

COMPARATIVE STUDY OF REMOVAL POLLUTANTS (HEAVY METALS) BY AGRICULTURAL WASTES AND OTHER CHEMICAL FROM THE AQUEOUS SOLUTIONS

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ABSTRACT

This study included the application of some experiments in the chemical treatment of some heavy metals elements by preparing biological surfaces that are adsorbed from natural and other chemical substances, as in preparing activated carbon prepared from charred pistachio shell with concentrated H_2SO_4 and Nano-Calcium Oxide prepared from $CaCl_2 \cdot 2H_2O$ with $NaOH$. The prepared materials were diagnosed with spectral techniques where the FTIR infrared spectrum proved the formation of carbonyl, hydrogen and oxygenated of the surface in activated charcoal and the hydroxyl and calcium oxide groups in the nano-calcium oxide, as the FE-SEM surface morphology was proven to form on coal blocks The surface is a network of irregular holes and a network of microscopic holes regular on the surface of nano- calcium oxide. As for X-ray diffraction technology, the crystal structures of the surface, its shapes and sizes, are shown, and that activated charcoal consists of that Many types of carbon in the form hexagonally and cuboid and rhomboid with a right angle, while technical proven size of the crystalline calcium oxide nanoscale which ranges between (54.68-67.86nm) cube-shaped. PIAC activated charcoal and n-Calcium oxide were used as sorbents in the removal of, Cd^{+2} , Pb^{+2} ions from aqueous solutions, a study of the effect of pH, contact time, multiple weights for surface and the primary concentration of ions in a horizontal removal method, and the removal of minimal concentrations of ions in large volumes of solutions by the process of preconcentration.

Keywords : pollution, activated carbon, nano-cao, pistachio shell., calsuim oxide

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دراسة - مقارنة إزالة الملوثات (المعادن الثقيلة) بوساطة المخلفات الزراعية

وأخرى كيميائية من المحاليل المائية

مثنى محمد سرحان

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الباحث

قسم الكيمياء - كلية التربية للعلوم الصرفة - جامعة الانبار - العراق

المستخلص

تضمنت هذه الدراسة تطبيق بعض التجارب في المعالجة الكيميائية لبعض العناصر المعدنية الثقيلة (Heavy Metals) بتحضير سطوح حيوية مازة من مواد طبيعية وأخرى كيميائية، كما في تحضير الكربون المنشط المحضر من قشور الفستق (Pistachio Shell) المفحمة بحامض الكبريتيك المركز واوكسيد الكالسيوم النانوي Nano-CaO المحضر من تفاعل كلوريد الكالسيوم المائي مع هيدروكسيد الصوديوم. تم تشخيص المواد المحضرة بالتقنيات الطيفية حيث اثبت طيف الاشعة تحت الحمراء FTIR تكون المجاميع الكربونيلية والهيدروجينية والاكسجينية للسطح في الفحم المنشط وتكون مجاميع الهيدروكسيل واوكسيد الكالسيوم في اوكسيد الكالسيوم النانوي، كما اثبتت تقنية المجهر الالكتروني الماسح للانبعاث FE-SEM مورفولوجيا السطح بتكون كتل من الفحم تنتشر على السطح شبكة من الثقوب غير منتظمة الشكل وشبكة من الثقوب الدقيقة المنتظمة على سطح اوكسيد الكالسيوم النانوي، اما تقنية حيود الاشعة السينية XRD اوضحت التراكيب البلورية للسطح واشكالها واحجامها، وان الفحم المنشط يتكون من انواع عديدة من الكربون بشكل سداسي ومكعب والشكل. استخدم الفحم المنشط PIAC واوكسيد الكالسيوم النانوي n-CaO كمواد ماصة في ازالة ايونات Pb^{+2} ، Cd^{+2} من المحاليل المائية، ودراسة تأثير الدالة الحامضية pH وزمن التلامس وتعدد الاوزان للسطح والتركيز الابتدائي للايونات بطريقة الازالة الافقية (طريقة الوجبة)، وازالة التراكيز الضئيلة من الايونات في احجام كبيرة من المحاليل بعملية المراكزة (preconcentration).

الكلمات المفتاحية: التلوث، المخلفات الزراعية، الفحم المنشط، اوكسيد الكالسيوم النانوي، قشورالفستق.

INTRODUCTION

Pure water free from pollutants is a key ingredient in green protected and sustainable environments on Earth (1). Water has a major role in industrial development in all aspects. Rapid industrialization and urbanization and the multiplicity of requirements for industries and the proliferation of factories to keep pace with the urgent need has led to increased pollution with heavy metals, the problem of our time (2, 3). Heavy toxic elements are found in water and concentrated as a result of human activities (4). Cadmium, zinc, copper, nickel, chromium, and lead are often discovered in industrial wastewater that arises from mining, smelting, battery manufacturing, battery tanning, petroleum refining, and petroleum industries (5). The high concentration of toxic metallic elements is very dangerous for humans and the ecosystem even at low levels (6), because of their non-degradable nature as they possess vital properties that cause them to accumulate and be concentrated in different parts of the human body and animal (7). Some of these minerals are an important component in metabolic processes, but they are toxic in increasing their concentration in the body, that Fe, Cu, Zn, Co and Mn are among the minerals necessary for their important role in biological systems. Provided that it does not accumulate in large quantities, it causes harmful health problems for humans and other organisms (8). The release of factory waste, washing water and sewage directly into the environment, including rivers and irrigation of soils with untreated wastewater that is transmitted to the organism by feeding on plant crops contaminated with heavy elements that cause many health problems is considered one of the most important sources of environmental pollution (9). Agricultural residues are among the first materials that have been widely recycled and condensed for their low economic and material cost and ease of handling, as in reeds waste (10), apricot stone, sawdust, palm veneer, peanut shell, coconut and cashew, wheat bran, crusts Hazelnut (11), onion husks, leaves of Elias, bamboo powder, pistachio peels. That have been chemically treated and converted into adsorbent materials that have the ability to

extract toxic elements. Nanoparticles of metal oxides are important materials due to their widespread applications in various aspects including chemical catalysis, sensors, electronic optical materials and environmental treatment. There are a lot of metal nanoparticles, including MgO, Al₂O₃ and TiO₂, and other oxides that have been manufactured in a number of ways including ultrasound, plasma method, biopolymer aids, combined chemical precipitation and direct thermal decomposition, Sol-gel for their high absorbability of heavy elements ions (12) that It is considered a major concern for the pollution of the environment and water because of its high toxicity with low concentrations, which led to great research efforts in the past few and current decades to search for the best ways to overcome the problems of environmental pollution resulting from improper disposal and the increase of toxic heavy metal proportions. What led to the development of analytical techniques to determine the concentrations of toxic metals and adsorption extraction procedures on nanoscale surfaces prepared at low costs and simple equipment available, such as the use of nano- calcium oxide.

MATERIALS AND METHODS

Preparation of activated carbon:

(1.0kg) pistachio shell were purified from suspended impurities and contaminants by washing them several times with distilled water to remove dust and other soluble materials. After drying at room temperature, it was ground into fine powder and sifting the granular particles using a sieve size of the holes (200-30 μm). The powder was treated by burning it with concentrated sulfuric acid (H₂SO₄.) With a ratio of one to two parts by weight and the process of potting continued for 24 hours to complete the carbonization process, the sample was washed several times with distilled water to get rid of the excess acid until Reach at pH = 4. It was dried at (80-100 °C) for three hours. and then grind it and sift it to sort the volumes using its sieve size (42 μm .) And then save the biochar Active acid (PIAC) in cans sealed inside dried glass (Desiccators) for the purpose of the study later.

Preparation of nano –calcium oxide

1.0M of aqueous calcium chloride was dissolved in dionic water by Sol-gel method and during stirring the solution quickly, 20ml of sodium hydroxide (2.0M) was added, while maintaining the value at (PH= 8). Then the solution was filtered and dried at a temperature of 60 °C for 24 hours(13) , then the precipitate was ground and calcinated at 900 °C for 4 hours, as nano-Calcium Oxide powder is formed.The ionic equation of the reaction is :



Preparation of standard solution for ions

By dissolving the weights needed from cadmium nitrate (0.274 g) and lead nitrate (0.1958 g) per 100 ml of dionic water to prepare standard solutions of cadmium and lead ions at a concentration of 1000ppm and by dilution prepared a series of standard solutions at a concentration of 100ppm per ion to study the factors affecting the removal of ions with the surface.

Adsorption of study by batch method

The effect of different experimental parameters with surfaces by batch-method was studied, which included mixing a (50mL, 100ppm) of ion with (1.0 g) of activated carbon prepared from pistachios shell, and mixing a (25 mL, 100 ppm) of ion with (30mg) of nano-calcium oxide. Acid function values were adjusted using dilute sodium hydroxide and hydrochloric acid solutions. As for the ratio of removal of ions after the process of separating the solution from the sorbent material, it was according to the following formula(14): $R\% = [(C_0 - C_e)/C_0] \times 100$

Where: **R%** ;the recovery percentage of metal ions , **C₀** and **C_e** are the initial and residual concentrations (ppm) of metal ions.

RESULTS AND DISCUSSION

.Characteristics of the adsorbents

Then diagnose Activated Carbon (PIAC) at laboratory temperature using the infrared spectrum within the range (400-4000) cm^{-1} as shown in Figure1 where appeared of Wide absorption beam at (3415 cm^{-1}) elongation due to the hydroxyl (OH) group, Absorption package at (3066 cm^{-1}) belonging to the C-H group, stretched into the aromatic ring and Absorption beams at (2862 cm^{-1}) and

(2925 cm^{-1}) vibration deformation due to Fiat C-H in the symmetrical and asymmetric CH_2 group (15), Absorption beam at (1735 cm^{-1}) vibration due to group C = O in the carbonyl group or the presence of carboxylic bonds (16). As the strength of these beams decreases at higher temperatures to (1701 cm^{-1}) and (1681 cm^{-1}) in the active coal due to the decomposition of carbonate compounds and too, Absorption beams at (1620 cm^{-1}) and (1510 cm^{-1}) refer to C = O (most likely COOH^-) (17) elongation in the aromatic ring or C = C within the aromatic ring in the two accents. This indicates the presence of the two accretions after burning. That is, the presence of these values indicates the correlation of the carbonyl group with the aromatic ring and also reflects the degree of cellulose charring (18, 19). As for the diagnosis of n-CaO prepared after the burning process (Calcination) at a temperature of 900°C, as shown in Figure (2) appeared Asharp absorption package at (3643.28 cm^{-1}) belongs to the group (OH) and most likely the remaining hydroxide from $\text{Ca}(\text{OH})_2$ or from the water molecules on the surface of the samples (moisture from the air) while recording the spectra (20) and Strong absorption beam at (541.96 cm^{-1}) stretched vibration of Ca-O.

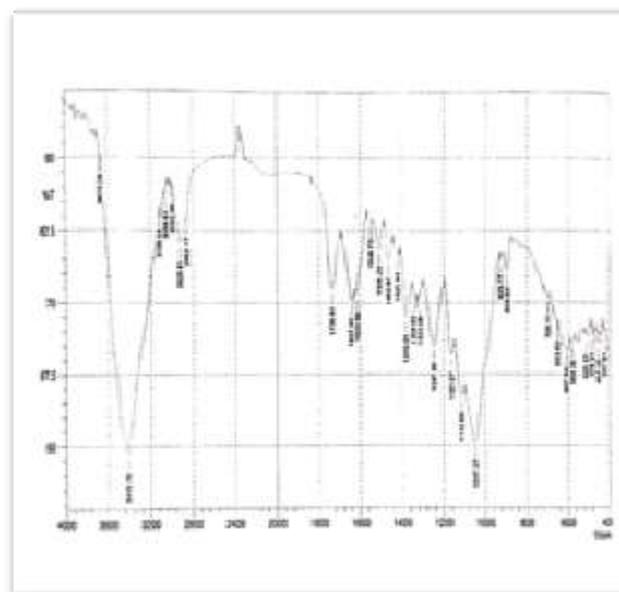


Figure1. FTIR of (PIAC).

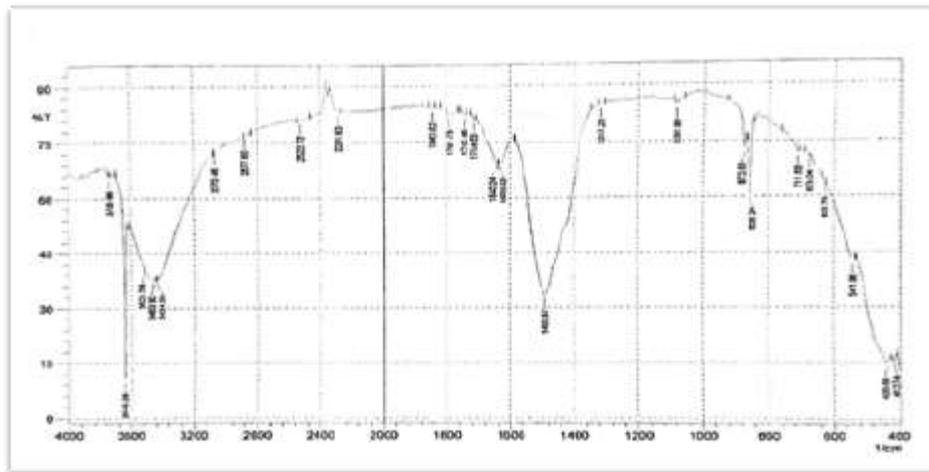


Figure 2. FTIR of nano- CaO.

A technique FE-SEM was used to monitor the physical morphology and morphological features of the prepared surfaces and to determine the structure and size of the particles, as it plays a fundamental role in understanding the nature of these substances reaching a level of accuracy to (1nm). Figure 3 shows the agglomeration of charred pistachio shells (PIAC) varying in size and shape, as these large blocks of biochar contain a network of micropores that are spread

irregularly on the surface due to the release of volatile substances. As for the crystals of the n-CaO oxide powder prepared by the Sol-gel method, as in Figure 4, the particles of the powder have been agglomerated and formed larger particles. XRD analysis which proved the nanoparticles by calculating the crystalline volume, which shows the large surface area of the prepared material and hence its high adsorption capacity(21).

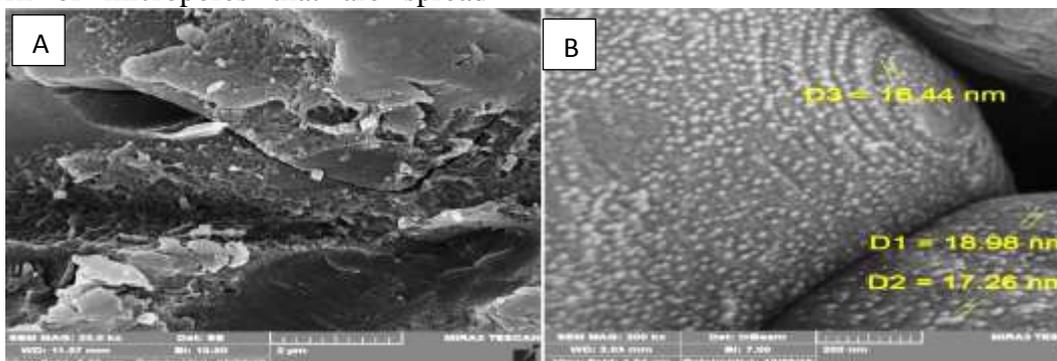


Figure 3. FE-SEM images of PIAC.

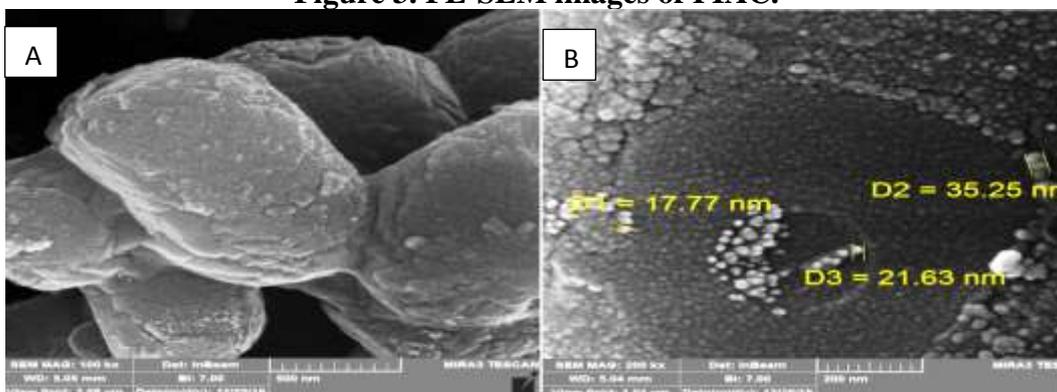


Figure 4. FE-SEM images of n-CaO.

XRD analysis showed the presence of cellulose, which is one of the important structural components of the primary cell wall of green plants as in charred pistachio crusts,

and through Figure 5 it was found that the main phase prevailing at the angle (26.1678), which indicates the presence of organic matter (15) significantly Also, the phase at the

angle (45.2043) shows the presence of the remaining salt, which was not completely removed during the soaking of the raw material. The proportion of coal formed is very large and formed in different phases, including Hexagonal, the existing rhombic form, Orthorhombic and Cubic shape. The X-ray diffraction technique also showed that the sol-gel prepared particles of the pure (CaO) substance as pure nanocomposite, type of cubic Centro symmetric and Polycrystalline (22), when observing the main phase prevailing at The angle (37.359°) as shown in Figure 6, and these results are in agreement

with the card number (00-048-1467). When calculating the value of the crystal volume using the (Scherer's Equation) (13) and according to the equation No. (1), it was found that the obtained sizes On it are nanoscale sizes ranging from (54.68 - 67.86) nm.

$$D = \frac{0.9\lambda}{\beta \cdot \cos \theta} \text{----- (1)}$$

Where : **D**= size of crystallite (nm) , **K** or **0.94** = constant of number or scherrer's constant , λ = wavelength of cu-k α (0.154nm) , β = full width at half maximum intensity (FWHM) in Radian , θ = Bragg angle .

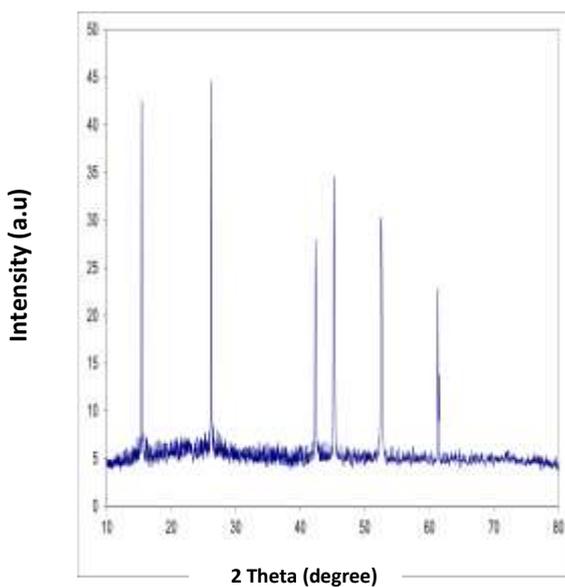


Figure 5. XRD patterns of PIAC

Experimental Parameters

Effect of pH : The effect of the acid function on the removal rate of Cd⁺², Pb⁺² ions has been studied when treated with (1.0g) of (PIAC) at a temperature of 25°C and continuous shaking for the duration (2h), at the values of the acid function ranging between (pH = 1- 8) The highest removal rate at pH = 6.0 is 97.00% for cadmium ion, shown in Figure 7. As for pH = 7.0, the removal rate for lead ion is 99.90%, shown in Figure 8), As for the study of the effect of the acidic function on the ratio of removal of ions when treated with (30 mg) of powder (n-CaO), the percentage of removal of cadmium ion at (pH = 7) is approximately (99.50%), as in Figure 9 The percentage of removal of lead

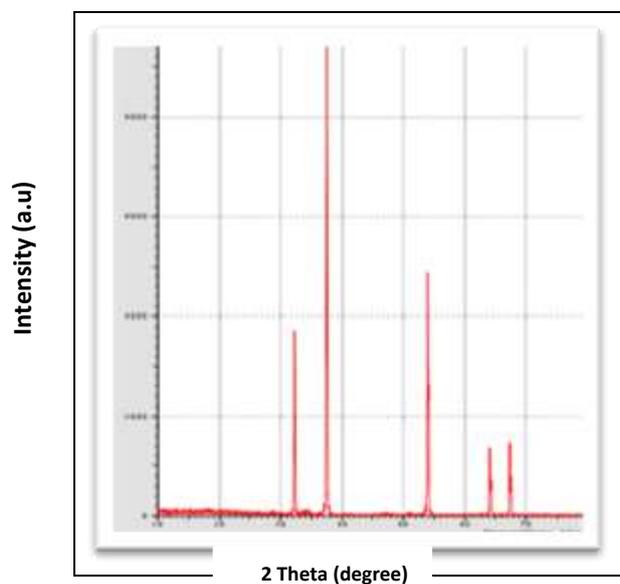


Figure 6. XRD patterns of n-CaO

ion is (99.90%) at (pH = 7) shown in Figure 10. The lower absorption of ions in the acid medium, i.e. when pH values are lower than the specified percentage of removal, is due to the presence of excess H ions that compete with the metal ions at adsorption sites (23). Where the metal ions condense on the surface due to the electrostatic repulsion with protons on the adsorbent surface (24). The percentage decrease of the removal of metal ions at the pH level is higher than the optimum adsorption ratio values due to the formation of soluble hydroxyl groups such as Pb(OH)₂, Cd(OH)₂, which are condensate complexes on the adsorbent surface competing with the metal ions in the locations Active adsorption.

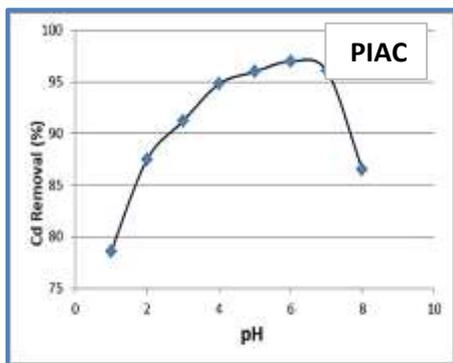


Figure 7. Effect of pH on removal Cd²⁺

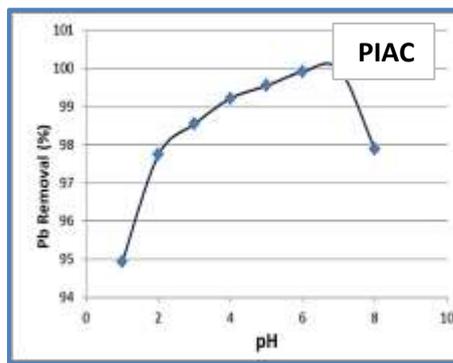


Figure 8. Effect of pH on removal Pb²⁺

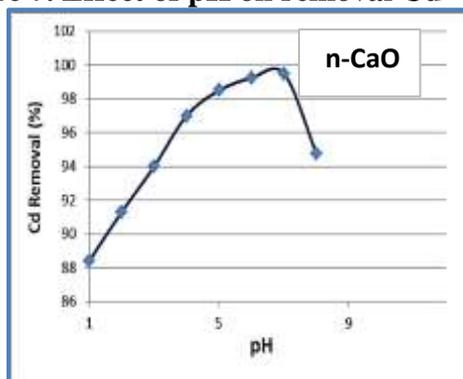


Figure 9. Effect of pH on removal Cd²⁺

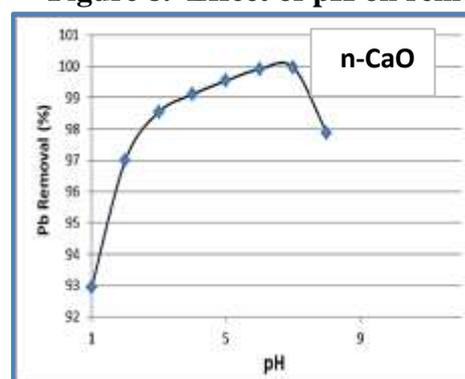


Figure 10. Effect of pH on removal Pb²⁺

Effect of contact time : The effect of contact time on the removal rate of Cd²⁺, Pb²⁺, was studied when treated with (1.0g) of powder (PIAC) and (30 mg) (n-CaO) at temperatures (45 ,55)⁰ C with a time ranging from (5 min - 3h) by fixing the acid function of each ion.As the results recorded the percentage of removal of adsorbed ions on activated carbon and nano- calcium oxide at a temperature of 45⁰C, the highest percentage of removal of cadmium ion was 99.10% with a contact time (80 min.) With PIAC, while it reached 96.10% with a contact time (100 min) with n-CaO as shown in Figure 11, while the highest lead clearance rate was 99.50% with(80 min) contact time with PIAC while 99.20% with (100 min) contact time with n-CaO as in Figure 12. At a temperature of 55⁰C, the percentage of cadmium ion removal was 97.20% at the time of contact (80 min) with

PIAC, while it was 96.00% at the time of contact (100 min) with n-CaO shown in Figure 13, and the lead ion removal rate was recorded 97.40% at the time of contact (80 min) with the PIAC, while it was 94.30% at the time of contact (100 min) with n-CaO shown in Figure 14. This shows that the effect of temperature differences is very little or almost non-existent on the time of ions contact with the surface .The adsorption ratio of the ions is very high at the fixed temperature of (45 , 55) ⁰C, and the adsorption speed of activated charcoal which is documented at a time of 80 min is greater than the adsorption speed of nano- calcium oxide which stopped at a time of 100 min. Thus, the adsorption process stops due to the adsorbent reaching the saturation limit at the specified contact time and its absorption capacity again (24).

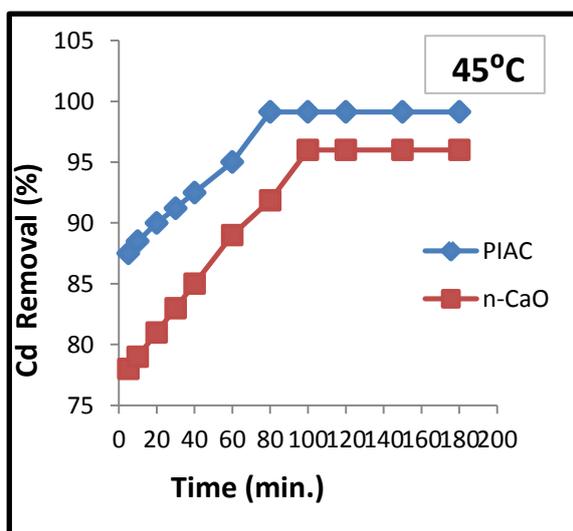


Figure 11. Effect of contact time on removal Cd⁺²

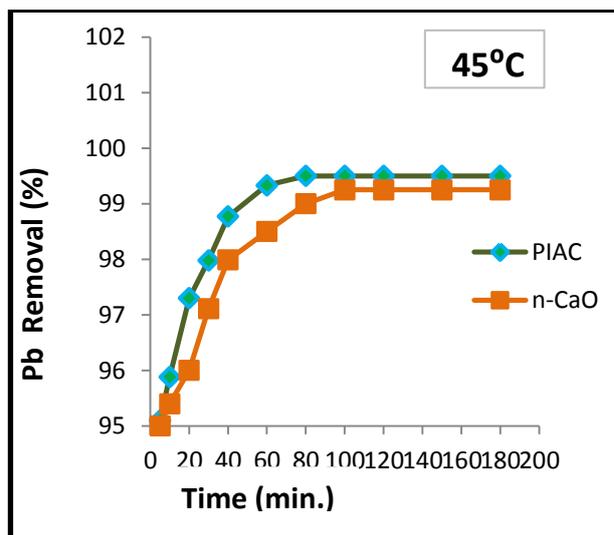


Figure 12. Effect of contact time on removal Pb⁺²

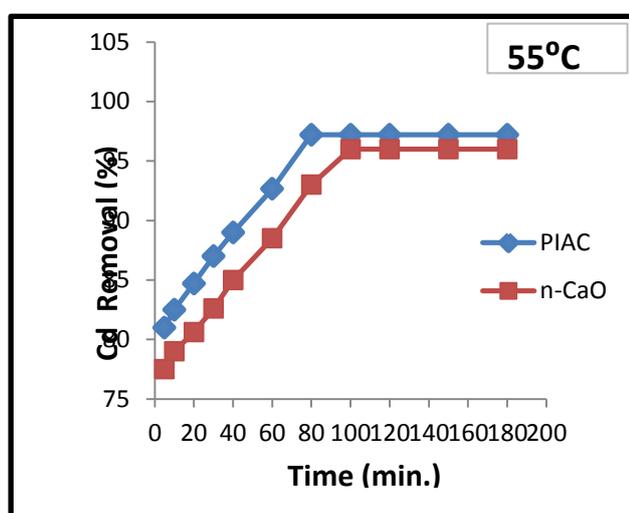


Figure 13. Effect of contact time on removal Cd⁺²

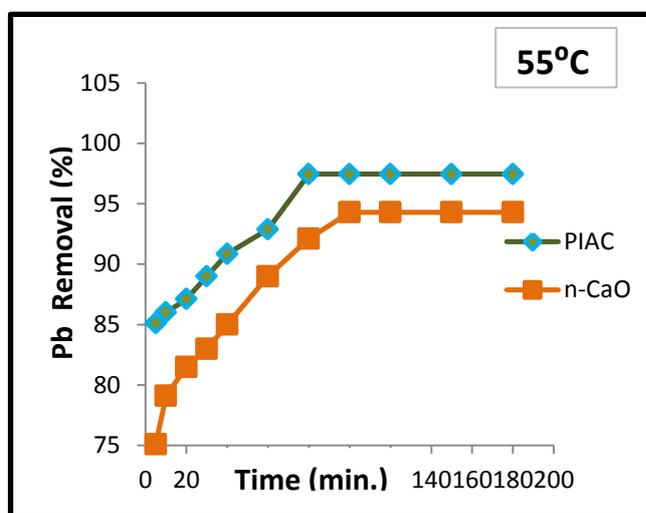


Figure 14. Effect of contact time on removal Pb⁺²

Effect of Initial Concentration of Ions : The effect of the initial concentration of ions in (10,30,50,70,100) ppm and the volume of 50mL was studied on the ratio of removal with the adsorbent substance 1.0g of activated carbon within the established working conditions, as it was found that the removal rate of Cd⁺², Pb⁺² ions absorbed by specific sites specific sites of the functional groups that make up biochar are large, and with increasing concentrations of ionic solutions the saturated specific sites are saturated and the exchange sites are filled with due to the excessive surface area of activated charcoal, that with an increase in the primary

concentration the ion removal rate increases with the surface, and that the highest removal rate was (91.12%) Cadmium ion and (93.50%) Lead ion at the highest concentration (100ppm) as shown in Figure (15). The highest removal rate of ions with 30 mg of nano-calcium oxide was (93.02%) for cadmium ion and (90.40%) for lead ion, at the concentration value of ions (100ppm), as in Figure 16, and as a result of surface area, high porosity, and adsorption capacity The larger the absorbent, the removal rate increases with the increase in the primary concentration of the metals(25).

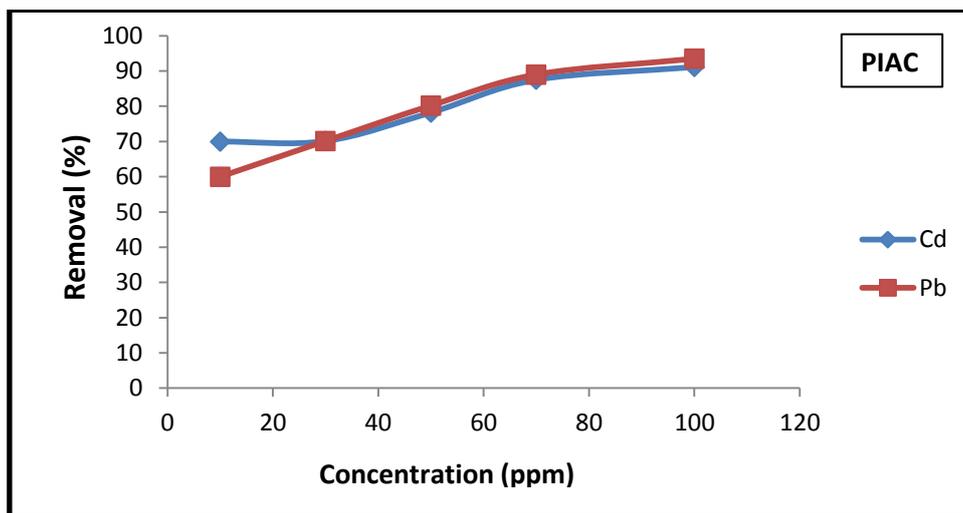


Figure 15. Effect of initial concentration on removal Cd⁺², Pb⁺² ions with PIAC

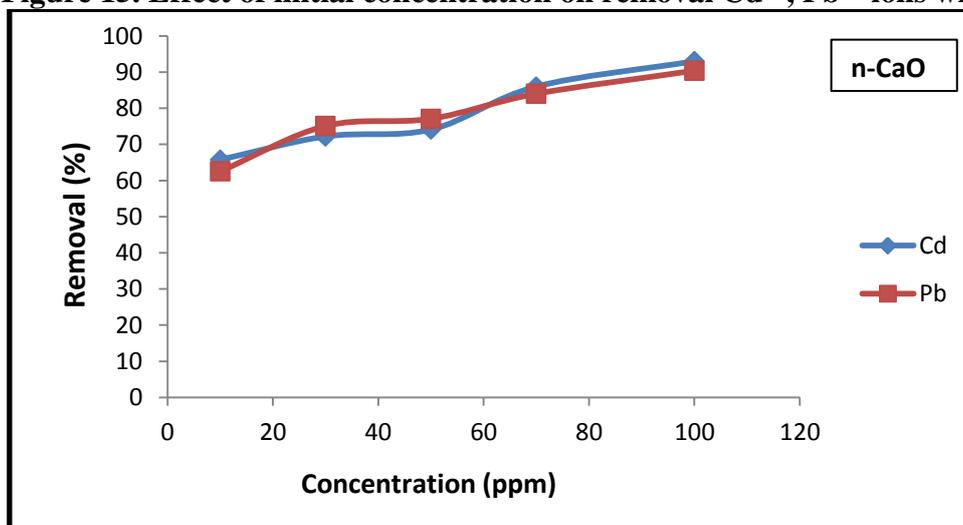


Figure 16. Effect of initial concentration on removal Cd⁺², Pb⁺² ions with n-CaO

Effect of Multiple doses : The effect of multiple doses of adsorbent material on the removal rate was studied for metal ions Cd⁺², Pb⁺², with activated carbon (0.1, 0.5, 1.0, 2.0, 2.5) g and nano-calcium oxide (10,20,30,40,50,60)mg at (25 °C) and shaking Continuous for (2 h), with fixing the acidic functions of each ion with fixed concentrations (100 ppm), it is observed that the adsorption ratio of the ions increases with the increase of the surface-absorbing dose until it reaches constant or very close values when increasing the weight, The adsorption efficiency increases

with increasing absorbed doses due to the increase in the surface area of the biomaterial, which in turn leads to an increase in the number of active sites for bonding with ions and does not stop at a certain limit, but has the ability to continue to increase if higher doses of the adsorbent material are used until a layer of ions is formed covering The surface prevents adsorption from occurring again (25). Therefore, the optimum absorption dose is at (1.0g) and (30mg) of activated carbon and nano-calcium oxide, respectively (26). As in Figure (17) and (18) .

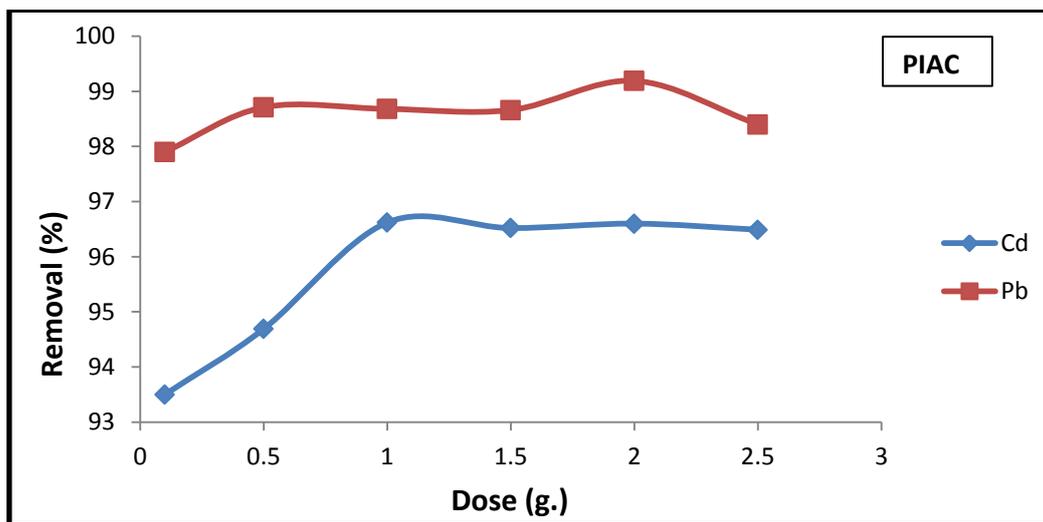


Figure 17. Effect of Multiple doses for PIAC on removal Cd⁺², Pb⁺² ions.

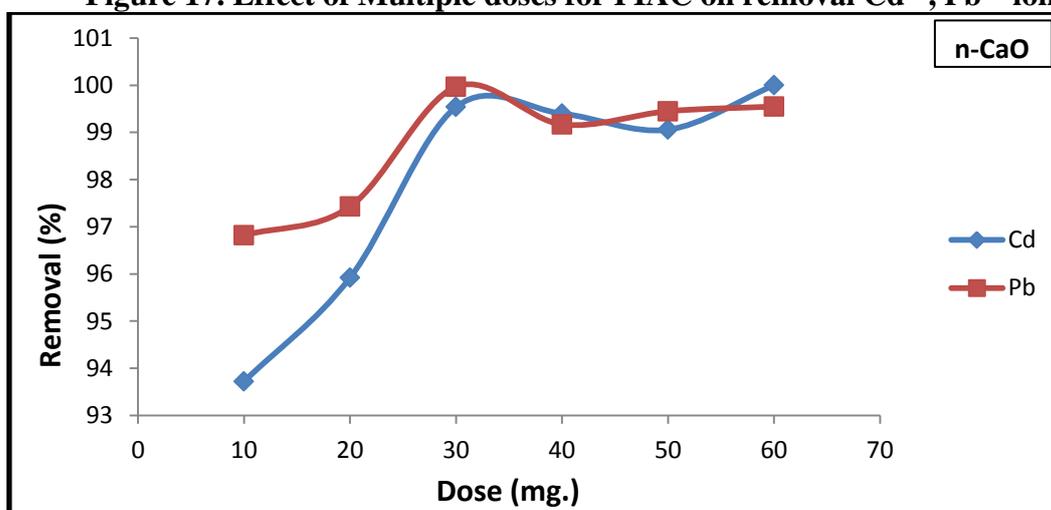


Figure 18. Effect of Multiple doses for n-CaO on removal Cd⁺², Pb⁺² ions.

Preconcentration method: Heavy metals are sometimes found in river water, irrigation, sewage, and industrial in small quantities, and despite this they cause high toxicity to the environment and the organism. In order to get rid of low concentrations of ions, the concentration process (increased concentration of ions) was used, which represents a higher removal. A possible percentage of minimal concentrations of ions in large quantities of solutions, which cannot be estimated by the available spectral methods, which included treatment of different volumes of solutions (250,500,1000) mL with a concentration (1.0

ppm) of ions, Cd⁺², pb⁺² with 1.0g of Activated charcoal, 30mg of nano-calcium oxide, and By estimating the concentrations of the ions studied in the leachate solution after the filtration process by the flame atomic absorption device, the ratio of the concentrations of ions in the leachate solution resulting from the treatment of different volumes with absorbent surfaces has reached (0.00 ppm) as in Table 1. These results demonstrate the success and importance of the concentration process and its application in the various fields of environmental elements (27).

Table 1. Shows removal of ions by pre-concentration method .

The adsorbent surface	Metal Ions	Sample volume /mL	Con. of Ions added/ppm	Con. of Ions in filtrate	Removal %
PIAC & n-CaO	Cd ⁺²	250	1.0	0.00	100
		500	1.0	0.00	100
		1000	1.0	0.00	100
	Pb ⁺²	250	1.0	0.00	100
		500	1.0	0.00	100
		1000	1.0	0.00	100

Conclusion : The current study showed that of pistachio shells can be burned with sulfuric acid to produce biochar which has proven to be very high in adsorption of heavy metals from standard solutions, and this proves the success of our work in investing neglected agricultural waste that is not usable in manufacturing a therapeutic substance for hazardous ions for the environment and the organism. The nano- calcium oxide of prepared by Sol-gel method, Conducting analytical techniques FTIR, XRD, FE-SEM, and this gives high visions of the structural properties and components as well as the produced surface morphology. Biochar properties have demonstrated high carbon content, porosity, and adsorption efficiency if compared to other types of activated charcoal prepared by researchers in previous studies of other types of agricultural waste. The removal ratio of the studied metal ions increases within the range (4-7) of the acidic function with activated charcoal and within the range (6.8-7.2) of the acidic function with nano- calcium oxide. The removal rate of ions increases at the contact time (80min) and (100min) of activated charcoal and nano-calcium oxide, respectively, at different temperatures. Also, the removal rate increases when there are multiple doses of the adsorbed surfaces until the surface is completely saturated with ions. By studying the comparison between activated charcoal and nano- calcium oxide when treated with standard solutions, the removal rate is approximately 98% at experimental parameters, and this leads us to the possibility of replacing costly nanomaterials that need accuracy in work and length of time, which has been proven by some studies Its toxic effect on the aquatic environment, especially fish, if concentrations exceed the limited quantities, with locally available materials that are inexpensive and easy to deal with in a short time such as peanut

shells to obtain the same proportions for removal.

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