



Facile Preparation of Copper and Tin Oxide Nanoparticles as Efficient Adsorbent of Heavy Metals from Wastewater

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Abstract: Heavy metal removal from waste water is essential to solve the global water crises. Transition metal oxide nanoparticles are promising candidates for these applications. Herein, Copper oxide and Tin oxide nanoparticles have been prepared via Facile and economic perception method starting from commercial precursors. The obtained nanoparticles were in flack-like shape and spherical shape for Copper oxide and Tin oxide nanoparticles, respectively. All prepared nanoparticles are in crystalline phases, where the prepared Copper oxide and Tin oxide nanoparticles were in monoclinic and tetragonal crystalline phases, respectively. The crystal size of Copper oxide and Tin oxide nanoparticles were 12 nm and 13 nm respectively. Cd and Pb ions were removed from wastewater by the obtained Copper oxide and Tin oxide nanoparticles. The adsorption processes were studied under various parameters, such as; contact time and pH values. The highest removal uptake was about ~99% of Pb ions were recorded for Copper oxide nanoparticles. This uptake process carried out after 30 min in a neutral medium (pH 7). While, Tin oxide nanoparticles removed about ~94% at the same conditions. On the other hand, Copper oxide nanoparticles removed about ~57% from Cd ions. This uptake process carried out after 30 min in a partially acidic medium (pH 6). While, Tin oxide nanoparticles removed about ~54% at the same conditions. Finally, it is highly recommended to use Copper oxide and Tin oxide nanoparticles as promising adsorbents for heavy metal removal applications.

Keywords: Copper Oxide Nanoparticles, Tin Oxide Nanoparticles, Heavy Metal Removal

1. Introduction

Water is the most essential resource for all types of life on earth. So, the availability of clean and affordable water is considered as the the most basic humanitarian goals, and remains a global basic challenge.

The current water supplies face massive challenges. Therefore, it is critical to apply a basic water treatment in the affected areas. Generally, human activities play a greater role in exacerbating water scarcity by contaminating natural water sources [1].

Industrial wastewater considered as one of the main pollution sources of water. Most of industrial wastewater was

discharged into natural water sources, such as; rivers, lakes and coastal areas. These caused serious pollution problems in the water environment, and therefore, grate negative effects to the eco-system and human's life. The industrial wastewater contains significant quantities of heavy metals, such as; copper, cadmium, zinc, silver, lead, chromium, nickel, vanadium, platinum, and titanium. Heavy metals-contaminated is produced from different industries, such as; anodizing-cleaning, electroplating, electro less depositions, milling, conversion-coating, and etching [2, 3].

Since, heavy metals considered as non-biodegradable and potentially toxic elements. They cannot be degraded or destroyed naturally unlike organic pollutants therefore persist in our environment so pose a different kind of challenge for

remediation [4].

Heavy metals are dangerous especially when they contaminate the aquatic ecosystem, the main source of heavy metals may be industrial or consumer wastes releasing heavy metals into rivers, streams, lakes, and groundwater [5].

Heavy metals pollutants cause serious health deceases, including reduced growth and development, cancer, organ damage, liver damage, nervous system damage, anemia, diarrhea, insomnia, nausea, Wilson's disease, gastrointestinal (GI) disorders, stomatitis, tremor, ataxia, paralysis, vomiting and convulsion, depression and death. Exposures to some even small dose of heavy metals, such as; lead and mercury may consider as a reason of autoimmunity development, where a human's immune system attacks its own cells. This phenomena cause various diseases, such as; kidney diseases, and rheumatoid arthritis. Children may receive higher doses of these heavy metals than adults, since they consume more food for their growth than adults [6].

In recent years, several techniques for the removal of heavy metals from the wastewater are development such as Chemical precipitation [7, 8], ion- exchange [9], reverse osmosis [10], and adsorption [6, 11].

There are many recent studies indicating that many of the nano metal oxides show a very favorable absorption of heavy metals in terms of high capacitance and selectivity, which may lead to deep removal of toxic metals to meet increasingly stringent regulations. They are considered as a promising adsorbent for water treatment applications due to their enormous surface area which could be increased by using various functionalized groups.

Metal oxides nanoparticles are effective, economic adsorbents for various pollutants, such as; dyes and heavy metals. The adsorption process is mainly controlled by complexation between ion pollutant and the oxygen in metal oxides [12].

Metal oxide nanoparticles could be used in various applications such as gas sensors, solar energy conversions biomedical, adsorbents, catalysis, pharmaceutical products, semiconductors, surface coatings, and in the medical.

Metal oxides nanoparticles demonstrate high removal efficiency of heavy metal from wastewater, due to their high surface area and much more surface active sites comparing to bulk materials [13].

Regarding to heavy metal pollutions, there has been a rising interest recently for the development of materials capable of removing these pollutants. Currently, metal oxides nanoparticles, such as; zinc oxide, ferric oxides, copper oxide, manganese oxides, magnesium oxides aluminum oxides, titanium oxides, and cerium oxides are identified as promising adsorbents for heavy metal removal from aqueous systems [14, 15].

Among all metal oxide nanoparticles we will focused CuO, SnO₂, where CuO-NPs attracts attention because of its large surface area, enhanced oxygen adsorption capability. Due to its high surface these nanoparticles are considered as promising candidate with enhanced photocatalytic activity [16]. The copper oxide nanoparticles (CuO-NPs) possess a

wide range of applications, using in removal of dyes [17], gas sensors [18], solar energy transformation [19], and remove heavy metals [20].

Tin oxide (SnO₂) is consider one of the most nanoparticles to be inspected recently; SnO₂ nanoparticles is a n-type semiconductor, which could be used in various applications such as in solid-state gas sensors [21], transparent conducting electrodes [22], rechargeable Li batteries [23, 24], and optical electronic devices [25], and as pollutant adsorbent, such as; heavy metal ions and dyes [26, 27], however the available literature on adsorption of heavy metal ions by Tin oxide nanoparticles is limited.

The current research aims to study the effect of nano copper oxide and tin oxide nanoparticles as adsorbent for lead and cadmium from wastewater. Hence, this study aims to study the adsorption behavior of lead and cadmium ions from water using the synthesized CuO and SnO₂ nanoparticles under different operating conditions to determine the optimum conditions for Pb and Cd removal. So, in order to determine the optimum condition for removing lead and cadmium from solution, adsorption studies were performed by evaluating various parameters, such as: pH, contact time, and initial concentration of lead and cadmium, adsorbent doses.

2. Materials and Methods

2.1. Chemicals and Reagents

The chemicals used in the experiment are analytic reagent grade. Copper(II) nitrate trihydrate Cu (NO₃)₂•3H₂O (98%) (Sigma-Aldrich), poly ethylene glycol (PEG) (Mwt 10000) (PANREAC, Spain), Tin (II) Chloride dehydrate SnCl₂•2H₂O (98%-101%) (Merck), Ethylene glycol, Ammonium hydroxide solution NH₃OH (25%) (Sigma Aldrich, Germany), Lead (II) Nitrate Pb(NO₃)₂ (99.9%) (Wako), Cadmium Chloride 2.5-Hydrate (99.9%) (Wako), sodium hydroxide (NaOH) (Extra pure) (Oxford), hydrochloric acid (HCl) (37%) (Fisher Scientific).

In all experiments double water distilled water was used, prepared and diluted and used to wash all glass.

2.2. Copper Oxide Nano-particle Preparation

Copper oxide Nano-particles were been prepared as following; 0.725 g of Cu (NO₃)₂•3H₂O was dissolved in 50 ml of PEG (poly ethylene glycol) was added into the solution. Then, sodium hydroxide (NaOH) added during stirred until the pH 11. During that, the mixture was heated in the microwave oven radiation with power 900 W for 1.45 minutes until complete dryness of the mixture then the precipitates were filtered and then washed by distilled water. The precipitate was dried in an oven for three hours at 75°C.

2.3. Tin Oxide (SnO₂) Nano-particle Preparation

Tin Oxide (SnO₂) Nano-particle were been prepared as following; 50 ml (0.1) of SnCl₂•2H₂O mixed with 10 ml of Ethylene glycol. Then added, Ammonium hydroxide solution (NH₃OH), during stirred until the pH 8. During the mixing

process the mixture was heated in the microwave oven radiation with power 900 W for 3 minutes until complete dryness of the mixture then the precipitates were filtered and then washed by distilled water. The precipitate was dried in an oven for three hours at 75°C.

2.4. Adsorption Procedure

The adsorption experiments of (Cadmium or Lead) removal from the polluted waste water using synthesized nanoparticle (Copper oxide or Tin oxide) as adsorbent materials.

The adsorption test was performed according to the following methodology:

Batch adsorption experiments were carried out at room temperature by shaking solution flasks at 150 rpm containing fixed dose of adsorbent (0.1g-0.4g) of (nanoparticle Copper oxide or Tin oxide) in (50) ml a predetermined concentration (25ppm-100ppm) of Cadmium or Lead metal solution during certain time and various pH (3-11) Experiments were carried out at initial pH value 7 for cadmium and 6 for lead. After finishing the mixing time intervals the adsorbent materials were separated from waste water contain (cadmium or lead) heavy metal by Centrifuge. Then the cadmium or lead heavy metal concentrations were determined after and before the treatment process using Inductive Coupling Plasma-Optical Emission Spectroscopy Optima (8300) (ICP-OES). The percentage of ions removal using each adsorbent material separately was determined using the following equation [28]:

$$\%R = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

Where R is the cadmium or lead removal, C_o and C_e are the initial and final concentration of the metal ions in solution, respectively.

In order to calculate the uptake capacity of the metal ion, the up take amounts per gram of prepared adsorbent material was evaluated from the change in solution concentration using the following equation [29]:

$$Q(\text{mg/g}) = \frac{V(C_o - C)}{M} \times 100 \quad (2)$$

Where Q is the uptake capacity (mg/g), V is the volume of the solution (ml) and M is the mass of the solid material (g).

3. Results and Discussion

3.1. Characterization of Adsorbents

3.1.1. X-Ray Diffraction Analyses

Figure 1 shows the XRD patterns of the prepared nanoparticles. The prepared CuO nanoparticles were highly crystalline than SnO₂ nanoparticles. Figure 1-a confirm that CuO nanoparticles was successfully synthesized by precipitation method using microwave heating technique. It is clearly noticed that the prepared sample are identical to the mono-phase of CuO with a monoclinic structure (ICDD card No. 048-1548). Figure 1-b confirm that SnO₂ nanoparticles

was successfully prepared by sol-gel method using microwave heating technique and the diffraction peaks indexed to the tetragonal SnO₂ phase (JCPDS Card No. 88-0287).

These results are in a good agreement with those published by other researchers [30, 31], as summarized in table 1.

The crystalline size of the prepared nanoparticles was calculated for XRD data by using Debye Scherer equation [20]:

$$D = 0.9\lambda / \beta \cos\theta \quad (3)$$

Where λ is the X-ray wave length, θ is the Bragg angle, β is the line broadening at half the maximum intensity in radians.

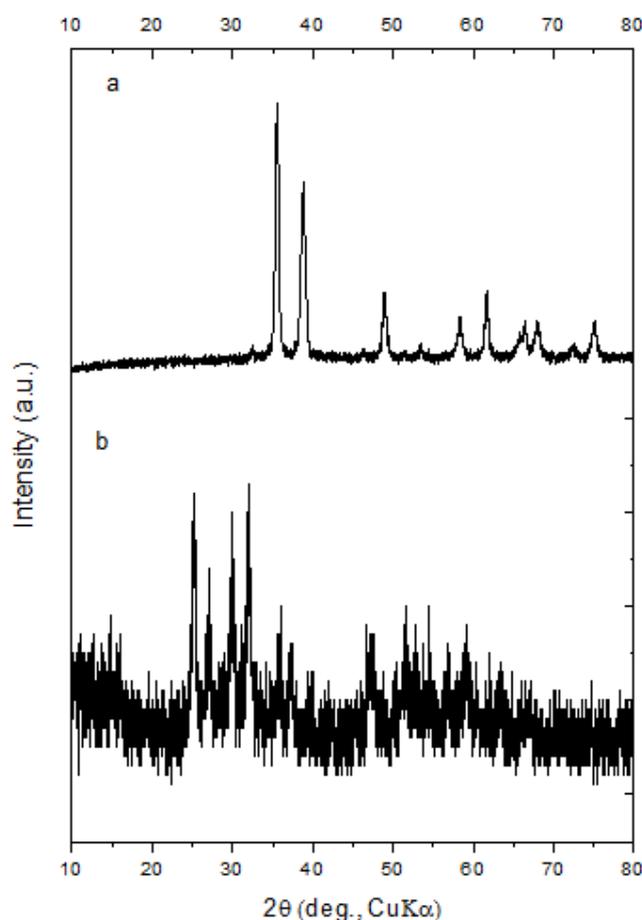


Figure 1. XRD patterns of prepared (a) CuO and (b) SnO₂ nanoparticles.

Table 1 summarizes the structural data of the prepared CuO and SnO₂ nanoparticles comparing to literature survey.

3.1.2. Scanning Electron Microscopic (SEM) Analyses

To evaluate the morphology of the prepared nanoparticles, CuO and SnO₂ nanoparticles were characterized by scanning electron microscopy (SEM). Figure 2 shows the SEM micrographs of the prepared nanoparticles. The prepared CuO nanoparticles were in large flake-like shape figure 2-a, while the prepared SnO₂ nanoparticles were in small spherical shape figure 2-b. These findings are in a good agreement with those published by other researchers [30, 31], as summarized in table 1.

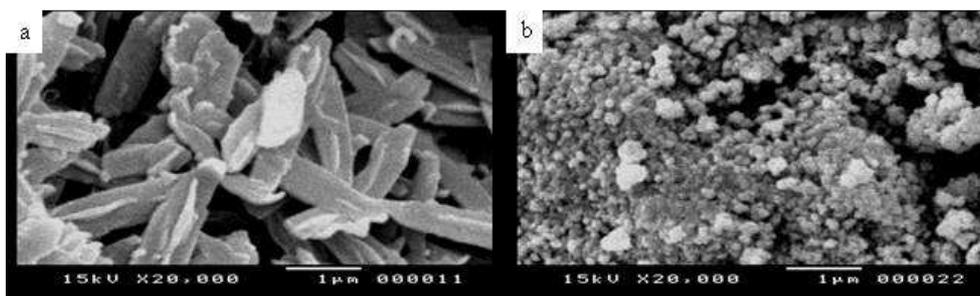


Figure 2. SEM micrographs of the prepared (a) CuO and (b) SnO₂ nanoparticles.

Table 1. The crystalline data of the prepared CuO and SnO₂ nanoparticles comparing to literature survey.

Nanoparticles	Crystalline phase	Crystal size (nm)	morphology	application	Reference
CuO	monoclinic	12	large flake-like shape	Water treatment	Current work
SnO ₂	tetragonal	13	small spherical	Water treatment	Current work
CuO	monoclinic	25	porous balls	N/A	[30]
SnO ₂	tetragonal	10	spherical	Water treatment	[31]

3.2. Adsorption Studies of Cadmium and Lead on CuO Nanoparticles

3.2.1. Effect of Contact Time

The removal of heavy metal (Cd and Pb) from aqueous solution was studied as function of contact time in the range of (0-120) min at (25) ppm initial concentration for both, pH 7 for Cd pH 6 for Pd at room temperature.

Figure 3 shows the effect of contact time on the adsorption of both of Cd and Pb using the prepared CuO nanoparticles as adsorbents. It is noticeable that, the adsorption of Pb is higher than Cd for CuO nanoparticles, Cadmium and Lead ions were rapidly removed by CuO nanoparticles (at 30 mints).

The adsorption rate could be classified into two main stages. In the first stages, the adsorption efficiency of the pollutants ion by the CuO nanoparticles increased rapidly due to the abundant availability of active binding sites on the CuO nanoparticles, and with gradual occupancy of these sites, the adsorption efficiency decreased in the last stages [32]. That means that the equilibrium status can be achieved after 30 minutes for both.

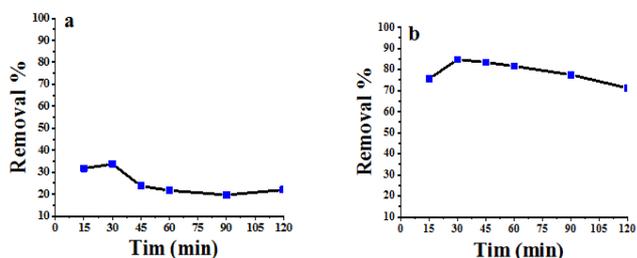


Figure 3. Graphical representation which shows the effect of contact time on the adsorption of (a) Cd@CuO (b) Pb @CuO. at adsorbent weight=0.1 g, 25 ppm initial concentration for both, pH 7 for Cd pH 6 for Pd, at room temperature.

3.2.2. Effect of pH Values

The creation of adsorbed sites depends mainly on the value

of solution pH. Where, the active sites on the surface of adsorbent can either be protonated or deprotonated with hydrogen and hydroxide ions. By other words, the surface charge of the adsorbent may be influenced by different values of solution pH [33].

Removal of (Cd and Pb) from aqueous solution was studied as function of pH in the range of (3-11) at (25) ppm concentration, contact time 30 mint, at room temperature. Figure 4 shows the effect of pH values on the adsorption of both of Cd and Pb using the prepared CuO nanoparticles as adsorbents. It is noticeable that, the highest adsorption values were recorded at alkaline media. On the other hands, hydrogen ion concentration (pH value) is considered as the main important parameters that affect the adsorption process of pollutants ions from wastewater. This is may be due to that, the solubility of the metal ions is mainly affected by the solution pH value. In addition to, hydrogen ion concentration may substitute some positive ions found in the active sites and impact the degree of ionization of the adsorbate during the reaction [34].

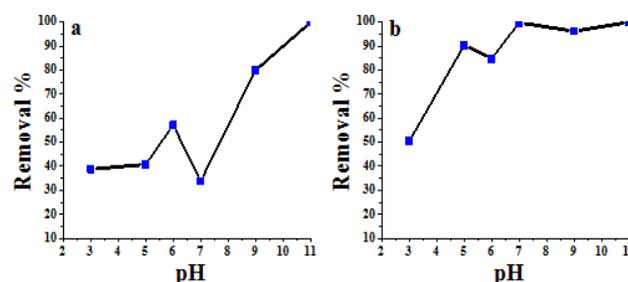


Figure 4. Graphical representation which shows the effect of pH values on the adsorption of (a) Cd@CuO (b) Pb @CuO. at adsorbent weight=0.1 g, 25 ppm initial concentration for both, contact time 30 min for both, at room temperature.

Figure 4-a Show the removal of Cd ions by CuO nanoparticles upon the initial pH on the sorption in range of (3-11). The metal removal from solution at pH beyond 8 did not provide any accurate results, where the pollutants ions are

precipitated as hydroxides. Therefore, the removal curve increased due to there was not Cadmium ions to be removed. By other words, the solution seems to be clear because of the metal precipitation [35]. The effect of pH on the adsorption behavior of nano CuO for Cd was shown in Figure 4. The initial pH of the solution significantly affected the adsorption capacity of the adsorbent, Removal of Cd ions increases gradually with increasing solution pH from 3 to 6. The maximum recorded value was reached at pH of 6. So, it was considered as optimum condition. At lower pH values, the metal ion removal was limited; this is due to the presence of H^+ ions which compete with the Cd ions for the adsorption sites.

The effect of initial pH on the adsorption of Pb ions onto CuO nanoparticles was evaluated within the pH range of (3-11) figure 4-b. Removing metal from solution at pH beyond 8 did not provide any accurate results, where the pollutants ions are precipitated as hydroxides. Therefore, the removal curve increased due to there was not Lead ions to be removed. By other words, the solution seems to be clear because of the metal precipitation [35]. Figure 4 shows the adsorption behavior of Pd ions by CuO nanoparticles upon changing initial solution pH value. It's clear that the initial solution pH value has a remarkable effect on the adsorption capacity. Removal of Pd ions increases gradually with increasing solution pH from 3 to 7. The maximum recorded value was reached at pH of 7. So, it was considered as optimum condition. At lower pH values, the metal ion removal was limited; this is due to the presence of H^+ ions which compete with the Pd ions for the adsorption sites.

3.3. Adsorption studies of Cadmium and Lead on SnO_2 Nanoparticles

3.3.1. Effect of Contact Time

The removal of heavy metal (Cd and Pb) from aqueous solution was studied as function of contact time in the range of (0-120) min at (25) ppm initial concentration for both, pH 7 for Cd pH 6 for Pd at room temperature.

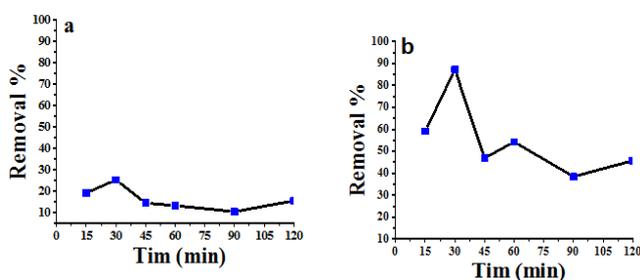


Figure 5. Graphical representation which shows the effect of contact time on the adsorption of (a) Cd@ SnO_2 (b) Pb @ SnO_2 . at adsorbent weight=0.1 g, 25 ppm initial concentration for both, pH 7 for Cd pH 6 for Pd, at room temperature.

Figure 5 shows the effect of contact time on the adsorption of both of Cd and Pb using the prepared SnO_2 nanoparticles as adsorbents. It is noticeable that, the adsorption of Pb is higher than Cd for SnO_2 nanoparticles, Cadmium and Lead was rapidly removed by SnO_2 nanoparticles (at 30 mints).

The adsorption rate follow the same sequence described earlier [32]. That means that the equilibrium status can be achieved after 30 minutes for both.

3.3.2. Effect of pH Values

The creation of adsorbed sites depends mainly on the value of solution pH. Where, the active sites on the surface of adsorbent can either be protonated or deprotonated with hydrogen and hydroxide ions. By other words, the surface charge of the adsorbent may be influenced by different values of solution pH [33].

Removal of (Cd and Pb) from aqueous solution was studied as function of pH in the range of (3-11) at (25) ppm concentration, contact time 30 mint, at room temperature. Figure 6 shows the effect of pH values on the adsorption of both of Cd and Pb using the prepared SnO_2 nanoparticles as adsorbents. It is noticeable that, the highest adsorption values were recorded at alkaline media. On the other hands, hydrogen ion concentration (pH value) is considered as one of the most important parameters that influence the adsorption behavior of pollutants ions from wastewater. It influence the solubility of the metal ions in the solution, replaces some of the positive ions found in the active sites and affects the degree of ionization of the adsorbate during the reaction [34].

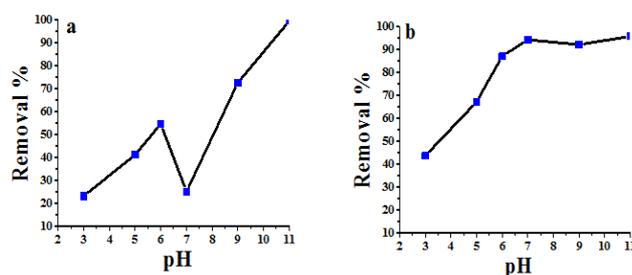


Figure 6. Graphical representation which shows the effect of pH values on the adsorption of (a) Cd@ SnO_2 (b) Pb @ SnO_2 . at adsorbent weight=0.1 g, 25 ppm initial concentration for both, contact time 30 mint for both, at room temperature.

Figure 6-a Show removal of Cd ions by SnO_2 nanoparticles at the initial pH on the sorption in range of (3-11). The metal removal from solution at pH beyond 8 did not provide any accurate results, where the pollutants ions are precipitated as hydroxides. Therefore, the removal curve increased due to there was not Cd ions to be removed. By other words, the solution appears to be clear because of the metal precipitation [35]. Figure 6 shows the adsorption behavior of Cd ions by SnO_2 nanoparticles upon changing initial solution pH value. It's clear that the initial solution pH value has a remarkable effect on the adsorption capacity. Removal of Cd ions increases gradually in solution with increasing pH from 3 to 6. The maximum recorded value was achieved at pH of 6. So, it was considered as better condition. At lower pH values, the metal ion removal was limited; this is due to the presence of H^+ ions which compete with the Cd ions for the adsorption sites.

Figure 6-b Show removal Pb ions by SnO_2 nanoparticles at

pH range (3-11). The metal removal from solution at pH beyond 8 did not provide any accurate results, where the pollutants ions are precipitated as hydroxides. Therefore, the removal curve increased due to there was not Lead ions to be removed. By other words, the solution appears to be clear because of the metal precipitation [35]. Figure 6 shows the adsorption behavior of Pd ions by SnO₂ nanoparticles upon changing initial solution pH value. It's clear that the initial solution pH value has a remarkable effect on the adsorption capacity. Removal of Pd ions increases gradually with

increasing solution pH from 3 to 7. The maximum recorded value was reached at pH of 7. So, it was considered as optimum condition. At lower pH values, the metal ion removal was limited; this is due to the presence of H⁺ ions which compete with the Pd ions for the adsorption sites.

Table 2 summarized the optimum adsorption conditions for all studied samples. The highest adsorption was recorded for sample CuO where removed 99.7% of Lead ions from wastewater. The optimum adsorption conditions were Contact time 30 mint and PH 7.

Table 2. The optimum adsorption conditions.

Sample code	Adsorbent	Pollutant	Highest adsorption R%	Adsorption conditions
Cd@CuO	CuO NP	Cd	57.14%	Contact time 30 mint and PH 6
Pb@CuO	CuO NP	Pb	99.7%	Contact time 30 mint and PH 7
Cd@SnO ₂	SnO ₂ NP	Cd	54.75%	Contact time 30 mint and PH 6
Pb@SnO ₂	SnO ₂ NP	Pb	94.34%	Contact time 30 mint and PH 7

4. Conclusion

Facile and economic perception method had been used to precipitate crystalline Copper and Tin oxide nanoparticles where CuO and SnO₂ nanoparticles with different morphologies have been synthesized by precipitation and sol gel method respectively using microwave heating technique. The produced CuO and SnO₂ nanoparticles were characterized by XRD and SEM. The XRD patterns and SEM micrographs approve the structure of the prepared pure CuO and SnO₂ nanoparticles.

Nanoparticles supply an efficient mechanism for the adsorption of Pb and Cd heavy metals from wastewater. In this research, CuO and SnO₂ nanoparticles have been used as adsorbent in batch adsorption experiments for the removal of lead and cadmium from aqueous solutions.

The adsorption behavior has been tested under various conditions, such as; pH values, contact time. The obtained results can be summarized as: The highest adsorption for both Pb and Cd were recorded after 30 minutes. The pH experiments showed that the governing factors affecting the adsorption characteristics of all CuO and SnO₂ nanoparticles are competition of the H⁺ ions with metal ions at low pH values, maximum adsorption at pH 7 for lead and 6 for cadmium. Removal percentage% of lead and cadmium heavy metals was found to increase, reach a maximum value with increase in contact time and pH values. These oxide nanoparticles are highly recommended to be applied in water treatment applications.

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