Adsorption of Lead (Pb^{+2}) and Cobalt (Co^{+2}) Ions from Wastewater using CdO Nanoparticles as an Adsorbent

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Abstract— This research focused on using Cadmium Oxide nanoparticles as adsorbent to remove heavy metals ions such as lead and cobalt from wastewater. Different parameters were studied to obtain the best results, such as contact time and adsorbent dosage. The highest results were obtained at 45 min contact time, 0.5 g/100 mL dosage and 50 mg/L initial concentration of metal ions at temperature 25 ^{o}C, which were 91.23% and 90.59% for lead and cobalt ions, respectively. The pseudo-second order was shown to have a high degree of fitness based on kinetic data. The adsorbent was characterized using a variety of techniques, including UV-visible, Fourier transform infrared spectroscopy (FTIR), XRD diffraction and Field Emission Scanning Electron Microscope (FE-SEM).

Keywords— Green synthesis, CdO nanoparticles, Lettuce leaves extract

1. INTRODUCTION

Environmental contamination is one of humanity's most significant problems. In latest years, it has increased at an extraordinary rate, attainment incredible proportions in terms of its impact on living things [1]. Heavy metals establish one of the most common contaminants in wastewater [2]. Heavy metal contamination is a serious environmental issue that has a significant effect on both the aquatic and terrestrial ecosystems due to their toxicity, non-degradability, and bioaccumulation [3]. Rapid industrialization and urbanization have caused contamination of the environment by heavy metals, and their rates of mobilization and transport in the environment have greatly accelerated since 1940s [4]. Heavy metals are considered hazardous due to these three characteristics: persistence, bioaccumulation, and toxicity (PBT) [5]. Heavy metals like Pb^{+2} and Co^{+2} ions are common in the wastewater from industries like electroplating, electronics, battery production, rubber factories, and paints [6]. Ion exchange, chemical precipitation, electrochemical extraction, and adsorption are all prevalent methods for extracting heavy metal ions from wastewater; however, adsorption may be the best option due to its high efficiency, low cost, and ease of use [7]. Kumar and co workers prepared a metal oxide nanoparticles such as ZnO and SnO2 with specific surface areas of 15.75 and 24.48 m2/g respectively were successfully synthesized by precipitation method and then employed as adsorbents for removal of Malachite Green Oxalate (MGO) and hexavalent Chromium (Cr) from aqueous solution[8]. Yang et al., exploited the synthysized nanomaterials extensively to remove heavy metals in water a series of nanomaterials, including carbon-based nanomaterials, zero-valent metal nanomaterials, metal oxide materials, and nanocomposites were discussed in detail [9]. The aim of this work

is to synthesis and study the effect of cadmium oxide nanoparticles (CdO NPs) on the removal of some metallic ions such as Pb^{2+} and Co^{2+} from wastewater.

2. MATERIALS AND METHODS

2.1. Chemical and reagents

Cadmium chloride ($CdCl_2$) and sodium hydroxide were obtained from sigma Aldrich. Lettuce leafs were obtained from gardens in Iraq.

2.2. Preparation of the Lettuce leaves Extract

To synthesis aqueous Lettuce leaves leaf extract, the steps involved for obtaining are: Collecting the Lettuce leafs leaf, washed thoroughly with tap and deionized water to remove any impurities then dry 24 hours. Grinding the dried part of the plant to a fine powder, boiling a determined quantity (20 g) of the dried powder with distilled water (100mL) and filter the resulted until no debris is present. Figure 1.

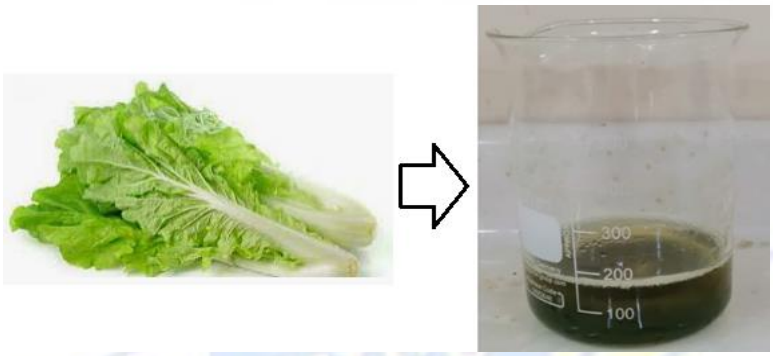


Fig.1. Lettuce leaves extract prepared

2.3. Synthesis of CdO NPs

Once the aqueous plant extract is obtained, 15-20 mL from it was added to an CdCl2 solution (1g dissolved in 100mL deionized water), NaOH solution (1M) drop wise very slowly, the Cd(OH)2 nanoparticles was formed, then calcination it at 550 °C to obtained CdO nanoparticles. The formation of $Cd(OH)_2$ and CdO nanoparticles are show in figure (2), which confirm by UV-vis spectrum figure (3).[10]

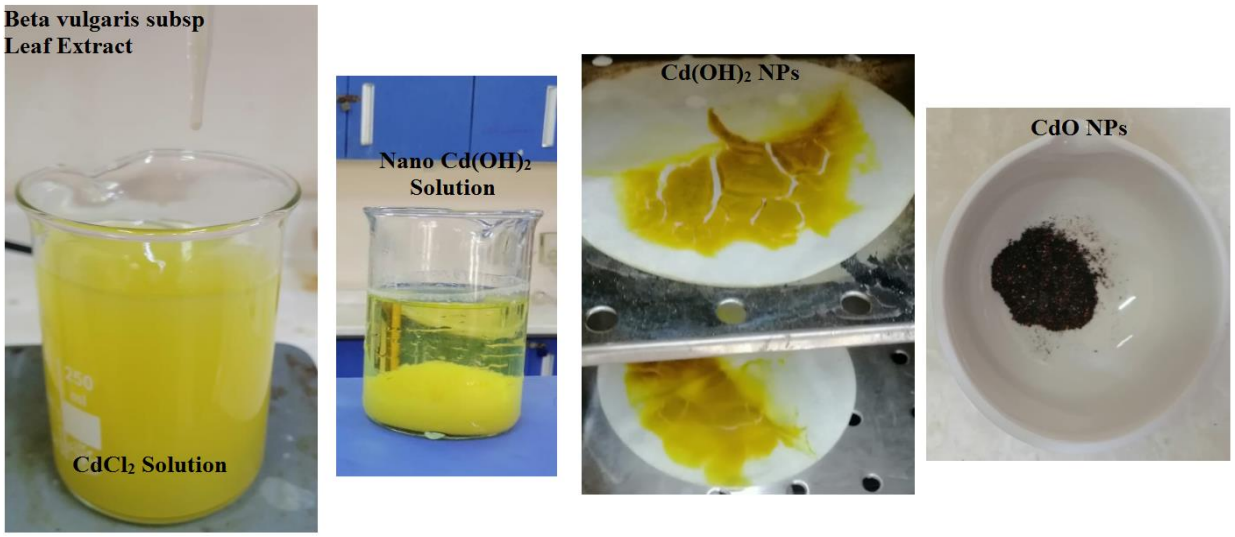


Fig.2. Synthesis of CdO NPs

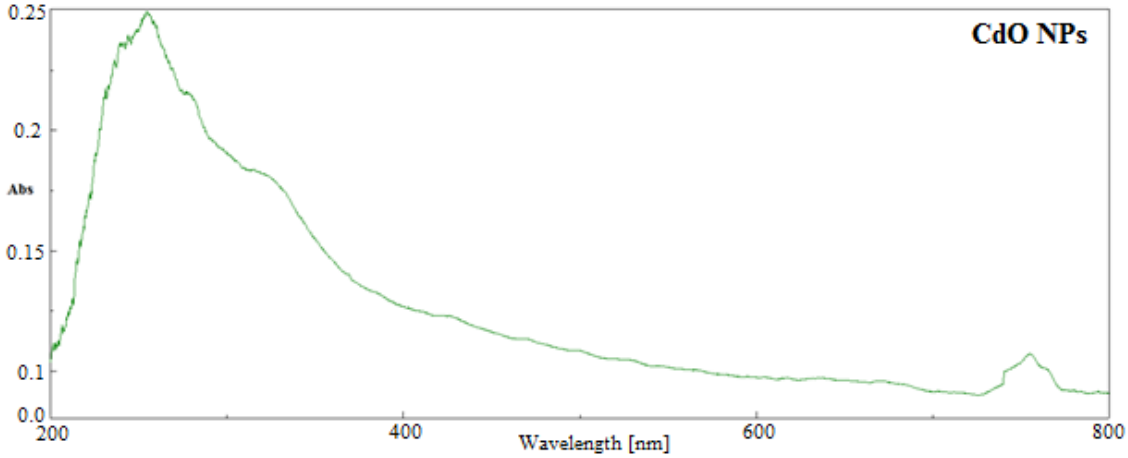


Fig.3. The UV absorbance spectrum for CdO nanoparticles.

3. Characterization

X-ray diffraction (XRD) analysis of CdO NPs sample was carried out on a Bruker instrument, German, using Cu Kα radiation. The surface morphological features such as shape and particle size and the composition of the CdO nanoparticles were measured using Field Emission Scanning Electron Microscope (FE-SEM) (Germany). The FTIR and UV– visible spectrum were recorded in the department of chemistry, college of education for pure science, university of diyala, Iraq.

4. Results and Discussion

The UV– visible absorption spectra of CdO nanoparticles are shown. in Fig. 3 although the wavelength of our spectrometer is limited by the light source, the absorption band of the CdO nanoparticles have been shows a blue shift due to the quantum confinement in sample compare with bulk CdO particles. This optical phenomenon indicates that these nanoparticles show quantum size effect. [14] UV-Vis spectra of CdO had a maximum absorbance at 300 nm.

The FTIR spectra of $Cd(OH)_2$ NPs and CdO NPs are shown in Figures (4 and 5). The FTIR spectrum of the $Cd(OH)_2$ NPs shows a strong peak at 3417cm^{-1} corresponding to the free OH group and peak at 1573 cm^{-1} caused by the bending bonded O-H group.

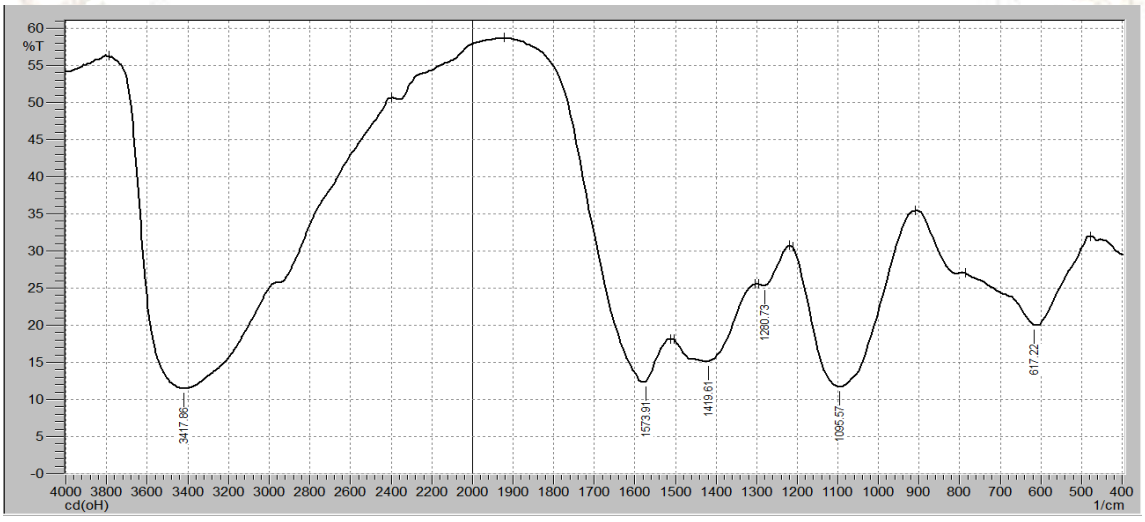


Fig.4. FTIR of $Cd(OH)_2$ nanoparticles.

Comparison of $Cd(OH)_2$ NPs and CdO NPs spectrum from 450-3900 cm^{-1} at room temperature showed several peaks. The modes of vibration of chemical bonds present in the CdO nanoparticles were analyzed from the FTIR spectrum and the functional groups were recorded in the range of 450-4000 cm^{-1}. Fig. 5 shows the FTIR spectrum of the CdO nanoparticles. The peak at 3510 cm-1corresponds to the formation of the O-H group in the adsorbed water molecule which plays an important role in the adsorption and antibacterial activity of the synthesized nanoparticles. The Cadmium–oxygen (Cd–O) bond is observed at 1095 cm-1it indicates the formation of CdO from cadmium chloride and show peaks lie at 532 cm^{-1} and 601 cm^{-1} which indicate the formation of CdO NPs.

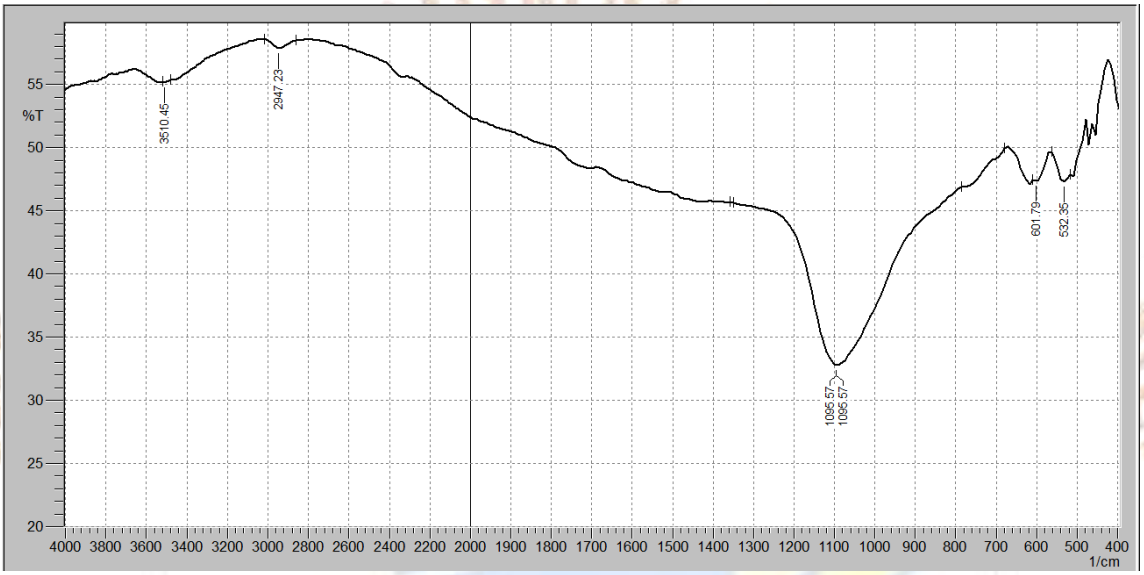


Fig.5. FTIR of CdO nanoparticles.

The XRD pattern of calcinated powder at 400 ºC for 2 h is shown in Fig. 6. The average particle size was estimated from the width at half-maximum (FWHM) as the diffraction peak of CdO, (111), (200) and (220) at 2θ values of 33.41, 38.60 and 55.54º using Debye-Scherrer's formula. It is observed that the average particle size is 32.4 nm.

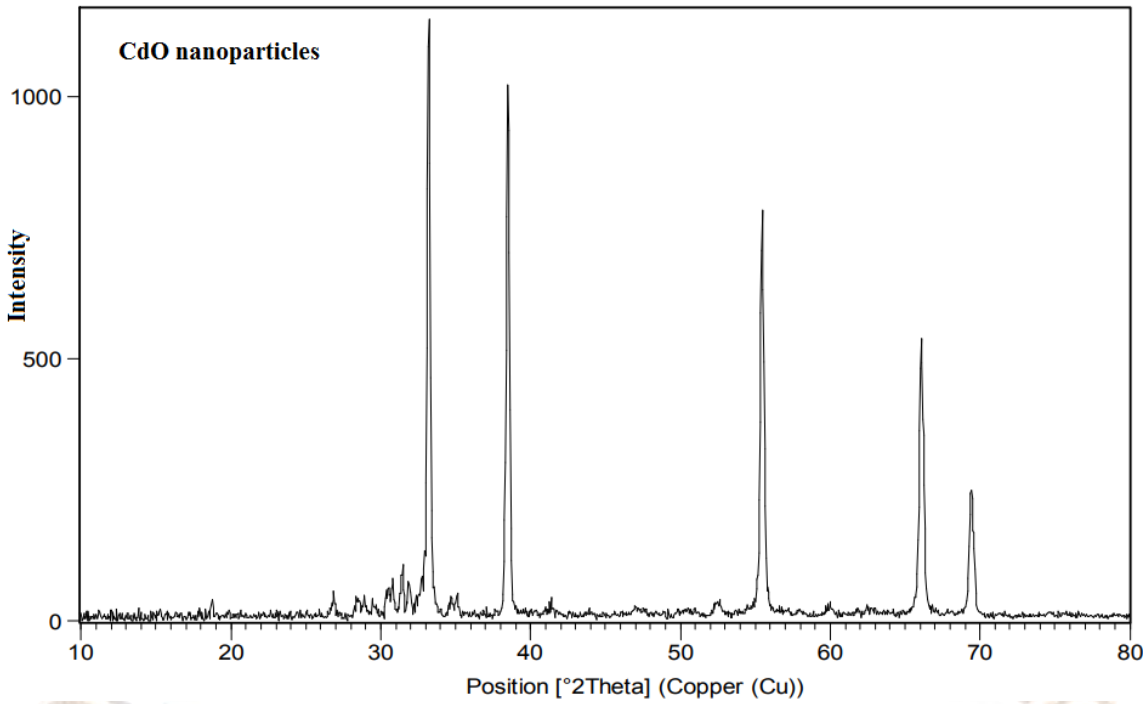
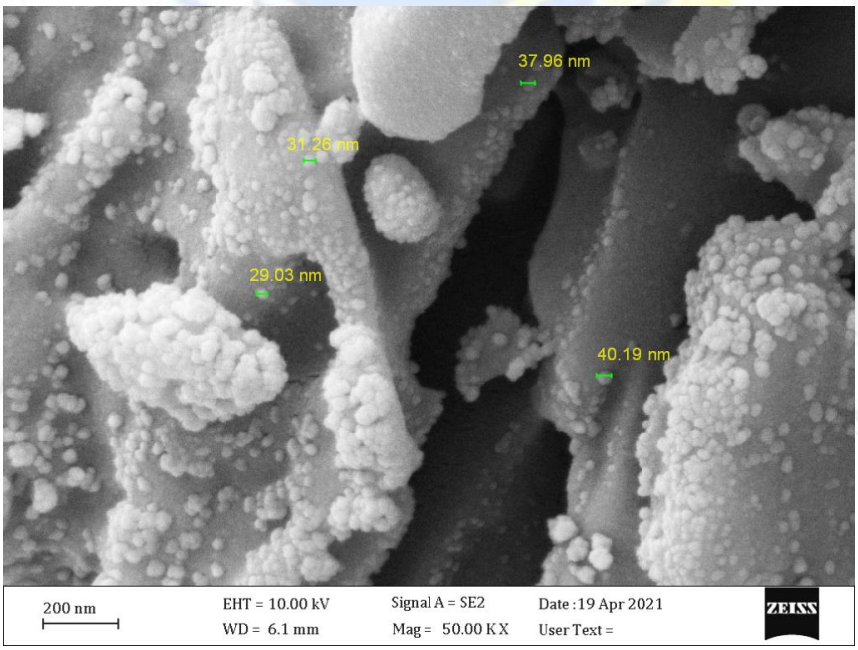


Fig.6. XRD pattern of CdO NPs calcinated at 400 ºC for 2 h

The Field Emission Scanning Electron Microscope micrograph of the $Cd(OH)_2$ and CdO nanoparticles shown in Fig. 7 and 8.

In figure 7, The morphology of the $Cd(OH)_2$ nanoparticles showed small sized, quasi-spherical particles of average diameter 29– 40 nm and observed that cadmium hydroxide nanoparticles are uniform, homogeneous and have been distributed separately. Strong preference for self-assembly of these particles [11].



The FE-SEM image of the CdO nanoparticles corresponding to the XRD pattern in Fig. 6 is shown in Fig. 8, it is clear that the prepared CdO nanoparticles have regular spherical shape and uniform size, with an average size of 43 nm.

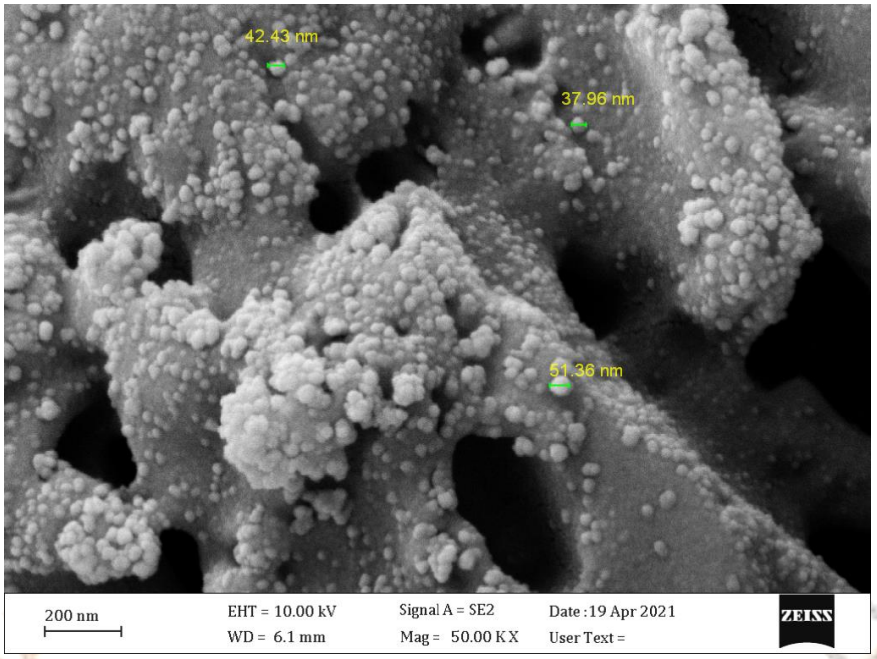


Fig.8. FE-SEM analysis of CdO NPs

4.1. Adsorption of Pb^{+2} and Co^{+2}

The removal of lead and cobalt ions using CdO NPs was calculated under a contact time (0–60) min., dosage of CdO NPs (0.1–1) g/100ml, and concentration of metals (10–100) mg/L. The percentage adsorption of Pb+2 and Co+2 ions from the solution (R%) and capacity of adsorption by CdO NPs qe (mg/g) were calculated according to Eq. (1) and Eq. (2), respectively [12].

$$R\% = (C_o - C_e)/ C_e * 100 \quad \text{-----1}$$

$$qe = V(C_o - C_e)/ m \text{ ------2}$$

Where: C_o corresponds to the lead and cobalt ions initial concentration and C_e is the residual concentration after adsorption, V is the solution volume (L), m is the mass of adsorbent (g).

4.1.1. Effect of Contact Time on Adsorption- The influence of contact time on adsorption of Pb^{+2} and Co^{+2} ions on CdO nanoparticles was investigated in the range of 0–60 min. Other conditions were constant (adsorbents 0.5 g/100 ml, initial metal concentrations 50 mg/l at a temperature of 25°C).The effect of contact time on the removal of metal ions is shown in Figure 9. It was observed that the adsorption of Pb^{+2} and Co^{+2}adsorption increased along with the contact time. The equilibrium was achieved at 45 min, because there were plenty of wide surface areas available. The adsorption rate becomes very slow as contact time increases due to the saturation of active sites of CdO NPs at equilibrium state. The maximum removal efficiencies for Pb^{+2} and Co^{+2} ions was 91.23% and 90.59% at optimum time 45 min.

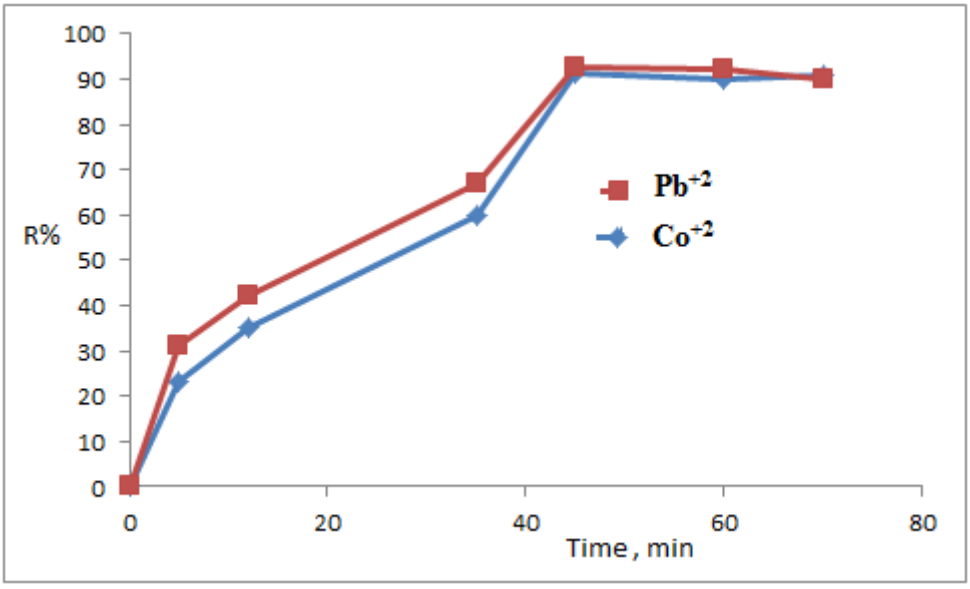


Fig.9. The effect of contact time on the % removed of Pb^{+2} and Co^{+2} by CdO NPs

4.1.2.Effect of Adsorbent Quantity on Adsorption-Through this study it was found that the capacity of adsorption of metal ions was highest when using the amount of 0.5g of CdO NPs. The influence of adsorbent quantity on the uptake of the Pb^{+2} and Co^{+2} ions are shown in figure 10, with increasing the quantity of samples, the lead and cobalt ions removal will increases too, this means that the increase the amount of CdO NPs increases the concentration removal of metal ions from wastwater. The effect of the adsorbent quantity of Pb^{+2} and Co^{+2} ions removal on the CdO NPs surfaces, was studied using different amount of the adsorbent (, 0.1, 0.2, 0.3, 0.4 and 0.5) g at (298) K, fixed concentration of metal ions (50) mg/L, contact time for each samples are (60) min.

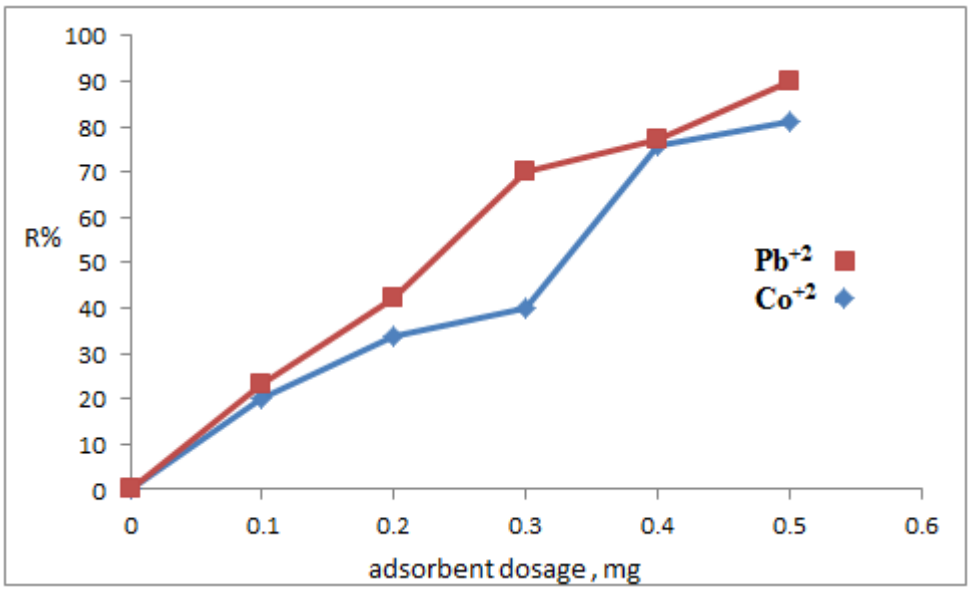


Fig.10. The effect of adsorbent quantity on the percent removed of Pb^{+2} and Co^{+2} ions by CdO NPs

4.2. Adsorption Kinetics

To investigate the adsorption process of metal ions onto synthesized CdO NPs, pseudo-second-order kinetic (2^{nd}) [9,12] was applied to the experimental data.

The pseudo-second-order kinetic model is shown as;

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t, \quad \text{.....3}$$

Where q_2 is the maximum adsorption capacity (mg g^{-1}) for the pseudo-second-order adsorption and k_2 is the equilibrium rate constant for the pseudo-second-order adsorption (gmg^{-1} min^{-1}),

The pseudo-second-order model assumed that the adsorption; in general, might be second order, the rate limiting step may be chemical adsorption involving sharing or exchange of electrons between the solid adsorbent and divalent lead and cobalt ions.

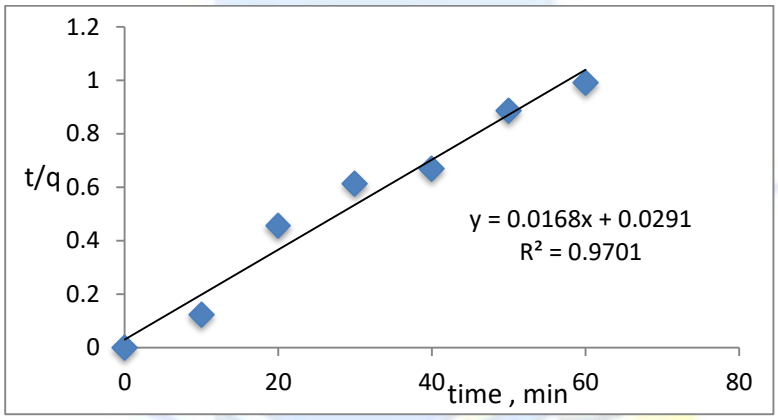


Fig11. Pseudo-second order plots for lead ion adsorbed on CdO NPs

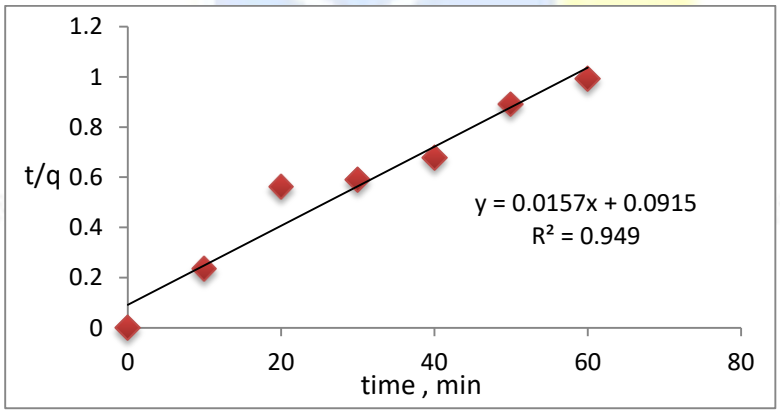


Fig11. Pseudo-second order plots for cobalt ion adsorbed on CdO NPs

5. Conclusions

The feasibility of using CdO NPs as adsorbent for the removal of Pb^{+2} and Co^{+2} ions from wastewater was investigated in this study. CdO nanoparticles were found to be a good efficient sorbent for removing these heavy metals ions from wastewater under the following optimum conditions: initial concentration 50 mg/L, , contact time 60 min and CdO NPs dosage 0.5 g/100 Ml at a temperature of 25°C. The batch experiments results showed that the maximum removal percentages achieved under optimum conditions for Pb^{+2} and Co^{+2} ions were 91.23% and 90.59%, respectively. The pseudo-second order was shown to have a high degree of fitness based on kinetic data. The UV-visible, FTIR, XRD and FE-SEM analyses revealed that the functional groups on the surface of CdO nanoparticles were detected and the morphology of the surface was studied.

6. References

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