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Preparation and Characterization of (Hyacinth plant / Chitosan) Composite as a Heavy Metal Removal

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Abstract:

In this study, the preparation and characterization of hyacinth plant /chitosan composite, as a heavy metal removal, were done. Water hyacinth plant (*Eichhorniacrasspes*) was collected from Tigris river in Baghdad. The root and shoot parts of plant were ground to powder. Composite materials were prepared at different ratios of plant part (from 2.9% to 30.3%, wt /wt) which corresponds to (30-500mg) of hyacinth plant (root and shoot) and chitosan. The results showed that all examined ratios of plant parts have an excellent absorption to copper (Cu (II)). Moreover, it was observed that 2.9% corresponds (30mg) of plant root revealed highest removal (82.7%) of Pb (II), while 20.23% of shoot removed 61% of Cd (II) within 24 hr. On the other hand, SEM images displayed a regular shape and high porosity of prepared samples, while FTIR spectra of composite materials showed the characteristic of raw materials bands, which give strong evidence of composite formation.

Key words: Biosorption**,** Chitosan**,** *Eichhorniacrasspes*, Heavy metals.

Introduction:

Eichhorniacrassipes is a free perennial aquatic plant. It results in a problem in many countries because of minimizing the oxygen level in water, reducing water circulation of water activities, hindrance, getting rid of fish and others (1). It is a floating macrophyte, which hold large quantities of toxic metals; some of which are important for plant growth. Water Hyacinth grows rapidly in water with a high level of nutrients like nitrogen and phosphorous. Lu et al. reported that the plants proved trace element absorption such as silver (Ag), Lead (Pb), Cadmium (Cd) and Copper (Cu) (2, 3). Water hyacinth is utilized at laboratory as a guide, and field scales to study the ability of industrial wastewater treatment from chemical, electrochemical, tannery, dairy, textile dyes, refinery, sugar, paper and rubber industries (4, 5). *E. crassipes* biomass is as biosorbent for the removal of toxic pollutants from aqueous solutions, since *E. crassipes* biomass is able to biosorb heavy metals and that was attributed to its ability tobiosorb to heavy metal (6-8). Chitosan is easily prepared from chitin.

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The Chemical modification of chitosan produces materials with a variety of physical and mechanical properties. (9, 10) Chitosan is not antigenic and is a well-tolerated implanted material. Films and fibers can be formed from chitosan by utilizing cross-linkers and adapted techniques for altering from other polysaccharides, such as treatment of amylose with epichlorohydrin. The basic technique of film and fiber casting of chitosan films and fibers was early developed (11-13). The release of heavy metal from the industries into the environment (water system) threatens the human life. The control of Pb(II), Cu (II) and Cd (II) has special importance for both organisms living in water and those that benefit from water. Water hyacinth has ability to remove pollutant from aquatic systems. High removal percentage of toxic heavy metals can be performed by biofiltration process without production of toxicity, secondary waste minimization, taking a short time to achieve and no toxicity limit for heavy metals. Among them, the adsorption technique is found to be the most effective (6, 14, 15). Biosorption is a biological method to protect environment, which is an alternative method to conventional waste treatment facilities. Its advantages are low operating cost, effective in dilute solution, secondary waste, minimization, taking a short time period and have no toxicity limit for heavy metals. In biosorption process, the physic-chemical interaction between the surface charge of microorganisms group and ions in solution were induced by complication process, (ion exchange, micro-precipitation and others) (16). In this study, composite sample were preparing from different ratios of dried water hyacinth root or shoot with chitosan and characterized. Moreover, removal of Pb(II), Cu (II) and Cd (II) by prepared composite was determined and optimized .

Materials and Methods:

Experimental part

Water hyacinth plant was collected from Tigris river in Baghdad. Chitosan of low molecular weight was supplied from ABCO Laboratories (Eng. Ltd., Gillingham, England). Sodium tripolyphosphate, (STPP) $Na_5O_{10}P_3$, molecular weight (367.86) was supplied from Mallinckrodt. Inc. (Paris, France).

Samples preparation

Preparation of hyacinth plant powder

Plant parts was washed with distilled water for several times and divided into two parts (root and shoot); the root and shoot were dried at (105 ºC) for 24hr and milled in a bladed mixer to less than 0.1mm and the powder were treated with 2M HCl for 24hr. The powder was washed several times with DW to reach pH 7. Thereafter, the powder was dried and milled again and stored in nylon package at room temperature until used.

Preparation of Microspheres

One gram of chitosan was dissolved in 40 ml of diluted acetic acid (2% v/v) to get the 1gm of chitosan beads. Plant root or shoot was added at ratio (2.9,4.3,5.6 ,6.97 ,8.25 ,8.69 ,10.66 , 20.3 and 30.3%, wt/wt) separately, as drops, into the chitosan solution during stirring process for 2 hrs and the mixture was treated with ultrasonic bath for 30 min. The solution was plunged through a capillary tube into a beaker continuous 100 mL of Sodium tripolyphosphate (STPP) solution at pH 8.6. The solution chitosan was poured into the STPP solution and took shape immediately. The hardened spheres were filtered; washed, become dry and saved in a dry container for future use. Waste water samples were collected from Hosainiya river in karbala city in Iraq ,and the dose of chitosan beads and all composite were 50 mg of beads in 100ml from waste water while the powder parts of hyacinth plant ratio was (2.9, 4.3, 5.6, 6.97, 8.25, 8.69, 10.66, 20.3 and 30.3%, wt) in 100 ml of waste water.

Instrumentations

FTIR

Fourier transformation of infrared (FTIR) spectra investigated were measured by Perkin-Elmer Fourier transformation of infrared spectrophotometer ((model 2000) over the wavenumber range of 400-4000 cm^{-1} in University of Baghdad /College of Education For Pure Science (Ibn-Al-Haitham).

Atomic absorption

The concentrations of Pb, Cu, Cd In altogethertasters were determined according to the standard method using Atomic Absorption Spectrometer Varian Spectra (220) with graphite furnace accessory and equipped with deuterium arc background corrector in University of Baghdad /College of Education For Pure Science (Ibn-Al-Haitham)

Scanning Electron Microscope (SEM)

The diameter and morphology of chitosan beads were examined by scanning electron microscopy (SEM) (Inspect S50, Holand). Sample was dispersed on glass slide and silver paste used as filament then viewed using an accelerating voltage of 15 kV at different magnifications in University of Baghdad /College of Education For Pure Science (Ibn-Al-Haitham).

Results and Discussions:

In order to examine the effect of adsorbent doses, absorbent microspheres of different concentration (2.9 ,4.3 ,5.6 ,6.97 ,8.25 ,8.69 ,10.66 , 20.3 and 30.3%, wt/wt) were used, together with (root and shoot) of hyacinth plant .Those results affirmed the viability to remove heavy metal from waste water, collected from Hosainiya river in karbala city in Iraq. The results showed the composite is successful in removing heavy metal compared with chitosan beads alone or powder parts of hyacinth plant alone. This was attributed to the unique hydrogen bonding from cellulose; lignin in present in root of hyacinth plant and high total dipole moment and chitosan could perform an attractive electrostatic interaction to deal with pb(ll) ,cu(ll), cd(ll) heavy metal. The best ratio was used for pb(ll) removal was (2.9%) wt; which decreased with root ratio, whereas it increased with shoot ratio up to 8.69%. These samples exhibited excellent ability for cu (ll) removal of (100%); however the worst was for cadmium where the response was at 8.36% of root, and its ability increased with shoot ratio to (61%). In general, the increase of adsorbent dosage is due to the viability of larger surface area and movement of absorption sites .It was noticed that at 8.25% root, the elimination develops very low as the external metal ions attentiveness and solution metal ions attentiveness come in balance with every other (17). The reduction in elimination proportion with a rise in the adsorbent dosage is mostly owing to the unsaturation of adsorption places over the adsorption reaction; wherever the collection of adsorption places would be principal to a reduction in the total surface area of the adsorbent leading to reduction in adsorb ions heavy metal.(18, 19). The results are show in Figs.1,2 ,3 and 4.

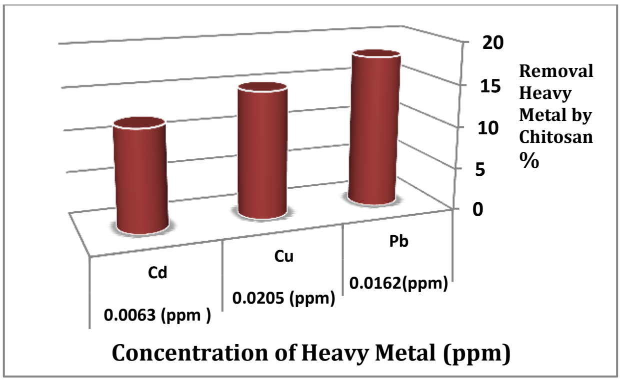


Figure 1. Removal percentage of Pb, Cu, Cd heavy metal in the presence of water hyacinth parts within 24 hr with different concentration of Heavy Metal (ppm)

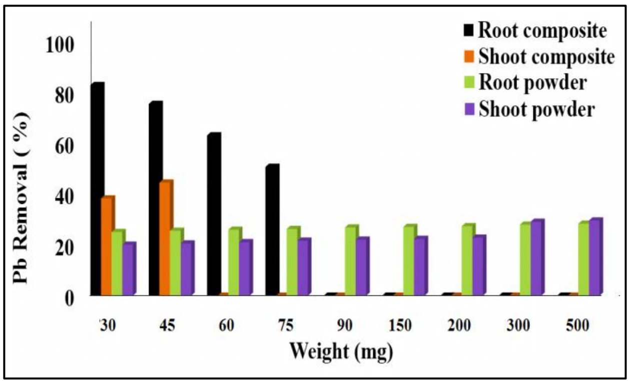


Figure 2. Removal percentage of Pb in the presence of water hyacinth parts within 24 hr and reference (0.0162 ppm)

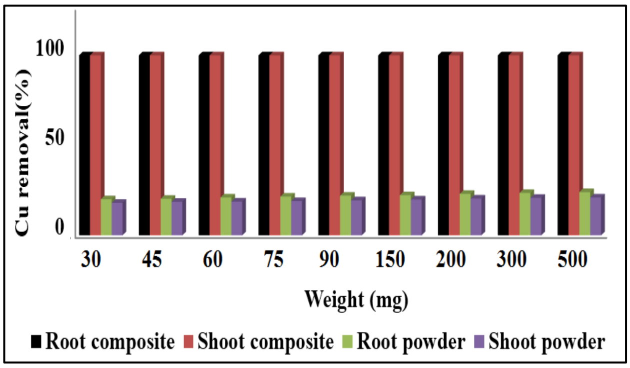


Figure 3. Removal percentage of Cu in the presence of water hyacinth parts within 24 hr and reference(0.0205 ppm).

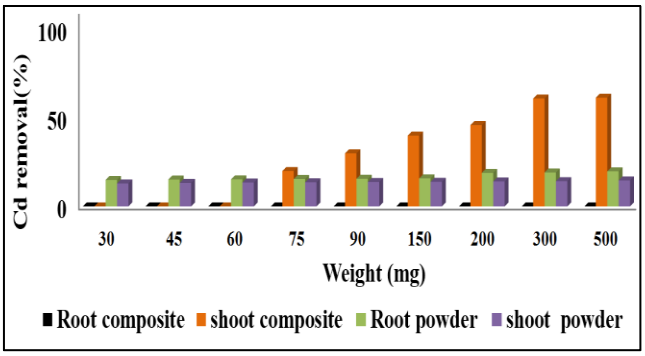


Figure 4. Removal percentage of Cd in the presence of water hyacinth parts within 24 hr and reference (0.0063 ppm).

The characteristics of the chitosan beads are shown in Fig.5. The band at (3365cm^{-1}) was attributed to (OH) stretching vibration. The band at 2920 cm^{-1} is attributed to C-H vibration for alkanes. The band at (2177) cm^{-1} was due to C=N, and the band at (1651 cm^{-1}) attributed to C=O stretch vibration of carboxyl ate. The appearance of the band at (1591 cm^{-1}) is attributed to the C=C aromatic; band at (1479 cm^{-1}) attributed to C-H deformation, and the band at (580 cm^{-1}) is attributed to (chloride, bromide, iodide. The results are in good agreement with those in (1). It is evident from Fig.6 that FTIR spectrum of shoot water hyacinth/chitosan composite include disappear of (OH) bands stretching vibration and cross-linked chitosan appearing at 1649 cm^{-1} and 1550 cm^{-1} matching to extending vibration (-POH) groups, which lowerdin comparison with root composite, made it less absorbance to heavy metal than root composite. The spectra show the characteristic bands of poly saccharide such as cellulose and proteins. The results showed that the water hyacinth plant contains carbon, crud protein, amino acids, phosphorus, cellulose, lignin, and flavonoids, which is agreement with (2).

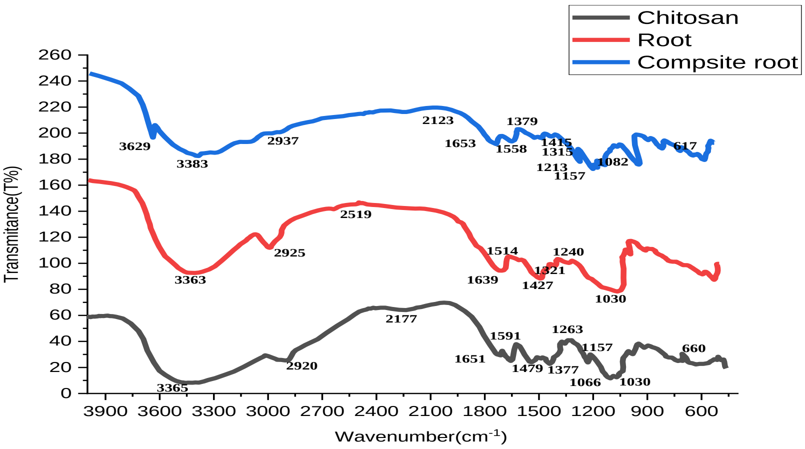


Figure 5. FTIR spectra of :(A) Chitosan beads; (B)Root powder hyacinth plant and (C) Chitosan beads with root powder hyacinth plant.

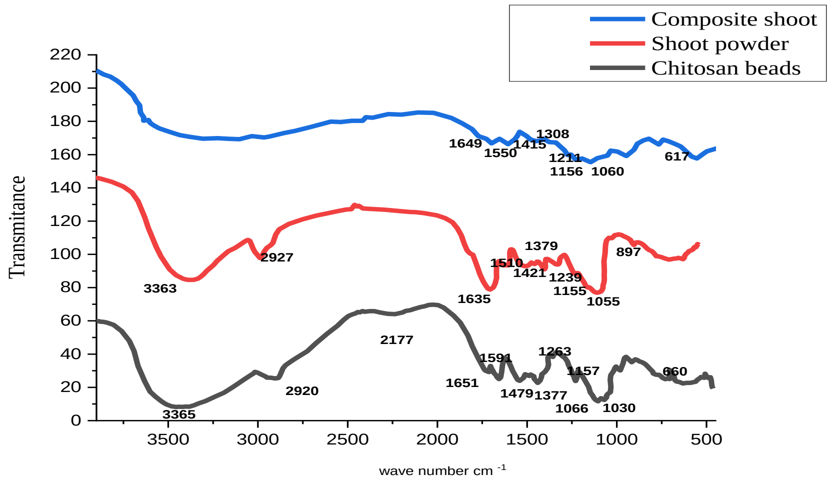


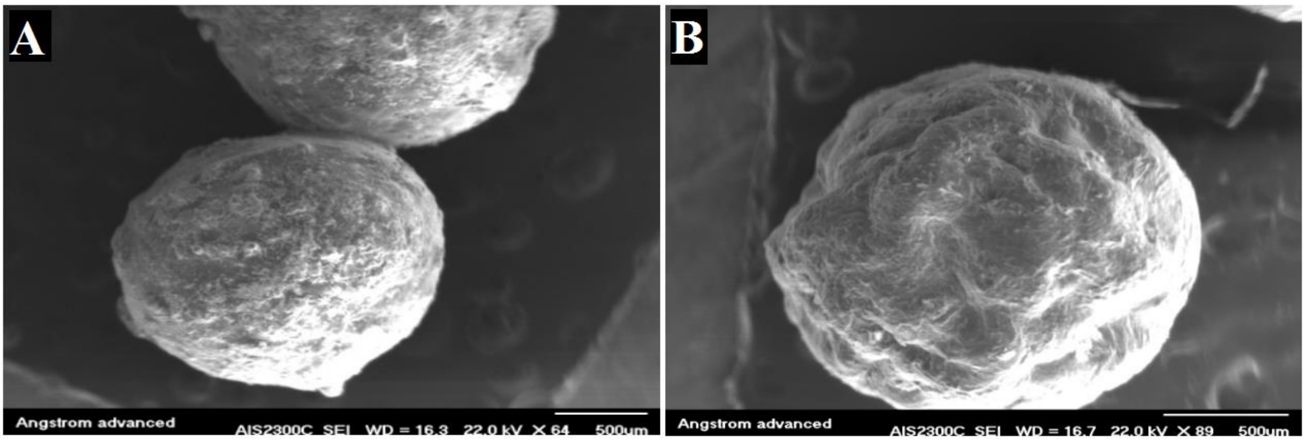
Figure 6. FTIR spectra of :(A) Chitosan beads; (B)Shoot powder hyacinth plant and (C) Chitosan beads with shoot powder hyacinth plant.

Figure 5 displays the FTIR spectra of root water hyacinth/chitosan composite that include the typical bands of cross-linked chitosan appearing at 1653 cm^{-1} and 1558 cm^{-1} matching to extending vibration of (P=O) of the (-POH)groups and extending vibration of $(NH^{3+)}$ group correspondingly. In addition, the band displays the central peaks of water hyacinth dry substance which seems at 1379-1315 cm^{-1} and 1213 cm^{-1} which matches to CH_3 umbrella style.

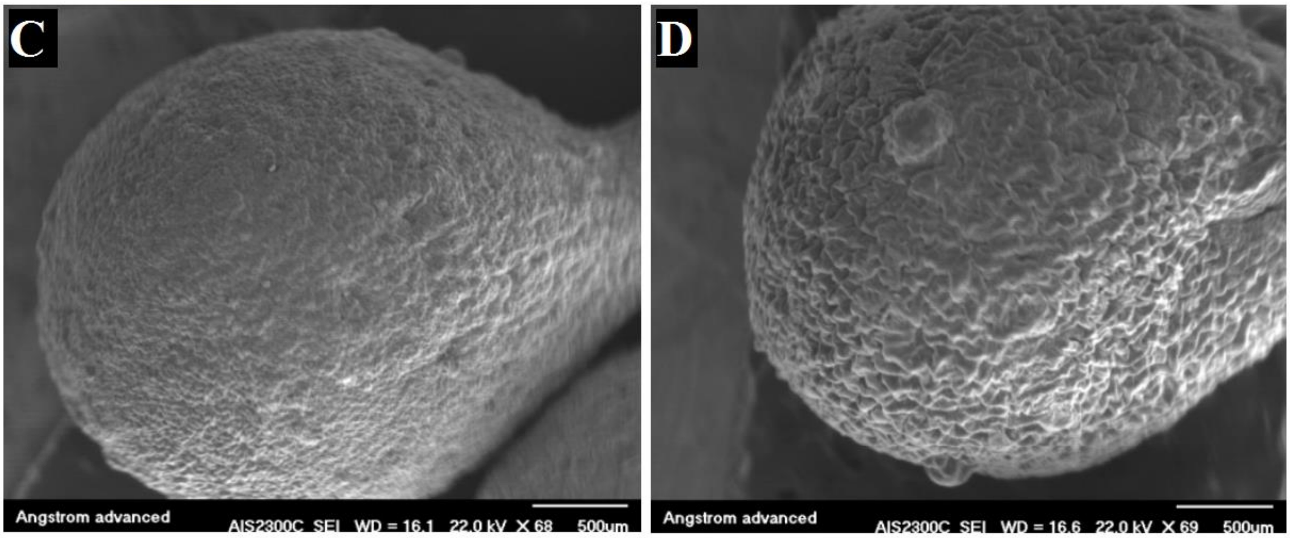
The nearby band agrees to CH3 umbrella mode. The band near1157 cm^{-1} is illustrative of the ant symmetric bridge extending of C-O-C groups in cellulose. After the overhead point out results, it could be determined that there are no new bands which gives the impression in the spectrum of water hyacinth/ chitosan composite providing a strong indication that the prepared beads is a composite. These result were enhanced with (SEM) results; which proved that the particles of (water hyacinths plant) are implanted in the matrix of cross-linked chitosan polymer as a composite material.

The SEM photographas of chitosan with root and shoot beads are illustrated in Fig.7.The samples investigated were as microsphere that showed very clear and bunch of poros; which are arranged homogenously. On microsphere examination, the microsphere has adiamter of approximalty (1mm), with surface and interior presenting high porosity (2).

(SEM) Image for beads, the results indicated that there is certain alteration in a water hyacinth plant external structure as a consequence of presenting chitosan to procedure plate like structure in dry phase. The picture of SEM microsphere of (chitosan\hyacinth plant) microsphere showed the particles structure of water hyacinth plant; it is mostly lignin and cellulose entrenched in cross linked chitosan matrix. Thus statistics might be a good approval to those obtained above by FTIR. The chitosan –based haycinth (root and shoot) were solid ,spherical;micro or nano size water carrior particley consitutting a matrix type structure; this is in agreement with that in(19).



(a) Dry Beads of chitosan and root hyacinth plant **(b) Wet Beads of chitosan and root hyacinth plant**



(c) Dry Beads of chitosan and shoot hyacinth plant **(d) Wet Beads of chitosan and shoot hyacinthplant**

Figure 7. SEM photographs of chitosan with root and steam beads

Conclusion:

The results of FTIR and SEM investigation designate that chitosan is cross-linked into water hyacinth particles to produce new composite, a structure that appear as spheres while plunged in solution. The composite is of compacted size; no oxygen ingesting is indicated for the elimination of heavy metal ions from wastewater during (24 h). From this work , it can be concluded that it is an easy and self-assembling way aimed at the low-cost sorbent made after dried water hyacinth/chitosan that offers high-sorption performance of Pb(II),cu (ll), cd(ll) and high viability of desorption. The most stimulating result of this microsphere attitude is that the machinery of the elimination procedure is an ion-exchange. These suitable features will donate to the recycle of microspheres as a new sorbent material in applied applications for elimination of heavy metals from wastewater. It is worth to mention here that there are so various methods used in the elimination of contaminants some of which are natural while the others are determined by chemical methods.

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Conflicts of Interest: None.

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تحضير ودراسة خصائص متراكبة زهرة النيل مع الجايتوسان لإزالة المعادن الثقيلة

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الخلاصة :

في هذه الدراسة، تم تحضير ودراسة خصائص متراكبة نبات زهرة النيل / الجايتوسان ، لإزالة المعادن الثقيلة. تم جمع نبات زهرة النيل من على ضفاف نهر دجلة في بغداد. اجزاء زهرة النيل من جذر وساق تم تنعيمها إلى مسحوق. المواد المتراكبة تحضر بنسب للجزء النباتي من (2.9% الى30.3% بنسب وزنيه) التي تقابل من (30 الى 500 ملي غرام)مع الجيتوسان. النتائج أظهرتأن جميع أجزاء النبات لها امتصاص ممتاز للنحاس الثنائي وصل إلى 100%. حيث أن نسبة (2.9 %) تقابل 30ملي غرام من إضافة زهرة النيل للجايتوسان أعطت أعلى إزالة للرصاص الثنائي تصل إلى 82.2% خلال 24 ساعة بينما أن نسبة أن نسبة 20.23% من إضافة ساق زهرة النيل إلى الجايتوسان أعطت إزالة 61% من الكادميوم الثنائي خلال 24ساعةومن ناحية أخرى أظهرت صور (SEM)إشكال منتظمة ومسامية عالية للنماذج بينما كانت اطياف(FTIR)اثبت على تكوين المتراكبة .

الكلمات المفتاحية: عميلة الامتزاز، الجايتوسان، زهرة النيل، المعادن الثقيلة.