Preparation of nanoparticles from CaO and use it for removal of chromium (II), and mercury (II) from aqueous solutions.

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Abstract. Calcium oxide (CaO) nanoparticles were prepared by the sol-gel strategy from CaCl₂ and calcinated the gathered powder at various temperatures (400, 500 and 600°C). Additionally, the basic qualities for the readied sorbent were researched by methods for powder X-beam diffraction examination (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM) while the textural properties were resolved from low temperature adsorption of N₂ at -196 °C. Great outcomes were acquired under the proper conditions. The capacity of CaO nanoparticles for evacuation of some overwhelming metal particles as chromium (II) and mercury (II) from aqueous solutions through adsorption has been researched. Every one of the analyses was completed by batch method. The impact of pH (2, 5, 7, 8 and 10), stirring time, temperature and the presence of different foreign ions has been researched. The expulsion rate going to 100 % of various metal particles at pH7, stirring time 30 min, room temperature (≈ 25°C) was accomplished and adsorbent dose 30 mg.

Keywords: Adsorption, nano-CaO, XRD, chromium (II) and mercury (II).

1. Introduction
The heavy metals pollution is of prevailing worry between the kinds of natural pollution because heavy metals have high toxicity. They don't molder into nontoxic items in water sources and gather in living bodies and acquiring high rate by the food chain [1]. Chromium has been broadly utilized in different businesses like material, cowhide, concoction industry, metal completing, paint industry and numerous different ventures [2]. Since chromium is a need dangerous, mutagenic and cancer-causing substance when present in overabundance, it is particularly required to expel chromium from effluents previously enabling it to enter any water framework or on to arrive [3]. Mercury has been perceived to make both intense and perpetual poisonous quality the focal sensory system, kidneys, lung tissues, and concepitive framework [4,5]. It might enter the body through gastrointestinal ingestion, skin contact, or aspiratory inward breath. Subsequent to entering the human body, mercury circles in the blood and is put away in the liver, kidneys, cerebrum, spleen, and bone, along these lines prompting a few medical issues, for example, loss of motion, genuine intestinal and urinary complexations, brokenness of the focal sensory system, and, in more serious instances of inebriation, demise, broadly known as the Minamata Bay mischance, Japan, in 1956 [6]. The removal of chromium (II) and mercury (II) particles from any sample of watery by exemplary techniques incorporates its deposition with soluble base hydroxide or lime, ion exchange, reverse osmosis and electrolytic precipitation[7]. These great techniques are costly and have a lot of disadvantages, for example, production of metal-bearing sludge or wastes, imperfect metal elimination and the elimination of secondary waste[8]. Among the traditional techniques of removing the heavy metal ions, adsorption method has been widely studied because it is easy to operate, efficient process and economical that can be used for the removal of chromium (II) and mercury (II) ions from aqueous solution[9,10]. Calcium oxide (CaO) is an important industrial compound, which is used as toxic-waste treatment agent,
catalyst, in paint as well as for other major applications and a collective in refractory, [11,12]. In addition, nanoparticles of metal oxide can be used as bactericide adsorbent. Calcium oxide (CaO) can show tremendous capacity and great as a dsorbent for many toxic chemicals [13,14]. Therefore, the purpose of this study is to reach a method characterized by speed, simplicity and high sensitivity to remove chromium (II) and mercury (II) ions from aqueous solutions by use nanoparticles of calcium oxide (CaO) and know the best appropriate conditions.

2. Experimental part
2.1. Materials
Stock solution (100 mg/l) of chromium (II) was production from (CrCl$_2$), stock solution (100 mg/l) of mercury (II) was production from (HgCl$_2$). CaCl$_2$ salt was utilized for the planning of sorbent. 100 mg/l of different particles stock solution was set up by gauging the asked for a sum in refined water. The anions were used as their potassium or sodium salts while the metal salts were used as their chlorides. Standard solution of HCl and NaOH were used for pH alterations. Every working solution was prepared by diluting with distilled water.

2.2. Preparation of nano-CaO sorbent
A proper quantity of CaCl$_2$ was a thaw in water and warmed to 40 °C. Then add 20 ml of NaOH (0.1M) to the solution when it was being mixed quickly. Following 30 minutes the response was warmed, sifting and washing at pH value was approximately eight were completed. Thus the forerunners of CaO such as Ca (OH)$_2$ was created which left for 24 hours at 65°C ±5°C to be dried. The dried antecedents were calcinated at 600,500 and 400 °C for 2 hours, Calcium oxide powder was created [13, 14]. The ionic condition of the response is as following:

\[
3 \text{ Ca}^{2+} + 6 \text{OH}^- \rightarrow 3 \text{Ca(OH)}_2 \rightarrow 3 \text{CaO} + 3 \text{H}_2\text{O}
\]

2.3. Sorbent characterization
Using a Philips PW 105 diffractometer using (Ni-sifted Cu Ka) radiation (1.540 A) at 45 keV, 35 mA, was recorded X-ray diffraction model of the adsorbent which prepared, and an examining range two hours of 18-80°. SEM (scanning electron microscope) it was implemented by using (a Jeol JSM-840) under high discharge, at an voltage of 200 keV. TEM (transmission electron microscopy) it was implemented by using a JEOL 2012 instrument with settling power 0.3 nm, the quickening strain being 220 keV. The specimens were kept onto carbon ribbon and covered with gold in a Blazers plasma sputtered (30 s at 35 mA). The area of surface of the readied adsorbent was calculated from(N$_2$) nitrogen adsorption contemplates led at(-195°C) using the high discharge traditional volumetric glass framework (BET).before to any adsorption estimation, the sample was removed excess gas at 300°C for 4 hours under a lessened pressure of 15-10 Torr.

2.4. Batch adsorption studies
The impact of different exploratory parameters, for example, the stirring time, temperature and the presence of different foreign ions have been investigated. For each test, 50 ml of a sample contains (chromium and mercury particles solution of a specific focus + a known amount from CaO sorbent) was taken in a 100 ml measuring utensil and afterward mixing happens with nonstop air stream rises at 250 rpm for a coveted time to realization equilibrium adsorption and to generate calcium carbonate formation at room temperature. Toward the finish of the required time interims, the sample was taken out and the solution was isolated from the adsorbent by sifting through a Whatman channel paper. The recuperation level of chromium and mercury particles (Removal%) was ascertained by the accompanying condition:

\[
\text{Removal\%} = \frac{(\text{Co} - \text{Ce})}{\text{Co}} \times 100
\]

Where: Co residual concentrations (mg/l) chromium and mercury particles separately.
2.5. Method for determination

The remaining concentration of chromium and mercury particles in the filtrate were measured by GBC, Sensia Series Atomic Absorption Spectrometry (electronic AAS) with an air-acetylene fire under the ideal instrumental conditions as appeared in table 1.

|               | Cr  | Hg  |
|---------------|-----|-----|
| Wave length, nm | 540 | 307.5 |
| Sensitivity, µg/ml | 0.04 | 0.020 |
| Working calibrating range, ppm | 3-10 | 2-6 |

Table 1. Optimum instrumental conditions of chromium and mercury.

3. Results and discussion

3.1. Calcination temperature effect on the prepared CaO nanoparticles

The (XRD) patterns of calcium oxide nano-particles were calcinated at 600, 500 and 400°C for 2 hours. The patterns show in figure 1, at 400°C has been observed different shapes of diffraction phases become clear at 19, 30 and 32 and in case increasing calcination temperature at (600°C) and (500°C) has been observed raise the crystallization of structure. The distinctness of diffraction peak at 30 with a little background confusion be visible tendency along (111) plane of reversal of cubic phase. Furthermore, transmission electron microscopy morphology of calcium oxide nano-particles calcinated at (500°C) is appeared in figure 2, which confirmed the nanoparticles of calcium oxide with a simple cubic structure and with a high surface area appeared in table 2.

![Fig.1 XRD pattern of nano-CaO sorbent.](image-url)
Fig. 2. A TEM image of nano-CaO sorbent calcinated at 500°C.

3.2. Scanning electron microscope (SEM)
The SEM picture of the sorbent test calcinated at various temperatures is appeared in figure 3 (a, b and c). Breaking down the morphology part of the nanoparticles by the explanation the pictures demonstrates that the combined size nanoparticles are under 100 nm. That implies the incorporated sorbent has nano measurement.

Fig. 3a. SEM image of CaO nanoparticles calcinated at 400°C.

Fig. 3b. SEM image of CaO nanoparticles calcinated at 500°C.
Fig. 3c: SEM image of CaO nanoparticles calcinated at 600°C.

3.3. Surface area measurement

The sorbent surface area was calculated by utilizing diverse techniques include BET strategy, S strategy and T Plot technique. The information got and organized in table 2 as follows:

| Calcination temperature, °C | $S_T$ (m$^2$.g$^{-1}$) | $S_B$ (m$^2$.g$^{-1}$) | $S_{BET}$ (m$^2$.g$^{-1}$) | $r_A$ (Å) | C |
|-----------------------------|------------------------|------------------------|---------------------------|-----------|---|
| 400°C                       | 19.1                   | 18.7                   | 19.6                      | 370       | 10.5 |
| 500°C                       | 72.0                   | 71.0                   | 71.49                     | 12445     | 5.1  |
| 600°C                       | 53.5                   | 52.9                   | 53.81                     | 13500     | 8.87 |

Table 2. Value of surface area calculated by different methods

3.4. Study of adsorption

3.4.1. pH effect

In order to know pH effect on the adsorption of chromium and mercury ions, the dose of adsorbent (30 mg) was related with chromium and mercury ions (10 mg/l) at different values of pH (10, 8, 7, 5 and 2) with 30 min contact time.

As shown in figure 4, the results appeared that the removal of chromium and mercury ions be as follows Cr$^{2+}$ < Hg$^{2+}$. Also, the removal % is low at (PH < 7) where the concentration of H$^+$ ion was high and this means that strong acidic medium, and therefore the surface of sorbent becomes high positive charged, thus lessening the attraction between sorbent and chromium and mercury ions.

When increasing the values of pH, removal % will increase. And be the best and highest proportion at pH range (7-10), and this can be explained as follows:

By with the pH increases (pH>5), the concentration of (H$_3$O$^+$ hydronium ion) is very low, the surface of the sorbent was high negative charged, thus the sites are easily available for chromium and mercury ions binding. So the competition between the proton and the ion is zero or very low, and the removal % chromium and mercury ions is increased then, at pH curve is shifted to alkaline region (pH>8) the removal% of chromium and mercury ions at most remains constant, therefore, the suitable pH of solution for maximum removal of chromium and mercury ions is 7.
3.4.2. The effect of stirring time
The removal % of chromium and mercury particles by calcium oxide nanoparticles as a role of time is exhibited in figure 5. The removal % of metal ions moved toward equilibrium inside 30 min for all chromium and mercury particles. The adsorption was fast at the initial stage because the primary concentration proportionality between the sorbent in solution and the number of active sites available on the sorbent surface at the beginning is very good, thus achieving a state of adsorption equilibrium as a result of the increase in the number of molecules that moves from the bulk liquid to the surface of the sorbent. Therefore, ascertained that 30 minutes and appropriate stirring time for all experiments of chromium and mercury ions at pH 7 in aqueous solutions.
3.4.3. Effect of temperature

The temperature has two most imperative effects on the adsorption procedure. In high temperature is basic to rise the dissemination rate of the adsorbent while differing the temperature will different the equilibrium limit of the adsorbent for a particular adsorbate. In this Investigation, a series of tests were directed on the sorption of 10 mg/l of chromium and mercury particles on 30 mg of sorbent at 338, 318, 298 and 283 K at pH7 and mixing time 30 min to inquire about the effect of temperature on the adsorption elements. The outcomes portrayed in (table 3) demonstrated that the adsorption limit ascends as the temperature rise bolstered that the procedure is endothermic in nature. By doing so, raising the temperature may speed up many slow adsorption steps and lead to the formation of new effective sites. In addition, at high temperature increases the movement of chromium and mercury ions from the bulk of the liquid to the surface of the sorbent. Thus this easy adsorption method possibly can use in industrial wastewater handling for the removal of different metal ions. That is because all the wastewater is hot.

| Temperature, K | Removal % for Hg$^{2+}$ | Removal % for Cr$^{2+}$ |
|---------------|--------------------------|-------------------------|
| 283           | 92.56                    | 99.78                   |
| 298           | 98.5                     | 99.5                    |
| 318           | 100                      | 100                     |
| 338           | 100                      | 100                     |

Table 3. Effect of temperature on the removal of chromium and mercury ions

3.4.4. Effect of various other ions

Under the ideal conditions chose for this search the removal % of 10 mg/l of chromium and mercury ions from an aqueous solution of pH 7 containing 30 mg of the sorbent happened at high concentration (1000 mg/l) of different cations and anions. Every one of the cations was used as their sulfates or chlorides whereas the anions were used as the potassium or sodium salts. The conceivable measures of every particle, giving a mistake of ± 4% in the removal % of chromium and mercury ions are appeared in table 4 checking of the information demonstrate that the removal % of chromium and mercury ions is relatively same amounts in all cases. This demonstrates there is no opposition between all foreign ions with chromium and mercury ions in order to access sorbents active sites.

| Foreign ions (1000 mg/l) | Removal % for Hg$^{2+}$ | Removal % for Cr$^{2+}$ |
|------------------------|-------------------------|-------------------------|
| PO$_4^{3-}$            | 98.9                    | 90.1                    |
| SO$_4^{2-}$            | 97.89                   | 99.6                    |
| Cl$^-$                 | 99.5                    | 99.7                    |
| Mg$^{2+}$              | 98.4                    | 93.5                    |
| Ca$^{2+}$              | 99.9                    | 100                     |
| Mn$^{2+}$              | 100                     | 93.5                    |

Table 4: Effect of various other ions on the recovery of different metal ion
Conclusion

According to this investigation, it could be concluded that:

- nano-CaO that prepared can be used as an effective and inexpensive sorbent for the elimination of different heavy metal ions (Cr\(^{2+}\), Hg\(^{2+}\)) from aqueous solutions.
- The process of adsorption which has advantages (compared to other separation methods) being low cost, easy, less time consuming, and is likely to be incorporated soon as clean water and wastewater treatment technique used in this research.
- The adsorption of metal ions happened mainly at the surface of the generated CaCO\(_3\) adsorbent.
- It happened of and/or deposition of metal hydroxide on the surface of the adsorbent.
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