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Synthesis of Nano-CaO Particles and Its Application for the Removal of Copper (II), Lead (II), Cadmium (II) and Iron (III) from Aqueous Solutions

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CALCIUM oxide (CaO) nanoparticles were synthesized by the sol-gel method from $CaCl_2$ and calcinated the collected powder at different tempratures (400, 500 and 600^oC). Moreover, the structural characteristics for the prepared sorbent were investigated by means of powder X-ray diffraction analysis (XRD), transmission electron microscope (TEM) and scanning electron microscope (SEM) while the textural properties were determined from low temperature adsorption of N_2 at -196 ^oC. Good results were obtained under the appropriate conditions. The ability of CaO nanoparticles for removal of some heavy metal ions as Fe(III), Pb(II), Cu(II) and Cd(II) from aqueous solutions through adsorption has been investigated. All the experiments were carried out by batch method. The effect of stirring time, pH (2, 5, 7, 8 and 10), adsorbent dose (5-40 mg/100 ml), temperature and the presence of different foreign ions has been investigated. The percentage of removal to about 100 % of different metal ions at pH7, room temperature (≈ 25^oC) was achieved, stirring time 30 min and adsorbent dose 30 mg.

Keywords: Sorption, XRD, Aqueous solution and Nano-CaO.

The heavy metals contamination is of dominant worry between the types of environmental contamination due to high toxicity of heavy metals and mobility. They do not decompose into nontoxic products in headwaters and collect in living bodies and obtaining high percentage by the food chain (1) .

Lead is the one of the important metals that is between the toxic heavy metals(2). Acid battery manufacturing, lead mining, printing, metallurgical alloying, glass industries and ceramics are considered the main sources of lead contamination in waste waters(3). The appearance of lead in drinking water at a very low concentration may cause like diseases as hepatitis, anemia, nephritic syndrome and encephalopathy(4). Lead intoxication of human lead to damage to the liver, kidney, brain, nervous system and reproductive system(5). Copper is very prevalent substance which widely used by electrical industries, in antifouling paints and in fungicides, which is considered toxic to humans due to

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*Correspondence author e-mail: shomirage@yahoo.com producing oxidative stress when takeing it up at high concentrations(6). Among the ionic types of copper, Cu(II) ions can have shocking impacts in aquatic solution, attaching easily to inorganic and organic matter based on solution pH(7). Cadmium is a highly toxic metal affecting the environment. When human intake high amount of Cd leads to blighter of renal system and kidney, skeletal deformity (Itai-itai), hypertension and cardiovascular diseases. Severe gastrointestinal irritation, anemia, muscular pain, teeth discoloration, possible necrotic changes in the liver and kidney can also occur, and loss of smell (8). Iron is one of the main components of the lithosphere and include nearly 5% of it. The presence of iron in drinking water at high concentration makes its taste very hateful (9). Due to iron storage disease, the liver becomes cirrhotic and leads to the cancer of the liver, which becomes the most diffuse cause of death between patients with hemochromatosis(10). In iron storage disease the intestine is unable to not allow entering unwanted iron. Instead this iron cumulative in the liver causing siderosis (11).

The elimination of copper, lead, cadmium and iron ions from aqueous solution by classic methods includes its deposition with alkali hydroxide or lime, electrolytic precipitation, ion exchange and reverse osmosis. These classic methods are expensive and have a lot of disadvantages such as production of metal-bearing sludge or wastes, imperfect metal elimination and the elimination of secondary waste.

Adsorption is an economical and efficient process that can be utilized for the elimination of copper, lead, cadmium and iron ions from aqueous solution.

Calcium oxide (CaO) is an exceptionally significant and important industrial compound, which is utilized as catalyst, toxic-waste treatment agent, an additive in refractory and in paint as well as for other major applications (12). Ultrafine metal oxide particles can be utilized as bactericide adsorbent. CaO has also shown great promise as a destructive adsorbent for toxic chemical materials (13).

Accordingly, this investigation aims to find a selective, simple and rapid method for the elimination of copper, lead, cadmium and iron ions from aqueous solutions by using nano-CaO as an effective sorbent under the recommended conditions.

Experimental

Materials

Lead (II) stock solution (100 $mg.L^{-1}$) was prepared from $Pb(NO_3)_2$, Copper (II) stock solution (100 $mg.L^{-1}$) was prepared from $CuSO_4.5H_2O$, Cadmium (II) stock solution (100 $mg.L^{-1}$) was prepared from $CdCl_2.8/3H_2O$ and Iron (III) stock solution (100 $mg.L^{-1}$) was prepared from $Fe_2(SO_4)_3$. $CaCl_2$ salt was used for the preparation of sorbent. 100 $mg.L^{-1}$of other ions stock solutions was prepared by weighing the requested amount in distilled water. The metal salts were utilized as their chlorides while the anions were utilized as their potassium or sodium salts. Standard aquatic solutions of NaOH and HCl were utilized for pH adjustments. All working solutions were made by diluting with distilled water.

Preparation of nano-CaO sorbent

An appropriate amount of $CaCl_2$ were dissolved in water and heated to 40 ^oC. While the solution was being stirred rapidly, 20 ml of NaOH (0.1M) was added to the solution. After 30 min the reaction was healted, filtering and washing steps at pH=8 were carried out. As a result the precursors of CaO; *i.e.* Ca $(OH)_2$ was produced which were left for 24 hr at 60^{o}C ±10^{o}C to be dried. The dried precursors were calcinated at 400,500 and 600^{o}C for 2 hr, Ca oxide powder was formed (14, 15) . The ionic equation of the reaction is as following:

$$3Ca^{2+} + 6OH^- \rightarrow 3Ca(OH)_2\downarrow \rightarrow 3CaO + 3H_2O$$

Sorbent characterization

X-ray diffraction model of the prepared adsorbent was recorded using a Philips PW 105 diffractometer utilizing Ni-filtered Cu Ka radiation (=1.540 A^o) at 40 keV, 30 mA, and a scanning range two hours of 18-80^o.Transmission electron microscopy (TEM) was carried out using a JEOL 2010 instrument with resolving power 0.2 nm, accelerating tension being 200 keV. Scanning electron microscope (SEM) was carried out utilizing a Jeol JSM-840 under high vacuum, at an acceleration voltage of 200 keV. The samples were deposited onto carbon tape and coated with gold in a Blazers plasma sputtered (30 s at 30 mA). The surface area of the prepared adsorbent was computed from nitrogen adsorption studies conducted at -196^{o}C using the high vacuum classical volumetric glass system (BET) befor any adsorption measurement, the sample was degassed at 250^{o}C for 3 hr under a reduced pressure of 10-5 Torr.

Batch adsorption studies

The influence of various experimental parameters such as: the stirring time, effect of pH and adsorbent dose was studied. For each experiment, 50 ml of a solution contains (different metal ions solution of a certain concentration + CaO sorbent with a known amount) was taken in a 100 ml beaker and then stirring occurs with continuous air stream bubbles at 250 rpm for a desired time to realization equilibrium adsorption and to generate calcium carbonate formation at room temperature. The pH was adjusted to the desired values using dilute solutions of NaOH and HCl. At the end of the required time intervals, the samples were taken out and the solutions were separated from the adsorbent by filtering through a Whatman filter papers.

The recovery percentage of different metal ions (Recovery %) was calculated according to the following equation:

$$\text{Recovery\%} = [(C_o - C_e)/C_o] \times 100,$$

where: C_o and C_e are the initial and residual concentrations ($mg.l^{-1}$) of different metal ions respectively.

Method for determination

The residual concentration of different metal ions in the filtrate were analyzed by GBC, Sensaa Series Atomic Absorption Spectrometry (computerized AAS) with air-acetylene flame under the optimum instrumental conditions as shown in Table 1.

TABLE 1. Optimum instrumental conditions of different metals.

	Fe	Cu	Cd	Pb
Wave length, nm	248.3	324.7	228.8	217
Working calibrating range, ppm	2-9	1-5	0.2-1.8	2.5-10
Sensitivity, µg/ml	0.05	0.025	0.009	0.06

Results and Discussion

Effect of calcination temperature on the prepared CaO nanoparticles

Figure 1 shows the XRD patterns of CaO nanoparticles calcinated at 400, 500 and 600°C for 1 hr, at 400°C different diffraction phases appeared at 18, 29.3 and 33.29 while increasing calcinations temperature at 500°C and 600°C increase the crystallization structure. The appearance of single diffraction peak at 29.3 with slitly background interference indicating orientation along (111) plane of reflection of cubic phase. Moreover, TEM morphology of CaO nanoparticles calcinated at 500°C is shown in Fig. 2, which confirmed the crystallization of CaO nanoparticles with a simple cubic structure and with high surface area as shown in Table 2.

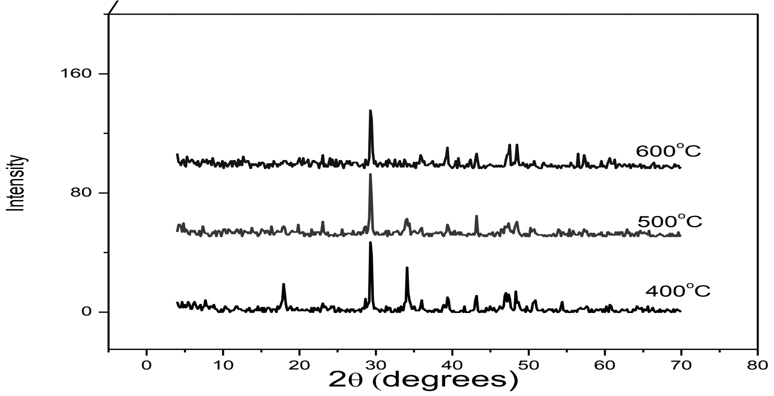

Fig.1. XRD pattern of nano-CaO sorbent.

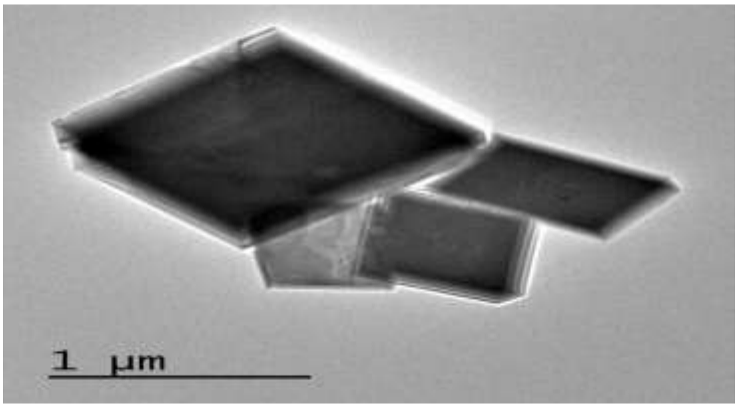

Fig. 2. TEM image of nano-CaO sorbent calcinated at 500°C.

Scanning electron microscope (SEM)

The SEM image of the sorbent sample calcinated at different tempratures is shown in Fig.3 (a,b and c). Analyzing the morphology aspect of the nanoparticles by studying the images indicates that the synthesized size nanoparticles are less than 100 nm. That means the synthesized sorbent has nano dimension.

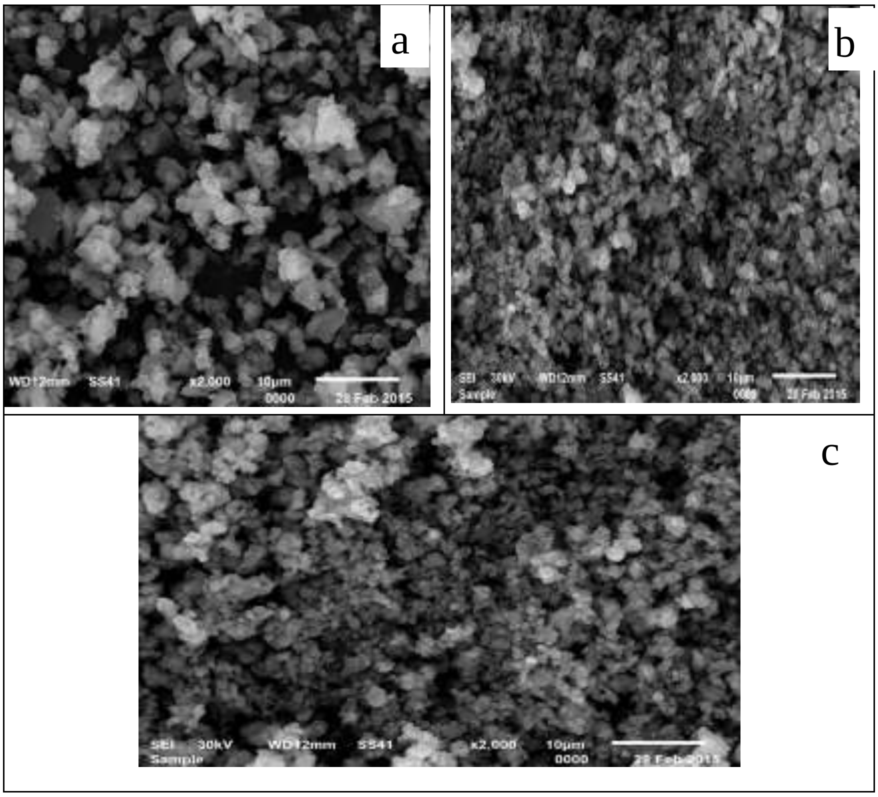

Fig. 3. SEM images of nano-CaO sorbent calcinated at a) 400°C, b) 500°C,and c) 600°C.

Surface area measurement

The surface area was determined for the prepared sorbent using different methods involve BET method, **S_{α_S}** method and T Plot method. The data obtained and tabulated in Table 2 as following:

TABLE 2.Value of surface area estimated by different methods: S_{BET} ,$S\alpha_s$ and S_T.

Calcination temperature, °C	**S_{BET} ($m^2.g^{-1}$)**	**S_{α_S} ($m^2.g^{-1}$)**	**S_T ($m^2.g^{-1}$)**	**r_A (A°)**	**C**
400°C	19.6	18.7	19.1	370	10.6
500°C	71.49	71.0	72.0	12440	5
600°C	53.81	52.9	53.5	13000	8.88

Adsorption study

The effect of pH

The adsorption of different metal ions count on the nature of the sorbent surface and the types distribution of different metal ions in the aquatic solution, which mainly depends on the pH of the solution, therefore, the pH is one of the most significant parameters impacting the sorption process of different metal ions.

To study the effect of pH on adsorption of different metal ions, the adsorbent dose (30 mg) was contacted with different metal ions (10 mg.L^{-1}) at different pH values(2, 5, 7, 8 and 10) with 30 min stirring time.

As seen in Fig. 4, experimental results showed that the elimination of metal ions under investigation followed the following trend: $Cd^{2+} < Cu^{2+} < Pb^{2+} < Fe^{3+}$. Also, the recovery % is low at strong acidic medium and this means that at high concentration of H^+ ion, the sorbent surface becomes more positively charged, thus diminishing the attraction between sorbent and different metal ions.

But with increasing the pH, recovery % will increase and reach maximum value at pH range (7-10) and these results can be explained as following:

When the pH increases (pH>5), the concentration of hydronium ion (H_3O^+) is very low, sorbent surface was more negatively charged, thus the sites are easily available for different metal ions binding. So, the effect of proton competition was decreased, and the recovery % of different metal ions is increased then, as pH curve is shifted to alkaline region (pH>8) the recovery % of different metal ions mainly still constant, therefore, the appropriate pH of solution for maximum uptake of different metal ions is 7.

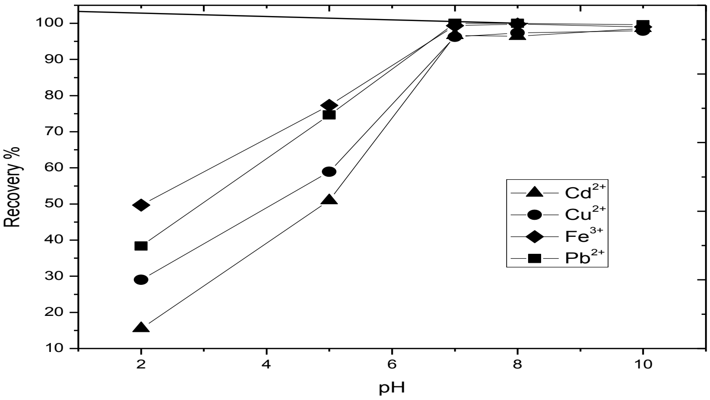

Fig. 4. The effect of pH on the recovery of different metal ions.

The effect of stirring time

The recovery % of different metal ions by CaO nanoparticles as a function of time is presented in Fig. 5. The percentage metal removal approached equilibrium within 30 min for all metal ions. The fast adsorption at the initial stage is because of the primary concentration gradient between the sorbate in solution and the number of vacant sites available on the sorbent surface at the beginning. Gradient increase in adsorption and so the realization of equilibrium adsorption may be because of limited mass transfer of the sorbate molecules from the bulk liquid to the surface of sorbent, so a time of 30 min was selected as a suitable stirring time for all experiments of different metal ions at pH 7 in aqueous solutions.

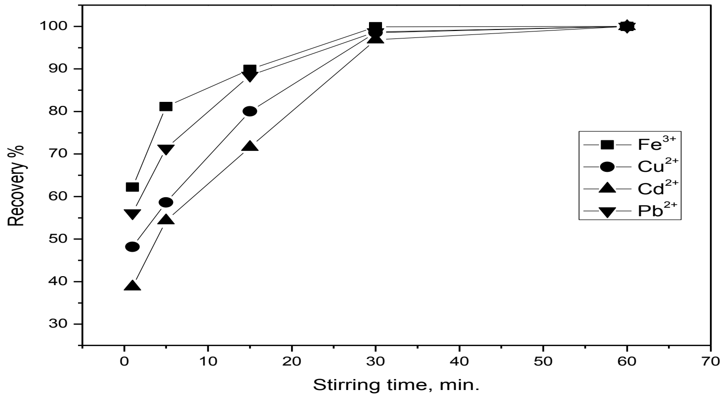

Fig. 5. The effect of stirring time on the recovery of different metal ions.

The effect of adsorbent dose

The dose of sorbent was a major parameter to control both availability and attain of sorption sites (16) . The impact of sorbent concentration on the recovery of different metal ions was studied by varying the dose of sorbent from 5-40 mg at constant value of pH=7, temperature=25°C and adsorbate concentration=10 mg.l^{-1}. The recovery % increases as the sorbent dose increases from 5-20 mg (for Fe^{3+} and Pb^{2+}), 5-30 mg (for Cu^{2+} and Cd^{2+}) then still constant as shown in Fig. 6. This is because the increased number availability of active adsorption sites arising because the intension in effective surface area resulting from the increases in dose of sorbent(17,18). Therefore, the optimum sorbent dose for maximum uptake of different metal ions is 30 mg.

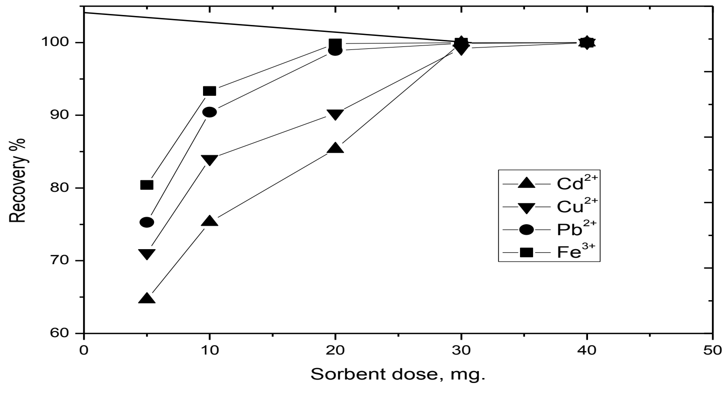

Fig. 6. The effect of sorbent dose on the recovery of different metal ions.

Effect of temperature

The temperature has two most important impacts on the adsorption process. In high temperature is common to rise the diffusion rate of the adsorbat while varying the temperature will vary the equilibrium capacity of the adsorbent for a specific adsorbate. In this investigation, a string of tests were conducted on the sorption of 10 mg.L^{-1} of different metal ions on to 30 mg of sorbent at 278, 298, 318 and 338 K at pH7 and stirring time 30 min to research the impact of temperature on the adsorption dynamics. The results depicted in Table 3 showed that the adsorption capacity rises as the temperature rises supporting that the process is endothermic in nature.

Such results may be credited to the formation of several new active sites on the adsorbent or to the speeding up of several slow sorption steps. Moreover, the increase of mobility of different metal ions from the bulk of solution to the sorbent surface should also be paid attention to. Since most liquid industrial wastes are generally spicy, the easy adsorption method given here possibly can be utilized in industrial wastewater handling for the elimination of different metal ions.

TABLE 3. Effect of temperature on the recovery of different metal ions.

Temperature, K	Recovery %for Fe^{3+}	Recovery % for Cu^{2+}	Recovery % for Cd^{2+}	Recovery % for Pb^{2+}
278	99.78	92.56	89.65	97
298	99.5	98.5	97.5	98.9
318	100	100	100	100
338	100	100	100	100

Effect of various other ions

Under the optimum conditions decided for this research the recovery % of 10 mg.l^{-1} of different metal ions from an aqueous solution of pH 7 containing 30 mg of sorbent was investigated at high concentration (1000 mg.l^{-1}) of various cations and anions. All the cations were utilized as their sulphates or chlorides whereas the anions were utilized as the corresponding potassium or sodium salts. The possible amounts of each ion, giving an error of ± 4% in the recovery % of different metal ions, are shown in Table 4; checking of the data shows that the recovery % of different metal ions is almost the same amount in all cases. This indicates that there is no competition between all the studied foreign ions with different metal ions for the interaction with the sorbent's active sites.

TABLE 4. Effect of various other ions on the recovery of different metal ions.

Foreign ions (1000 mg.l^{-1})	Recovery %for Fe^{3+}	Recovery % for Cu^{2+}	Recovery % for Cd^{2+}	Recovery % for Pb^{2+}
PO_4^{3-}	100	98.9	90.1	99.9
SO_4^{2-}	100	97.89	99.6	93.2
Cl^-	99.93	99.5	99.7	91.72
Mg^{2+}	99.72	98.4	93.5	97.34
Ca^{2+}	100	99.9	100	100
Mn^{2+}	100	100	93.5	100

Adsorption mechanism

The prepared nano-CaO sorbent may undergo the following reactions which lead to the formation of $CaCO_3$ in situ,

$$CaO_{(s)} + H_2O_{(l)} \text{---->} Ca(OH)_{2(s)}$$
$$Ca(OH)_{2(s)} + CO_{2(g)} \text{---->} CaCO_{3(s)} + H_2O_{(l)}$$

So the adsorption occurred actually on the surface of $CaCO_3$.

When $CaCO_3$ (sparingly dissoluble salt) is suspended with water, Ca^{2+}, $CaHCO_3^+$, $CaHO^+$ and HCO_3^- are created as surface charged types and their existence can play a role in aqueous solution pH. Moreover, H^+, $OH^-$and HCO_3^- are considered as possible determining ions in addition to Ca^{2+} and $CaCO_3$, the separation of these groups may lead to an alkaline or acidic surface (negative or positive charge of surface).

At pH<5, the elimination of metal ions may be due to a potential ion exchange mechanism among these ions and calcium containing $CaCO_3$.

In the pH values $^{(7-10)}$, where the maximal elimination of metal ions occurred, sorption may be electrostatically in nature and occurs between $Pb(OH)^+$,$Cd(OH)^+$, $Cu(OH)^+$, $Fe(OH)^{2+}$ and $Fe(OH)_2^+$ the predominant types in this pH values and the negatively charged surface of sorbent and/or deposition of metal carbonate on adsorbent surface.

Conclusion

According to the present investigation, it could be concluded that:

1. Prepared nano-CaO can be utilized as an effective and inexpensive sorbent for the elimination of different heavy metal ions (Cd^{2+}, Cu^{2+}, Pb^{2+} and Fe^{3+})from aqueous solutions.
2. Adsorption process which has advantages (compared with other separation methods) of being low cost, easy, less time consuming and in prospect to be soon incorporated as a clean technology to treat water and wastewater has been utilized in this search.
3. The adsorption of metal ions takes place mainly at the surface of the generated $CaCO_3$ adsorbent.
4. It could take place through sorption of hydrolytic types and/or deposition of metal hydroxide on the surface of adsorbent.

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تحضير جزيئات نانومترية من اكسيد الكالسيوم وتطبيقها في إزالة عناصر النحاس (II) والرصاص (II) والكادميوم (II) والحديد (III)

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تم تحضير جزيئات أكسيد الكالسيوم النانومترية بطريقة SOL-GEL من كلوريد الكالسيوم $CaCl_2$ وتحميص الناتج في ثلاث درجات حرارة مختلفة هي (400 م^{o} و 500 م^{o} و 600 م^{o}) . وقد تم دراسة الخصائص للمادة المازة بواسطة حيود الأشعة السينيه (XRD) وفحص المجهر الالكتروني (SEM,TEM) بينما يتم تحديد الخواص التكوينيه بعملية الإمتزاز لغاز النتروجين (N_2) في درجات حرارة منخفضة تصل الى حوالي (-196 م^{o}). حيث حصلنا على نتائج جيده في الظروف المناسبة. وقد تم التحقق من القدره الجيده لجزيئات أوكسيد الكالسيوم النانومتريه على ازالة بعض ايونات العناصر الثقيلة من المحاليل المائية من خلال عملية الإمتزاز.

اجريت جميع التجارب بطريقة (batch method) وقد تم دراسة مجموعه من التاثيرات منها وقت فترة التحريك او التقليب ودرجة الحامضيه والقاعديه (2,5, 7, 8, 10) وكذلك الجرعه المستخدمه من المادة المازه من (5 ملغ / 100 مل الى 40 ملغ / 100 مل)؛ ودرجات الحرارة ؛ ووجود ايونات غريبة مختلفة. وقد تم تحقيق نسبة ازالة تصل الى حوالي 100% من ايونات العناصر المختلفة ؛ عند ظروف معينه تتمثل في درجة حامضيه تساوي (7)؛ وفي درجة حرارة الغرفه (25 م^{o}).