An-Najah National University

Faculty of Graduate Studies

Phytofiltration of Chromium (Cr) and Manganese (Mn) from polluted waters using *Luffa Cylindrica*

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This Thesis is submitted in Partial Fulfillment of the Requirements for the Degree of Master of Environmental Science, Faculty of Graduate Studies, An-Najah National University, Nablus - Palestine.
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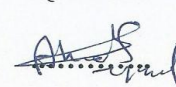Phytofiltration of Chromium (Cr) and Manganese (Mn) from polluted waters using *Luffa Cylindrica*

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This Thesis was Defended Successfully on18/10/2015, and approved by:

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Dedication

First of all, my greatest gratitude to Allah,

To my family, specially my father and mother ….

To my dear "Yousef"…

To my country "Palestine "…

 To my teachers and partners …

To all who help and encourage me in any way…

Acknowledgments

First of all, I am so grateful to Allah, who gives me the patience and power to finish my thesis.

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الاقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل عنوان:

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Phytofiltration of Chromium (Cr) and Manganese (Mn) from polluted waters using *Luffa Cylindrica*

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Declaration

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

Student's Name: اسم الطالب: آيات توفيق حسن أبو شرية

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Date: التاريخ: ٢٠١٥/١٠/١٨

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Abstract

The phytofiltration potential of *Luffa Cylindrica* (sponge and seeds) to remove Mn^{2+} and Cr^{3+} from aqueous solutions was studied. The effect of various parameters on the removal process was investigated. Such parameters included; pH, initial concentration of metal ion, temperature, and contact time. The binding capacity of seeds with the metal ion (mg/g) was determined. The effect of the presence of other competing ions was also studied. Adsorption isotherms were investigated, the reaction order and Gibbs free energy were determined. The results showed that the maximum percent removal of Cr^{3+} by sponge and seeds were 42% and 40% respectively, while were 82% and 78% for the removal of Mn^{2+} respectively. The optimum pH was 5.0 for the removal of Cr (III) and 7.0 for Mn (II). The percent removal of metal ions was optimum at initial concentration of 5 mg/L, a temperature range of 35℃ - 40℃, and a contact time of 30 minutes. The equilibrium concentration of metal ions in solution was followed by using flame atomic absorption spectrometry. Binding capacity of seeds was 1.7 mg/g for Cr (III) and 3.4 mg/g for Mn (II). The results of the uptake of Cr (III) by seeds fit well with the Langmiur adsorption isotherm, while Freundlich adsorption isotherm was found to be

more applicable for the removal of Mn (II) by seeds. The binding of both metal ions with seeds followed a second order kinetics. The values of Gibbs free energy were also determined.

Chapter One
Introduction

There has been an increasing concern regarding the accumulation of heavy metals in the environment. These metals are considered as a threat to both human health and environment, especially when their tolerance levels are exceeded. This is due to the fact that, unlike many substances, toxic heavy metals are not biodegradable over time, and accumulate in the environment. Therefore, there is a necessary demand for toxic heavy metal sequestration in order to immobilize their release in environment. Heavy metals such as manganese, arsenic, nickel, lead, cadmium and chromium reach the bodies of water mainly from industrial waste and landfill run off.

1.1. Heavy metals

Heavy metals are chemical elements that have a specific gravity that is at least five times the specific gravity of water; e.g., arsenic, 5.7, cadmium, 8.65, mercury, 13.546 (Graeme and Pollack, 1998).

Heavy metals enter the water system from various sources, as agricultural sources due to use of fertilizers and pesticides that reach the water bodies as runoff, in addition to sewage effluents (Gupta et al., 2009). Heavy metals are the most toxicological species found in industrial effluents due to mining, painting, etc…, (Abdel- Ghani et al., 2009). They accumulate in living tissues by food chain, multiplying the danger (Einschlag, 2011a).

The greatest toxicity of heavy metals comes from its ability to form highly stable ligands with organic compounds in the body. Since they are

bioaccumulative; they bound with organic compounds, modify the biological organic molecule that in many cases result in malfunction, change the main ingredients of the affected cells, lead to death of the cells in many cases (David and Norman, 1986).

In the present study, chromium (III) and manganese (II) were investigated.

1.1.1 Manganese (II)

Manganese is a very common metal that can be found everywhere on earth, manganese compounds exist naturally in the environment as solids in the soils, small particles in the water and as dust particles in air. It is not only essential for humans to survive, but it is also poisoning when very high concentrations are present in a human body (Lenntech). National Secondary Drinking Water Regulations for manganese is 0.05 ppm (EPA). Humans have the greatest role in increasing the concentrations of manganese in the environment through certain activities, as industrial activities and burning fossil fuels. These concentrations can also enter surface water, groundwater and sewage water. For some animals, the lethal dose is quite low, which means that smaller dose of manganese decrease the chance for them to survive when they exceed the essential dose. Manganese substances can cause lung, liver and vascular disturbances, decline in blood pressure, failure in development of animal fetuses and brain damage. When manganese uptake occurs through the skin, it can cause tumors and coordination failures. Finally, laboratory tests with test animals have shown that severe manganese poisoning should even be able

to cause tumor development with animals. In plants, manganese can cause both toxicity and deficiency symptoms, especially when the pH of the soil is low (Lenntech).

1.1.2 Chromium (III)

There are different forms of chromium, such as Cr (III) and Cr (VI). Chromium enters the air, water and soil in all forms, through natural processes and human activities. The main human activities that increase the concentrations of chromium (III) and chromium (VI) mainly in water are steel, leather and textile manufacturing. Through coal combustion, chromium will end up in the air; eventually settle in waters or soils. In water, chromium will absorb on sediment and become immobile; a large part of the chromium that ends up in water will eventually leach out (Lenntech). EPA regulated limit in drinking water for Cr (III) and Cr (VI) is 0.1 ppm (Primary Drinking Water Rules, 1992). Chromium (III) is less mobile, less toxic and is mainly found bound to organic matter in soil and aquatic environments (Salt et al., 1994; Zavoda et al., 2001). Plants usually absorb only chromium (III), the essential kind of chromium for organisms, but if concentration exceeds a certain value, it can disrupt the sugar metabolism and cause heart conditions, even at too low dose (Lenntech).

Chromium toxicity in plants is observed at multiple levels, from reduced yield, through effects on leaf and root growth, to inhibition on enzymatic activities and mutagenesis (Salt et al., 1994; Zavoda et al., 2001). Generally, chromium doesn't accumulate in the bodies of fish, but disposal

of metal products in surface waters increase chromium concentrations to high value, that can damage the gills of fish that swim near the point of disposal.

In animals, chromium can cause respiratory problems, decrease the immunity toward disease and cause birth defect (Lenntech).

1.2. Traditional techniques for removing heavy metals

The traditional techniques used to remove heavy metals from polluted water involve filtration (using activated charcoal), ion exchange resins, flocculation and chemical precipitation. These aforementioned techniques are costly and deleterious for both human health and the environment (Anderson, 1973; petruzzelli et al., 1997). Although precipitation is the most common one, but it only reduces the dissolved metal concentration to solubility product level which for many metals exceeds the discharge permit standards and thus needs extra cleaning stages (Gardea-Torresdey et al., 2004). Ion exchange resins have been widely used to remove heavy metals from waste water, but they are expensive and generate leachate that harms the human health (petruzzelli et al., 1997). Flocculation techniques are dependent basically on the use of flocculants to clean wastewater, but they are expensive and produce sludge and saline effluent (Semerjian and Ayoub, 2003). Filtration technique depends on the material of filtrate, the most common one is the charcoal that is used to remove organic contaminants from aqueous solution, the extensive use of it for metal removal from industrial effluents is expensive (Lima et al., 2002), when the

plant biomass is the material used in filtration process, the technique then is called phytofiltration.

1.3. Phytofiltration

Phtyofiltration is a subset of the bioremediation technology. Bioremediation is a large term that means using biological agents as bacteria or plants to remove or neutralize contaminants in polluted soil or water.

Bioremediation is a relatively new technique that appeared in the 1980s and received significant interest since it has proven to be a very promising technique in the cleaning of effluents from the contaminants in an environmentally friendly manner (Gardea-Torresdey, et al., 1996a; Volesky, 2001).

Bioremediation process includes: phytofiltration; the use of dead or inactivated biomass to remove heavy metals from contaminated water (Miller, 1996; Gardea-Torresdey et al., 2004) and phytoremediation; a green technology that uses living plants to remove contaminants from environment or renders them harmless (Berti and Cunningham, 2000; Salt et al., 1994). Phytoremediation can be accomplished by phytoextraction, phytovolatization, phytodegradation, phytostabilization, and rhizofiltration. Rhizofiltration; using plant root as a filter to absorb pollutants mainly heavy metals from aqueous systems (Zhu et al., 1999; Dushenkov et al., 1995). Phytoextraction; removal of heavy metals from the soil by direct

uptake of metals into plant roots that translocate into the upper parts of plant to be harvested latter (Cluis, 2004). Phytodegradation; also called phytotransformation, is a contaminant destruction process, it is a Phytoextraction mechanism, but differs in that, after the contaminants are translocated in the aerial portions of the plant, they are converted to a less toxic form, plant-produced enzymes which found in rhizosphere metabolize the contaminants (Singh and Labana, 2003). Phytostabilization; plants stabilize the contaminants by chemically immobilizing them in the soil, thus avoiding risk of their leaching in ground water or spreading in the air that reducing their bioavailability in the environment (Prasad and de Oliveira Freitas, 2003).

Phytovolatization; Plants are used to volatilize the volatile contaminants (as mercury), by extracting them from the soil then converting to gas which is released by transpiration from leaves (Ghosh and Singh, 2005a; Ghosh and Singh, 2005b; Raskin et al., 1997).

Biosorbents are cheap and readily available; they obtained either from nature or from certain process as a waste byproduct (Bailey, et al., 1999). It has been proven by many researchers that using biomaterials derived from different kinds of dead cheap biomass have a good ability to bind toxic contaminants from waste water (Gardea-Torresdey, et al., 2004; 1998a; Tiemann, 1998; Sawalha et al., 2006; Abu shqair et al., 2000). Dead biomass shows better properties than of living organisms; dead biomass is not affected by high concentrations of pollutants, and needs no

maintenance, in contrast to living organisms which affected by high concentrations of pollutants and need nutritional supply (Gardea-Torresdey, et al., 1996c).

Faced with the demand for new material that is more efficient, inexpensive, biodegradable, and environmentally friendly, the use of plant material (*Luffa Cylindrica*) for the purification of toxic products in aqueous effluents has received a significant credibility in recent years (Laidani et al., 2010).

1.4. *Luffa Cylindrica*

Luffa [*Luffa cylindrica (L.) Roem syn L. aegyptiaca Mill*], commonly called sponge gourd, smooth loofa, vegetable sponge, and bath sponge is a member of cucurbitaceous family (Bal et al., 2004). The fruits and classification of the plant are shown in figure 1 and table I.

(a) (b)
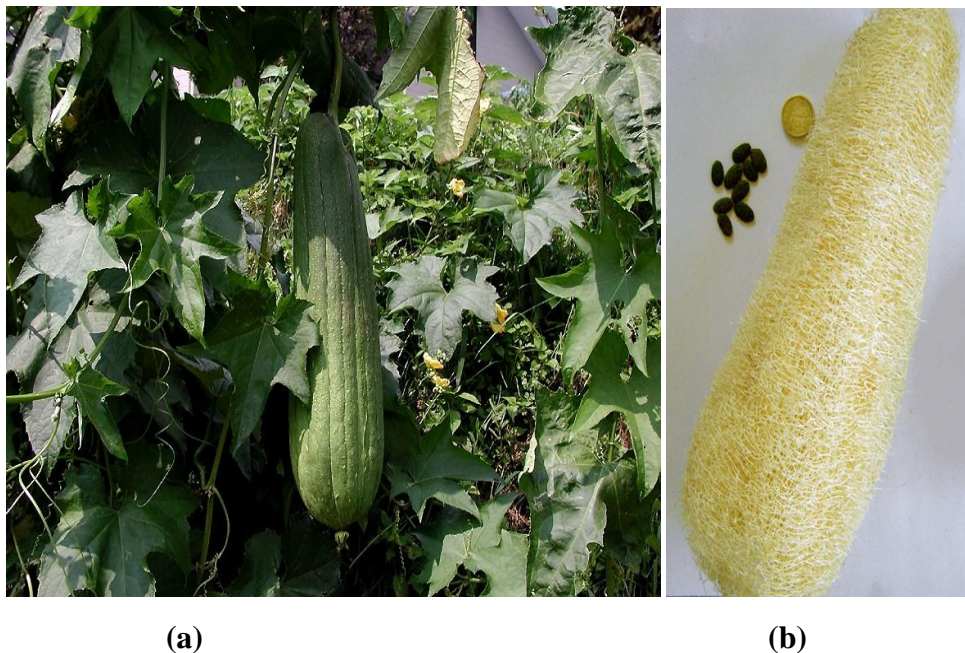
Figure 1: *L.Cylindrica;* (a) young fruits, (b) matured fibers with seeds.

Table I : Scientific classification of *L.Cylindrica* (Kirtikar and Basu, 1973).

Kingdom	Plantae
Division	Mangoliophyta
Class	Mangoliosida
Order	Cucurbitales
Family	Cucurbitaceae
Genus	Luffa
Species	Cylindrica

L. cylindrica is a lignocellulosic material consisted mainly of cellulose, hemicelluloses and lignin (Rowell et al., 2002). The fibers are composed of 60% cellulose, 30% hemicelluloses and 10% lignin. The fruits of *L.cylindrica* are smooth and have cylindrical shape (Mazali and Alves, 2005). One mature Luffa sponge produces at least 30 seeds, some can produce more and more (Newton, 2006). The seeds are black and contain 40% protein and 40% oil. Seeds need to be germinated at 25ºC and grown on transplanted when the soil temperature is about 18ºC. The flower of *L. cylindrica* is yellow and blooms on August - September. *L. cylindrica* grows about 12 cm long (Lee and Yoo, 2006). Both male and female flowers found on the plant with a much larger number of male flowe*r*s (Stephens, 2012). *Luffa* is a sub-tropical plant, which demands warm summer temperatures and long frost-free growing season. It is an annual climbing vegetable which produces fruit containing fibrous vascular system. The indigenous areas of *Luffa* species is difficult to assign with accuracy, tropical countries of Asia and Africa are very familiar in cultivation of *Luffa* species. Indo-Burma is documented to be the center of

diversity for *Luffa* species. The main commercial production countries are China, Korea, India, Japan and Central America (Bal et al., 2004).

The roasted seeds are edible and can be pressed to obtain oil, the oil has been used in soap manufacture in the United States, since the toxic seedcake is rich in nitrogen and phosphorous, it can be used as fertilizer (Lee and Yoo, 2006).

Young fruits are edible (can supply some antioxidant constituents to human body) (Oboh et al., 2009), and matured fibers have wide applications, generally used in washing ships and cars and manufacturing slippers or baskets (Lee and Yoo, 2006). After revealing the outer complex network of strict fibers and separating seeds; it can be used for bathroom and cleaning utensils, as shock absorbers, as a sound proof linings, as packing materials, as filters in factories, as soles of shoes (Bal et al., 2004), as adsorbent for removal of heavy metal [such as manganese, Lead, Chromium, Copper, etc] in contaminated water (Demir et al., 2008), as sequestration matrix for plant, algae, bacteria and yeast (Iqbal and Zafar, 1993a; 1993b), and they can also be recycled into mats or pillows when they finally wear down (Newton, 2006).

In addition, the *Luffa* that was reported to be a ribosome- inactivating protein separated from *Luffa* seeds is also effective against growth of parasites, protozoa, insects, fungi and HIV (Ng et al., 2011).

1.5. Objectives

The objective of this research is to determine the phytofiltration potential of *Luffa Cylindrica* to remove Mn (II) and Cr (III) from aqueous solution. This includes investigating the optimum conditions for phytofiltration e.g., pH, temperature, adsorption time, binding capacity, concentration of metal ions, effect of other competing ions. The kinetics of the biosorption process, as well as, the adsorption isotherms will be explored.

1.6. Novelty

There are numerous studies in the literature about using plant fibers, but very few are for fibers of *Luffa Cylindrica* (Laidani, 2010). No previous research studied the *seeds* of *Luffa Cylindrica* alone as a biosorbent in cleaning waste water from the heavy metals discussed in this work.

This research studies the biosorption of Mn (II) and Cr (III) by both sponge and seeds of *Luffa Cylindrica* at optimum batch conditions. More focus will be given to the seeds.

1.7. Hypothesis

This research was conducted under the hypothesis that both the sponge and seeds of *Luffa Cylindrica* are able to uptake certain amounts of the heavy metals (Mn (II) and Cr (III)) from their aqueous solutions.

1.8. Previous studies

▪ One study investigated the phytofiltration potential of *Luffa Cylindrical* by using its seeds and sponge mixture powder for removal of Ni^{2+}, Pb^{2+}, Cu^{2+} and Zn^{2+} from the aqueous solution. The highest percent removal of 1000 mg biomass was 98.2, 95.2, 87.6 and 43.5 for Pb^{2+}, Zn^{2+}, Cu^{2+} and Ni^{2+} respectively at pH 5.0 and contact time of 2 hours. (Einschlag, 2011).

▪ Another study showed that the *Luffa Cylindrica* sponge has a great potential for heavy metals removal in water systems. (Adie et al., 2013).

▪ One of the studies discussed the biosorption of lead by fibers and modified fibers of *Luffa Cylindrica* in batch experiment. The highest percent removals were 82.72% for the native fibers, and 94.93% for the modified ones (Saueprasearsit et al., 2010).

▪ A study determined the percent removal of metal ions present in the produced water as a secondary treatment by sponge powder of *Luffa Cylindrica*, the removal was up to 92.31%, 88.64%, 85.71% and 66.67% for Cr^{3+}, Zn^{2+}, Pb^{2+} and Cd^{2+} respectively (Oboh et al., 2009).

▪ One of the studies found that Durian Peel is an effective biosorbent in removal of Cr^{6+} from an aqueous solution; the maximum adsorption capacity was 10.67 mg/g (Saueprasearsit, 2011).

▪ A study determined the phytofiltration potential of Saltbush (*ATRIPLEX CANESCENS*) to remove heavy metals from contaminated waters in good percentages (Sawalha, et al., 2006).

▪ Another study discussed the using of some decaying leaves to remove certain heavy metals and showed a good potential (Abu Shqair, et al., 2000).

▪ One study determined the adsorption capacity of alfalfa binding to cadmium (II), chromium (III), chromium (VI), lead (II), and zinc (II) that were per gram of biomass: 7.1 mg Cd (II), 7.7 mg Cr (III), 43 mg Pb (II), and 4.9 mg Zn (II) (Gardea-Torresdey et al., 1998b).

Chapter Two

Methodology

2.1. Collection and treatment of biomass

Luffa Cylindrica (seeds & sponge) were purchased from local market. Seeds were washed with distilled water, oven dried at 70 ºC for three days, then ground to pass through 425 Micron sieve.

Sponge was washed with distilled water, oven dried at 70 ºC for five days.

The seeds were treated according to Gardea-Torresdey et al., 1996b. For each metal ion in this study, 0.50g native seeds were washed twice with 0.01 M HCl followed by deionized water to remove any substance that may interfere with metal binding. Then mixed with 100 mL of deionized water (biomass concentration is about 5mg biomass per mL of water). The pH of the seeds slurry was adjusted as the natural pH of each metal ion solution (pH = 4 for Cr (III), pH = 6 for Mn (II)). A 5.0 mL aliquot of the biomass mixture was added to each of three tubes and centrifuged for 5 minutes at 3000 rpm. The supernatants were discarded and the obtained biomass pellets were saved for further use.

For each of the two metal ions in this study, a 0.1g native *Luffa* sponge was immersed in DI water adjusted to pH values as the natural chromium and manganese solutions for 15 minutes.

For each parameter studied, a set of controls was kept and treated as the biomass solutions.

2.2. Preparation of solutions of chromium and manganese

$Mn(NO_3)_2 . 4\,H_2O$ (4.5638g/L) and $Cr(NO_3)_3 . 9H_2O$ (7.6995g/L) were used to prepare 1000 ppm manganese and 1000 ppm chromium solutions respectively.

2.3. Preparation of stock hard cation solutions

$MgCl_2 . 6H_2O$ (8.3580g/L), $CaCl_2 . 2H_2O$ (3.6628g/L) were used to prepare 1000 ppm magnesium and 1000 ppm calcium solutions respectively.

2.4. Preparation of calibration curves

A fresh 50 ppm metal ion solution was prepared daily by successive dilution of the stock 1000 ppm solution. Then 5, 10, 15 and 20 ppm solutions were prepared by diluting 10, 20, 30 and 40 mL respectively from the 50 ppm standard solution into 100 mL volumetric flasks. Deionized water was used as a blank. Volumetric flasks were soaking on 0.1 M HNO_3 before used. The concentration of the metal ion was followed by measuring the absorbance of the solution by flame atomic absorption spectrometry (FAAS). A calibration curve of absorbance versus concentration was constructed at the time of analysis. Calibration coefficient (R^2) was at least 0.999 for all analyses. Deionized water was aspirated into the instrument before and after the analysis of each sample to prevent interferences, and a

separate control of 10 ppm for each metal solution was read every 5 samples.

2.5. Metal quantification

The amount of metal ion that was sorbed and the percent removal of metal ion by biomass were calculated by applying equations 1 and 2 respectively:

$$q \ = \ \frac{C_o - C_f}{m} \cdot V \qquad (1)$$

$$\% \ Removal \ = \ \frac{C_o - C_f}{C_o} \cdot 100 \qquad (2)$$

Where q is the amount of metal ion sorbed by the biomass (mg/g); C_0 is the initial metal ion concentration; (mg/L), C_f is the final ion concentration (mg/L) after the biosorption occurred, V is the volume of aqueous solution (L) in contact with the biomass, and m is the mass (g) of biomass.

2.6. Instrumentation

- (ICE 3000 SERIES, Thermo Scientific) Flame atomic absorption spectrometer with acetylene-air flame was used for absorption measurements.
- JENWAY (3510) pH Meter was used to measure pH.
- (Centurion, Scientific Ltd) Centrifuge was used for separation.

2.7. Studied parameters

2.7.1 Effect of time

The binding time intervals studied were 5, 15, 30, 50 and 70 minutes. For each time interval, the obtained biomass pellets and the treated sponges were mixed with metal ion solutions. All samples were stirred at 20 ℃ for the appropriate time intervals at an agitation speed of 120 rpm. Then, samples of seeds were centrifuged for 5 minutes at 3000 rpm, sponges were removed from their mixtures, the supernatants and mixtures were saved for metal quantification using AAS.

2.7.2 Effect of initial concentration

5, 10, 15, and 20 ppm solutions of both metals were prepared from their stock solutions. For each concentration, the obtained biomass pellets and the treated sponges were mixed with an appropriate concentration of metal ion solution. All the samples were stirred at 20 ℃ for 20 minutes at agitation speed of 120 rpm. Then, seed samples were centrifuged and the sponges were removed from mixtures. The supernatants and mixtures were saved for metal quantification.

2.7.3 Effect of temperature

The effect of temperature was investigated at different degrees, 15, 25, 35, 45 and 55 ℃. For each temperature, the pellets and the treated sponges were mixed with metal ion solutions. All the samples were stirred at

appropriate temperatures for 20 minutes at agitation speed of 120 rpm. After that, seeds samples were centrifuged and the sponges were removed. The supernatants and mixtures were saved for metal quantification.

2.7.4 Effect of pH

The procedure of studding effect of pH was performed according to (Tsezos and Deutschmann, 1990). The seeds slurry and native sponge were adjusted to pH values: 2 – 9 by either adding 0.1 M HCl or 0.1 M NaOH. For each biomass sample, respective pH adjusted metal solutions were added to the respective biomass samples. All samples were stirred at temperature of 20 ºC for 20 minutes at agitation speed of 120 rpm, after centrifuging of seeds samples and removing of sponges from mixtures, the supernatants and mixtures were collected for metal quantification.

2.7.5 Capacity studies

Seeds pellets were reacted with metal ion solution at the optimum parameters. The mixtures were shaken for 20 minutes at temperature of 40 ºC and agitation speed of 120 rpm, centrifuged, decanted and the supernatants were kept for metal analysis. The same biomasses were resuspended several times with a fresh aliquot of the metal solution and centrifuged until the biomass was saturated (i.e the metal concentration in the supernatant was as the initial solution). The capacity was assumed to be the difference in metal concentration between the controls and the supernatants of the reacted samples of each reaction cycle and was

calculated using a sum of the individual cycles (Gardea-Torresdey et al., 1996b).

2.7.6 Effect of competing ions

The effect of competing ions on the removal of Cr^{3+} and Mn^{2+} ions by seeds was studied at the optimum parameters.

5, 10, 15 and 20 ppm of single metal solutions and single hard cation solutions were prepared. The same set of concentrations was prepared for both metal solutions.

The seeds pellets were obtained as previously mentioned. At each concentration, the obtained biomass pellets were mixed with an appropriate concentration of bimetal solution; other pellets were mixed with an appropriate concentration of metal hard cation solution. All the samples were stirred at 40 ℃ for 20 minutes at agitation speed of 120 rpm, centrifuged at 3000 rpm for 5 minutes; the supernatants were collected for metal quantification using AAS.

2.8. Statistical analysis

All the studied parameters were performed in triplicate for statistical purpose. The 95% confidence intervals were calculated. The relative standard deviation did not exceed 4.5%.

Optimum conditions for analysis of chromium and manganese by AAS spectrophotometer are shown in table (II).

Table II : Optimum conditions for analysis of chromium (III) and manganese (II) by FAAS spectrophotometry.

Metals	Wavelength (nm)	Bandpass (nm)	Lamp current %
Cr (III)	357.9	0.5	100
Mn (II)	279.5	0.2	75

Chapter Three

Results and Discussion

3.1. Effect of Time

Contact time is one of the most important parameters that must be taken into account for waste water treatment applications. Figures 2 and 3 show the percent removal of metal ions by seeds and sponge respectively at different contact times. The data is shown in tables (1) and (2).
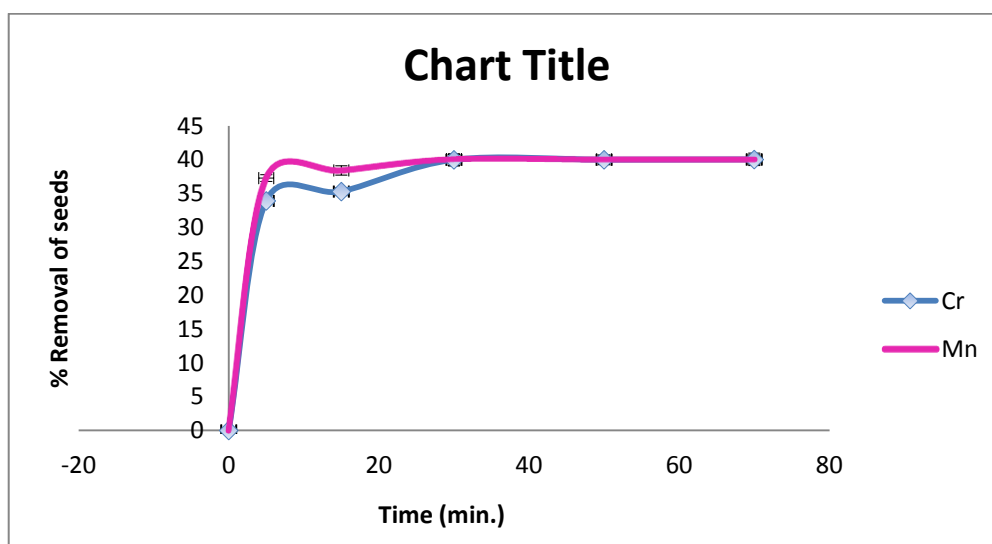
Figure 2: Effect of contact time on the % removal of metals by seeds.
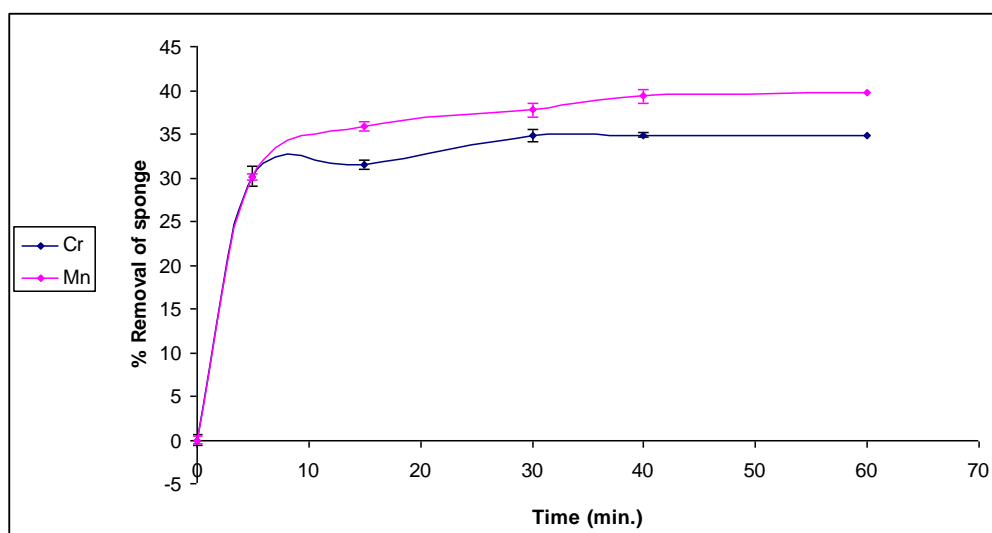
Figure 3: Effect of contact time on the % removal of metals by sponge.

The results show that the percent removal of both is large at small contact times, then an equilibrium is reached after a certain time. Initially, a large number of vacant sites are available for binding, after a certain time (10 – 15 min); these sites become saturated with metal ions, the remaining sites are difficult to be occupied because of the repulsive forces that form between metal ions (Lu et al., 2009).

3.2. Effect of Temperature

The effect of temperature on the removal of metal ions is shown in figures 4 and 5 (tables (3) and (4)). The percent removal slightly increases as the temperature increases to a limit value.
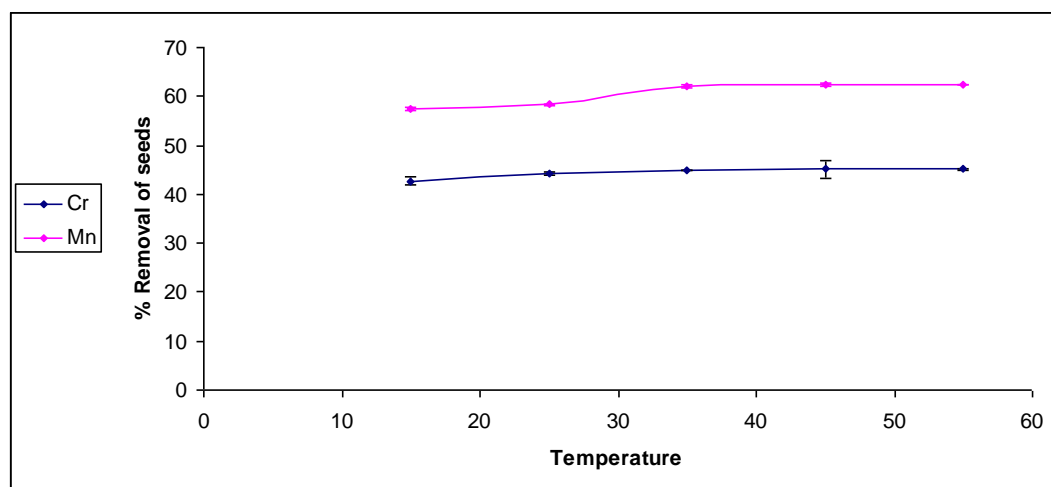
Figure 4: Effect of temperature on the % removal of metals by seeds.
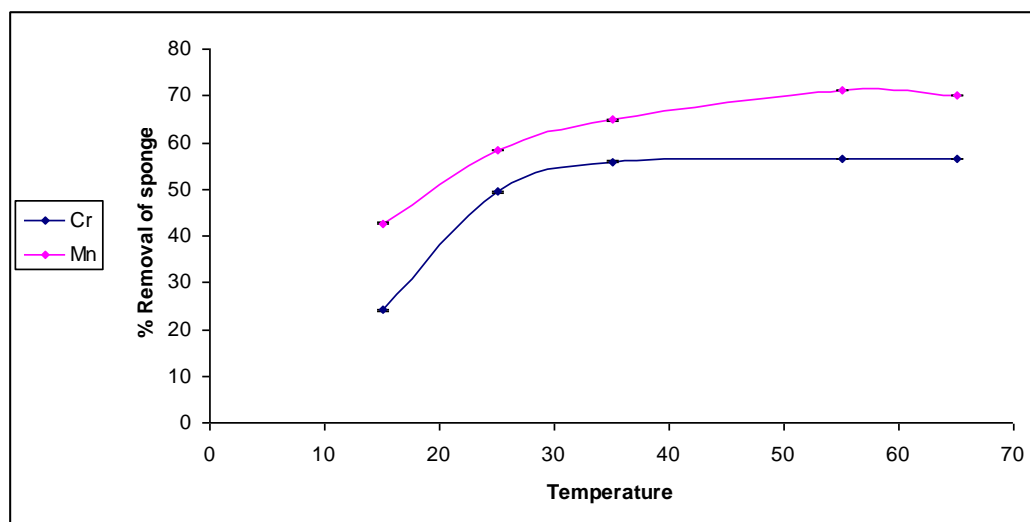
Figure 5: Effect of temperature on the % removal of metal ions by sponge.

As expected, increasing temperature will increase the rate of diffusion of metal ions on the outer layer and in the inner pores of biomass (Babarinde et al., 2006). Also, an increase in temperature results in increase in mobility of large metal ions, which indicates that the adsorption process is endothermic, leads to swelling effect within the internal structure of biomass that in turn, encourages the metal ions to penetrate further and increase in the kinetic energy of adsorbent particles that increase the collision between adsorbent and adsorbate molecules results in enhancing the removal of metals from adsorbent surface (Guo et al., 2009).

3.3. Effect of initial concentration

Figures 6 and 7 illustrate the effect of initial metal ions concentration on their removal by both biomasses (tables 7 and 8). As can be seen, increasing the initial metal ion concentration decreases the percent removal of the metal ions by both seeds and sponge. At low concentration, most metal ions will occupy the available sites of biomass. As concentration of

these ions increases, the sites will be filled until saturation, more ions have no empty sites to be occupied (removal is decreased).
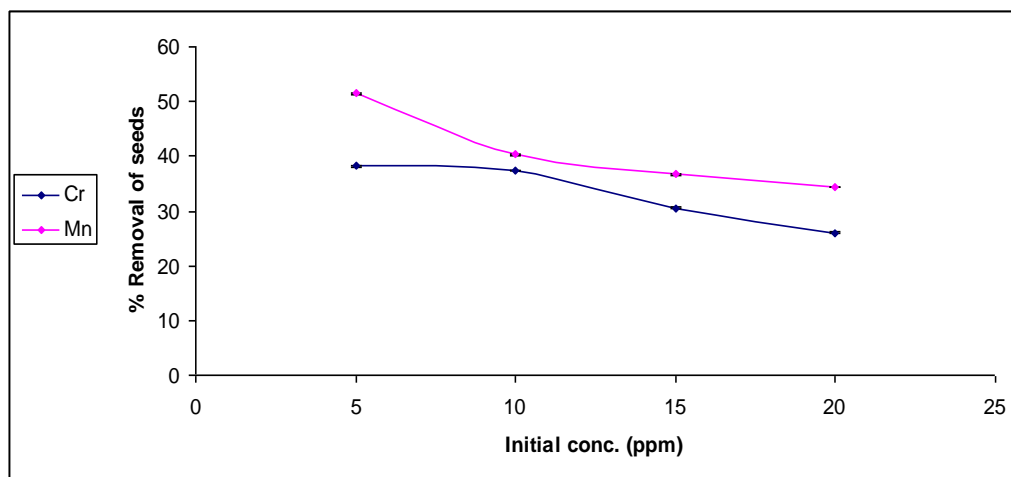
Figure 6: Effect of initial metal ion concentration on the % removal of metals by seeds.
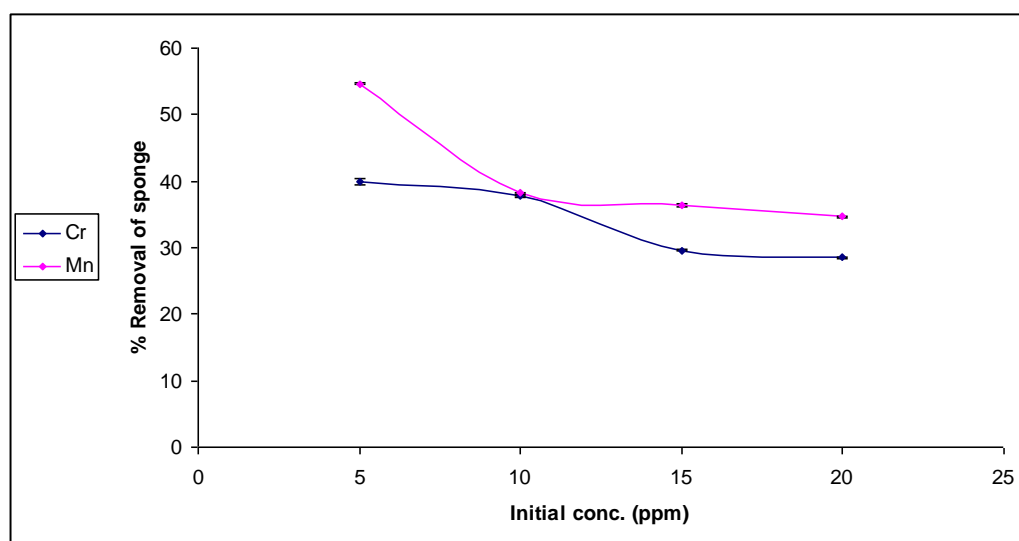
Figure 7: Effect of initial metal ion concentration on the % removal of metals by sponge.

3.4. Effect of pH

The pH of solution is a significant variable in sorption studies since it affects the charge of biomass surface, degree of ionization of metal ions,

and the extent of dissociation of functional groups present on the active site of biomass (Nandi et al., 2009).

Figures 8 and 9 show the percent removal of metal ions by both biomasses at different pH values. (Data is shown in tables (5) and (6)).
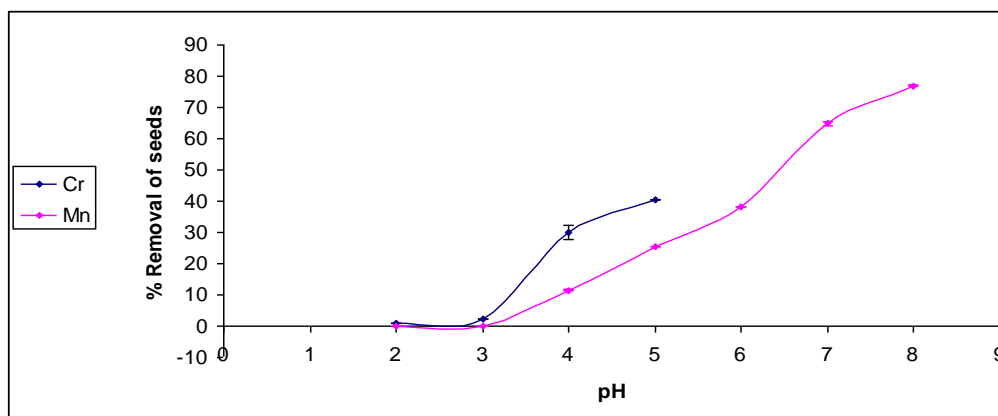
Figure 8: Effect of pH on the % removal of metals by seeds.
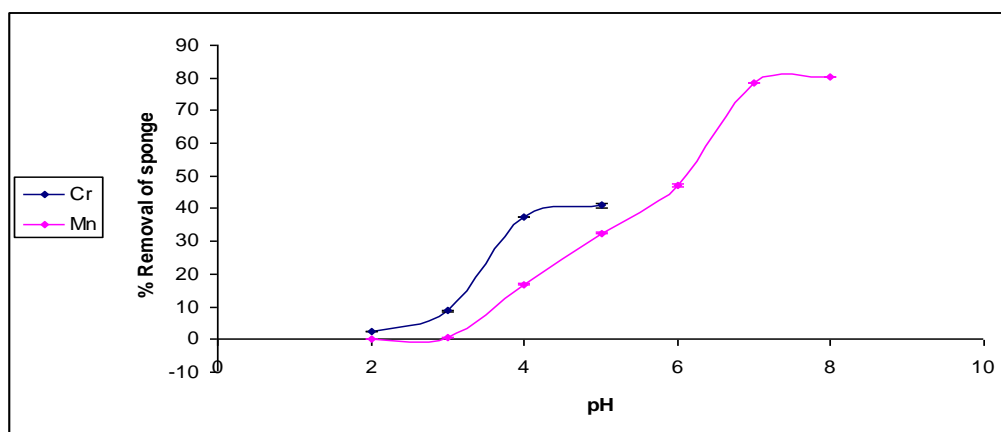
Figure 9: Effect of pH on the % removal of metals by sponge.

For Mn (II); both biomasses showed the same percent removal trend at all values of pH. At pH 2.0 and 3.0, the seeds did not show any binding, while the percent removal was too small for sponge: 0.26% and 0.54% respectively. At pH of 4.0 − 8.0, both biomasses showed an increase in the average percent removal of Mn with higher values for the sponge. The

maximum removal was $\approx 77\%$ and $\approx 80\%$ by seeds and sponge, respectively.

As it can be seen obviously from figures above, the average percent removal of Mn at pH 7.0 and 8.0 for both biomasses are close from each other, so, for environmental and economical considerations; pH 7.0 is the optimum value in which the percent removal of Mn was $\approx 65\%$ and $\approx 78\%$ by seeds and sponge respectively.

For Cr (III); both biomasses had the same average percent removal trend with increasing pH values. At pH $2.0 - 3.0$, the biomasses showed small percent removal. The percent removal increased with increasing pH values to $4.0 - 5.0$ with higher removal by the sponge. The maximum removal occurred at pH 5.0, which was 40.5% and 41% for seeds and sponge, respectively.

In the acidic medium, a large number of strong competing hydrogen ions occupy the available sites on biomass, preventing metal ions from interacting with the biomass. As the pH of the solution increases; the density of positive charge decreases on the surface of biomass due to absence of hydronium ions that in turn, enhances the binding with positive metal ions (Patnukao et al., 2008).

At pH values greater than 5 and 8 for Cr (III) and Mn (II) respectively, metals begin to precipitate. These conclusions agreed with calculations of solubilites of the hydroxides of Cr (III) and Mn (II) (i.e. $Cr(OH)_3$) and

$(Mn(OH)_2)$, respectively. The solubility product constant (k_{SP}) for chromium and manganese hydroxides are (6.3×10^{-31}) and (1.6×10^{-13}) respectively. These values predict that chromium and manganese begin to precipitate as hydroxides at pH values (5.3 and 9.6), respectively.

Tables (III) and (IV) show some optimum pH values for binding of Mn (II) and Cr (III) to different adsorbents.

Table III : pH values for binding of Mn (II) to different adsorbents.

Adsorbents	pH	References
Crab shell particles	6	(Vijayaraghavan et al., 2011)
Activated zeolite with NaCl	6	(Taffarel and Rubio, 2009)
Activated carbon from coconut shells	7	(Moreno-Piraján, 2011)

Table IV : pH values for binding of Cr (III) to different adsorbents.

Adsorbent	pH	References
Alfalfa	5.0	(Gardea-Torresdey et al., 1998b)
C. Sphagnum peat moss, its Humin and Humic acid	4.0-5.0	(Gardea-Torresdey et al., 1996c; De la Rosa et al., 2003)
Petiolar felt-sheath of palm	4.0	(Iqbal et al., 2002)
Sorghum (*Sorghum bicolor*)	4.5-5.0	(Cano-Rodriguez et al., 2002)

3.5. Binding capacity

Table (12) represents the amount of Mn (II) and Cr (III) adsorbed from solution by the seeds after each cycle at optimum conditions.

Figure 10 shows that the seeds became saturated with Cr (III) ions after nine cycles, by using sum of amount of metal ions that was adsorbed in each cycle; the binding capacity of Cr (III) ions with seeds was 1.65 mg/g.

The figure shows also that the seeds became saturated with Mn (II) ions after ten cycles with binding capacity of 3.36 mg/g.
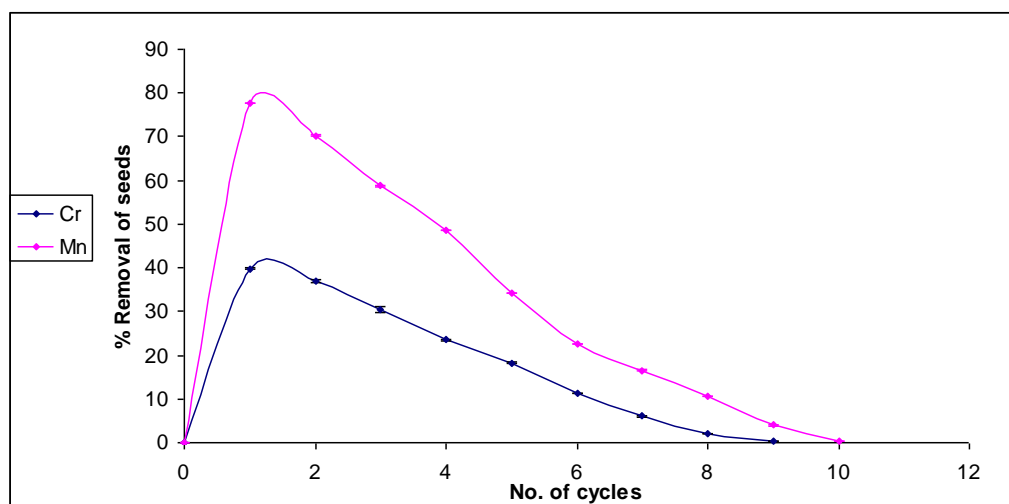
Figure 10: Binding capacity of metals with seeds.

3.6. Effect of competing ions

Generally, water pollution is caused by more than one heavy metal ion. Interferences between them can affect their binding to biomass when existing in the same solution. For example, arsenic binding to sorghum biomass was increased by the presence of iron ions (Gardea-Torresdey et al., 1997).

Figure 11 shows the effect of Mn (II) ions on the percent removal of Cr (III) ions by seeds. The percent removal was negligibly increased when Mn (II) ions were present. Figure 12 shows the effect of Cr (III) ions on the

percent removal of Mn (II) ions by seeds. The percent removal was decreased notably when Cr (III) ions were present. Table (9) shows the necessary data.
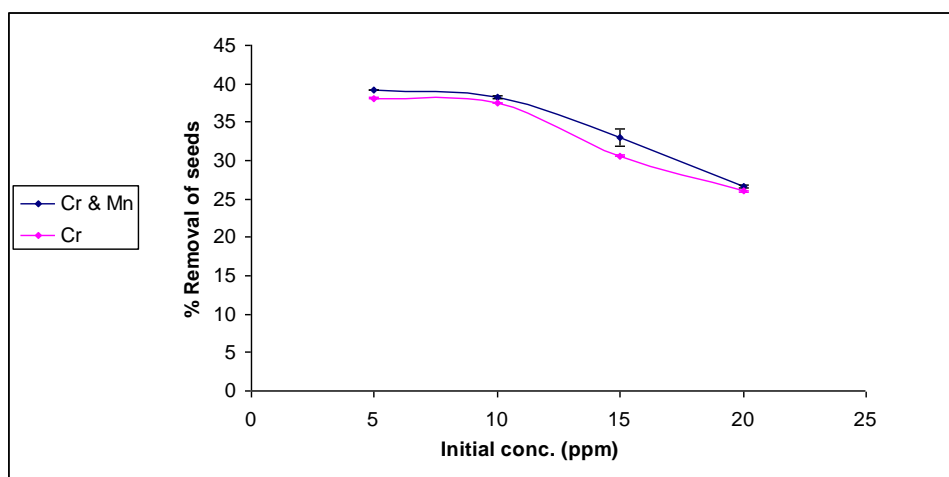
Figure 11: Effect of Mn^{2+} ions on the percent removal of Cr^{3+} by seeds.
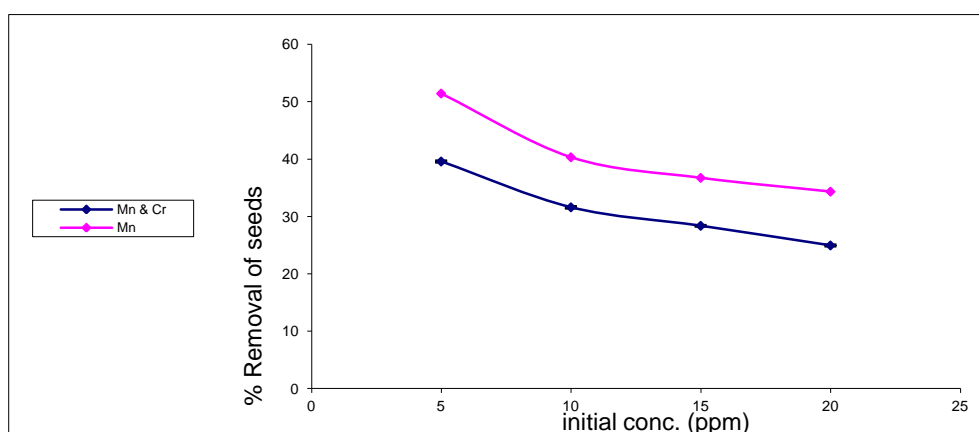
Figure 12: Effect of Cr^{3+} ions on the percent removal of Mn^{2+} by seeds.

Since hard ions are already available in water systems, it will be very important to know how they can affect the binding of a biomass to different metal ions. This study examined the effect of Ca^{2+} and Mg^{2+} on the percent removal of Cr (III) and Mn (II) by seeds. The results are shown in figures 13 and 14. (Data is shown in tables (10) and (11)).
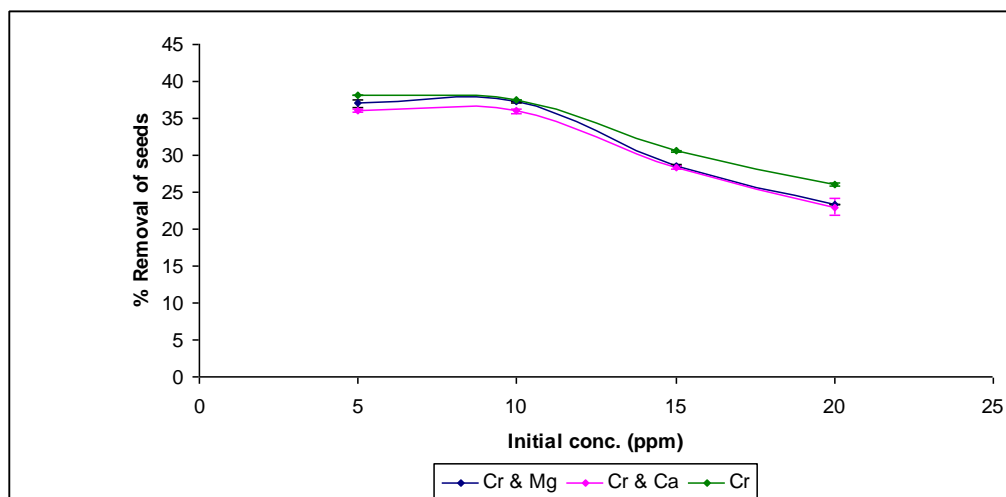
Figure 13: Effect of hard ions on the percent removal of Cr^{3+} by seeds.
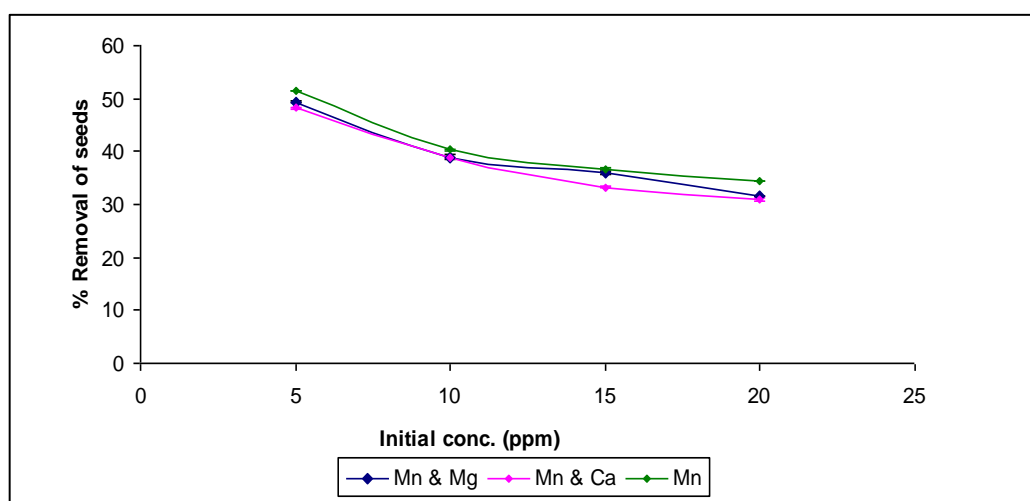
Figure 14: Effect of hard ions on the percent removal of Mn^{2+} by seeds.

From the figures above, both Ca^{2+} and Mg^{2+} decreased the removal in a negligible way in agreement with many researchers. Generally, hard ions have no effect on the biosorption of heavy metals (Gardea-Torresdey et al., 1997; Drake and Rayson, 1996; Parsons et al., 2003).

3.7. Phytofiltration potential of *Luffa Cylindrica*

At the optimum conditions (pH 5.0 and 7.0 for Cr (III) and Mn (II) ions, respectively, initial concentration of metal ion 5 mg/L, temperature (35℃ -

40℃) and a contact time of 15 minutes); the average percent removal of Cr (III) ions by sponge and seeds from aqueous solutions were 42% and 40% respectively. While were 82% and 78% for Mn (II) by sponge and seeds, respectively. This shows that the seeds of Luffa have a comparable phytofiltration potential to the sponge for both Cr (III) and Mn (II) ions.

3.8. Application of adsorption isotherms

The process of removal of heavy metals from polluted aqueous solutions using non living biomass is a physic-chemical process with uncontrolled metabolic mechanism(s) (Davis et al., 2003). Adsorption isotherms are used to explain the equilibrium of metal ions that occurs between the solid phase of biomass and the aqueous solution. These models might determine some kinetic and thermodynamic parameters that can give a clearer image about the binding mechanism (Altun et al., 1998). The more known non-linear models are Langmiur and Freundlich isotherms.

Langmiur model suggests that the uptake of metal ion is monolayer occurred on homogeneous surface with no different energies for all binding sites and no interactions between adsorbed molecules (Lin and Juang, 2002; Romero-Gonzalez et al., 2005).

The linearized form of the Langmiur model is given by:

$$\frac{1}{q_e} = \frac{1}{q_{max}\,K_a}\,\frac{1}{C_e} + \frac{1}{q_{max}} \qquad (3)$$

Where:

q_e = Is the quantity of metal uptake per unit mass of biomass at equilibrium (mg/g)

q_{max} = Is the maximum uptake of metal per unit mass of biomass (mg/g)

K_a = Is Langmiur constant (L/mg) that relates to the energy of adsorption that quantitatively indicates the affinity between adsorbed ions and adsorbent

C_e = Is the concentration of metal ion in solution at equilibrium (mg/L)

Therefore, a plot of $\frac{1}{q_e}$ versus $\frac{1}{C_e}$ gives a straight line of slope $\frac{1}{q_{max}\,K_a}$ and intercept $\frac{1}{q_{max}}$.

Freundlich model also suggests a monolayer uptake of metal ion on a biomass. It differs from Langmiur in that it assumes that the distribution of energy of the active binding sites of a biomass is heterogeneous, with interactions between adsorbed molecules that make the affinities of binding sites of biomass to vary with these interactions; those with stronger affinities are occupied first (Davis et al., 2003).

The linearized form of the Freundlich model is given by:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{4}$$

Where:

q_e = Is the quantity of metal uptake per unit mass of biomass at equilibrium (mg/g)

K_f = Is the maximum adsorption capacity (L/mg)

n = Is the adsorption intensity (relates to the strength of affinities of binding sites (Davis et al., 2003))

C_e = Is the concentration of metal in solution at equilibrium (mg/L)

Therefore, a plot of $\ln q_e$ versus $\ln C_e$ gives a straight line of slope $\frac{1}{n}$ and intercept $\ln K_f$.

For adsorption of Mn (II) ions on seeds, the experimental data were better fitted to the Freundlich equation ($R^2 = 0.9936$) than Langmiur equation ($R^2 = 0.977$) as seen in figures 15 and 16, (table (14)). The parameters are shown in table (VII).
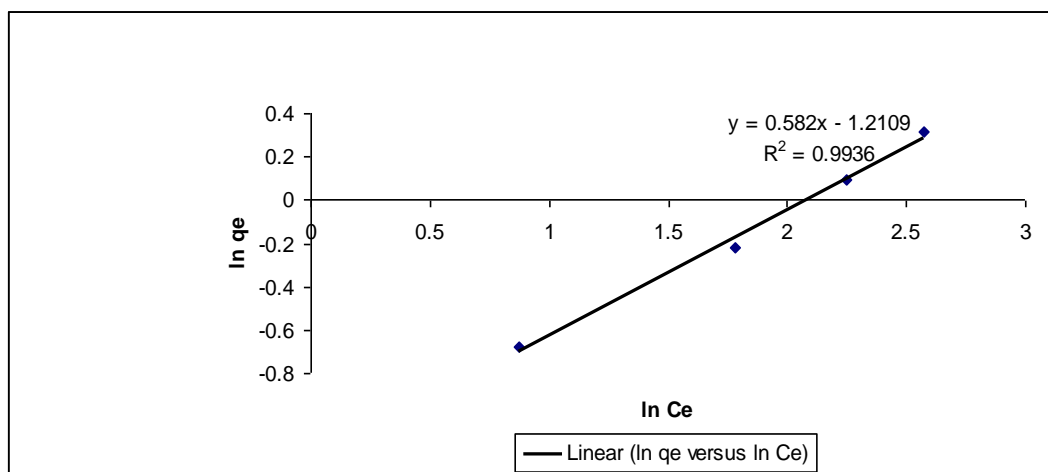
Figure 15: Applying Freundlich adsorption isotherm on the adsorption of Mn (II) on seeds.
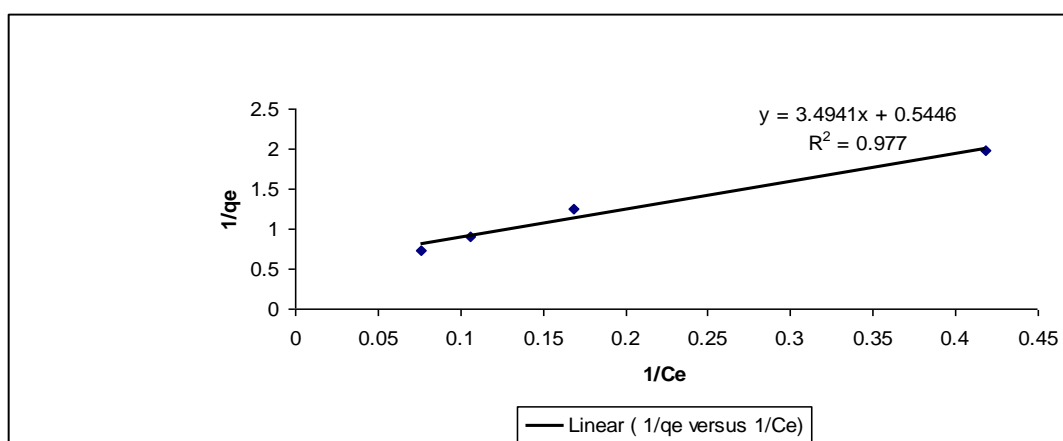
Figure 16: Applying Langmiur adsorption isotherm on the adsorption of Mn (II) on seeds.

While, for adsorption of Cr (III) on seeds, the experimental data were better fitted to the Langmiur equation ($R^2 = 0.9657$) as seen in figures 17 and 18, (table (13)) than Freundlich equation ($R^2 = 0.9212$). The parameters are shown in table (VII).

$$y = 0.6476x - 1.6347$$
$$R^2 = 0.9212$$
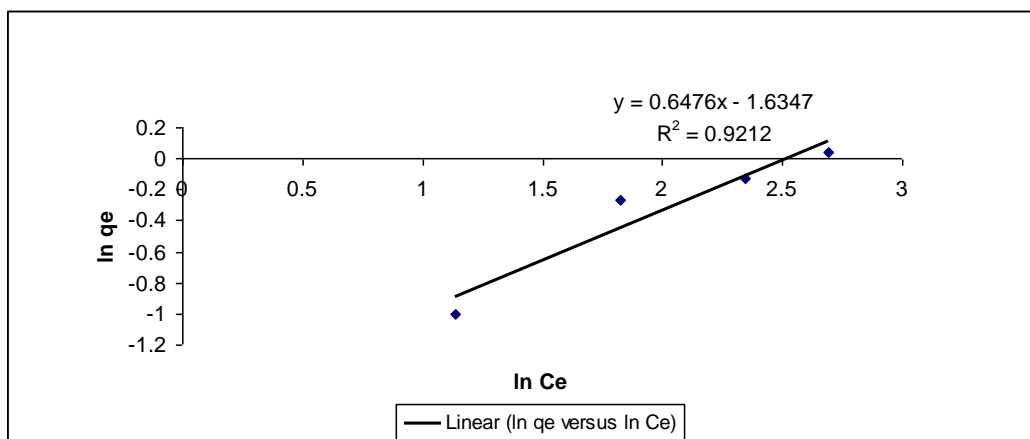
Figure 17: Applying Freundlich adsorption isotherm on the adsorption of Cr (III) on seeds.

$$y = 6.962x + 0.4073$$
$$R^2 = 0.9657$$
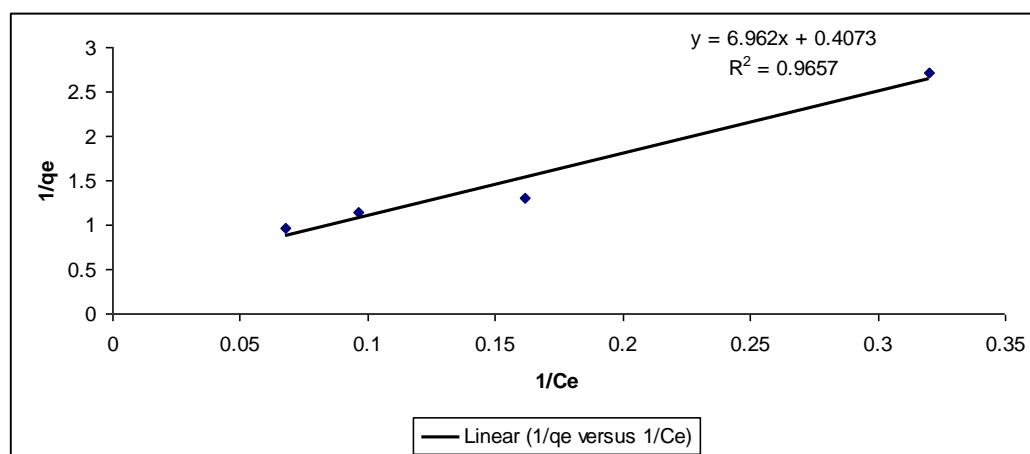
Figure 18: Applying Langmiur adsorption isotherm on the adsorption of Cr (III) on seeds.

Table VII : Adsorption isotherms parameters for both Cr^{3+} and Mn^{2+}.

Adsorption isotherms	Parameters	Cr^{3+}	Mn^{2+}
Langmiur	K_a	0.0585	0.1558
	q_m	2.455	1.8362
	r^2	0.9657	0.977
Freundlich	K_f	0.195	0.2979
	n	1.544	1.7182
	r^2	0.9212	0.9936

3.9. Rate order of the adsorption process

Uptake of each metal ion from different initial concentrations of the metal can be used to study the dependency of the rate of adsorption on the concentration of metal ion left in solution. Thus, the reaction order of the adsorption process can be determined.

Figures 19 and 20 show the loss of various concentrations of each metal ion by seeds with time. (Tables (15) and (16)).
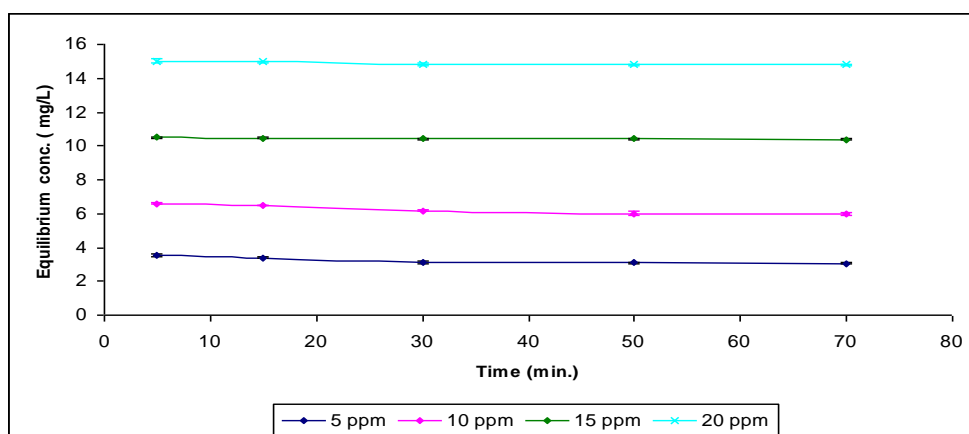
Figure 19: Loss of various concentrations of Cr (III) ions by seeds with time.
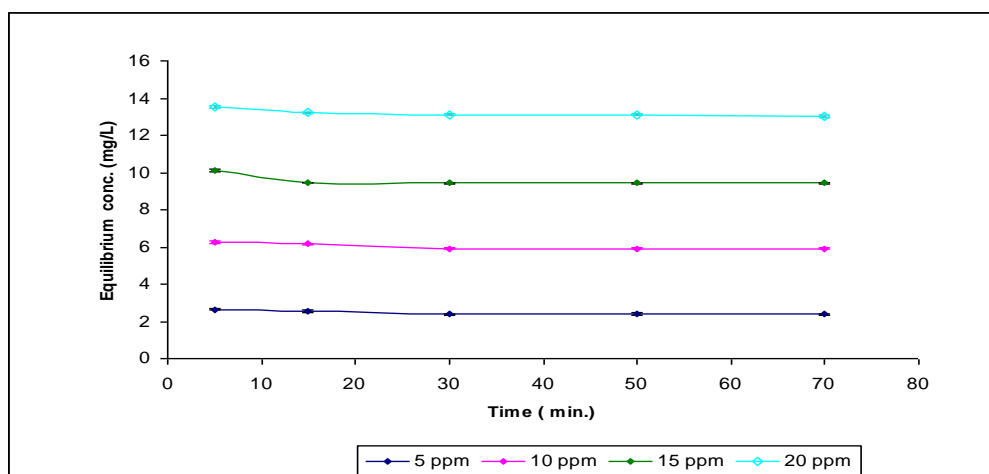
Figure 20: Loss of various concentrations of Mn (II) ions by seeds with time.

The pseudo first order rate equation (Lagergren, 1898) can be expressed as:

$$\log\,(\,q_{eq}\,-\,q_t\,) = \log q_e\,-\,\frac{K_{1,ad}}{2.303}\,t \qquad\qquad (\,5\,)$$

Where, q_t (mg/g): is amount of adsorbed metal on biomass at time (t), q_{eq} (mg/g): is amount of adsorbed metal on biomass at equilibrium, $K_{1,ad}$ (L/min.): is the rate constant of pseudo first order model. If the previous equation is applicable, the adsorption rate is the pseudo first order reaction. $K_{1,ad}$ can be obtained from the slope of the plot of $\log\,(\,q_{eq}\,-\,q_t\,)$ versus t. Figures 21 and 22 show the applied first order reaction for each metal ion with seeds.
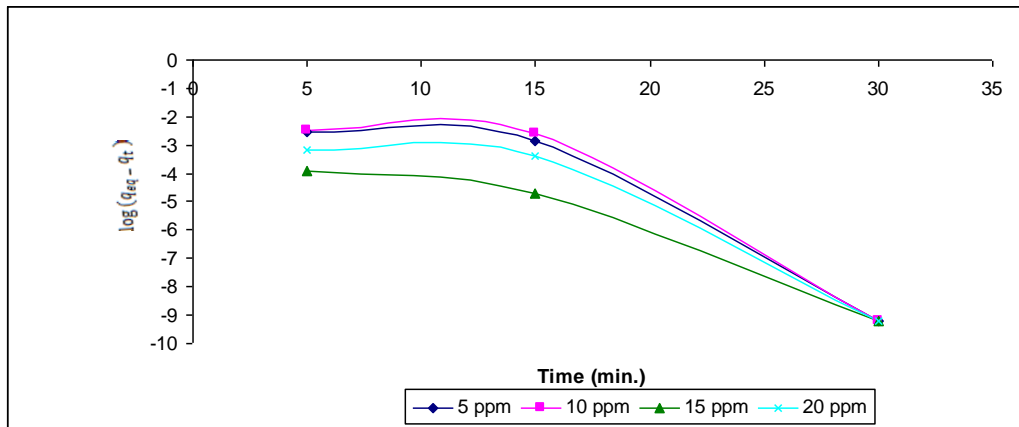
Figure 21: Applying a pseudo first order reaction on binding of Cr (III) ions with seeds.
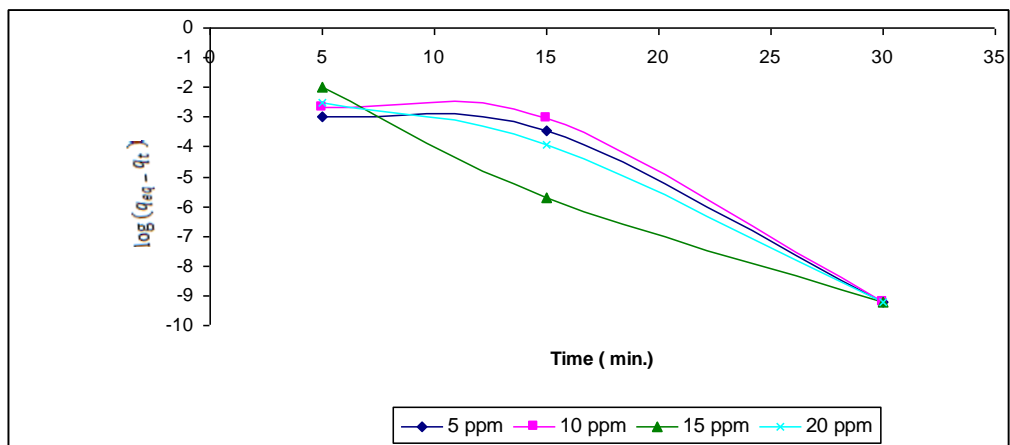
Figure 22: Applying a pseudo first order reaction on binding of Mn (II) ions with seeds.

The pseudo second order rate equation (Ho and Mckay, 1998) is expressed as:

$$\frac{t}{q_t} = \frac{1}{K_{2,ad}\, q^2_{eq}} + \frac{1}{q_{eq}}t \qquad (6)$$

Where, q_t (mg/g): is amount of adsorbed metal on biomass at time (t), q_{eq} (mg/g): is amount of adsorbed metal on biomass at equilibrium, $K_{2,ad}$ (g/mg.min.): is the rate constant of pseudo second order model. If the previous equation is applicable, then the plot of $\frac{t}{q_t}$ versus t should give a linear relationship. $K_{2,ad}$ and q^2_{eq} can be obtained from the intercept and slope of the plot, respectively.

Figures 23 and 24 show the plots of pseudo second order reaction for Cr (III) and Mn (II), respectively. The data is shown in tables (17) and (18).
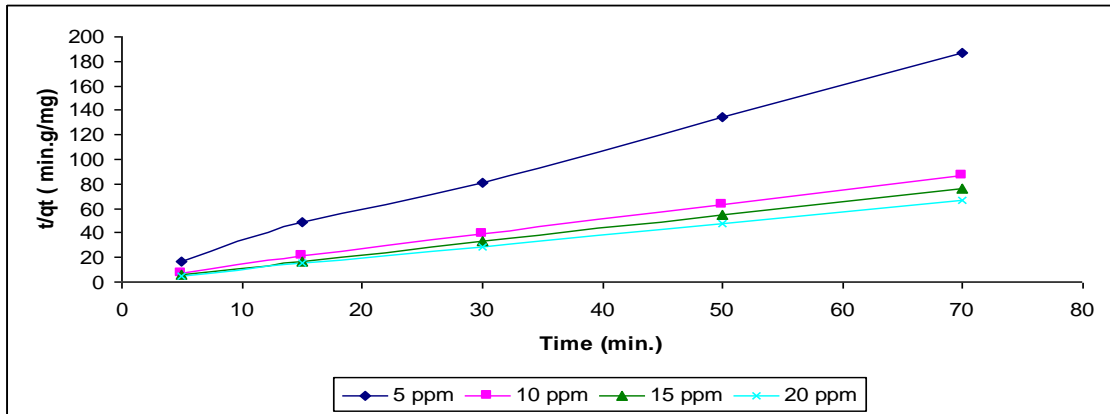
Figure 23: Applying a pseudo second order reaction on binding of Cr (III) ions with seeds.
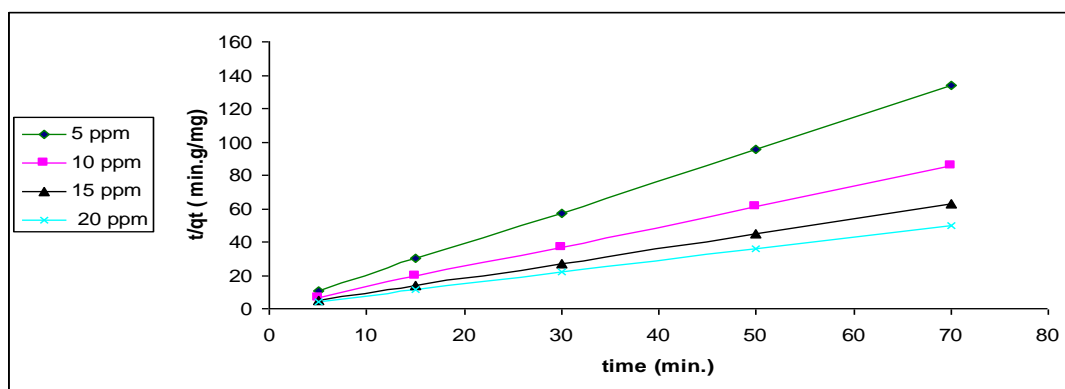
Figure 24: Applying a pseudo second order reaction on binding of Mn (II) ions with seeds.

Applying a pseudo second order reaction for both metal ions gave linear curves in contrast to pseudo first order. The experimental data fitted well the pseudo second order kinetics; it was noticed that Cr^{3+} and Mn^{2+} had regression values (R^2) for pseudo second order higher than for pseudo first order. This result agrees with similar studies carried out using the same biomass (Einschlag, 2011b). Parameters of first and second order reactions for Cr^{3+} and Mn^{2+} are shown in table (VIII).

Table VIII : Parameters of first and second order reactions for Cr^{3+} and Mn^{2+} ions.

Metals	Conc. ppm	pseudo first order			pseudo second order		
		R^2	$K_{1,ad}$	q_{eq}	R^2	$K_{2,ad}$	q_{eq}
Cr	5	0.869	0.642	0.617	0.998	1.116	0.387
	10	0.850	0.652	0.934	0.9992	0.603	0.823
	15	0.929	0.505	$5.22*10^{-3}$	1	6.438	0.918
	20	0.863	0.583	0.092	1	2.424	1.048
Mn	5	0.886	0.597	0.128	0.9999	2.505	0.529
	10	0.879	0.629	0.381	0.9999	1.797	0.825
	15	0.983	0.655	0.129	0.9999	1.860	1.125
	20	0.9573	0.634	0.245	0.9999	1.334	1.402

3.10. Gibbs free energy, $\Delta G°$

The equilibrium constant K_c for the biosorption of Cr (III) and Mn (II) ions by seeds of *Luffa Cylindrica* can be obtained from the intercept of ln (q_e/C_e) versus q_e in Khan and Singh equation (Sawalha et al., 2006) (Figure 25), (tables (19) and (20)), or from the slope of the plot of q_e versus C_e as show in equation (7) (Romero-Gonzalez et al., 2005) (Figure 26) (tables (21) and (22)) or can be obtained from Langmiur in equation (3).

$$K_c = \frac{q_e}{C_e} \tag{7}$$
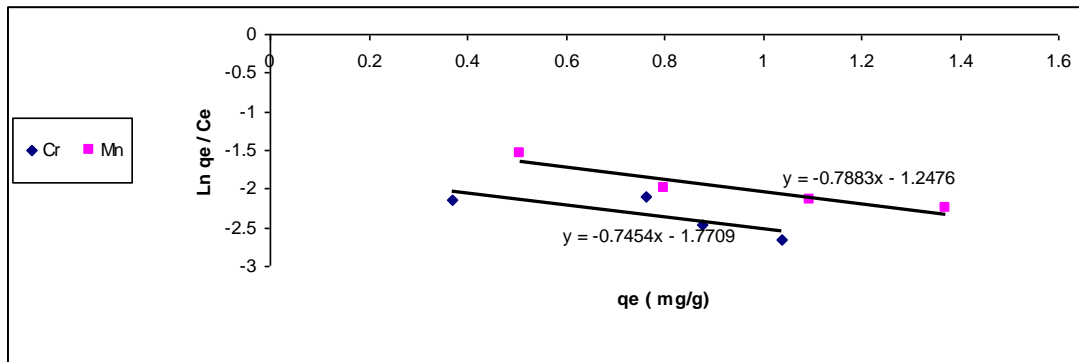
Figure 25: Khan and Singh plots of ln (q_e/C_e) versus q_e for Cr (III) and Mn (II) adsorption on seeds at 20°C.
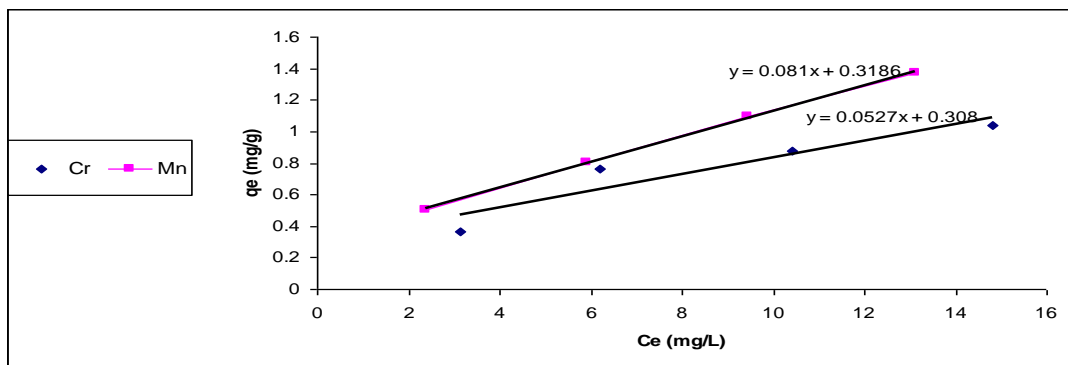
Figure 26: Adsorption of Cr (III) and Mn (II) ions on seeds at 20 °C using q_e versus C_e plot.

The negative values of K_c for Cr (III) and Mn (II) mean a non linear fitting of these metal ions by using Khan and Singh (Sawalha, et al., 2006). Using q_e versus C_e plot shows more fitted data for biosorption of both metal ions.

Thermodynamic parameters for the biosorption of Cr (III) and Mn (II) by seeds are shown in table (IX).

Table (IX): Thermodynamic parameters for the biosorption of Cr (III) and Mn (II) by seeds at 20 C°. (K_c is the equilibrium constant; $\Delta G°$ is the Gibbs free energy)

Metal	Khan and Singh		q_e versus C_e plot	
	K_c	$\Delta G°(KJ/mol)$	K_c	$\Delta G°(KJ/mol)$
Cr (III)	-1.7709	not applicable	0.0527	7.1694
Mn (II)	-1.2476	not applicable	0.081	6.1224

The change in the Gibbs free energy $\Delta G°(KJ/mol)$ for biosorption of both metal ions by seeds was calculated according to equation (8):

$$\Delta G° = -RT \ln K_c \tag{8}$$

Where, T is the temperature (Kelvin); R is the gas constant (8.314 J/ mol. K). The positive values of $\Delta G°$ for Cr (III) and Mn (II) in table 1, indicate that biosorption of both metal ions by seeds are non spontaneous processes. This could be an explanation for the little binding capacity of these metal ions shown by seeds.

Conclusion

Using *Luffa Cylindrica* sponge and seeds as biosorbents is a good alternative in removal of heavy metals from aqua systems; it is a promising method for waste management and environmental treatment.

Studied adsorption parameters as pH, initial concentration of metal ion, temperature and contact time have an effect on the removal of Mn (II) and Cr (III) by both biomasses.

The optimal percent removal of Cr (III) ions by sponge and seeds were 42% and 40%, respectively. While were 82% and 78% for removal of Mn (II) ions, respectively. The suitable conditions for binding of both biomasses were at pH 5.0 and 7.0 with Cr (III) and Mn (II) ions, respectively, initial concentration of 5 mg/L, temperature (35℃ - 40℃) and contact time (15 minutes).

Tables

Table (1): Effect of contact time on the % removal of metals by seeds. (5 mg/mL biomass, 10 ppm metal ion, 20 ºC, 120 rpm).

Time (min.)	% Removal of Cr^{3+}	% Removal of Mn^{2+}
5	33.92	37.29
15	35.30	38.42
30	39.99	40.11
50	40.00	40.06
70	40.03	40.07

Table (2): Effect of contact time on the % removal of metals by sponge. (6.66 mg/mL biomass, 10 ppm metal ion, 20 ºC, 120 rpm).

Time (min.)	% Removal of Cr^{3+}	% Removal of Mn^{2+}
5	30.13	30.06
15	31.49	35.84
30	34.85	37.77
40	34.88	39.38
60	34.90	39.74

Table (3): Effect of temperature on the % removal of metals by seeds. (5mg/mL biomass, 10 ppm metal ion, 15 min., 120 rpm).

Temperature (ºC)	% Removal of Cr^{3+}	% Removal of Mn^{2+}
15	42.68	57.57
25	44.15	58.30
35	44.89	62.07
45	45.16	62.44
55	45.18	62.40

Table (4): Effect of temperature on the % removal of metals by sponge. (6.66 mg/mL biomass, 10 ppm metal ion, 15 min., 120 rpm).

Temperature (ºC)	% Removal of Cr^{3+}	% Removal of Mn^{2+}
15	24.13	42.73
25	49.40	58.29
35	55.94	64.82
55	56.61	71.13
65	56.50	70.00

Table (5): Effect of pH on the % removal of metals by seeds.
(5mg/mL biomass, 10 ppm metal ion, 15 min., 20 ºC, 120 rpm) .

pH	% Removal of Cr^{3+}	% Removal of Mn^{2+}
2	0.97	Negligible
3	2.35	Negligible
4	30.00	11.57
5	40.57	25.53
6		38.29
7		64.82
8		76.92

Table (6): Effect of pH on the % removal of metals by sponge.

(6.66 mg/mL biomass, 10 ppm metal ion, 15 min., 20 ºC, 120 rpm).

pH	% Removal of Cr^{3+}	% Removal of Mn^{2+}
2	2.53	0.25
3	8.69	0.54
4	37.59	16.87
5	41.00	32.61
6		47.25
7		78.35
8		80.25

Table (7): Effect of initial metal ion concentration on the % removal by seeds. (5mg/mL biomass, natural pH values, 15 min., 20 ºC, 120 rpm) .

Initial concentration (ppm)	% Removal of Cr^{3+}	% Removal of Mn^{2+}
5	38.14	51.43
10	37.51	40.32
15	30.60	36.72
20	25.97	34.32

Table (8): Effect of initial metal ion concentration on the % removal by sponge. (6.66 mg/mL biomass, natural pH values, 15 min., 20 ºC, 120 rpm).

Initial concentration (ppm)	% Removal of Cr^{3+}	% Removal of Mn^{2+}
5	40.00	54.66
10	37.75	38.18
15	29.63	36.36
20	28.49	34.64

Table (9): Effect of the presence of one metal on the percent removal of the other by seeds. (5mg/mL biomass, optimium pH values (for each metal), 15 min., 40 ºC, 120 rpm).

Initial concentration (ppm)	% Removal of Cr^{3+} in presence of Mn^{2+}	% Removal of Mn^{2+} in presence of Cr^{3+}
5	39.20	39.58
10	38.25	31.59
15	33.00	28.369
20	26.56	24.95

Table (10): Effect of hard ions on the percent removal of Cr^{3+} by seeds. (5mg/mL biomass, pH =5.00, 15 min., 40 ºC, 120 rpm).

Initial concentration of Cr^{3+} (ppm)	% Removal of seeds in presence of Mg^{2+}	% Removal of seeds in presence of Ca^{2+}
5	37.00	36.01
10	37.20	36.00
15	28.56	28.40
20	23.35	23.00

Table (11): Effect of hard ions on the percent removal of Mn^{2+} by seeds. (5mg/mL biomass, pH: 8.00, 15 min., 40 ºC, 120 rpm).

Initial concentration of Mn^{2+} (ppm)	% Removal of seeds in presence of Mg^{2+}	% Removal of seeds in presence of Ca^{2+}
5	49.38	48.26
10	39.00	38.80
15	36.04	33.25
20	31.58	30.90

Table (12): Binding capacity for seeds with metal. (5mg/mL biomass, 5 ppm metal ion, optimium pH values (for each metal), 15 min., 40 ºC, 120 rpm).

no. of cycles	% Removal of Mn^{2+}	q (mg/g)	% Removal of Cr^{3+}	q (mg/g)
1	77.60	0.76	39.85	0.39
2	70.25	0.68	37.00	0.36
3	58.69	0.57	30.59	0.29
4	48.59	0.47	23.56	0.23
5	34.25	0.33	18.26	0.17
6	22.58	0.22	11.26	0.11
7	16.58	0.16	6.00	0.05
8	10.59	0.10	2.06	0.02
9	4.00	0.03	0.28	0.002
10	0.23	0.002	0.28	0.0028
		$q_{total} = 3.36$		$q_{total} = 1.65$

Table (13): Application of Langmiur adsorption isotherm on % removal of Cr^{3+} by seeds.

$1/q_e$	$1/C_e$
2.71149	0.32009
1.3108	0.16166
1.1381	0.09606
0.9619	0.06756

Table (14): Application of Freundlich adsorption isotherm on the % removal of Mn^{2+} by seeds.

$ln\ q_e$	$ln\ C_e$
-0.6809	0.87129
-0.2228	1.778741
0.0917	2.24499
0.31562	2.57377

Table (15): Loss of various concentrations of Cr^{3+} by seeds with time.

Cr	5 ppm	10 ppm	15 ppm	20 ppm
Time (min.)	C_{eq} (mg/L)	C_{eq} (mg/L)	C_{eq} (mg/L)	C_{eq} (mg/L)
5	3.53	6.60	10.51	15.01
15	3.40	6.47	10.45	14.97
30	3.12	6.18	10.41	14.80
50	3.09	6.0	10.40	14.79
70	3.07	5.99	10.39	14.78

Table (16): Loss of various concentrations of Mn^{2+} by seeds with time.

Mn	5 ppm	10 ppm	15 ppm	20 ppm
Time (min.)	C_{eq}	C_{eq}	C_{eq}	C_{eq}
5	2.64	6.27	10.12	13.52
15	2.54	6.15	9.45	13.21
30	2.39	5.92	9.44	13.11
50	2.38	5.92	9.42	13.11
70	2.38	5.92	9.41	13.01

Table (17): Applying second order equation on the % removal of Cr^{3+} seeds.

Cr^{3+}	5 ppm		10 ppm		15 ppm		20 ppm	
Time (min.)	q_t mg/g	$\dfrac{t}{q_t}$	q_t mg/g	$\dfrac{t}{q_t}$	q_t mg/g	$\dfrac{t}{q_t}$	q_t mg/g	$\dfrac{t}{q_t}$
5	0.29	17.22	0.67	7.37	0.89	5.59	0.99	5.01
15	0.31	48.38	0.68	21.86	0.90	16.57	1.00	14.92
30	0.36	81.34	0.76	39.32	0.91	32.82	1.03	28.87
50	0.37	134.04	0.79	62.71	0.91	54.65	1.04	48.05
70	0.37	187.31	0.80	87.42	0.91	76.40	1.04	67.15

Table (18): Applying second order equation on the % removal of Mn^{2+} by seeds.

Mn^{2+}	5 ppm		10 ppm		15 ppm		20 ppm	
Time (min.)	q_t mg/g	$\dfrac{t}{q_t}$	q_t mg/g	$\dfrac{t}{q_t}$	q_t mg/g	$\dfrac{t}{q_t}$	q_t mg/g	$\dfrac{t}{q_t}$
5	0.47	10.59	0.74	6.70	0.97	5.12	1.29	3.86
15	0.49	30.60	0.76	19.51	1.10	13.53	1.35	11.05
30	0.52	57.47	0.81	36.78	1.11	26.98	1.37	21.78
50	0.52	95.71	0.81	61.30	1.11	44.82	1.37	36.30
70	0.52	133.89	0.81	85.78	1.11	62.71	1.39	50.08

Table (19): Applying Khan and Singh equation on the % removal of Cr^{3+} by seeds.

$ln\dfrac{q_e}{C_e}$	q_e (mg/g)
-2.13	0.36
-2.09	0.762
-2.47	0.87
-2.65	1.03

Table (20): Applying Khan and Singh equation on the % removal of Mn^{2+} seeds.

$ln\dfrac{q_e}{C_e}$	q_e(mg/g)
-1.55	0.50
-2.00	0.80
-2.15	1.09
-2.25	1.37

Table (21): A plot of q$_e$ versus C$_e$ for the % removal of Cr^{3+} by seeds.

q_e(mg/g)	C_e(mg/L)
0.36	3.12
0.762	6.18
0.87	10.41
1.03	14.80

Table (22): A plot of q$_e$ versus C$_e$ for % removal of Mn^{2+} by seeds.

q_e(mg/g)	C_e (mg/L)
0.50	2.39
0.800	5.92
1.09	9.44
1.37	13.11

References

1. Abdel-Ghani, N. T., Ahmad, K. H., El-Chaghaby, G. A., Lima, E. C., 2009. **Factorial Experimental Design for Biosorption of Iron and Zinc Using Typha Domingensis Phytomass.** Desalination 249: 343–347.

2. Abu- shqair, I., Salim, R., Al-subu, M., Swaileh, K., 2001. **Removal of Dissolved Copper from Polluted Water Using Plant Leaves: Effect of Acidity and Plant Species.** Rev.Int. Contam. 17 (2) 91-96.

3. Adie, D.B., Igboro, S.B., Daouda, N., 2013. *Determination of the Filter Potential of Luffa Sponge (luffa aegyptiaca) in Water Quality Analysis*, **American International Journal of Contemporary Research** , 3(3),120-123.

4. Altun, O., Ozbelge, H.O., Dogu, T., 1998. **Journal of Colloid and Interface Science**, 198(1), 130-140.

5. Anderson, W.P., 1973. **Ion Transport in Plant, Academic Press**, London and New York, pp. 340-399.

6. Bailey, S. E., Olin, T. J., Bricka, R. M., Adrian, D., 1999. **Water Resources.** 33 (11), 2469–2479.

7. Bal, K.E., Bal, Y., Lallam, A., 2004. **Gross Morphology and Absorption Capacity of Cell-Fibers from the Fibrous Vascular System of Loofah (*Luffa cylindrica*).** Textile Res. J. 74: 241-247.

8. Berti, W., Cunningham, S. D., 2000. **Phytostabilization of metals. IN Raskin, I. & Ensley, B. D. (Eds.) Phytoremediation of toxic metals:**

using plants to clean-up the environment. New York, John Wiley & Sons.

9. Cano-Rodriguez, I., Perez-Garcia, J.A., Gutierrez-Valtierra, M., Gardea -Torresdey, J.L., 2002. Rev. Mex.Ing. Quim. 1–3, 97–103.

10. Cluis, C., 2004. *Junk-greedy Greens: phytoremediation as a New Option for Soil Decontamination*. **BioTeach Journal**, 2**,** 61-67.

11. David, W. O., Norman, H. N., 1986. **Principles of Modern Chemistry. Saunders Golden Sunburts Series Printed by the Dryden Press**. 383 Madison Avenue, New York. N. Y.10017. USA.

12. Davis, T.A., Volesky, B., Mucci, A., 2003. **Water Research**, 37(18), 4311-4330.

13. De la Rosa, G., Gardea-Torresdey, J. L., Peralta-Videa, J.R., 2003. **Journal of Hazardous Materials**. 97 (1–3), 207–218.

14. Demir, H., Top, A., Balkose, D., Ulku, S., 2008. *Dye Adsorption Behavior of Luffa cylindrica Fibers.* **Journal of Hazardous Materials;** 153:389-394.

15. Drake, L. R., Rayson, G. D., 1996. **Analytical Chemistry**, 68 (1), 22A–7A.

16. Dushenkov, V., Motto, H., Raskin, I., Kumar, N. P., 1995. **Rhizofiltration: the Use of Plants to Remove Heavy Metals from Aqueous Streams**. Environmental Science Technology, 30**,** 1239-1245.

17. Einschlag, F.S., 2011a.**Waste Water _Treatment and Reutilization, In Tech, Chp.** 10, p. 195-212.

18. Einschlag, F.S., 2011b.**Waste Water _Treatment and Reutilization, In Tech, Chp**. 10, p. 13.

19. Gardea-Torresdey, J. L., Cano-Aguilera, I., Webb, R., Tiemann, K. J., Gutierrez- Corona, F., 1996. **Journal of Hazard Materials , 48**, 171–180.

20. Gardea-Torresdey, J. L., de la Rosa, G., Peralta-Videa, J. R., 2004. **Pure and Applied Chemistry**, 76(4), 801-813.

21. Gardea-Torresdey, J. L., Tang, L., Salvador, J.M., 1996a. *J. Hazard. Mater.* **48** (1–3), 191–206.

22. Gardea-Torresdey, J. L., Tiemann, K. J., Gonzalez, J. H., Cano-Aquilera,I., Henning, J. A., Towsend, M. S., 1996b. **Journal of Hazard Materials, 49**, 205-216.

23. Gardea-Torresdey, J. L., Tiemann, K. J., Gonzalez, J. H., Henning, J. A., Towsend, M. S., 1996c. **Journal of Hazard Materials, 48**, 181–190.

24. Gardea-Torresdey, J. L., Tiemann, K. J., Gonzalez, J. H., Rodreques,O., Gamez, G., 1998a. **Journal of Hazardous Materials**, 57, 29-39.

25. Gardea-Torresdey, J. L., Tiemann, K. J., Gonzalez, J. H., Rodreques,O., Gamez, G., 1998b. **Phytofiltration of Hazardous Cadmium, Chromium, Lead and Zinc Ions by Biomass of Medicago Sativa Alfalfa, University of Texas at El Paso.**

26. Gardea-Torresdey, J. L., Tiemann, K. J., Gonzalez, J. H., Rodríguez, O., 1997. *J. Hazard. Mat.er.* **56**, 169–179.

27. Ghosh, M., Singh, S. P., 2005a. **A comparative study of cadmium phytoextraction by accumulator and weed species.** *Environmental Pollution,* 133**,** 365-371.

28. Ghosh, M., Singh, S. P., 2005b. **A review on phytoremediation of heavy metals and utilization of its byproducts**. *Applied Ecology and Environmental Research,* 3**,** 1-18.

29. Graeme, K., Pollack C., 1998. *Heavy metal toxicity, Part I: Lead and metal fume fever.* **Journal of Emergency Medicine,** Volume 16, Issue 2, Pages 171-177.

30. Guo, S., Li, W., Zhang, L., Peng, J., Xia, H., Zhang, S., 2009. **Kinetic and equilibrium adsorption study of lead (II) onto the low cost adsorbent-Eupatorium adenophorum spreng, Process Safety and Environmental Protection,** 87 (5): 343-351.

31. Gupta, N., Prasad, M., Singhal, N., Kumar, V., 2009. **Modeling the Adsorption Kinetics of Divalent Metal Ions onto Pyrophyllite Using the Integral Method**. Ind. Eng.Chem. Res., 48 (4), 2125-2128.

32. Ho, Y. S. and Mckay, G., 1998. "**Sorption of Dye from Aqueous Solution by Peat,"** Chemical Engineering J., 70, 115.

33. http://water.epa.gov/drink/contaminants/secondarystandards.cfm Accessed on 2015, may, 30.

34. http://www.lenntech.com/periodic/elements/v.htm#ixzz3GvoFwWGc, Accessed on 2015, may, 20.

35. Iqbal, M., Zafar, S.I., 1993a. **The use of fibrous network of matured dried fruit of *Luffa aegyptiaca* as immobilizing agent.** Biotechnol. Tech. 7: 15-18.

36. Iqbal, M., Zafar, S.I., 1993b. **Vegetable sponge: A new immobilizing medium for plant cells.** Biotechnol. Tech. 7: 323-324.

37. Iqbal, M., Saeed,A., Akhtar, N., 2002. *Bioresource Technol*. **81**, 151–153.

38. Junior, O.K., Gurgel, L.V.A., de Freitas, R.P., Gil, L.F., 2009. **"adsorption of Cu (II), Cd (II) and Pb (II) from aqueous single metal solutions by mercerized cellulose and mercerized sugarcane bag asse chemically modified with EDTA dianhydride (EDTA)," Carbohydrate Polymers,** vol. 77, no.3, pp, 643-650.

39. Lagergren, S., 1898. "**zur Theorie der sogenannten adsorption geloster stöffe, Kungliga Sevenska Vetenskapsakademiens,**" Handlingar, 24, 1.

40. Laidani, Y., Hanini, S., Henini, G., 2010. **Valorization of Luffa for Water Treatments Copper Chargers. Study of the Possibility of Regeneration by Chemical Desorption**. Oman, pp. 1.

41. Lee, S., Yoo, J.G., 2006. **Method for preparing transformed luffa cylindrica Roem (World Intellectual property organization)**,http://www.wipo.int/pctdb/en/wo.jsp?IA=KR2004002745&DISPLAY=STATUS

42. Lima, I.M., Wartelle, L.H., Marshall, W.E., 2002. **Preprints of Extended Abstracts presents at the ACS National Meeting, American**

Chemical Society, Division of Environmental Chemistry, 42(2), 112-116.

43. Lin, S.H., Juang, R.S., 2002. **Journal of Hazardous Materials**, 92(3), 315-326.

44. Lu, D., Cao, Q., Cao, X., Luo, F., 2009. *Removal of Pb (II) using the modified lawny grass, Mechanism, Kinetics, Equilibrium and Thermodynamics studies.* **Journal Hazardous Materials**, 166 (1): 239-247.

45. Mazali, I.O., Alves, O.L., 2005. **Morphosynthesis: high fidelity inorganic replica of the fibrous network of loofa sponge (***Luffa cylindrica***).** An Acad. Bras. Ciên. 77(1): 25-31

46. Miller, R., 1996. **Phytoremediation: Technology Overview report, Ground Water Remediation Technologies Analysis Center**.

47. Moreno-Piraján, J. C., Garcia-Cuello, V. S., Giraldo, L., 2011. "**The removal and kinetic study of Mn, Fe, Ni and Cu ions from wastewater onto activated carbon from coconut shells,"** Adsorption, vol. 17, no. 3, pp. 505–514.

48. Nandi, B.K., Goswami, A., Purkait, M.K., 2009. *"adsorption characteristics of brilliant green dye on kaolin"*, Journal of Hazardous Materials, Vol. 161, no.1, pp. 387-395.

49. Newton, A., 2006. **More On How To Grow A Luffa, Green Living**, How To, www.groovygreen.com/groove/?p=710, 28.05.2015.

50. Ng, Y.M., Yang, Y., Sze, K.H., Zhang, X., Zheng, Y.T., Shaw, P.C., 2011. *Structural characterization and anti-HIV-1 activities of*

arginine/glutamate-rich polypeptide Luffin P1 from the seeds of sponge gourd [Luffa cylindrica]. **Journal of Structural Biology**; 174:164-172.

51. Oboh, I., Aluyor, E., Audu, T., 2009. *Luffa cylindrica - an emerging cash crop.* **African Journal of Agricultural Research Vol. 4 (8)**, pp. 684-688.

52. Oboh, I., Aluyor, E., Audu, T., A., 2009. *Post-treatment of produced water before discharge using luffa cylindrica.* Leonardo Electronic *Journal of Practices and Technologies*. P. 57-64.

53. Parsons, J. G., Gardea-Torresdey, J. L., Tiemann, K. J., Gamez, G., 2003. *Anal. Chim. Acta.* **478** (1), 139–145.

54. Patnukao, P., Kongsuwan, A., Pavasan, P., 2008. *Batch studies of adsorption of copper and lead on activated carbon from Eucalyptus camaldulensis Dehn .Bark*. **Journal of Environmental Sciences**, 20.

55. Petruzzelli, D., Mascolo, G., Barile, G., Tiravanti, G., Marton, A., 1997. **Reactive & Functional Polymers**, 35(1/2), 89-98.

56. Prasad, M. N. V. , De oliveira freitas, H. M., 2003. *Metal hyperaccumulation in plants - Biodiversity prospecting for phytoremediation technology*. **Electronic Journal of Biotechnology**, 6.

57. Primary Drinking Water Rules (sec. 141.32 (e) (20)), **Federal Regulations, The Burea of National Affairs, Inc**. (1992).

58. Raskin, I., Smith, R. D. , Salt, D. E. 1997. **Phytoremediation of metals: using plants to remove pollutants from the environment.** *Current Opinion in Biotechnology,* 8**,** 221-226.

59. Roberts, J.D., Caserio, M.C., 1977. **Basic Principle of Organic Chemistry**, Benjmin, W.A.,Inc., Menlo Park, Calif, USA, 2nd edition.

60. Romero-Gonzalez, J., Peralta-Videa, J.R., Rodriguez, E., Ramirez, S.L., Gardea-Torresdey, J.L., 2005. **Journal of Chemical Thermodynamics**, 37(4), 343-347.

61. Rowell, R.M., James, S.H., Jeffrey, S.R., 2002. **Characterization and factors effecting fibre properties**, In Frollini E, Leao, AL, Mattoso LHC, (ed.), Natural polymers and agrofibres based composites. Embrapa Instrumentacao Agropecuaria, san Carlos, Brazil pp.115-134.

62. Salt, D. E., Kumar, P. B. A. N., Dushenkov, S. , Raskin, I. 1994 Phytoremediation: A New Technology for the Environmental Cleanup of Toxic Metals. **International Symposium Research on Conservation and Environmental Technology for Metallic Industry**. Toronto, Canada.

63. Saueprasearsit, P., **Adsorption of Chromium (Cr^{+6}) Using Durian Peel, 2011. International Conference on Biotechnology and Environment Management IPCBEE vol.18, IACSIT Press, Singapoore**.

64. Saueprasearsit, P., Nuanjaraen, M., Chinlapa, M., 2010**. *Biosorption of Lead (Pb^{+2}) by Luffa Cylindrica Fiber*. Enviromental Research Journal** 4(1): 157-166.

65. Sawalha, M., Gardea-Torresdey, J., Gurian, P., Chianelli, R., Walton, J., Saupe, G., 2006.**Thermodynamic and Isotherm Studies of the Biosorption of Cu(II), Pb(II), and Zn(II) onto the leaves Biomass of Saltbush (*Atriplex canescens*),** chp.5, P., 80.

66.   Semerjian, L., Ayoub, G.M., 2003. **Advances in Environmental Research,** 7(2), 389-403.

67. Shukla, S. R., Pai, R, S., Shendarkar, A. D., 2006. **"Adsorption of Ni (II), Zn (II) and Fe (II) on modified coir fibres," Separation and Purification Technology,** vol. 47, no. 3, pp. 141–147.

68.   Singh, V., Labana, S., 2003. **Phytoremediation: an overview of metallic ion decontamination from soil.** *Appli. Microbiol. Biotechnol.,* 61**,** 405-412.

69.   Stephens, J.M., 2012. **Gourd, Luffa — Luffa cylindrica (L.) Roem., Luffa aegyptica Mill.,** and Luffa acutangula (L.) Roxb.1, University of Florida, IFAS Extemsion.

70.   Taffarel, S, R., Rubio, J., 2009, **"On the removal of Mn^{2+} ions by adsorption onto natural and activated Chilean zeolites,"** Minerals Engineering, vol. 22, no. 4, pp. 336–343.

71.   Taffarel, S, R., Rubio, J., 2010.   "**Removal of $^{Mn2+}$ from aqueous solution by manganese oxide coated zeolite,"** Minerals Engineering, vol. 23, no. 14, pp. 1131–1138.

72.   Teimann, K, J., 1998. **Study of Alfalfa Phytofiltration Technology to Clean Heavy Metal Contaminated Waters, Doctoral Dissertation**, University of Texas at El Paso.

73.   Tsezos, M., *Deutschmann*, A. A., 1990. **Journal of Chemical Technology and Biotechnology,** 48, 29-39.

74.   Üçer, A., Uyanik, A., Aygün, Ş, F., 2006. "**Adsorption of Cu (II), Cd (II), Zn (II), Mn (II) and Fe (III) ions by tannic acid immobilized**

activated carbon," Separation and Purification Technology, vol. 47, pp. 113–118.

75. Vijayaraghavan, K., Winnie, H, Y, N., Balasubramanian, R., 2011. "**Biosorption characteristics of crab shell particles for the removal of manganese (II) and zinc (II) from aqueous solutions,**" Desalination, vol. 266, no. 1–3, pp. 195–200.

76. Volesky, B., 2001. *Hydrometallurgy .***59**, 203–216.

77. Zavoda, J., Cutright, T., Szpak, J., Fallon, E., 2001. **Uptake, Selectivity, and Inhibition of Hydroponic Treatment of Contaminants**. *J. Environ. Eng.,* 127**,** 502.

78. Zhu, Y. Z., Pilon-Smits, E. A. H., Tarun, A. S., Weber, S. U., Jouanin, L., Terry, N., 1999 . **Cadmium Tolerance and Accumulation in Indian Mustard Is Enhanced by Overexpressing g-Glutamylcysteine Synthetase1.** *Plant Physiol.,* 121**,** 1169-1177.

جامعة النجاح الوطنية

كلية الدراسات العليا

استخدام تقنية الامتصاص الحيوي لإزالة عنصر الكروم (Cr) والمنغانيز (Mn)
من الماء الملوث باستخدام نبات اللوف المتسلق

إعداد

آيات توفيق حسن أبو شربة

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ب

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الملخص

تم دراسة قدرة نبات اللوف المتسلق (كإسفنج وبذور) على إزالة أيونات عنصر الكروم (Cr^{3+}) والمنغانيز (Mn^{2+}) من المحاليل المائية باستخدام تقنية (phytofiltration.)

تم دراسة تأثير بعض العوامل المختلفة على عملية الإزالة مثل: درجة الحموضة، درجة الحرارة، تركيز أيون العنصر الابتدائي والوقت اللازم. كذلك تحرت الدراسة مدى السعة الارتباطية للبذور لأيونات العناصر، تأثير بعض الأيونات المنافسة للارتباط، وأوجدت Isotherms ورتبة التفاعل و $\Delta G°$.

خلصت الدراسة الى أن للإسفنج والبذورقدرة على إزالة أيونات الكروم (Cr^{3+}) من محلوله بنسبة أقصاها 42% و 40% على الترتيب و 82% و 78% على الترتيب لأيون المنغانيز (Mn^{2+}). كما أن لدرجة الحموضة أثرا واضحا حيث بلغت نسبة الإزالة قيمتها القصوى عند درجة حموضة 5 لأيونات الكروم (Cr^{3+}) و 7 لأيون المنغانيز (Mn^{2+})، وكان تركيز الأيون الابتدائي 5 ملغرام/ليتر، درجة حرارة ما بين 35 – 40 س° والوقت اللازم 15 دقيقة لكلا أيونات العنصرين .

أظهرت الدراسة أيضا أن للبذور مقدرة على استيعاب 1.65 ملغرام/غرام من (Cr^{3+}) و 3.36 ملغرام/غرام من (Mn^{2+}).

تم متابعة تراكيز أيونات العناصر باستخدام جهاز طيف الامتصاص الذري (باستخدام اللهب).

وُجد أن Langmiur adsorption isotherm كان الأفضل تطبيقا على ازالة أيونات الكروم

(Cr^{3+}) بينما كان Fruendlich adsorption isotherm الأفضل لإزالة أيونات المنغانيز

(Mn^{2+}). كما تم تقدير رتبة التفاعل بين أيونات كل عنصر والبذورفكانت من الدرجة الثانية.