Egyptian Journal of Chemistry
http://ejchem.journals.ekb.eg/

Heavy Metals Biosorption Using Dry Biomass of *Lotus Corniculatus* L. And *Amaranthus Viridis* L.

Moussa, H. R. [a*]; Mamdouh S. Serag [b]; Mohamed Adel Elgendy [b] and Marwa T. Mohesien [b]

[a]*Radioisotope Department, Nuclear Research Center, Atomic Energy Authority, Dokki, 12311, Giza, Egypt.*
[b]*Department of Botany and Microbiology, Faculty of Science, Damietta University.*

Abstract

Metal pollution issues is becoming increasing day by day common in Egypt and elsewhere due to rapid growth the human population, industrialization foundries, smelters and urbanization. Heavy metals are the major problematic pollutants which poses a significant threat public health, as they are continual and non-biodegradable. Thus, their phytoremediation becomes inevitable and extensive efforts to apply the absorption technique which seems to be a promising alternative, less expensive, high efficiency that is being used widely for removal of heavy metal from aqueous media. In the present study the dry mass of two weeds, *Lotus corniculatus* and *Amaranthus viridis* were used as adsorbents to study the process of biosorption. The studied plants have not gained much importance and are common in the Egyptian waste lands. For the present study different concentration (10, 50 and 100 ppm) of four heavy metals (cadmium, chromium, lead and zinc) were tested for the adsorption by the two plants. Results showed that the adsorption process was very rapid for the two weeds (90% of equilibrium adsorption capacity was achieved) for the removal of the tested heavy metals (cadmium, chromium, lead and zinc). The FT-IR, XRD and phytochemical tests analyses have been carried out in order to find the structural and chemical composition (functional groups) of the dry biomass of the two plants to clearly establish a protocol for the adsorption mechanism involved for removal of heavy metals by eco-friendly and cost effectiveness technique. The experimental results indicated that the feasibility of using effective, easy, and abundantly available dry biomass of the tested weeds can be easily converted to good adsorbent without any pretreatment.

Keywords**:** Heavy metals; Adsorption technique; *Amaranthus viridis; Lotus corniculatus*.

1. Introduction

Heavy metals in water originated from wastewater of numerous industries [1]. The presence of heavy metals in aqueous water streams have become a major problem due to their harmful impacts on human health and on the fauna and on biota of aquatic ecosystem [2].

Different techniques are used for the removal of heavy metals from aqueous solutions: ion exchange [3], chemical precipitation [4], membrane separation [5], electrochemical coagulation [6], photo-catalysis [7], reverse osmosis [8], and electro dialysis [9]. All these techniques are over the top expensive and furthermore not really compelling.

Recently, impressive consideration has been inspired to the investigation of utilization of agricultural dry biomass as adsorbents. Adsorption technique is known as a convenient, minimal expense, being eco-friendly, harmless to the ecosystem, achievability for physical and chemical modification efficient, and great adsorption limit of heavy metals from wastewater. The flexibility in design and operation, high removal effectiveness and the opportunities for the greater part of the adsorbents to be recovered and reuse by reasonable desorption process have made adsorption process acquiring its prevalence [10,11].

In Egypt, *Lotus corniculatus* (*Fabaceae*) is growing wild in the Mediterranean region, Nile banks, cultivated ground and wetlands [12]. there are few studies for anti-cancer and antioxidant effects [13], as contraceptives, for the treatment of sexually transmitted diseases and treatment of peptic ulcers, proanthocyanidins, tannins, flavonoids, oleanolic acid, and saponins were identified in these species [14].

*Amaranthus viridis L.*is an annual herb, from family (Amaranthaceae) a decoction of the entire

---

Corresponding authors: Helal Ragab Moussa, e mail: helal_moussa@hotmail.com
Receive Date: 11 May 2022, **Revise Date:** 27 July 2022, **Accept Date:** 07 August 2022
First Publish Date: 07 August 2022
DOI: 10.21608/EJCHEM.2022.137954.6073

plant is used as antioxidant, antihyperlipidemic and antidiabetic, [15]. Antifungal lectin and antiproliferative [16]. The root juice is used to treat inflammation during urination and constipation [17].

In the present context, the dry biomass of two plants, *Lotus corniculatus* and *Amaranthus viridis* were used as adsorbents to test their biosorption efficiency for removal of some heavy from aqueous solution.

2. MATERIALS AND METHODS

2.1. Experimental Design and Apparatus Description

In the present study, the dry biomass of *Lotus corniculatus* and *Amaranthus viridis* were used for the removal of some heavy metals from its aqueous solution. Both the plants were collected from *Damietta Governorate*, Egypt and cut into small pieces and washed several times with double distilled water, dried in oven at 55 °C for five days, then stored in at room temperature.

The Extract was prepared by Solid-liquid extraction using soxhlet apparatus in this process solutes were removed from solid using liquid solvent, in present study ethanol is taken as polar solvent and water as non-polar solvent.

In the present study different weight of dry masses (0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4 gm) of two plants, *Lotus corniculatus* L. and *Amaranthus viridis* L. were used as adsorbents to study the process of biosorption. Three concentrations (10, 50 and 100 ppm) of four heavy metals (cadmium, chromium, lead and zinc) were tested for the adsorption by the two plants, pH 6.0 was chosen as the optimum pH for the adsorption system.

Various analysis such as FTIR, XRD and phytochemical tests had been carried out in Central Laboratory of Elemental and Isotopic Analysis (CLEIA), Nuclear Research center, Atomic Energy Authority in order to find the structural and chemical composition (functional groups) of the dry biomass of the two weeds to clearly establish a protocol for the adsorption mechanism involved for removal of tested heavy metals.

Heavy metals determination in the two plants were done using atomic absorption spectroscopy (shimadzu). Standard operating parameters were set. The hollow cathode lamps for Cr, Cd, Pb and Zn (shimadzu) were used as radiation source and fuel was air acetylene. All the samples and standard were run in duplicate.

2.2. Fourier transform infrared analysis (FT-IR)

FT-IR analysis was performed using (NICOLET iS10 model instrument) the spectra were recorded in the range 400 – 4000 cm^{-1}.

2.3. X-Ray diffraction (XRD) technique

X-Ray Diffraction (XRD) allows one to ascertain the molecular structure of a crystalline material by diffracting X-rays through the sample [18]. An XRD analyzer obtains interference patterns reflecting lattice structures by varying the angle of incidence of the X-Ray beam **(Rigaku MicroMax-007 X-ray diffraction system,** McCrone Associates, Inc.**, China).**

3. RESULTS AND DISCUSSION

3.1. Removal of heavy metal using dry biomass of *Lotus corniculatus* and *Amaranthus viridis*:

The plot of adsorption percentage opposed to amount of adsorbent at different concentration of heavy metal (10, 50 and 100 ppm) in aquatic solution is shown in Figure (1 and 2).

In case of *Lotus corniculatus* (Figure 1), it is observed that at a concentration of 10 ppm of heavy metals the adsorption rate reaches a value of 93, 82, 90 and 73 % respectively, for cadmium (3.5 g), chromium (2 g), lead (2 g) and zinc (2.5 g).At a concentration of 50 ppm of heavy metals the adsorption efficiency reaches a value of 58, 45, 72 and 39 % respectively, for cadmium (2.5 g), chromium (2.5 g), lead (2.5 g) and zinc (4 g).At a concentration of 100 ppm of heavy metals the adsorption percentage reaches a value of 44, 40, 62 and 39 % respectively, for cadmium (2 g), chromium (4 g), lead (3 g) and zinc (4 g) as shown in Figure (1).

Whereas, in case of *Amaranthus viridis* (Figure 2) it was observed that at a concentration of 10 ppm of heavy metals the adsorption percentage reached a value of 90, 68, 75 and 42 %, respectively for cadmium (4 g), chromium (2.5 g), lead (3 g) and zinc (3.5 g). Also, at a concentration of 50 ppm of heavy metals the adsorption percentage reached a value of 52, 42, 48 and 28 %, respectively, for cadmium (2.5 g), chromium (3 g), lead (3.5 g) and zinc (3.5 g). At a concentration of 100 ppm of heavy metals the adsorption rate reached a value of 45, 27, 44 and 10 % respectively, for cadmium (3.5 g), chromium (3.5 g), lead (4 g) and zinc (4 g). In case of 100 ppm multiple species solution much higher quantity of adsorbent is required (Figure 1 and 2) for the two weeds.

The purification of 100 ppm of cadmium, chromium, lead and zinc from aqueous solution at various bio sorbent amount of *Lotus corniculatus* and *Amaranthus viridis* were examined. Results showed that ion uptake increased when dry biomass of the two plants take-up increments [19,20]. But with further increase in bio-adsorbent after a defined/specific quantity the adsorption becomes constant and afterward further abatements. This decrease is inferable from metal concentration shortage in the aquatic solution.

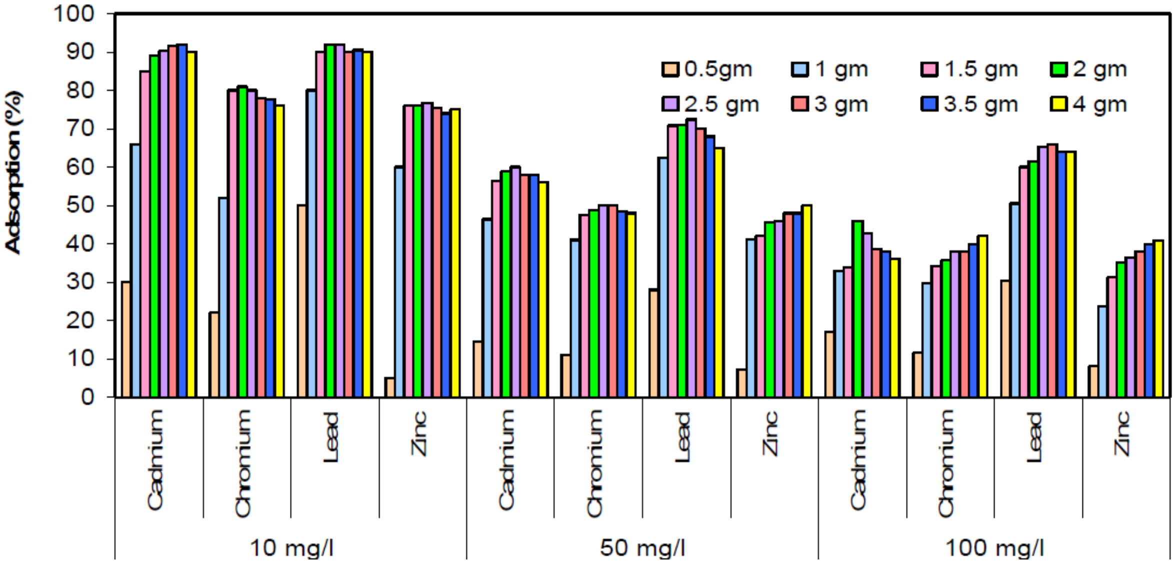


Figure 1: Impact of adsorbent quantity variation of *Lotus corniculatus* on the adsorption of different concentrations (10, 50 and 100 ppm) of four heavy metals (cadmium, chromium, lead and zinc) from aqueous solution.

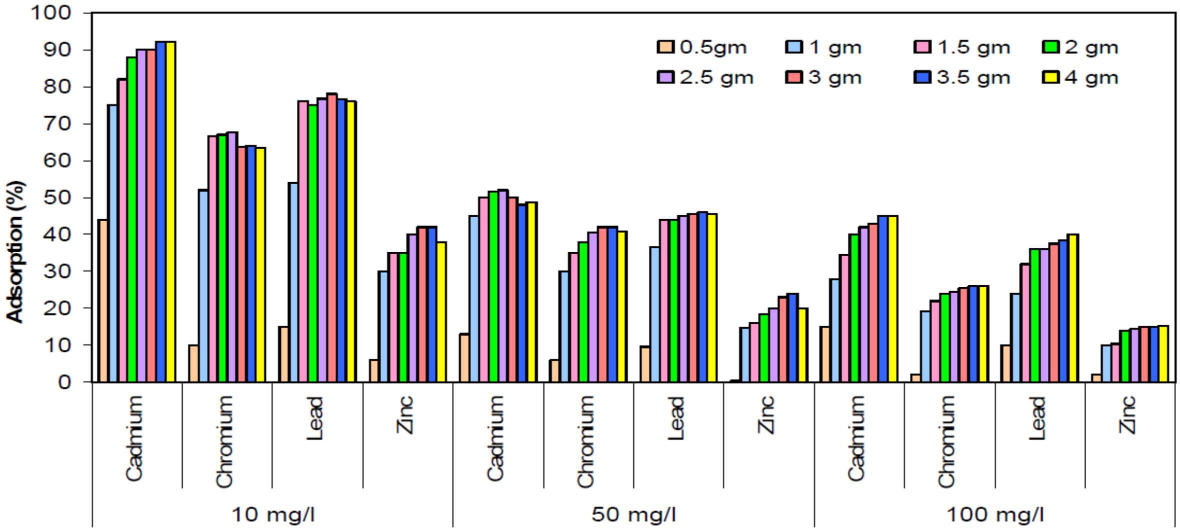


Figure 2: Impact of adsorbent quantity variation of Amaranthus viridis on the adsorption of different concentrations (10, 50 and 100 ppm) of four heavy metals (cadmium, chromium, lead and zinc) from aqueous solution.

Using the bio-sorbents there was an increase in metal uptake up to 4 g biomass for selected heavy metal ions.

The expansion in adsorption rate with the increment in amount of adsorbent at a particular concentration of metal ions in single as well as multiple species can be explained on the basis that with the increase in the quantity of dry biomass of *Lotus corniculatus* and *Amaranthus viridis* the availability of ionic sites increments, since the concentration of metal ions in aquatic solution is fixed, initially more ions get exchanged with the metal ions but after the saturation is reached adsorption diminishes (Figure 1 and 2).

However, at higher concentration (50 and 100 ppm) the adsorption rate is low when the quantity of adsorbent is small, the expansion in the quantity of adsorbent outcomes in the increment of adsorption rate, because the total sites of adsorption are increased. But the impedance and rivalry between available binding sites at higher biomass densities caused a decline in the particular adsorption limit of the biosorbent as in the case of the various species solution [20,21].

3.2. Fourier transform infrared analysis (FT-IR) and X-ray diffraction (XRD) technique

FT-IR analysis and XRD technique was carried out in order to know the chemical and structural composition of the dry biomass of the two weeds *Lotus corniculatus* and *Amaranthus viridis* that played a strong role in the adsorption of heavy metals (Figure 3, 4, 5, 6 and 7). The adsorption rate behaviour of dry biomass towards metal ions is a function of the chemical composition of the biomass. FT-IR absorption bands of the dry biomass of *Lotus corniculatus*, (Figure 3A and 6) recorded major characteristic bands which included: 3400-2950 cm^{-1} indicate O-H stretch which may be carboxylic group. Also, O-H and N-H stretching, vibration band obtained at 3420 cm^{-1} indicate phenolic groups. FT-IR absorption bands at 2400-1800 cm^{-1} show $C \equiv N$ or $C \equiv C$, but at 1190 cm^{-1}C-O stretch is obtained this all suggesting carboxylic group which is accountable for heavy metal binding.

FT-IR absorption bands of the dry masses of *Amaranthus viridis* (Figure 3B and 7**)** recorded peak at 3200-2850 cm^{-1} showed C-H stretch which may be of benzene. FT-IR absorption bands at peak at1550-1400 cm^{-1}in bending may be of methylene group or nitro or aromatic double bond stretch. Peak at 1150 cm^{-1} show C-O-C stretch of ether. FT-IR spectrum of the dry-biomass of the two plants focuses only on a few groups such as hydroxyls, ether, amide, carboxylic and hydro carbons supporting for the adsorption of heavy metals.

FT-IR spectra of the polar and non-polar extract of the dry biomass of the two plants *Lotus corniculatus* and *Amaranthus viridis* are shown in Figure (4, 5, 6 and 7).

The polar spectra of *Lotus corniculatus* (Figure 4A and 6) demonstrated that peaks at 3600-3200 cm^{-1} showed broad O-H stretch of carboxylic acid. Also C=O stretch at 1750-1700 cm^{-1} also suggesting presence of carboxylic acid group, also C-O stretch at 1240 cm^{-1}shows carbonyl group, thus the main functional groups are mainly benzene and carboxylic acid (Figure 4A and 6).

The polar spectra of *Amaranthus viridis* (Figure 4B and 7) shows the O-H stretch and bond stretch peaks which are hide peaks and not appearing as strong peaks, the groups may be benzene, C-O-C, C=O, CH_2 and CH_3.

FT-IR spectra of the non-polar extract of the dry biomass of the two plants *Lotus corniculatus* and *Amaranthus viridis* are shown in Figure (5, 6 and 7).

The non-polar spectra of *Lotus corniculatus* (Figure 5A and 6), similarly show hydroxyl or carboxylic groups as peaks obtained at 3600-3200 cm^{-1} having a broad O-H stretch and C=O stretch was also obtained at 1760 cm^{-1}indicatingcarbonyl group may be carboxylic acid. In addition, stretch of C=C at 1650-1600 cm^{-1} is the indication of benzene. FT-IR spectra at 1350 cm^{-1} could be attributed to C-O stretching of carbohydrates, sulfoxides, polysaccharides-like substances or alcohol. Thus the major functional groups recognized are mainly benzene and carboxylic acid (Figure 5A and 6).

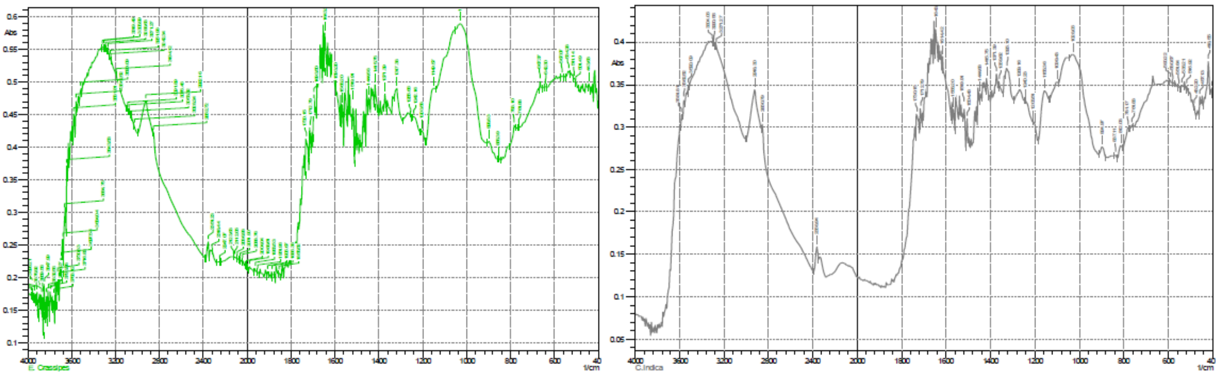
FT-IR spectra of the non-polar extract *Amaranthus viridis* (Figure 5B and 7), show at intensity of 3000–3800 cm^{-1} indicate hydroxyl (-OH) group stretching, and at intensity of 1600–1700 cm^{-1} indicate carbonyl (–C=O) stretching. Dry biomass extracts the major groups further reported were OH, C-O-C, CH_2, CH_3, C=O, COOH and benzene. The main functional groups responsible for adsorption process are the hydroxyls, amides, carbonyls, phosphonates, phosphodiester, carboxylic and carboxylate groups. Some of these groups are present in the dry biomass of the selected plants and interact with the metal ions and it directly seems that these functional groups responsible for in heavy metals binding process [20-25].

This may indicate the involvement of hydroxyl groups in the binding of Cr and Cd (Figure 5B and 7). The presence of slight changes in the peak regions refers to the presence of adsorption. Interestingly, the peaks get shifted with the presence of metal ions indicate an interaction of heavy metals with these functional groups.

The important role of metal adsorption includes electrostatic forces as wells as specific chemical interaction [21**,**26]. Also, the relation between the metal uptake efficiency and the amount of acidic groups is related to the number of carboxylic groups (weak acid) occurring in the biomass. These groups play the prevailing role in metal binding [20**,**21].

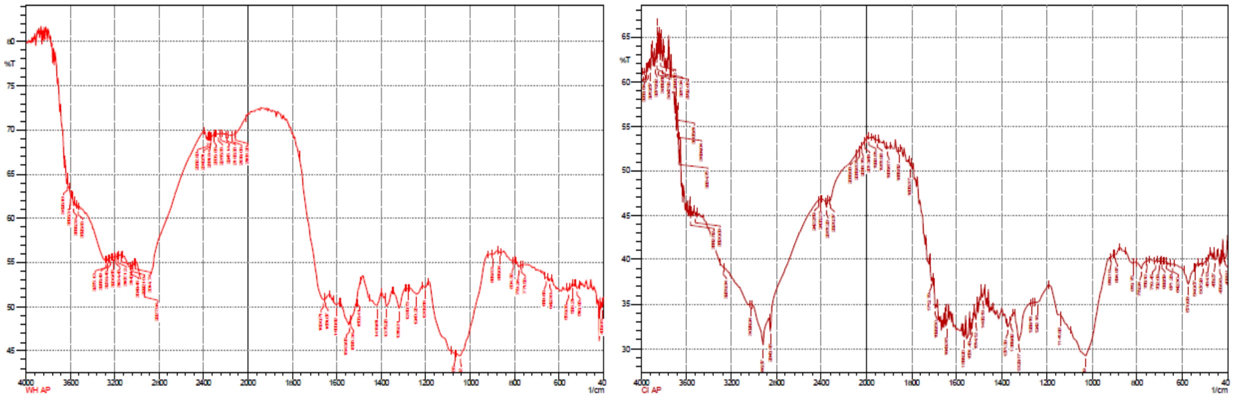
In our study, pH 6.0 was chosen as the optimum pH for the adsorption system. Many adsorption studies report pH 5.0 - 6.0 as the optimum pH for heavy metals (cadmium, chromium, lead and zinc) adsorption by various biosorbents [27-30].

The presence of functional groups on the surface of biosorbents was confirmed using FTIR analysis. In addition, FTIR analysis provides information on possible mechanisms involved in metal ion adsorption. From FTIR study, the formation of new absorption bands, the change in absorption intensity, and the shift in wavenumber of functional groups could be due to interaction of metal ions with active sites of biosorbents. The metal ions bound to the active sites of the biosorbents through either electrostatic attraction or complexation mechanism. The electrostatic attraction was between metal ion and carbonate group. Meanwhile, the complexation mechanism involved electron pair sharing between electron donor atoms (O and N). Results from this study suggest hydroxyls, amides, carbonyls, phosphonates, phosphodiester, carboxylic and carboxylate are the main adsorption sites in *Lotus corniculatus* L. and *Amaranthus viridis* L. [31].



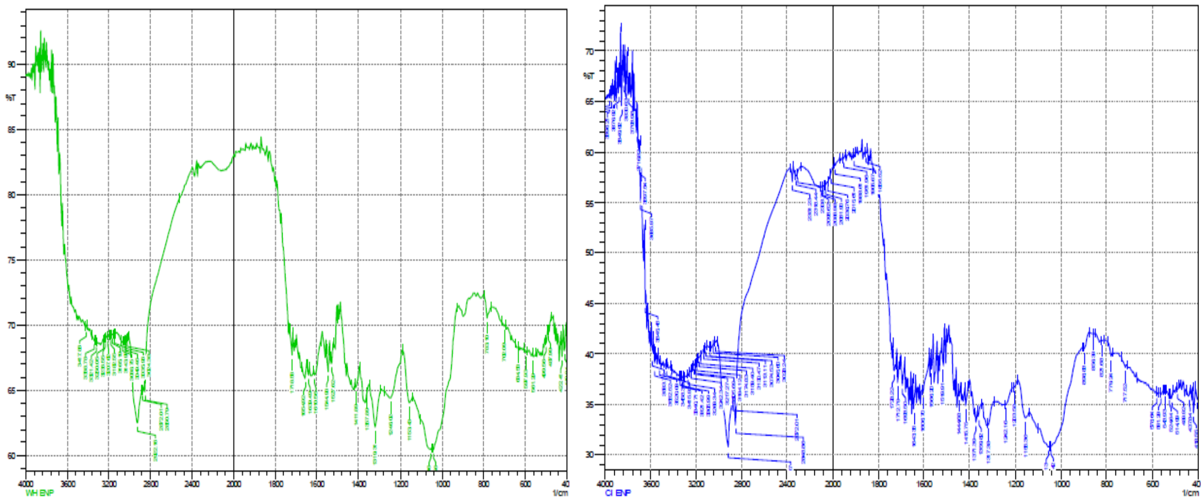
Lotus corniculatus (A) *Amaranthus viridis* (B)

Figure 3: Fourier transform infrared analysis (FT-IR) for the dry biomasses absorbance *in Lotus corniculatus* (A) and *Amaranthus viridis* (B).



Lotus corniculatus (A) *Amaranthus viridis* (B)

Figure 4: Fourier transform infrared analysis (FT-IR) for the dry biomasses polar- extract *in Lotus corniculatus* (A) and *Amaranthus viridis* (B).



Lotus corniculatus (A) *Amaranthus viridis* (B)

Figure 5: Fourier transform infrared analysis (FT-IR) for the dry biomasses non polar-extract *in Lotus corniculatus* (A) and *Amaranthus viridis* (B).

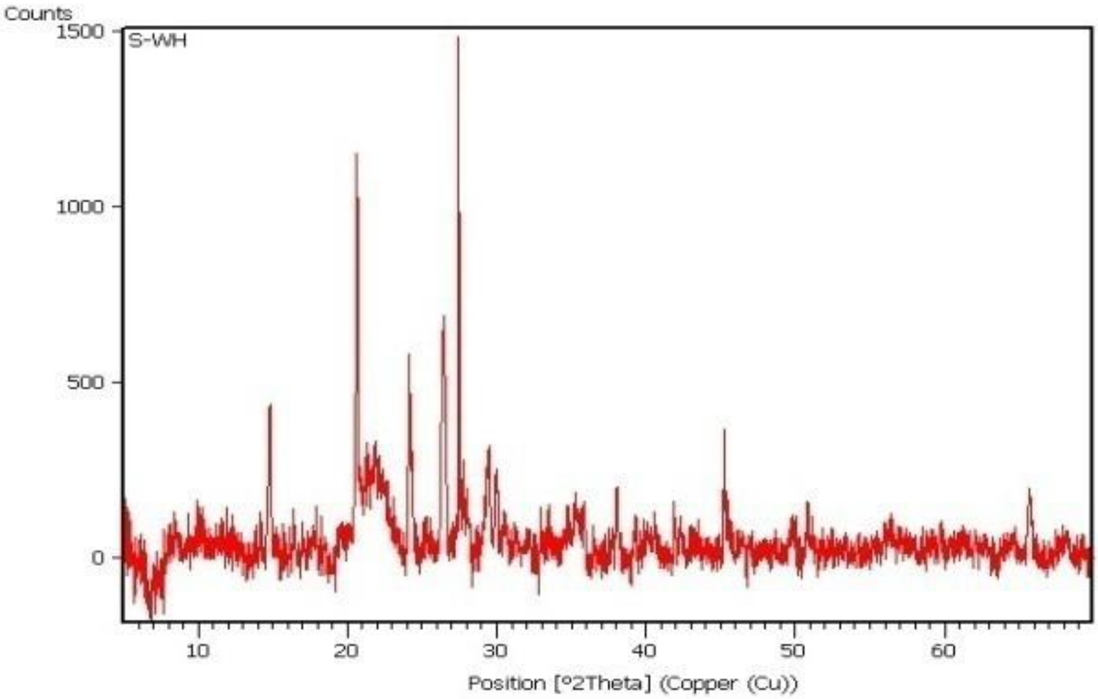


Figure 6: X-ray diffraction analysis (*XRD*) for the dry biomasses *in Lotus corniculatus* L.

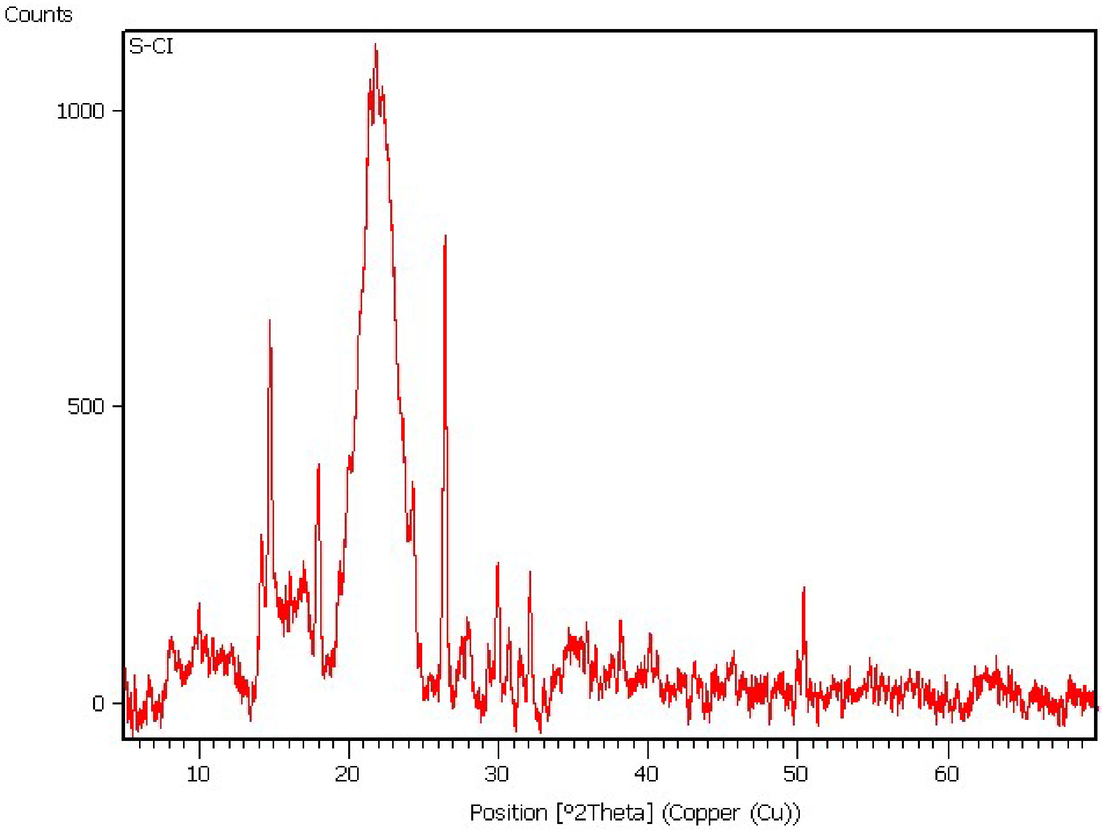


Figure 7: X-ray diffraction analysis (*XRD*) for the dry biomasses *in Amaranthus viridis* L.

4. CONCLUSION

Results showed that the adsorption process was very rapid for the two weeds (90% of equilibrium adsorption capacity were achieved) for the removal of the tested heavy metals (cadmium, chromium, lead and zinc). The experimental results indicated that the feasibility of using effective, easy, and abundantly available dry biomass of agricultural wastes can be easily converted to good adsorbent without any pretreatment. The FT-IR, XRD and phytochemical tests analyses were used to determine the surface functional groups and physico-chemical properties of the two weeds.

In countries, with the push for fast commercial improvement coupled with lack of awareness about metallic toxicity, there's an urgent want for growing an economical and eco-friendly technology. Adsorption technique gives numerous advantages, inclusive of fee effectiveness, high efficiency, minimization of chemical/biological sludge, and regeneration of biosorbent with opportunity of metallic recovery. Further, studies are needed to be carried out to get conclusive results for utilizing various adsorbents for wastewater treatment**.**

5. Conflicts of interest

There are no conflicts to declare.

6. REFERENCES

[1] Moussa, H. R. and Sabah Mohamed El-Gamal (2017). Does Exogenous Application of Melatonin Ameliorate Boron Toxicity in Spinach (*Spinacia oleracea* L.) Plants?. International J. of Vegetable Science, 23 (3): 233-245.

[2] Taty-Costodes VC, Fauduet H, Porte C, Ho YS (2005) Removal of lead (II) ions from synthetic and real effluents using immobilized *Pinus sylvestris* sawdust: adsorption on a fixed-bed column. J Hazard Mater 123(1–3):135–144

[3] Elkady M, Shokry H, Hamad H (2016) Effect of superparamagnetic nanoparticles on the physicochemical properties of nano hydroxyapatite for groundwater treatment: adsorption mechanism of Fe(II) and Mn(II). RSC Adv 6:82244–82259

[4] Rostamnezhad N, Kahforoushan D, Sahraei E, Ghanbarian S, ShabaniM (2015) A method for the removal of Cu(II) from aqueous solutions by sulfide precipitation employing heavy oil fly ash. Desalination Water Treat. 57(37):1–10

[5] Nędzarek A, Drost A, Harasimiuk FB, Tórz A (2015) The influence of pH and BSA on the retention of selected heavy metals in the nanofiltration process using ceramic membrane. Desalination 369: 62–67

[6] BazrafshanE, Mohammadi E, Ansari-Moghaddam A, Mahvi AM (2015) Heavy metals removal from aqueous environments by electrocoagulation process—a systematic: review. J Environ Health Sci. Eng. 13:74–89

[7] Hamad HA, Sadik WA, Abd El-latif MM, Kashyout AB, Feteha MY (2016) Photocatalytic parameters and kinetic study for degradation of dichlorophenol-indophenol (DCPIP) dye using highly active mesoporous TiO2 nanoparticles. J Environ Sci., 43:26–39

[8] Abu Qdais H, Moussa H (2004) Removal of heavy metals from wastewater by membrane processes: a comparative study. Desalination 164(2):105–110

[9] Ebbers B, Ottosen LM, Jensen PE (2015) Comparison of two different electrodialytic cells for separation of phosphorus and heavy metals from sewage sludge ash. Chemosphere 125:122–129

[10] Shih M (2012) Kinetics of the batch adsorption of methylene blue from aqueous solutions onto rice husk: effect of acid-modified process and dye concentration. Desalination Water Treat 37(1–3):200–214

[11] Ali RM, Hamad HA, Hussein MM, Malash GF (2016) Potential of using green adsorbent of heavy metal removal from aqueous solutions: adsorption kinetics, isotherm, thermodynamic, mechanism and economic analysis. Eco Eng 91:317–332

[12] Boulos L (2004) Flora of Egypt**.** Cairo: Al Hadara Publishing.

[13] Khalighi-Sigaroodi F, Ahvazi M, Hadjiakhoondi A, Taghizadeh M, Yazdani D, Khalighi-Sigaroodi S, Bidel S (2012) Cytotoxicity and antioxidant activity of 23 plant species of *Leguminosae* family. Iran J Pharm Res 11: 295.

[14] El Mousallami AM, Afifi MS, Hussein SA (2002) Acylated flavonol diglucosides from *Lotus polyphyllos*. Phytochemistry 60: 807–811.

[15] Ashok KBS, Lakshman K, Jayaveea KN, Sheshadri SD, Saleemulla K, Thippeswamy BS, Veerapur VP (2011). Antidiabetic, antihyperlipidemic and antioxidant activities of methanolic extract of *Amaranthus viridis* Linn in alloxan induced diabetic rats. Exp. Toxicol. Pathol., 3:11-16.

[16] Kaur N, Dhuna V, Kamboj SS, Agrewala JN, Singh J (2006). A novel antiproliferative and antifungal lectin from Amaranthus viridis Linn seeds. Protein Pept. Lett., 13(9): 897-905

[17] Manandhar NP (2002). Plants and People of Nepal Timber Press. Oregon, p. 6.

[18] Fitzpatrick, M.E., Fry, A.T., Holdway, P., Kandil, F.A., Shackleton, J., and Suominen, L., "Determination of Residual Stresses by X-ray Diffraction", Measurement Good Practice Guide No. 52, (Issue 2), NPL, UK, 2005.

[19] Peng, H., Liu, Y. G., Zeng, G. M., Li, X. and Zhang, W. (2009). Biosorption of Cu (II) and Zn (II) by intact and pre-treated biomass of *Oscillatoria planctonica*. *International J. of Environment and Pollution*, vol. 38 (1-2), pp. 1-14.

[20] Gadd GM (2009) Biosorption: critical review of scientific rationale, environmental importance and significance for pollution treatment. J Chem Technol Biotechnol 84(1):13–28

[21] Subhas Sarkar and S. Adhikari (2018). Adsorption Technique for Removal of Heavy Metals from Water and Possible Application in Wastewater-Fed Aquaculture. Wastewater Management Through Aquaculture pp 235-251.

[22] Yun YS, Park D, Park JM, Volesky B (2001) Biosorption of trivalent chromium on the brown seaweed biomass. Environ Sci Technol 35: 4353-4358.

[23] Horsfall, Michael Jnr, Spiff, Ayebaemi (2004). Recovery of lead and cadmium ions from metal-loaded biomass of wild cocoyam (*Caladium bicolor*) using acidic, basic and neutral eluent solutions. Journal of Corrosion Science and Technology, 2:12-18.

[24] Pradhan S, Singh S, Rai LC (2007) Characterization of various functional groups present in the capsule of Microcystis and study of their role in biosorption of Fe, Ni and Cr. Bioresour Technol 98: 595-601.

[25] Michalak I, Chojnacka K, Witek-Krowiak A (2013) State of the art for the biosorption process—a review. Appl Biochem Biotech 170(6):1389–1416

[26] Borda MJ, Sparks DL (2008) Kinetics and mechanisms of sorption-desorption in soils: a multiscale assessment. In: Violante A, Huang PM, Gadd GM (eds) Biophysico-chemical processes of heavy metals and metalloids in soil environments. Wiley, Hoboken, pp 97–124.

[27] Rafatullah M, Sulaiman O, Hashim R, Ahmad A (2010) Adsorption of Copper(II) onto Different Adsorbents. Journal of Dispersion Science and Technology, 31, 918-930.

[28] Mahmoud GA (2013) Adsorption of Copper(II), Lead(II), and Cadmium(II) Ions from Aqueous Solution by Using Hydrogel with Magnetic Properties. Monatshefte for Chemie-Chemical Monthly, 1-10.

[29] Chen G, Fan J, Liu R, Zeng G, Chen A, Zou Z (2012) Removal of Cd(II), Cu(II) and Zn(II) from Aqueous Solutions by Live Phanerochaete Chrysosporium. Environmental Technology, 33, 2653-2659.

[30] Al-Jariri JS, Khalili F (2012) Adsorption of Zn(II), Pb(II), Cr(III) and Mn(II) from Water by Jordanian Bentonite. Desalination and Water Treatment, 21, 308-322.

[31] Putra WP, Kamari A, Yusoff S, Ishak CF, Mohamed A, Hashim N, Isa IM (2014) Biosorption of Cu(II), Pb(II) and Zn(II) ions from aqueous solutions using selected waste materials: Adsorption and characterisation studies. Journal of Encapsulation and Adsorption Sciences 04(01): 25-35.