وأظهرت صور مجال الانبعاث المسح المجهرية (FE-SEM) أن Ag₂O-NPs لها شكل كروي ، ووجود إشارات لعنصر الفضة التي تعود للجسيمات النانوية لأكسيد الفضة أكدت بواسطة طيف تحليل الأشعة السينية المشتت للطاقة (EDX). تم إجراء تجارب الامتزاز من أجل تحديد تأثير وقت التلامس ، وجرعة الممتزات ، ودرجة الحرارة على سعة الامتزاز ، وكذلك لتتبع إزالة Ni (II) و Pb (II) بواسطة

جسيمات Ag_2O النانوية. أظهرت التجارب أن 50 دقيقة كانت اختيارًا جيدًا كوقت التلامس المثالي لإزالة أيونات $Ni(II)$ و $Pb(II)$ ، والكمية المثلى للامتصاص حوالي 200 (مجم / لتر) ، ودرجة الحرارة المثلى التي يمكن استخدامها إزالة أيونات $Ni(II)$ و $Pb(II)$ هي 298 كلفن. أظهرت النتائج أنه يمكن إزالة كل من $Ag(I)$ و $Ni(II)$ بشكل فعال من المحاليل المائية.

لكلمات المفتاحية : المعادن الثقيلة، الامتزاز، المواد النانوية ، أكسيد الفضة

INTRODUCTION

It is known that as technology advances, ecological issues are getting worse, one of the major problems is pollution of heavy metals that have negative effects on health human and other living organisms [1, 2]. Toxic heavy metals are metallic elements that have a density about five times higher than that of water, include nickel, lead, mercury, cadmium, and cobalt[3]. In recent years, heavy metal pollution has increased dramatically. As a result of the continuous development in the industrial and agricultural fields. Wastewater, agricultural pesticides, tanneries, excessive use of plant fertilizers, municipal waste and burning fossil fuels are the main sources of heavy metal toxicity[4, 5]. The majority of heavy metals have been shown to be poisonous, carcinogenic, and pose a significant risk to human health[6]. In order to mitigate this problem, various physical and chemical methods are widely used for removal toxic heavy metals from aqueous solution. Chemical methods include ion exchange[7], reverse osmosis[8], membrane filtration[9], chemical precipitation[10], flotation[11], and coagulation[12]. However, all these methods are low efficiency, expensive, and lead to generation of toxic by-products[13]. While adsorption technique is considered one of the most suitable techniques for removing heavy metals ions from polluted water due to its high efficiency, safe, simple, clean and low cost[14-16]. Different adsorbents such as crab shell, dried aerobic activated sludge , seaweeds, activated carbon prepared from almond husk, and waste factory tea, chelating minerals, activated carbon, and biopolymers[17]. Several studies have been conducted using these adsorbents, in a study published by Davis et al.[18], in which brown algae were used as adsorbents to remove toxic heavy metals like cadmium Cd^{+2} , lead (Pb^{+2}) , copper (Cu^{+2}), chromium (Cr^{+3}), and Zinc (Zn^{+2}). Similarly, another study was conducted by Iqbal et al.[19], using a bio-adsorbent (petiolar felt

sheath of palm (PFP)) to study the adsorption and removal of most heavy metals such as nickel, lead, cadmium, copper, zinc and chromium from polluted water. But because there is no single adsorbent material that is characterized by the ability to absorb all types of pollutants, in addition to the fact that the old technologies are conventional and limited in their applications. Therefore, the search for new adsorbent materials with higher efficiency has been of interest to many researchers [20]. Nanomaterials have met the requirements because of their high adsorption

capabilities because they have a larger surface area and more active sites to interact with metal species[21, 22]. It is worth mentioning that adsorption processes using nanotechnology are low-cost and require less infrastructure[23]. There are many factors that control the adsorption process of heavy metals on surfaces, including temperature, adsorbed ion concentration, contact time, and pH[24]. One of the most widely used nanoparticles is silver oxide (Ag_2O), which has a distinct set of multifunctional properties including catalysis, photochemical, medicinal effects, a high adsorption ability, and is non-toxic, which makes it more promising for the removal of toxic heavy metals[25].

The aim of this work is to remove nickel (II) and lead (II) ions based on adsorption by silver oxide nanoparticles and to identify the thermodynamic parameters of the adsorption process.

Materials and Methods:

Materials used

Standard solutions of nickel (II), lead (II) ions were prepared at a concentration of 1000 mg/L of $\text{Ni}(\text{CH}_3\text{CO}_2)_2$ and PbCl_2 in deionized water. Also, different concentrations (20, 40, 60, 80, and 100) mg /L of standard stock solutions were prepared for each metal ion. Then, using atomic absorption, the concentrations were determined and the absorbance of the solutions measured with wavelength at $\lambda_{\text{max}} = 312$ nm for nickel and $\lambda_{\text{max}} = 283.32$ nm for lead ions.

Adsorbate

Standard stock solutions of nickel (II) and lead (II) ions (1000 mg/L) were prepared from the salts of $\text{Ni}(\text{CH}_3\text{CO}_2)_2$ and PbCl_2 in deionized water, many concentrations of each metal ion (20, 40, 60, 80, and 100 mg/L) were created. To determine the amounts of metals by atomic absorption, the absorbance of these solutions was measured at $\lambda_{\text{max}} = 312$ nm for nickel and $\lambda_{\text{max}} = 283.32$ nm for lead. A series of volumetric flasks with 0.1 g of silver oxide nanoparticles and 50 ml of either copper (II) or nickel (II) ion solution with Co of 100 mg/L were added. These substances are placed to a water bath shaker at varying rates of rotation (185 rpm) and temperature (298 K) at various time intervals (10, 20, 30, 40, and 50 min). After that, samples are filtered to prevent nanoparticle interference before with the analysis. Atomic absorption was used to calculate the metal solution concentrations. Contact time, adsorbent amount, and temperature are the elements that have been investigated as influences on the adsorption of the two metals onto silver oxide nanoparticles. The two-metal removal percentage was calculated using the equation below.[26, 27].

$$R \% = \frac{(C_o - C_e) * 100}{C_o} \dots\dots (1)$$

Where: (R%) is the percentage removal of metals; (Co) is the initial concentration of metal ions that were initially present in the system (in mg/L); and (Ce) is the concentration of copper and nickel ions that have been removed (in mg/L).

RESULT AND DISCUSSION

Characterization of Silver oxide nanoparticle

X-ray diffraction

The XRD pattern of Ag₂O-NPs is depicted in Figure (1). All of the cubic phase structure's pattern peaks in Table 1 can be well matched with the diffraction peaks of (111), (200), (220), and (311). The Debye-Scherrer equation was used to determine the average crystallite size, which was determined to be 38.69 nm. The presence of expansive and sharp peak were observed, which indicates the crystallite size and purity of Ag₂O-NPs[28].

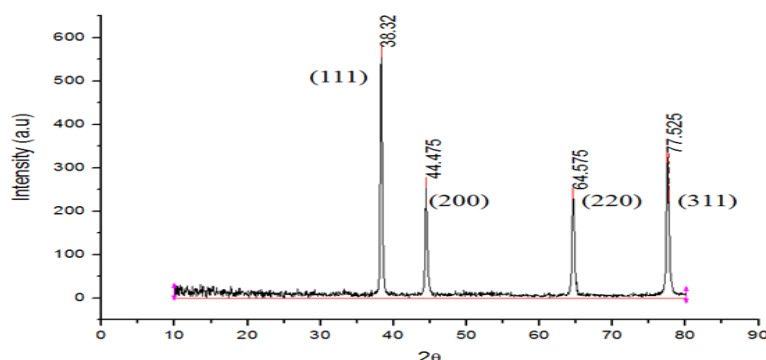


Figure1: X-ray diffraction pattern of Ag₂O-NPs

Table (1) XRD data of Ag₂O-NPs

| Pos. [°2Th.] | FWHM Left [°2Th.] | d-spacing [Å°] | Height [cts] | Rel. Int. [%] | hkl | D,nm | δ | ε |
|--------------|-------------------|----------------|--------------|---------------|-----|-------|----------|----------|
| 38.3163 | 0.246 | 2.34915 | 561.43 | 100 | 111 | 35.72 | 0.000784 | 0.002146 |
| 44.4621 | 0.246 | 2.03767 | 260.33 | 46.37 | 200 | 36.45 | 0.000753 | 0.002145 |
| 64.5933 | 0.3444 | 1.44288 | 232.63 | 41.44 | 220 | 28.52 | 0.001229 | 0.003001 |
| 77.4962 | 0.1968 | 1.23173 | 318.44 | 56.72 | 311 | 54.09 | 0.000342 | 0.001713 |

FT-IR analysis

As shown in Figure (2), FTIR spectrum (400 to 4000 cm^{-1}) confirms the presence of synthesized Ag_2O - NPs. The broad peak at 3309 cm^{-1} was related to O-H group. The peak at 544 cm^{-1} corresponding to Ag–O bond[29]. The peaks at 1457 and 1354 cm^{-1} was related to bending vibrations of $-\text{CH}_3$ symmetrical and asymmetrical. The peaks at 1623 cm^{-1} to roughly 1650 cm^{-1} related to O-H bending mode or the C=C stretching vibrations.

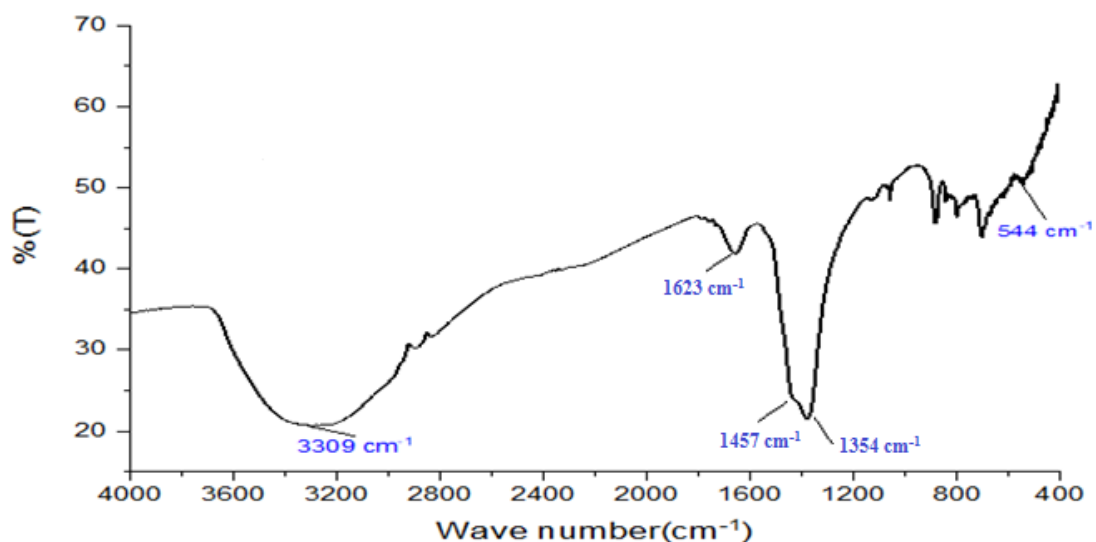


Figure 2: FT-IR analysis of Ag_2O -NPs

FE-SEM images of Ag_2O -NPs.

The FE-SEM images of Ag_2O -NPs are shown in Figure (3). The surface morphology of Ag_2O -NPs showed spherical shape agglomerated with average size about 47.45 nm, this value was further supported from the calculations made on the XRD pattern[30].

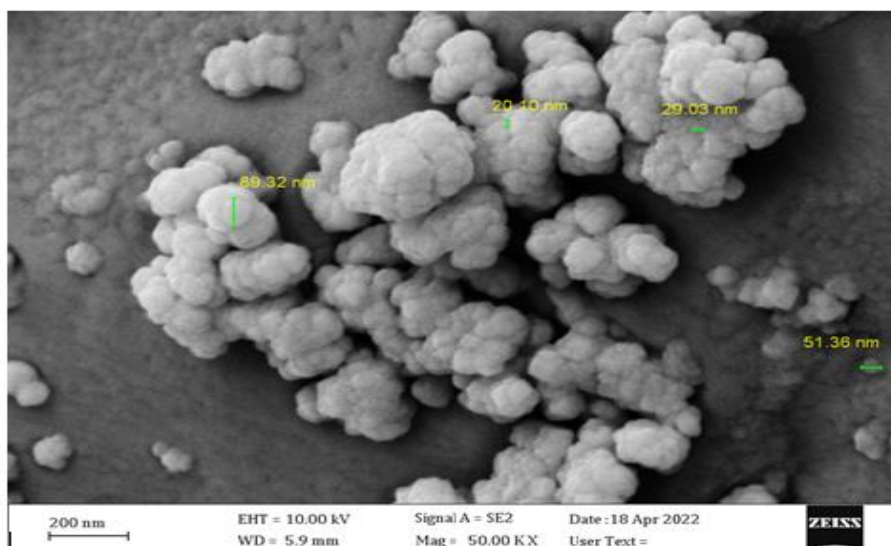


Figure 3: FE-SEM image of Ag₂O-NPs

Energy-dispersive X-ray (EDX) study

The energy dispersive spectra of the produced Ag₂O-NPs is shown in Figure (4), which demonstrates that silver is one of the component elements. Surface plasmon resonance causes the usual signal peak of silver nanoparticles to be at 3 keV. The quantitative data of Ag₂O-NPs produced by biosynthesis is shown in Figure (4). The inset of Figure (4) depicts the existence of elements like Ag, O, and C.

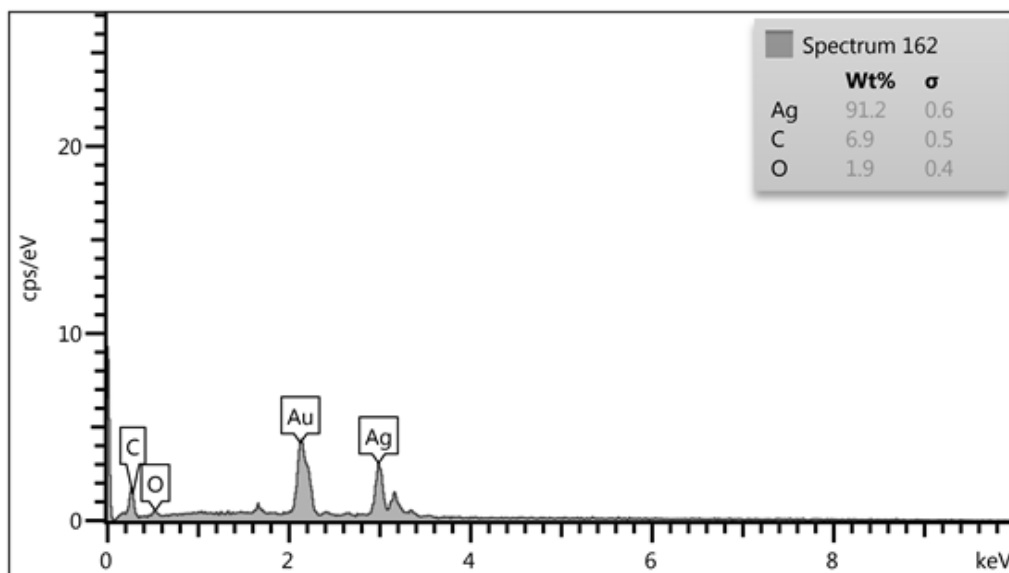


Figure 4: Energy-dispersive X-ray (EDX) spectroscopy of synthesized Ag₂O-NPs.

Removal Ni (II) and Pb (II) ions on Ag₂O-NPs surface

Contact time effect

The influence of contact time on the adsorption of Ni(II) and Pb(II) ions on (Ag₂O-NPs) was investigated at (10, 20, 30, 40, and 50) minutes at (298)K, concentration (100) mg/L of metal ion. The percentage removal of Ni (II) and Pb (II)ions changes with contact time, as shown in Tables 2 and 3, respectively. It can be seen from them that an equilibrium period of about (50) min is needed for the adsorption of both ions on the Ag₂O-NPs. The percentage removal of Ni(II) and Pb(II) ions for surfaces decreases at the beginning of contact time with both ions, followed by a gradually increasing percentage removal of Ni(II) and Pb(II) ions for surfaces because the rapid initial rate increase followed by a slow rate at later period could be due to availability of excess adsorption sites on the adsorbent[31]. The initial high adsorption rate may have been brought on by ion exchange, which was followed by a gradual chemical reaction involving the active groups of the metal ions on the sample. [32], and the remaining vacant surface sites are difficult to occupy the remaining unoccupied surface spots. The metal ions have to traverse further and deeper into the pores encountering much larger resistance[33].

Table 2: Effect of contact time on the adsorption of Ni (II) ion on (Ag₂O-NPs) at 298 K .

| Time,min | C ₀ mg/L | Ct mg/L | R % |
|----------|---------------------|---------|--------|
| 10 | 100 | 52.222 | 47.778 |
| 20 | | 39.732 | 60.268 |
| 30 | | 35.544 | 64.456 |
| 40 | | 31.222 | 68.778 |
| 50 | | 12.182 | 87.818 |

Table 3: Effect of contact time on the adsorption of Pb (II) ion on (Ag₂O-NPs) at 298 K .

| Time,min | C ₀ mg/L | Ct mg/L | R % |
|----------|---------------------|---------|--------|
| 10 | 100 | 61.204 | 38.796 |
| 20 | | 60.009 | 39.991 |
| 30 | | 58.997 | 41.023 |
| 40 | | 52.069 | 47.931 |
| 50 | | 45.042 | 54.958 |

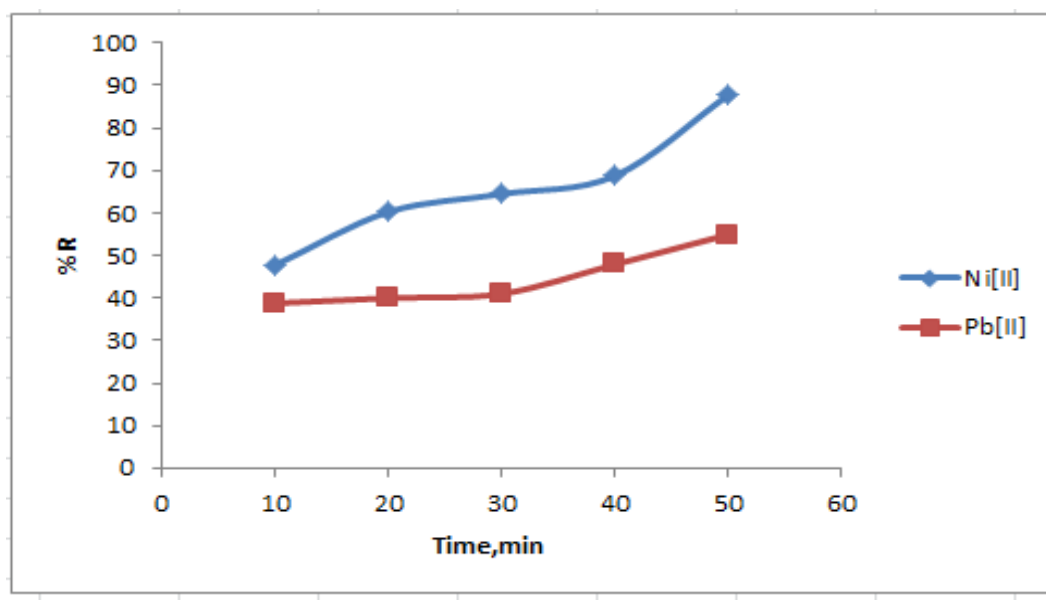


Figure 5: Effect of contact time on the removal (%) of Ni (II) and Pb(II) ions on Ag₂O-NPs at 298 K.

Adsorbent quantity effect

The influence of adsorbent amount on the removal of Ni (II) and Pb (II) ions on the Ag₂O-NP surfaces was investigated using fixed amounts of adsorbent (50, 100, 150, 22, and 250 g) at 298 K, different concentrations of Ni (II) and Pb (II) ions (100 mg/L), and a contact time of 60 min for both ions.

The influence of adsorbent quantity on the uptake of the metals Ni (II) and Pb (II) ions onto Ag₂O-NPs is shown in Tables 4 and 5 and in Figure 6. Metals removal increases as the amount of Ag₂O-NPs prepared by the Arundo leaf extract method increases, implying that increasing the amount of oxide nanoparticles increases the metals removal percentage.

Table 4: Effect of adsorbent quantity on the adsorption of Ni (II) ions on Ag₂O-NPs at 298 K .

| W,mg | C ₀ mg/L | C _e mg/L | R % |
|------|---------------------|---------------------|--------|
| 50 | 100 | 42.173 | 57.827 |
| 100 | | 39.543 | 60.457 |
| 150 | | 37.014 | 62.986 |
| 200 | | 33.154 | 66.846 |
| 250 | | 32.594 | 67.406 |

Table 5: Effect of adsorbent quantity on the adsorption of Pb (II) ions on Ag₂O-NPs at 298 K.

| W,mg | C ₀ mg/L | C _e mg/L | R % |
|------|---------------------|---------------------|--------|
| 50 | 100 | 55.215 | 44.785 |
| 100 | | 54.182 | 45.812 |
| 150 | | 50.498 | 49.502 |
| 200 | | 50.219 | 49.781 |
| 250 | | 49.178 | 50.822 |

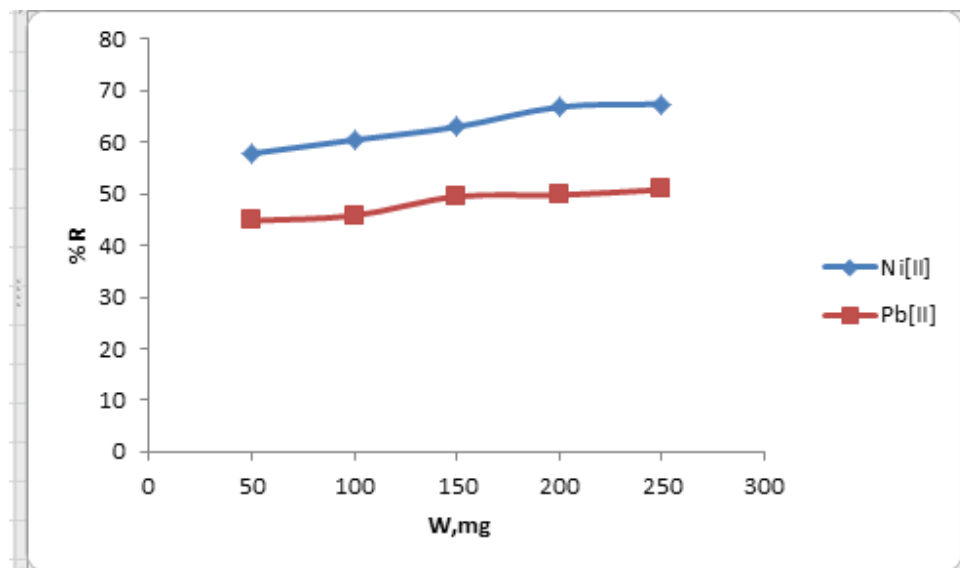


Figure 6: Effect of adsorbent quantity on the removal (%) of Ni (II) and Pb(II) ions on Ag₂O-NPs at 298 K.

Temperature effect

The influence of temperature on the amount of adsorption of Ni (II) and Pb (II) ions on Ag₂O-NPs was examined at various temperatures (298, 308, 318, 328, 328, and 338) using 0.1 gram of the surface at an initial concentration of 100 mg/liter. The contact time was constant at 60 minutes. Figure (7) shows the general shape of the Ni (II) and Pb (II) ions (Ag₂O-NPs). The data showed that the percentage of removal decreases with increasing temperature, and this proves that the removal of individual metals is exothermic in nature for each of the nickel-lead ions present at the surface (Ag₂O-NPs). As the temperature increases, a decrease in the absorption rate may weaken the strength of the interaction between the active sites on the adsorption surface and the single metal ions. [34].

Table 6: The effect of temperature on the adsorption of Ni (II) ions on Ag₂O-NP_s.

| T,K | C ₀ mg/L | C _e mg/L | R % |
|-----|---------------------|---------------------|--------|
| 298 | 100 | 21.106 | 78.894 |
| 308 | | 32.712 | 67.288 |
| 318 | | 41.648 | 58.352 |
| 328 | | 44.823 | 55.177 |
| 338 | | 45.548 | 54.452 |

Table 7: The effect of temperature on the adsorption of Pb(II) ions on Ag₂O-NP_s.

| T,K | C ₀ mg/L | C _e mg/L | R % |
|-----|---------------------|---------------------|--------|
| 298 | 100 | 38.303 | 61.697 |
| 308 | | 41.911 | 58.089 |
| 318 | | 46.432 | 53.568 |
| 328 | | 55.592 | 44.408 |
| 338 | | 61.611 | 38.389 |

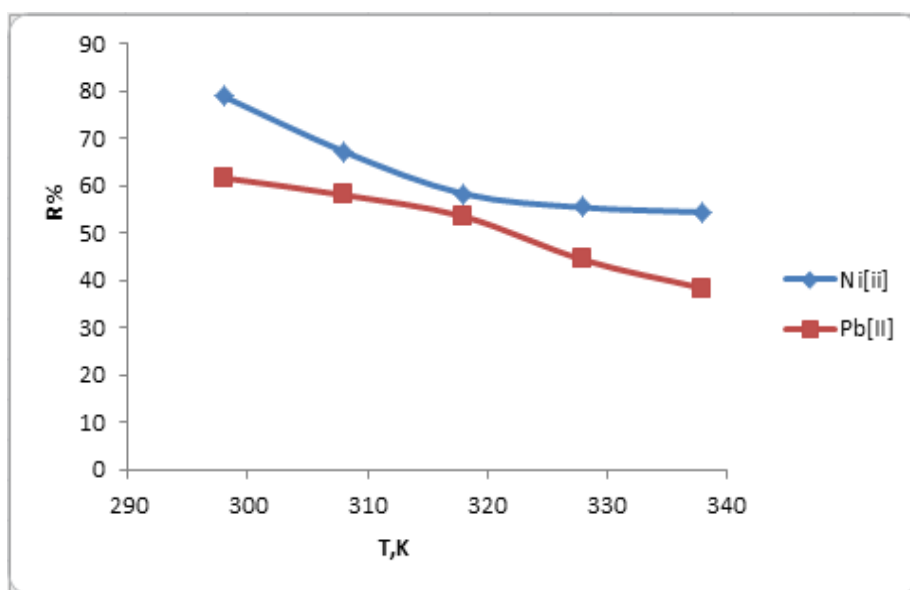


Figure 7: The effect of temperature on removal (%) of Ni (II) and Pb(II) ions on Ag₂O-NP_s.

CONCLUSIN

The main focus of this study is the removal of nickel and lead by adsorption technology using silver oxide nanoparticles as an adsorbent. The adsorption surface properties of silver oxide nanoparticles were studied in this work. The results indicated the presence of silver in the biomass, as the FT-IR spectra showed the presence of carboxyl and hydroxyl groups. which can easily bind with metal ions to remove them from aqueous solution, the percentage removal of Ni (II) and Pb (II) ions was 96.45% and 96.03%, respectively. The results indicate that Ag₂O-NPs highly efficient adsorbent for removing heavy metal ions.

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