Biosorption of Cu Ions from Sewage Water Using Water Hyacinth as a Low Cost Biosorbent

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Abstract

Biosorption of heavy metals is an effective technology for the treatment of Iraqi sewage water; an analytical technique used Atomic absorption spectroscopy of flame to estimate the ions of heavy metals and to monitor adsorption capacity and adsorption isotherms.

Results are presented showing the sorption of Cu(II) from solutions as adsorbed by biomass of Powder stems of water hyacinth plant as adsorbent surface.

At room temperature, Packed column method experiments were conducted to determine the adsorption properties of the biomass and it was observed that the adsorption capacity of the biomass strongly depends on some factors such as flow rate, particles size adsorbent, weight of adsorbent, initial concentration of adsorbed and effect of PH, and that the maximum (highest) adsorption capacity was 100% of Cu(II) ions solution at 70ppm using 1gm packed column with 300micron of powder stems plant, This attributed to the increase in the number of active sites on the plant .

The isotherm adsorption data were analyzed using Langmuir and Freundlich, Adsorption isotherms were also obtained and maximum removal of Cu(II) of dry weight biomass at a pH of 7.0 in 4 drop/min, obeys to Freundich's equations through correlation values R^2 obtained.

Results indicate the model was good fits for experimental data based on correlation coefficient, R^2 values. The Freundlich n (1.587) shows that the biosorption was spontaneous, good and physical. The results indicated that the biomass of hyacinth water plant is suitable for the development of efficient biosorbent for the removal and recovery of Cu(II), from Iraqi Sewage water.

Kee words: Heavy metals, Water hyacinth (Eichhornia crassipes), Biosorption, Cu(II).

1.INTRODUCTION

Heavy metals are toxic contaminants, because they are harmful to living organisms even in low concentrations, due to toxicity and carcinogenic properties that can accumulate in living tissues causing various diseases and disorders. The main toxic metal ions that pose a danger to humans as well as other life forms are Cr, Pb C, V, Cu, Ni, Cd, Hg and Fe, the removal of these toxic pollutants from wastewater are one of the most important environmental issues. The high solubility of these minerals in water, combined with their high reactivity and resistance to biodegradation, makes them an important toxic substance to be monitored in the aquatic environment. Since all heavy metals are non-biodegradable, removals from polluted tables must be of environmental quality standards (1). The US Environmental Protection Agency (EPA) regulations call for lowering heavy metals content in wastewater. Recently there is a considerable interest in developing cost effective and environmentally friendly technologies for the remediation of soil and wastewater polluted with toxic trace elements (6). Several methods have been used to remove heavy metal ions from wastewater, including chemical deposition, chemical oxidation / reduction, flotation, reverse osmosis, ion exchange, process membrane, super filtration, electrochemical technology and biological process (2-3). Adsorption is the most attractive method because of its simplicity, High comfort and effective removal. In common absorption processes, activated carbon and synthetic resins are usually used to gain high removal efficiency. However, due to the high cost of production, the removal of water using these two pipettes is rather expensive (4-5). Plants have the ability to accumulate nonessential metals such as Cu, and this ability could be harnessed to remove pollutant metals from the environment (7). Plants based bioremediation technologies have received recent attention as strategies to clean-up contaminated soil and water (8).Since 1990’s the adsorption of heavy metal ions by low cost renewable organic materials has gained momentum (9-10).The utilization of seaweeds, moulds, yeasts, and other dead microbial biomass and agricultural waste materials for removal of heavy metals has been explored (11). Agricultural materials particularly those containing cellulose shows potential metal biosorption capacity.The basic components of the agricultural waste materials biomass include hemicellulose, lignin, extractives, lipids, proteins, simple sugars, water hydrocarbons, starch containing variety of functional groups that facilitates metal complexation which helps for the sequestering of heavy metals (12-13). Industrial wastes and agricultural waste and agricultural by-products materials being economic and ecofriendly due to their unique chemical composition, availability in abundance, renewable, low in cost and more efficient are seem to be viable option for heavy metal remediation (14). Water hyacinth (Eichhornia crassipes) is a noxious weed that has attracted worldwide attention due to its fast spread and congested growth, which lead to serious problems in navigation, irrigation, and power generation. On the other hand, when looked from a resource angle, it appears to be a valuable resource with several unique properties. As a result, research activity concerning control (especially biological control) and utilization (especially wastewater treatment or phytoremediation) of water hyacinth has boomed up in the last few decades (15).

2. Experimental

2.1 Materials and Chemicals

Water hyacinth, $CuCl_2$.2H2O,

2.2 Instrumentation

Analytical Balance, Grinding Machine, Hiraeus oven, pH meter

2.3 Collection of Water Hyacinth (Eichhornia crassipes)

The water hyacinth used in this research was obtained and collected from Alaubaidi District, Baghdad, Iraq .

2.4 Water Hyacinth Preparation Grain

The hyacinth (root, stalks, Leaves) part washed several times with tap water to remove any epiphytes and insect larvae grown on plants. The plants dried, Next, the hyacinth was cut into smaller parts, after that, it was placed in plastic tanks under natural sunlight for five days, and then in an oven at 95˚C for 12 hours. The grains were then filtered using mesh 300 micron, after grinded in an electric grinding machine(16).

2.5 Preparation of stock solutions.

All chemicals used in the present work were of analytical grade. The stock solution of Cu^{+2} ions was prepared in 100 g L^{-1} concentration using 0.0269 g $CuCl_2.2H_2O$ (Purity% 98.0%, Source England) in 100ml of volumetric flask. then diluted to appropriate concentrations.

2.6 Preparation of buffer solutions.

Three phthalate and phosphate buffer solutions of pH values (5.5, 7, and 8) were prepared

Respectively (22). Also a three stock solutions of the prepared $Cu+^2$ of 500 ppm concentration were prepared in 100 ml volumetric flask using the above buffer solutions.

2.7 Column method

Continuous flow adsorption experiments were conducted in a cylindrical glas column (1.2 cm internal diameter and 10 cm height). At the bottom of the column, a 0.2 mm plastic sieve was attached followed by glass wool. Known quantities of adsorbent (1g) were placed into the column, yielding bed heights of 5 cm. copper solutions of known concentrations were pumped downward through the column bed. Samples were collected at the column outlet at different time intervals and were analyzed for copper concentration by Atomic Absorption spectrophotometer (AA-7000, SHIMADZU, Japan) at 324.8 nm. The inlet concentration was varied from 10 to 70 mg/L and the flow rate was varied from 2 to 6 drop/ min) or (0.1 to 0.3 mL/min) at a fixed inlet concentration (500 ppm).

2.8 Analysis of Metal Ions

The concentration of Cu (II) ions in the biosorption media was determined using Atomic absorption Spectrophotometer (AA-7000, SHIMADZU, Japan), equipped with air acetylene burner. Analytical wavelength was set at 324.8 nm. and then The amount of Cu (II) ions adsorbed, *q* (mg/g) was calculated by:

$$Qe= Co - Ce * V/ W$$

where **Co** and **Ce** (mg. L^{-1}) are the liquid-phase concentrations of phenol at initial and sampling times, respectively; **V** is the volume of the solution and **W** is the mass of dry adsorbent used.

3. Results and Discussion

Biosorption of heavy metal ions onto the surface of a biological material is affected by several factors, such as initial solution concentration, initial biomass concentration and flow rate (contact time)..

3.1 Effect of adsorbate initial concentration ($C_\circ$) of Cu^{+2} ions

To study the adsorbate concentration on a fixed weight surface of adsorption1g water hyacinth plant bed at different PH values (5.5, 7and 8) using buffer solutions, and at room temperature (25±2) °C. Plotting C_o(values from against removal % of $Cu+^2$ ions as shown in (table 1 and Fig.1).

Table (1) Values of removal present with change of adsorbate initial concentration.

C_o(ppm)	R%
10	99.65%
20	99.79%
30	99.89%
40	99.90%
50	99.96%
60	99.98%
70	100%

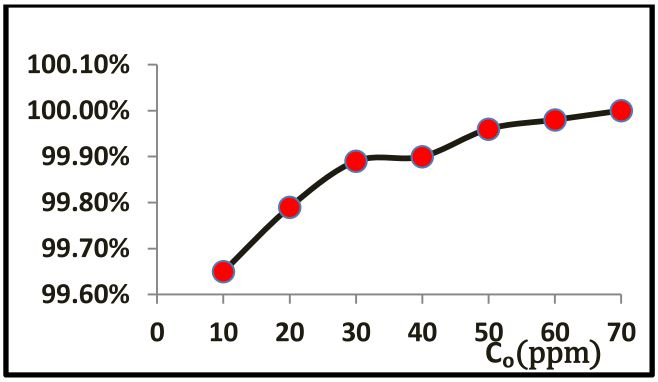

Figure 1. Effect of initial solution concentration on the removal of Cu(II) by water hyacinth

(amount of biosorbent = 1.0 g, temperature = 25 ^oC and contact time = 50 min)

When we notice the graph we find that the highest adsorption of Cu^{+2} ions occurs at PH=7. Figure 1 illustrates the adsorption of Cu(II) ion by water hyacinth as a function of initial metal ion concentration. This increase continues up to 70 ppm for Cu^{+2} and beyond this value, there is not a significant change at the amount of adsorbed metal ions. This plateau represents saturation of the active sites available on the biosorbent samples for interaction with metal ions. It can be concluded that the amount of metal ions adsorbed into unit mass of the water hyacinth at equilibrium (the adsorption capacity) rapidly increases at the low initial metal ions concentration and then it begins to a slight increase with increasing metal concentration in aqueous solutions in 70 ppm for copper. These results indicate that energetically less favorable sites become involved with increasing metal concentrations in the solution. The metal uptake can be attributed to different mechanisms of ion exchange and adsorption processes of the plant surface(17).

3.2 Effect of pH.

pH were studied and their impact on the adsorption of Cu^{+2} ions On the surface of waer hyacinth plant by preparing three Cu^{+2} ions solutions of constant concentration (20) ppm adjusted to different pH values (5.5, 7and 8) using buffer solutions. Then passage (10 ml) of each solution through a three columns of 1g plant bed with constant flow rate (4 drops min^{-1} at room temperature (25±2) °C, then by measuring the absorbance of these solutions after passing through the adsorption column, calculation of removal % of Cu^{+2} ions by the plant bed, and plotting removal present against the pH values as shown in (Fig. 2) it's found that the best pH value of adsorption of Cu^{+2} ions on plant bed was (pH=7), and that is due to the neutral character of Cu^{+2} ions as shown in (table 2 and Fig.2).

Table (2) Values of removal present with change PH solutions.

	root	stalk	Leave
PH	R%	R%	R%
5.5	99.91%	99.91%	99.92%
7	99.86%	99.85%	99.95%
8	99.86%	99.92%	99.79%

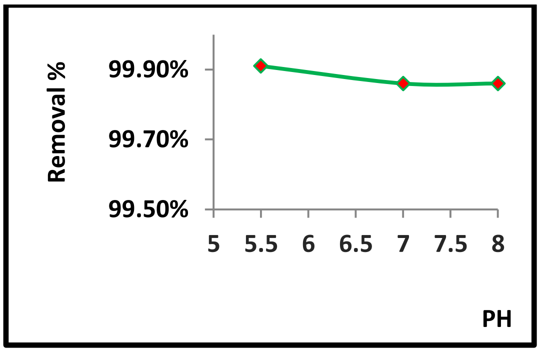

Fig. 2. Effect of pH on adsorption of Cu+^{2} ions on water hyacinth plant.

3.3 Effect of plant weight.

Seven different plant weight columns ranged from (0.2 – 1.2 g) plant bed were prepared for the passage(10 ml) of Cu^{+2} ions solution at pH = 7 and concentration of (20) ppm with constant flow rate of (4 drops/ min.) at room temperature (25±2) C°, then by measuring the absorbance of these solutions after passing through the adsorption column, calculation of removal percent of Cu^{+2} ions by the plant bed, and plotting removal percent against the clay weight as shown in (table 3 and Fig. 3) it's found that the highest adsorption of Cu^{+2} ions occurs on plant bed of 1.0 g weight. This means increasing absorption with increasing weight of clay to the upper limit of plant capacity, and adsorption surface area.

Table (3) Values of removal present with change plant weight.

(Weight gm)	R%
0.2	99.90%
0.4	99.92%
0.6	99.93%
0.8	99.98%
1.0	100%
1.2	100%

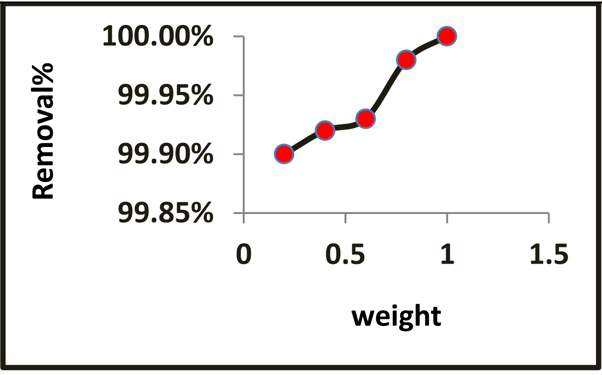

Fig.3. Effect of plan weight on adsorption removal persent of Cu^{+2} ions.

4. Adsorption Isotherms.

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among Cu^{+2} and adsorbent waer hacinth, based on a set of assumptions that are mainly related to the adsorbents, the type of coverage and possibility of interaction between the adsorbate species. Adsorption data are usually described by adsorption isotherms, such as Langmuir, Freundlich, isotherms (19). The set of experimental results as presented in fig.(4) at room temperature (25±2) were fitted with the Langmuir, Freundlich, models.Adsorption isotherms were obtained and the adsorptive capacity interpreted using both models.

4.1 The Langmuir isotherm.

The Langmuir model (20) is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The Langmuir isotherm is given by:

$$q_e = q_m k_1 Ce / 1 + K_1 Ce$$

The constants in the Langmuir isotherm can be determined by plotting (1/qe) versus (1/Ce) and making use of above equation rewritten as:

$$1/ q_e = 1/q_m + 1 /q_m K_L * 1 / Ce$$

Where qm (mg/g) and KL (L/mg) are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively. The values of qm and KL can be evaluated from the intercept and the slope of the linear plot of experimental data (Table4) of (1/qe) versus (1/Ce) (Fig.5), and were found to be -0.01418 mg/ g and -1.3×10^{-9} L/mg, respectively. Also the isotherm data fits the Langmuir equation well where the coefficient of determination (R^2= 0.9661).

4.2 The Freundlich isotherm.

The Freundlich isotherm model (21) is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved. Freundlich adsorption isotherm is the relationship between the amounts of ligand adsorbed per unit mass of adsorbent,qe, and the concentration of the copper at equilibrium (Ce).

$$\mathbf{q_e = K_f * Ce^{1/n}}$$

The logarithmic form of the equation becomes

$$\mathbf{Log\ qe = log\ K_f + 1/n\ log\ Ce}$$

Where K_f and n are the Freundlich constants, the characteristics of the system. K_f and n are the indicators of the adsorption capacity and adsorption intensity, respectively. The ability of Freundlich model to fit the experimental data was examined. For this case, the plot of log Ce vs. log qe was employed to generate the intercept value of K_f and the slope of n. from (Fig.6) The Freundlich constants K_f and n were found to be 1.5194 and 0.8967respectively. The Freundlich isotherm is more widely used but provides no information on the monolayer adsorption capacity in contrast to the Langmuir model. Freundlich isotherm fitted well with the coefficient of determination (R^2=0.9789).

Table 4 -Experimental data of the Adsorption Isotherms.

		Adsorption isotherms		**Langmuir equation**		**Freundlich equation**	
Metal Ion	C_o (mg/L)	C_e (mg/L)	Qe (mg/g)	1/Ce	1/Qe	Log C_e (mg/L)	Log Qe (mg/g)
Cu(II)	140	139.9257	0.000743	0.00714	1345.8950	2.1458	-3.1290
	175	174.9193	0.000807	0.00571	1239.1573	2.2428	-3.0931
	210	209.8897	0.001103	0.00476	906.6183	2.3219	-2.9574
	245	244.8744	0.001256	0.00408	796.1780	2.3889	-2.9010
	280	279.9670	0.001556	0.00357	642.6735	2.4471	-2.8079
	315	314.8242	0.001758	0.00317	568.8282	2.4980	-2.7549
	350	349.8095	0.001905	0.00285	524.9343	2.5438	-2.7201

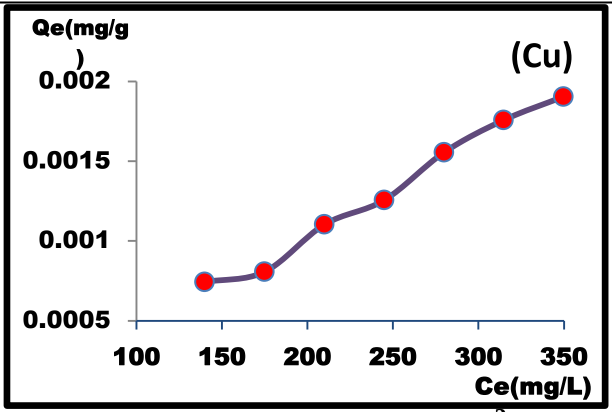

Fig.4. Adsorption isotherm of Cu+^{2} at pH = 7

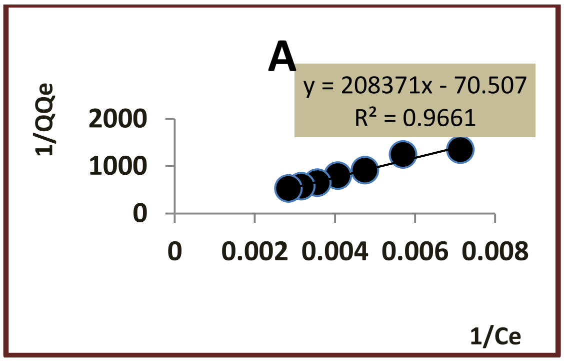

Fig.5. Langmuir linear adsorption isotherm of Cu+2

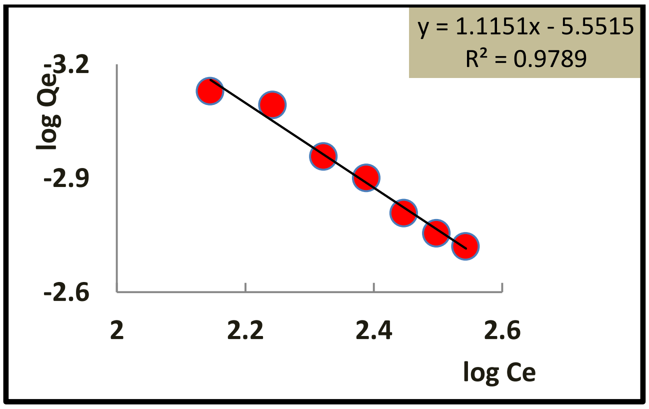

Fig. 6. Freundlich linear adsorption isotherm of Cu+^{2} ions.

5. Effect of flow rate (contact time).

Adsorption of Cu+^{2} ions was measured at five different flow rates for aqueous solution (20) ppm, concentration. From (Fig.7), the plot reveals that removal percent of is Cu+^{2} ions higher at low flow rates. This is probably due to higher contact time at these low flow rates. Adsorption can be viewed as a two-stage process, with a rapid initial adsorption, followed afterwards by a much slower rate. This is attributed to the high values of concentration gradient in the beginning of the adsorption processes, representing a significant driving force for phenol transfer between the solution and the adsorbent surface.(23) (Table2) show the calculated parameters that illustrate the importance of flow rate and contact time.

Table 2 :Effect of contact time on the adsorption of Cu+^{2} ions

20					Initial Conc. (ppm)
6	5	4	3	2	Flow Rate (drop/min)
0.30	0.25	0.20	0.15	0.10	Flow Rate (ml/min)
33.33	40.00	50.00	66.66	100.00	Time (t) (min)
0.1619	0.1506	0.1110	0.0909	0.0489	Equilibrium Conc.(C_t) (ppm)
99.19	99.24	99.44	99.54	99.75	Removaal%
0.19838	0.198404	0.19889	0.19909	0.19952	q_e (mg/g)
0.19889					q_t (mg/g)
7.58306	7.629301		-8.512205	-7.36979	Ln(qe-qt)
168.010	201.608	251.395	334.821	501.202	t/qe
50.00					Equilibrium Time (min)

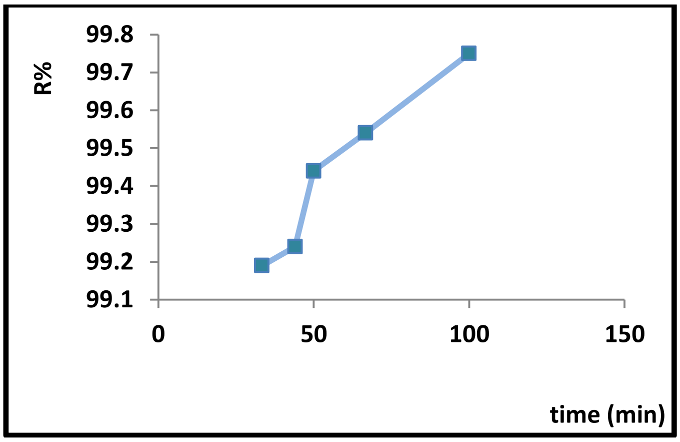

Fig.7. Effect of flow rate on adsorption removal % of Cu+^{2} ions on water hyacinth(1g).

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ألخلاصة

يعتبر الامتزاز الحيوي للمعادن الثقيلة تقنية فعالة لمعالجة مياه الصرف الصحي العراقية. التقنية تالحليلية تستخدم مطيافية الامتصاص الذري اللهبي لتقدير أيونات المعادن الثقيلة ولرصد قدرة الإدمصلص(الامتزاز) وآيزوثيرمات الامتزاز.

وتبين النتائج المعروضة ان امتزاز النحاس (الثاني) من الحلول كماة ممتزة بواسطة مسحوق سيقان من الكتلة الحيوية نبات زهررة النيل (صفير الماء) كسطح ماز.

في درجة حرارة الغرفة ، أجريت تجارب طريقة عمود معبأة لتحديد خصائص الامتزاز للكتلة الحيوية ولوحظ أن قدرة الامتتزاز للكتلة الحيوية تعتمد بشدة على بعض العوامل مثل معدل التدفق ، حجم الجزيئات الممتزة ، وزن المازة ، التركيز الأولي للمادة الممتزة وأثر PH ، وأن أقصى سعة امتزاز (أعلى) كانت 100% من محلول أيونات Cu(II) عند 70ppm باستخدام عمود 1gm معبأ بـ 300micron من مسحوق ساق النبات، وهذا يعزى إلى الزيادة في عدد المواقع النشطة على النبات.

تم تحليل بيانات آيزوثيرمات الامتزاز التي تم الحصول علىها iباستخدام آيزوثيرمات امتزاز لانكماير وفريندلش والحد الأقصى لازالة ايونات Cu(II) من الوزن الجاف للكتلة الحيوية عند درجة الحموضة 7 في 4drop/min، تطيع إلى معادلات Freundich من خلال قيم الارتباط R^2التي تم الحصول عليها.

تشير النتائج ان البيانات التجريبية المستندة إلى معامل الارتباط قيم R^2 ان النموذج مناسباً وان ثابت فريندليش n هو (1.587) أن عملية الامتزاز هو فيزيائي وان العملية كانت تلقائية, أشارت النتائج إلى أن الكتلة الحيوية لنبات زهرة النيل مناسبة لتطور مواد مازة كفؤه لإزالة واسترجاع Cu(II) ، من مياه الصرف الصحي العراقية.