

# Biosorption of Selected Heavy Metal Ions from A Multi-Metal Aqueous Solution using Water Hyacinth (*Eichhornia Crassipes*) Root Powder

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**ABSTRACT:** Batch assessment of WATER HYACINTH (*EICHHORNIA CRASSIPES*) activated root powder as a potential bioadsorbent for the sorption of Cu (II), Pb (II), Zn(II), Mn(III) and Cd(II) ions from a multi-metal aqueous solution, under various reaction parameters of initial metal ion concentration,  $P^H$  and Contact time were studied at room temperature and pressure. The residual metal ions in solution were determined using atomic absorption spectrophotometer (AAS), 2008 model GF-3000 Australia. Data obtained were tested with Langmuir and Freundlich adsorption isotherms models in order to determine the suitable model. In terms of the effect of initial metal ions concentration on the adsorption process, the adsorbent adsorbed the five heavy metal ions from the multi-metal solution in high percentage, in the average order of Pb(II), 100% > Mn (III), 99.95% > Cd(II), 99.86% > Cu (II), 99.76% > Zn (II), 99.73%, respectively. In terms of  $P^H$ , the adsorbent adsorbed Cu (II), Pb (II), Zn (II) metal ions from solution 100%, from  $P^H$  2-9 while Mn (III) and Cd(II) were adsorbed 100% from  $P^H$  6-9, respectively. Mn (III) and Cd(II) were  $P^H$  dependent. In terms of contact time, Cu (II) and Pb (II) ions were adsorbed within 5 minutes from solution while Zn (II), Mn(III) and Cd(II) were adsorbed 100% within 20 minutes. Langmuir adsorption isotherms gave a better description of the process, the maximum sorption capacity ( $q_m$ ) is 2.040 mg/g for Cu(II), 10.000mg/g for Pb (II), 3.780mg/g for Zn (II), 1.550mg/g for Mn(III) and 1.380mg/g for Cd (II) ions respectively. Considering the biomass adsorption favourability factor "R", "R" value fell between 0 and 1, thus the adsorbent is good and the process favourable. The study revealed that WATER HYACINTH root powder has the potential and favourable in adsorbing Cu (II), Pb (II), Zn(II), Mn(III) and Cd(II) ions from a multi-metal aqueous solution.

**Index Terms:** Water-Hyacinth, Biosorption, Adsorption, Adsorbent, Heavy metals, Multi-metal, Langmuir, Freundlich, Isotherm, Atomic Absorption Spectrophotometer (AAS).

## 1. Introduction

Man's perception of environmental pollution existed before the industrial revolution. According to Edward and Botkin, 1982, the king of England in the 13<sup>th</sup> century advised parliament to ban the use of soft coal, culprits were punished by death.

Naturally pollutants exists in the environment as wild bush fire, volcanic eruptions, though irregularly and most times at minimum concentrations, though in some places abnormal high concentration is experienced, such as in Bangladesh, for arsenic in drinking water in excess of 50µg/l. (Islam et al., 2007). Wastes generation is inevitable. There will be no pollution problems if wastes are eliminated as they are produced (Edward and Botkin, 1982).

Metals are not degradable; they accumulate in the environment until they reach toxic levels. Metals may undergo biotransformation or biomagnification to become lethal. All heavy metals are hazardous at certain concentration above their safe limits. Their presence in water and the food chain is a serious problem that must be tackled to avert possible death

Water is polluted when it's no longer fit for its intended purpose. Amongst the various pollutants, such as, heavy metals, fertilizers, solid wastes, sewage, plastics, etc, heavy metals are of serious concern because they are not degradable. Heavy metal is defined as any metal that has specific gravity greater than 4(four) . Ten (10) heavy metals are essential to life forms including humans in trace amount, which may be toxic at higher level, these include Cu, Zn, As,

Se, etc (Holum, 1986; Addison- Wesley, 1987). Some heavy metals do not have any known function to lives even at trace level, such as, Ge, Sr, Rb, etc. Cd, Hg, and Pb, are toxic at trace level and are referred to as the family of the big three (Volesky and Schiewer, 1999; Aderhold et al., 1996).

Heavy metals in human system above the safe limits have often led to bones and organelle problems. In plants, it ranges from stunting growth to loss of biodiversity, etc. Since heavy metals do not degrade, they undergo bioaccumulation and/or biotransformation in water, sediments and in life forms (Yetis et al., 1998; Matheickal and Yu, 1996; Ademoroti, 1996).

The toxicity of heavy metals in humans and plants cannot be over said. Toxicity result when toxic heavy metals at safe limits undergo biomagnifications or biotransformations aided by aquatic microbes, such as, S- Adenosyl Methionine (SAM). Mercury (Hg) at safe level (0.01mg/l), undergo biotransformation to methylmercury, a very deadly organomercury compound (Ademoroti, 1996). Methylmercury is capable of crossing biological boundaries/membrane because it is lipophilic. In the early 1950's Japanese scientists reported that 43 persons died from consuming fish caught in minamata bay due to high level of mercury discharged into the bay by a chemical company without treatment (Ademoroti, 1996). In 1955, Japanese physicians reported cases of people that drank from Zintu River contaminated with high level of cadmium (Cd), due to industrial and mining wastes. At mere sneezing and coughing, patients' bones were being broken due to loss of calcium (David and Miller, 1991). The governments of Sweden ban the use of alkylmercury as herbicide in agriculture in 1960,

and other uses, as reported by the Swedish scientists, because Mercury was building-up in fresh water fishes. Canadian scientists in 1969 reported that, fresh water fish was contaminated with mercury which led to the closure of Lake St. Clair and other lakes, and area of St. Lawrence River system to commercial fishing (Ademoroti, 1996). In 1976, a chemical processing company loaded toxic wastes into Love Canal in New York, which made dogs sniffed to death and some suffered sores that never healed. There were several cases of loss of pregnancies, blood and liver problems (Botkin and Edward, 1982). Cadmium causes liver, kidney and loss of red blood cells problems. (Addison-Wesley, 1987). Lead (Pb) causes brain damage, induces convulsion and mental retardation in children (Ademoroti, 1996). These heavy metals are not easily passed out from the body. e.g., cadmium stays in the human body for decades. Selenium up to  $4\mu\text{g/g}$  in food is toxic and causes accumulation of fluid throughout the body and liver problems (Ademoroti, 1996).

The conventional methods of effluents and wastewater treatment has been in use but with some limitations, such as high cost of operations, environmental unfriendly, disposal problems due to large volumes of sludge and sometimes ineffective, inability to recover metals from waste especially from sludge. The conventional methods include: precipitation, coagulation, sedimentations or centrifugation, reduction, osmosis and reverse osmosis, membrane separation, evaporative recovery, ion exchange, solvent extraction, electrode dialysis and electrolysis (Chong et al., 2000; Yetis et al., 1998; Ademoroti, 1996). The use of ion-exchange to remove metals from wastewater has some limitations, such as, non-resistance to thermal and osmotic shock, interference in metals removal in the presence of Ca and Mg ions (Aderhold et al., 1996; Kuyucak, 1990). Ion-exchange is not always selective to allow effective recovery of metals present in industrial effluent (Kratochvil et al., 1997). Membrane method has some limitations, such as, limited flow rates, instability of membrane in the presence of salt and acid and bad smell by inorganic and organic species (Aderhold et al., 1996). Ion-exchange resins, electrolysis and membrane method are expensive and complex to practice. (Atkinson et al., 1998; Kapoor and Viraraghavan, 1995). Osmosis and reverse osmosis, dialysis, electrodialysis and evaporation are also expensive (Aderhold et al., 1996). Solvent extraction is limited to stream containing more than  $1\text{g/l}$  of the targeted metal (Kratochvil et al., 1997). These limitations have led to cost effective alternative biomethods, such as biosorption (Volesky, 1990), sorption onto purified biopolymers (Jang et al., 1995), adsorptive filtration using coated sands (Benjamin et al., 1996), and adsorption on magnetic iron oxides (Chen et al., 1991), etc. The use of biomaterials as alternative to the conventional methods is due to their ability to accumulate heavy metals and degrade organic compounds (Kumar et al., 1995), coupled with their abundance, environmental friendliness and cost effectiveness. Metal biosorption ability is attributed to the

following mechanisms at the cell walls of the biomass, such as, micro-precipitation, ion-exchange, adsorption, complexation, co-ordination and chelation (Volesky and Schiewer, 1999; Greene and Darnall; 1990). All these mechanisms do occur at same time, yet independent of each other in the overall metal uptake process (Asma et al., 2005). Several biomaterials that been used for sorption studies include living and non-living biomass.

Islam et al., (2007), used biomass of Jute stick powder (JSP), Jute leaf powder (JLP), Sugarcane powder (SP), Lily leaf powder (LLP), fish eyes powder (FEP), eggs shell powder (ESP), Dheki (pleris) vegetable powder (DVP), Fern (*Dryopteris ramosa*) plant powder (FPP), and water hyacinth root powder (WHRP) for removing arsenic from potable water independently. The adsorption capacity are 91.80%, 90.81%, 92.80%, 90.60%, 81.53%, 98.72% and 88.80% respectively. The part of the biomaterials used was washed with ordinary and distilled water. The result obtained fit into Langmuir and Freundlich adsorption isotherms respectively.

In the metal sorption study of Pb, Cu, and Cd ions using brewery biomass, Jae-young et al., (2005), observed that with increasing temperature the maximum sorption were, Pb:  $96.4\text{mg/g}$ , Cu:  $48.9\text{mg/g}$  and Cd:  $14.3\text{mg/g}$  at  $308\text{K}$ . The result fit into Langmuir adsorption isotherm. The biosorption was endothermic reaction.

Cd (II), Cu (II) and Zn (II) biosorption kinetics was studied using cassava (*manihot esculenzacranz*) peeled waste by Horsfall et al., (2005). The result revealed exothermic reaction. The rate determining step was physisorption and the adsorption process was described as a pseudo-second order model. The rates co-efficient ranges between  $1.39 \times 10^{-2}\text{min}^{-1}$  and  $5.94 \times 10^{-2}\text{min}^{-1}$  Cd (II),  $1.46 \times 10^{-3}\text{min}^{-1}$  and  $5.8 \times 10^{-3}\text{min}^{-1}$  Zn(II). The data showed fast and stable process. The monolayer sorption capacity using Langmuir isotherm ranges between,  $5.88\text{--}26.3\text{mg/g}$  Cd(II),  $33.3\text{--}90.9\text{ mg/g}$  Cu(II) and  $22.2$  to  $83.3\text{mg/g}$  Zn (II), respectively.

Nomanbhay and Palanisamy (2005), used chitosan coated oil palm shell charcoal to remove Cr(II) and Cr(VI) from industrial wastewater. The equilibrium data using Langmuir isotherm model gave the maximum capacity values per gram of Chitosan as  $154\text{mg/g}$  Cr.

The sorption of Cd, Pb and Ni from industrial waste water was studied by Mahvi et al., (2005), using tea waste ( $0.5$  and  $1.5\text{g}$ ). For single system, Pb ( $5\text{mg/l}$ ),  $94\text{--}100\%$  was removed from the water, Ni,  $85.7\%$ , and Cd,  $77.2\%$ . The mixed system of Pb, Cd, and Ni under same concentration, the uptake of Pb decreased by  $3.5\%$  and Ni decreased by  $13.2\%$  respectively.

Salano et al., (2005), used phormospsis Sp in the adsorption of  $870\mu\text{mol/g}$  Pb,  $390\mu\text{mol/g}$  Cu,  $230\mu\text{mol/g}$  Cd,  $150\mu\text{mol/g}$  Zn and  $110\mu\text{mol/g}$  of Ni ions at pH 4-6 for 2 hours. At barely 10 minutes about 70% of the overall adsorption process had already been completed. The biosorbent was treated with heat and alkali, which showed that the biosorbent as well as its nitrogen content suggested that, chitosan and glucan are

the main components. Based on information on Lewis base sites, the reaction was a complexation reaction.

Caladium bicolor (wild cocoyam) sorption of Pb and Cd was studied by Horsfall and Spiff (2004b), the uptake capacity of the metal ions per gram of biomass for Pb (II) 12.95mg/g and Cd (II) 10.76mg/g in a single metal system. For a mixed system Pb(II) was 7.81mg/g and Cd (II) was 2.50mg/g.

Both single and mixed system kinetics of the sorption mechanism was pseudo-second order model.

Cassava (Manihot esculenzacranz) biomass waste modified with mercaptoacetic acid (MMA) for sorption of Cu (II) and Cd (II) was studied by Horsfall et al., (2004). Data evaluation using Langmuir isotherm showed the uptake capacity to be 127.3mg/g Cu(II), and 119mg/g Cd (II) respectively. The rate coefficient was evaluated by kinetics to be Cu(II),  $2.04 \times 10^{-3} \text{ min}^{-1}$  and Cd (II),  $1.98 \times 10^{-3} \text{ min}^{-1}$  respectively.

Minamisawe et al., (2004), studied the adsorption behaviour of Cd(II) and Pb (II) at pH 2-6.7 on the biomaterials; chitosan, coffee, green tea, tea yuzu, aloe and onto the inorganic adsorbent, activated carbon and zeolite. Between pH 4-6.7 all the biomaterials took up metal ions with chitosan being more efficient.

Montes et al., (2003), studied the adsorption capacity of copper using natural and modified radiata bark pine. The observed maximum uptake capacity on natural bark within 90-120 minutes was between 20-50mg/g dried bark.

The activated bark uptake was between 45-60mg/g dried bark with little dependence on pH. Cu adsorption kinetics in acid media was pseudo-first order model. The rate constant increased with pH. Under same experimental condition, the activated bark was almost three times more efficient than the natural bark. The study revealed that, in some cases pretreatment boosts sorption.

The biosorption of Pb (II) from water using coconut fibres was studied by Ebhoaye and Asia (2003). The study showed that, the level of Pb (II) adsorbed increased per unit mass of the adsorbent with initial metal ions concentration. With temperature, Pb (II) adsorbed increased, this suggested chemical interaction was predominant in the process. When the pH was reduced from 6-2, the level of Pb (II) adsorbed reduced meaning that Pb (II) adsorbed can be desorbed at pH 2.0. The amount of Pb (II) adsorbed when a unit mass of the adsorbent was fully covered was 28.57mg, independent of temperature.

Abia et al., (2002), studied the biosorption of Cd (II), Cu(II) and Zn(II) using cassava (manihot esculenzacranz) biomass. The result showed that the uptake was  $0.2303 \text{ min}^{-1}$ , Cd(II),  $0.0051 \text{ min}^{-1}$  Cu(II), and  $0.004 \text{ min}^{-1}$  Zn(II) for 0.5M thiolation level. For 1.00M thiolation,  $0.109 \text{ min}^{-1}$  Cd(II),  $0.0069 \text{ min}^{-1}$  Cu(II) and  $0.0367 \text{ min}^{-1}$  Zn(II) respectively. The sorption rate was rapid, such that within 60 minutes of mixing 60-80% of the ions were adsorbed. Thiolation increased the level of bonding sites, hence increased biosorption.

Yan and Viraraghavan (2000), carried out a comparative study on the effects of pretreatment on the sorption of Pb (II),

Cd(II), Ni(II) and Zn(II) using mucor rouxii. Pretreatment using detergent, alkali-NaOH, salt-  $\text{Na}_2\text{CO}_3$  and acid salt  $\text{NaHCO}_3$  maintained the sorption capacity compared to live mucor rouxii. Pretreating M. rouxii using HCl,  $\text{H}_2\text{SO}_4$  and  $\text{C}_2\text{H}_4\text{O}_2$  showed reasonable reduction in the bioaccumulation capacity and with  $\text{CaCl}_2$  and NaCl reduced the bioaccumulation capacity slightly. Pretreatment methods revealed reduction in biomass compared to autoclaved biomass, but still effective.

Biomaterials employed in the above sorption experiments showed very encouraging, effective and efficient uptake of various metals from water, single or mixed metal solutions alike.

The researcher desires to determine the potential of Eichhornia Crassipes (water hyacinth) root powder, for the biosorption of Cu(II), Pb(II), Zn(II), Mn(III) and Cd(II) ions from a multi-metal aqueous solution under reaction conditions of metal ions concentration, pH, contact time and to determine the suitable adsorption isotherm model.

No work has been reported using E-crassipes root powder to remove five heavy metal ions simultaneously from aqueous solution.

## 2.0. EXPERIMENTAL

### 2.1. Sample Collection

The sample "Eichhornia Crassipes" was collected from the middle of Warri River by Mc-Ivar market in the morning. The roots were chopped-off from the stem, rinsed with treated water to eliminate debris and sand before bagging them in clean polyethene to the laboratory (Islam et al., 2007).

### 2.2. Sample Preparation and Activation

The water hyacinth roots were washed mildly with distilled water and detergent to eliminate colour, odour, debris, sand and oil, thereafter with plenty of distilled water until the water became clear (Allen Stewart, 1974). The roots were air dried for a week, thereafter placed in Griffin oven heater at  $180^\circ\text{C}$  for 2 hours to further dry them to ease grinding into powder. 850 $\mu\text{m}$  sieve was used, only particle that came out were used. The washing with detergent and oven heating exposes active sites and activate the biomass for sorption process.

### 2.3. Equipments and Materials

The apparatus and equipments used are: standard volumetric flasks, beakers, measuring cylinders, spatula, conical flasks, wash bottle, glass rod, graduated pipette, Hach pH meter-model HQ20 with automatic temperature meter, Lark electronic balance-model LP-502A, Milano 850 $\mu\text{m}$  sieve, Griffin oven heater with thermostat, GBC multi-lamp atomic absorption spectrophotometer-2008, model-GF 3000, and masking tape. The materials used are 0.1M  $\text{HNO}_3$  acid, 0.1M NaOH, distilled water, water hyacinth root powder, buffer solutions, Analytical grade  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{CuSO}_4$ ,  $\text{ZnSO}_4$ ,  $\text{MnPO}_4$  Salts and Whatmann no. 45 filter papers.

Batch study was done at room temperature (25°) and 1 atmosphere pressure. The results obtained were tested with Langmuir and Freundlich isotherms to know the suitable model.

#### 2.4. Effect of Metal Ions Concentration on Adsorption

The effect of metal ions concentration were studied by preparing 10mg/l of the five soluble heavy metal salts - Cu(II), Pb(II), Zn(II), Mn(III) and Cd(II) mixed solution and adjusted to pH 5.0 ± 0.02, by addition of acid or base.

The same procedure was used to prepare 20mg/l, 30mg/l, 40mg/l, 50mg/l, 60mg/l, 70mg/l, 80mg/l, 90mg/l and 100mg/l, respectively. After vigorous agitation, 100ml was taken from each multi-metal solution into ten separate labelled bottles. 5g of the adsorbent was put into each bottle and automatically agitated for an hour. The mixture was filtered separately into different 50ml labelled bottles for metal ions determination using AAS (Islam et al., 2007; Lagrega et al., 1994).

#### 2.5. Effect of Contact Time on Adsorption

The effect of contact time on metal ions adsorption by *E. crassipes* was studied. 10mg/l standard solution of the multi-metal solution was prepared. 100ml were taken into 9 labelled 50ml bottles and adjusted to pH 5.0 ± 0.02. 5g of the adsorbent was put into each bottle labelled, 5 minutes, 10 minutes, 15 minutes, 20 minutes, 25 minutes, 30 minutes, 40 minutes, 50 minutes, and 60 minutes, respectively. Each bottled mixture was automatically agitated for the set time, thereafter filtered into 50ml plastic bottle for AAS analysis of metal ions. (Islam et al., 2007; El-Chaghaby et al., 2008).

#### 2.6. Effect of pH on Adsorption

The effect of pH on adsorption was done by preparing 10mg/l of the five heavy metal solution together. 100ml was taken into eight separate bottles labelled pH 2.0±0.02, 3.0±0.02, 4.0±0.02, 5.0±0.02, 6.0±0.02, 7.0±0.02, 8.0±0.02 and 9.0±0.2 and their pH were adjusted to pH 2.0±0.02 to 9.0±0.02. 5g of the adsorbent was added to each solution bottle and agitated for one hour. Each mixture was filtered into 50ml labelled bottle and taken for AAS analysis (El-Chaghaby et al., 2008).

#### 2.7. Quality Assurance

The filtrates obtained from the batch study were analyzed several times and the AAS was calibrated at intervals to ensure accuracy.

#### 2.8 Evaluation of Biosorption Efficiency

##### 2.8.1 Computation of Amount of Heavy Metal Ions Removed

The concentration of Cu(II), Pb(II), Zn(II), Mn(III) and Cd(II) ions removed were computed by the mass balance equation expressed as:

$$q_e = \frac{V}{M} (C_o - C_e) \quad \text{--- (1)}$$

(Chug and Hashim, 2001).

Where:  $C_o$  = initial metal ion concentration (mg/l)

$C_e$  = Final or equilibrium concentration of metal ion (mg/l)

$V$  = Volume of initial metal ion concentration used (l)

$M$  = Mass of the bioadsorbent used (g)

$q_e$  = Metal concentration retained in the adsorbent (mg/g) at equilibrium.

The percentage removal of metal ion from solution was computed by the equation:

$$\%R = \frac{(C_o - C_e)}{C_o} \times 100 \quad \text{--- (2)}$$

(El-Chaghaby et al., 2008)

"OR"

$$\%R = \left( \frac{C_R}{C_o} \right) \times 100 \quad \text{--- (3)}$$

Where:  $C_R = C_o - C_e$  = amount of metal removed at equilibrium (mg/l)

$C_o$  = initial metal ion concentration (mg/l)

$C_e$  = equilibrium concentration of metal ion (mg/l)

$\%R$  = Percent removal of metal ion.

The Langmuir and Freundlich adsorption isotherms were used to determine the sorption capacity and intensity respectively.

### 3.0. RESULTS AND DISCUSSION

The biosorption study of *E. Crassipes* in removing Cu(II), Pb(II), Zn(II), Mn(III) and Cd(II) ions from a multi-metal aqueous system was effective, good and favourable with respect to initial metal ions concentration, contact time and pH on the adsorption process respectively.

#### 3.1. EFFECT OF CONCENTRATION ON ADSORPTION

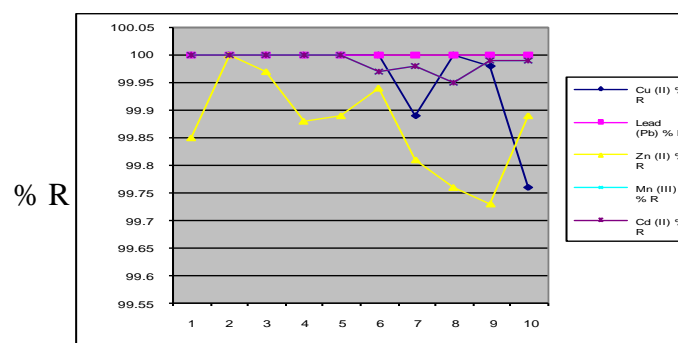


Fig. 3.1: Effect of Initial metal ion conc.(mg/l)  $C_o$  on the adsorption of the five heavy metal

**Table 3.1: Effect of Metal Ions Concentration on Adsorption**

Amount of Metal Adsorbed at Equilibrium ( $q_e$ ) (mg/g)

Co(mg/l)	Cu	Pb	Zn	Mn	Cd
10	0.200	0.200	0.199	0.200	0.200
20	0.400	0.400	0.400	0.400	0.400
30	0.600	0.600	0.599	0.600	0.600
40	0.800	0.800	0.799	0.800	0.800
50	1.000	1.000	0.998	1.000	1.000
60	1.200	1.200	1.199	1.199	1.199
70	1.390	1.400	1.397	1.399	1.399
80	1.600	1.600	1.596	1.599	1.598
90	1.790	1.800	1.795	1.799	1.800
100	1.990	2.000	1.997	1.999	2.000

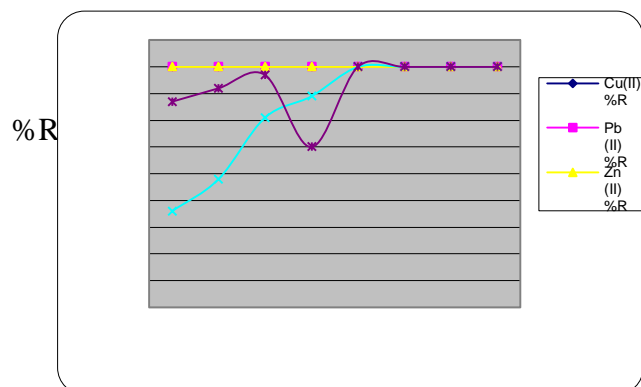
At 25°C, biomass 5g, Time 1hour, volume 100ml

Figure 3.1, shows the percentage removal of Cu(II), Pb(II), Zn(II), Mn(III) and Cd(II) ions from the multi-metal aqueous system onto the *E. Crassipes* biomass at an initial metal ion concentration of: 10mg/l, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mg/l at pH 5. The minimum percentage removal for Cu(II) was 99.76%; Pb(II), 100%; Zn (II), 99.73%; Mn(III), 99.99% and 99.86% for Cd, respectively.

Table 3.1, shows the adsorption capacity of the biomass, which increased from 0.200-1.990 mg/g for Cu(II); 0.200-2.000mg/g for Pb(II); 0.199-1.997 mg/g for Zn(II); 0.200-1.999 mg/g for Mn(III) and 0.200-2.000 mg/g for Cd(II) ions respectively.

The efficiency slightly decreased as the initial metal ions concentration increased, except for Pb(II) ions adsorption which did not decrease, indicating a stronger bond and higher affinity for Pb(II) ions than for others. According to Reimann (2007); Zheng *et al.* 2004, Pb is the most strongly bound element in typical organic material. The slight decrease in the efficiency of the biomass showed that the binding sites were near saturation due to increase in the initial metal ions concentrations. The heavy metal ions were adsorbed in the order of: Pb>Cd>Mn>Cu>Zn. The presence of toxic Pb (II) ions did not inhibit the high level adsorption of other heavy metals. This trend was reported by Saeed *et al.*, 2005; Adesola *et al.*, 2008; Ronbanchob *et al.*, 2004.

### 3.2. EFFECT OF pH ON ADSORPTION



**Fig 3.2:** Effect of pH on the adsorption of the five heavy metal ions by the bioadsorbent.

#### Effect of pH on Metal ions Adsorption

**Table 3.2: Amount of Metal ions Adsorption at Equilibrium ( $q_e$ ) (mg/g)**

pH	Cu	Pb	Zn	Mn	Cd
2	0.200	0.200	0.200	0.198	0.199
3	0.200	0.200	0.200	0.199	0.199
4	0.200	0.200	0.200	0.199	0.199
5	0.200	0.200	0.200	0.199	0.199
6	0.200	0.200	0.200	0.200	0.200
7	0.200	0.200	0.200	0.200	0.200
8	0.200	0.200	0.200	0.200	0.200
9	0.200	0.200	0.200	0.200	0.200

At 25°C, conc. (10mg/l), volume 100ml, adsorbent 5g, time 1hour.

The effect of pH on the adsorption of Cu(II), Pb(II), Zn(II), Mn(III) and Cd(II) ions was done using 10mg/l of the metal salts, 5g of the adsorbent and pH range of: 2,3,4,5,6,7,8 and 9, to determine the best pH for optimal adsorption of the metal ions.

Fig. 3.2 represents the pattern of adsorption of the metal ions by *E. Crassipes* biomass. The percentage removal of metal ions was very high, with Cu (II), Pb (II) and Zn (II) ions being 100%.

The removal of Mn (III) and Cd (II) ions at pH 2 was 99.46% and 99.87%, they increased to 100% from pH 6-9 respectively. Thus, Mn (III) and Cd (II) ions were best removed at pH 6-7 by the bioadsorbent. This trend of increasing pH with increasing sorption of the metal ions indicated that, the biomass did not reach equilibrium and that there are abundant binding sites for more metal ions, perhaps due to small concentration of metal ions and large amount of adsorbent used. The adsorbent efficiency was not limited by pH, but rather enhanced the process. This fast and stable adsorption showed that adsorption took place at the cell

walls of the adsorbent, and ion-exchange was responsible coupled with available sites. Jae-young, et al., 2002; Beveridge and Murray, 1980, experienced similar pattern of increasing adsorption with increasing pH, the reason was not clear, but was attributed to the different binding sites with different ionizing patterns in adsorbing each metal ions. Therefore, pH variations are not a limiting factor for *E. Crassipes* to adsorb these metal ions.

### 3.3. EFFECT OF CONTACT TIME ON ADSORPTION

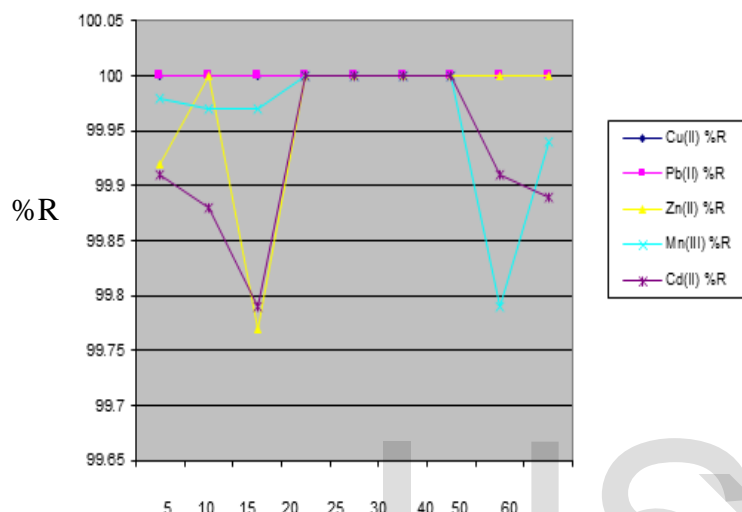


Fig. 3.3: Effect of contact time on the adsorption of the five heavy ions by the adsorbents

**Table 3.3: Effect of Contact time on metal ions adsorption.**

**Amount of Metal ions Adsorption at Equilibrium ( $q_e$ )(mg/g)**

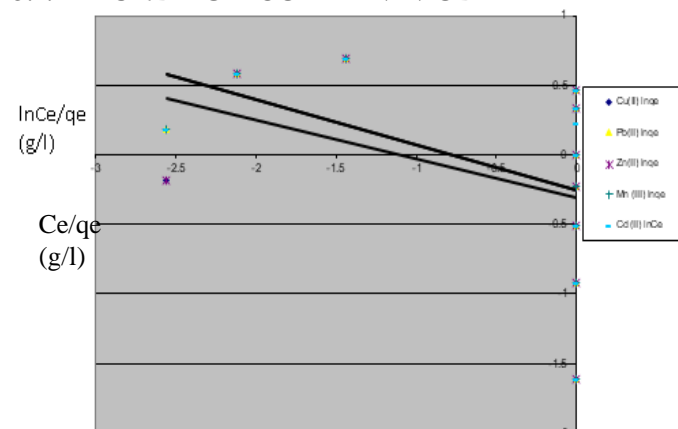
Time(min)	Cu	Pb	Zn	Mn	Cd
5	0.200	0.200	0.199	0.199	0.199
10	0.200	0.200	0.200	0.199	0.199
15	0.200	0.200	0.199	0.199	0.199
20	0.200	0.200	0.200	0.200	0.200
25	0.200	0.200	0.200	0.200	0.200
30	0.200	0.200	0.200	0.200	0.200
40	0.200	0.200	0.200	0.200	0.200
50	0.200	0.200	0.200	0.199	0.199
60	0.200	0.200	0.200	0.199	0.199

At 25°C, volume 100ml, pH 5.0, conc. (10mg/l), adsorbent 5g. The results revealed that Cu (II) and Pb (II) ions were adsorbed 100% within 5minutes and were stable for 60min. Zn (II) ions were adsorbed 100% within 10min., fell to 99.77% but rose to 100% at 20min, and became stable till the end. This fall and rise of Zn (II) ions suggested competitive adsorption process among the metal ions in solution. Mn (III) and Cd (II) ions took 20min to reach equilibrium from 99.98%

and 99.91% at 5min, to 100% at 20min. Both were stable till 40min but fell to 99.94% and 99.89% at 60min. The speed with which Cu(II) and Pb(II) ions were removed 100% within 5min reflected a pseudo-first order process. In all, three heavy metal ions were adsorbed from solution 100%, except for Mn (III) and Cd (II) ions, meaning that this adsorbent within this experimental conditions absorb these metal ions within 5-20min. The very fast sorption process exhibited by *E. Crassipes* indicated a physico-chemical process at the cell wall surface, and ion-exchange was dominant. The adsorption of Mn(III) and Cd(II) ions from 100% to 99.94 and 99.89% therefore indicated a physisorption process. For Cu(II), Pb(II) and Zn(II) ions chemisorption process prevailed. Thus, the study revealed physisorption and chemisorption processes with chemisorption being dominant. The speed with which Cu(II) and Pb(II) ions were adsorbed indicated that the adsorbent sites for adsorbing Cu(II), Pb(II) and Zn(II) ions were abundant and unsaturated, suggesting that all metal ions, do not bind to same sites, further showing that the adsorbent has specific sites for metal ions with similar affinity for these sites, which leads to competition. This is even more true because within same time frame Mn(III) and Cd(II) ions attained equilibrium meaning that sites for Mn(III) and Cd(II) adsorption were saturated, hence they came to equilibrium. Ronbanchob, et al., 2008, observed similar behaviours of heavy metal ions adsorption from mixed system/ solution. According to Beveridge and Murray, 1976, these differential metal bindings of cell walls might be due to the differences in binding strength or to the binding selectivity of cell wall components as known for *B. Subtilus*. Rho, (1997), attributed the high phosphorus content in the cell wall of *S. viridochromogenes* perhaps to be responsible for its superior metal adsorbing capacity. From the foregoing, this may be responsible partly, for the very high percentage adsorption of Cu(II), Pb(II), Zn(II), Mn(III) and Cd(II) ions coupled with large adsorbent mass of 5g.

Effluents containing these heavy metal ions can be highly and effectively removed from aqueous solution with the appropriate adsorbent mass and conditions.

### 3.4. FREUNDLICH ISOTHERM MODEL



**Fig.3.4.** Freundlich adsorption equilibrium isotherm for the five heavy metals ions on to the adsorbent



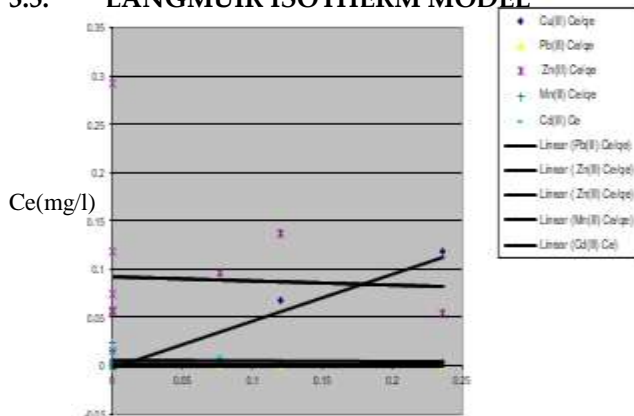
**Table 3 4. Parameters of Freundlich Isotherm for the five metal ions**

Heavy metals	$K_f$	$R^2$	$1/n$
Cu(II)	0.736	0.1524	0.2771
Pb (II)	0.000	0.0000	0.0000
Zn(II)	1.393	0.1241	0.1841
Mn(III)	0.527	0.6324	0.2531
Cd(II)	1.242	0.1256	0.1197

The essence of equilibrium sorption studies is to describe the surface properties and affinity for sorbates by the sorbent through some constants (El-Chaghaby et al., 2004).

The Freundlich isotherm was used to describe the sorption capacity ( $K_f$ ) and sorption intensity ( $1/n$ ) of the adsorption process. Fig.3.4 represents the graph obtained on application of the isotherm data to Freundlich equation. The isotherm described the adsorption study relatively well based on the  $K_f$ ,  $R^2$  and  $1/n$  values. However, in-terms of adsorption intensity values ( $1/n$ ), the sorbent had more affinity for Pb(II) ions than Cu(II), Mn(III), Zn(II) and Cd(II) respectively. Comparing the adsorption capacity  $y$  ( $K_f$ ) values, Pb(II) ions was 100%, hence the  $K_f$  values is 0.0000, signifying that the bioadsorbent had more affinity for Pb(II) ions. The coefficient of determination values ( $R^2$ ) from regression plot are shown in fig. 3.4, Pb(II) ions were adsorbed below ppm level. According to Jamode et al., 2004, if  $1/n < 1$ , bond energies increases with surface density, if  $1/n > 1$ , bond energies decrease with surface density, and if  $1/n=1$ , all surface sites are equivalent. In table 3.4,  $1/n$  values for all metal ions were less than (1) unity, meaning that during the sorption process bond energies increased with surface density, resulting to more sorbates being adsorbed from solution.

### 3.5. LANGMUIR ISOTHERM MODEL



**Fig.3.5.** Langmuir adsorption equilibrium isotherm for the five heavy metals ions on to the adsorbent

**Table 3.5. Parameters of Langmuir Isotherm for the five heavy metal ions**

Metal ions	R	$R^2$	$q_m$ (mg/g)	$K_L$ (L/g)
Cu(II)	0.000448	0.9262	2.040	222.800
Pb(II)	1.000	0.000	10.000	0.000
Zn(II)	0.0251	0.0716	3.780	3.890
Mn(III)	0.999	0.9737	1.550	$7.75 \times 10^{-6}$
Cd(II)	0.999	0.9847	1.380	$5.53 \times 10^{-5}$

To obtain the maximum sorption capacity by the sorbent, the experimental data were correlated with Langmuir isotherm. Fig. 3.5 presents the graph of Langmuir isotherm while table 3.5 presents the essential parameters:  $R^2$ ,  $q_m$  (mg/g),  $K_L$  (L/g) and  $R$  were obtained from the graph respectively. The coefficient of determination " $R^2$ " values shows that Langmuir isotherm model gave a good description of the sorption process. The maximum adsorption capacity ( $q_m$ ) values shows that the bioadsorbent (E-Crassipes) had higher capacity for Pb (II) than other ions. The energy of the sorption process ( $K_L$ ) for Cu(II) was highest and Pb(II) was least. According to Ganjidoust et al., 1992, adsorption process is favourable when the isotherm data is between zero and one (0 and 1). Therefore, the E-Crassipes adsorption of the five heavy metal ions was favourable because the favourability factor or separation factor " $R$ " values in table 4.5 are between 0 and 1.

## 4.0 CONCLUSION

The batch assessment of Eichhornia Crassipes activated root-powder as a potential bio-adsorbent for the sorption of: Cu(II), Pb(II), Zn(II), Mn(III) and Cd(II) ions from a multi-metal aqueous solution was studied and the better isotherm model determined.

In terms of the effect of initial metal ions concentration on the adsorption process, the adsorbent adsorbed the five heavy metal ions from the mixed solution in high percentage, in the average order of Pb(II), 100% > Mn(III), 99.95% > Cd(II), 99.86% > Cu(II), 99.76% > Zn(II), 99.73%, respectively. The amount of metal ions adsorbed ( $q_e$  mg/g) increased with increase in initial metal ions concentration as shown in table 1. The percentage of adsorption decreased with increase initial metal ions concentration.

The effect of contact time on the adsorption process revealed that the process was very fast, such that, within 5 min. Cu(II) and Pb(II) were adsorbed 100% from solution while Zn(II),

Mn(III) and Cd(II) took 20 min. for 100% adsorption. Generally, within 20 min. all five metal ions were adsorbed 100%.

The effect of pH variations on the adsorption process revealed that, Cu(II), Pb(II) and Zn(II) ions adsorption were pH independent, because 100% was achieved from pH 2-9. Mn(III) and Cd(II) ions were pH dependent with maximum adsorption from pH 6-9, respectively. The speed of the adsorption process suggested ion-exchange process was dominant, and occurred at the cell wall surface of the biomass.

The Langmuir and Freundlich equilibrium expression fitted the isotherm data, but Langmuir model gave a better description of the sorption process. Considering the biomass adsorption favourability, "R" value fell between 0 and 1, meaning that the adsorbent is good and the process favourable.

E. Crassipes (Water hyacinth) activated root powder is effective for adsorbing these heavy metal ions from a multi-metal aqueous solution.

## 5.0. RECOMMENDATIONS

1. Government, oil companies, corporate organizations, entrepreneurs etc., should invest in the processing of water hyacinth for heavy metal ions removal from waste-water because it is effective.

2. This will open-up the inland water ways, drastically reduced marine accident, increase marine movement and eliminate disease vectors.

3. The process is cheap, environment friendly and biodegradable.

## REFERENCES

Abia, A. A., Horsfall, M. Jnr. and Didi, O. (2002). Studies on the use of Agricultural By-product for the Removal of Trace Metals from Aqueous Solutions. *Journal of Applied Science and Environmental Management*, 6(2), 89-95.

Addison-Wesley (1987). Chemistry. USA: Addison-Wesley Pub. Co. Inc.

Ademoroti, C.M.A. (1996). Environmental Chemistry and Toxicology. Ibadan: Foludax Press Ltd.

Aderhold, D., Williams, C.J and Edyvean, R.G.J. (1996). The Removal of Heavy Metal ions by Seaweeds and Their Derivatives. *Bioresource Technol.*, 58, 1-6.

Adesola, N.A.B., Oyesiku, O.O., Babalola, J.O. and Olatunji J.O. (2008). Isothermal and Thermodynamic Studies of the Biosorption of Zinc(II) Ions by Calymperes Erosus. *Journal of Applied Sciences Research*, 4(6), 716-721.

Allen Stewart (1974). Chemical Analysis of Ecological Materials (2nd ed.), London: Black well Scientific Publication.

Asma, S., Igbal, M. and Waheed Akhtar (2005). Removal and Recovery of Lead (II) from single and Multimetal (Cd, Cu, Ni, Zn) Solutions by Crop Milling Waste, (Black gram husk). *Journal of Hazards Materials*, 117(1), 65-73.

Atkinson, B. W., Bux, F. and Kasan, H. C. (1998). Consideration for Application of Biosorption Technology to Remediate Metal-Contaminated Industrial Effluents. *Water S. A.*, 24, 129-135.

Benjamin, M. M. Sletten, R. S., Bailey, R. P. and Bennet, T. (1996). Sorption and Filtration of Metals Using Iron Oxide-Coated Sand. *Water Res.*, 30, 269.

Beveridge, T. J. and Murray, R.G.E. (1976). Uptake and Retention of Metals by Cell Walls of Bacillus Subtilis. *Journal Bacteriol.*, 127, 1502-1518.

Beveridge, T. J. and Murry, R.G.E. (1980). Sites of Metal Deposition in the Cell Wall of Bacillus Subtilis. *Journal Bacteriol.*, 141, 876-887.

Chen, W.Y., Anderson, P.R. and Hoisen, T.M. (1991). Recovery and Recycle of Metals from Waste water with Inorganic



- based Adsorption Process. Res. J. Water Poll. Control Fed., 63, 958-968.
- Chong, A. M. Y., Wong, Y. S. and Tam, N.F.Y. (2000). Performance of Different Microalgal Species in Removing Nickel and Zinc from Industrial Wastewater. *Chemosphere*, 41, 251-257.
- Chug, K. H. and Hashim, M. A. (2001). Desorption of Copper from Polyvinyl Alcohol Immobilized Sea Weed Biomass. *Acta Biotechnol.*, 24 (24), 295-306.
- David, G. L. and Miller, T. G. (1991). *Chemistry: A Contemporary Approach* (3<sup>rd</sup> ed.). USA: Wadworth Pub. Co. Inc.
- Ebhoaye, J.E. and Asia, I. O. (2003). Lead(II) Ions Binding Capacity of Coconut Fibres. *Advances in Natural and Applied Sciences. Research*, 1(II)20.
- Edward, A.K. and Botkin, D.B. (1982). *Environmental Studies*. Ohio: Bell and Howell Co.
- El-Chaghaby, G. A, Abdel – Ghani, N.T. and El-Nashar, R.M. (2008). Removal of Cr(III) and Pb(II) from solution by Adsorption onto Casuarina Glauca Tree Leaves. *EJEAFChe.*, 7(7), 3126-3133.
- Ganjidoust, H. Deyhool, F., Samadian, M. and Chen, H.Y.(ED). (1992). *Proceedings of the International Conference on Environmental Protection and Control Technology*, Kulalampur, Malaysia. 3, pp.903- 912.
- Greene, B., Darnall, D. W. (1990). Microbial Oxygenic Photoautotrophs (Cyanobacteria and Algae) for Metal Ion Binding. In: *Microbial Metal Recovery*. Ehlich, H.L. and Brierley, C. L. (eds.) Pp. 227-302, USA; McGraw-Hill Book Co.
- Holum, J.R.(1986). *Fundamental of General Organic and Biological Chemistry*. USA: John Wiley and Sons. Inc
- Horsfall, M. Jnr and Spiff, A. I. (2004b). Kinetic Study of Divalent Metal Ion Sorption on Caladium Bicolor (Wild Cocoyam) Biomass surface. *Journal of Corrosion Science and Technology*, 2,12-18.
- Islam, M.J., Hossain, M.R., Yousuf, A. and Subham, M., A. (2007). Removal of Arsenic from Drinking Water using Bioadsorbents. *Pro. Pakistan Acad. Scie.*, 44, (3), 157-164.
- Jae-young and Jae-Heon Kim (2002). Heavy Metal Biosorption and its Significance to Metal Tolerance of Streptomycetes. *The Journal of Microbiology*, 51-54.
- Jae-young and Jae-Heon Kim (2005). Heavy Metal Biosorption and its Significance to Metal Tolerance of Streptomycetes. *The Journal of Microbiology*, 51-54.
- Jamode, A. V., Sapkal, V.S. and Jamode, V. S. (2004). Defluoridation of Water using Inexpensive Adsorbents. *J. Indian Inst. Sci.*, 84 163-171.
- Jang, I. K., Nguyen, D. and Geesey, G. G. (1995). Effect of pH on the Absorption of Cu(II) by Alginate gel. *Water Res.*, 29, 315-321.
- Kapoor, A., and Viraraghavan, T. (1997). Heavy Metal Biosorption sites in *Aspergillus niger*. *Bioresource Technol.*, 61, 221-227.
- Kratochvil, D., Volesky, B. and Demopoulos, G. (1997). Optimizing Cu Removal/Recovery in a Biosorption Column. *Water Res.*, 31, 2327-2339.
- Kuyucak, K. N. (1990). Feasibility of Biosorbents Applications. In: *Biosorption of Heavy Metals*. Volesky, B. (ed), Pp. 371-378. USA: McGraw Hill Book Co.
- KUMAR, P.B.A.N.; MOTTO, H. and RASKIN, I. 1995b Rhizofiltration: The Use of Plants to Remove Heavy Metals from Aqueous Streams. *Environmental Science and Technology*, 29, (5), 1239-1245.
- Lagrega, M. D., Buchingham, P.L. and Evans, J.C. (1994). *Hazardous Waste Management*. USA; McGraw Hill Book Co.
- Mahvi, A. H., Naghipour, D., Vaezi, F. and Nazmara, S. (2005). Tea Waste as an Adsorbent for Heavy Metal Removal from Industrial Waste waters. *American Journal of Applied Sciences*, 2(1), 372-375.
- Matheickal, J.T. and Yu, Q. (1996). Biosorption of Lead from Aqueous Solutions by Marine Algae. (*Ecklonia radiata*). *Water Sci. Technol.*, 34,1-7.
- Minamisawa, M., Minamisawa, H., Yoshida, S. and Takai, N. (2004). Adsorption Behaviour of Biomaterials onto Chitosan, Coffee, Green Tea, Tea Yuzu, Aloe and Japanese Coarse Tea. *J. Agric. Foodchem.* 52 (18), 5606-5611.
- Montes, S., Valero, E.O., Morales, L., Vilches, A. and Schmidts, R. (2003). Adsorption Capacity of Copper of Natural and Modified Radiata Back Pine. *Journal of the Chilean Chemical Society*, 48 (4),1.
- Normanbhay, S.M. and Palanisamy, K. (2005). Removal of Heavy Metals from Industrial Waste water using Chitosan

- Coated oil-palm- shell-charcoal. *Electronic Journal of Biotechnology*, 8(1), 1-15.
- Reimann, C., Arnoldussen, A., Englmaier, P., Filzmoser, P., Finne, T. E., Garrett, R. G., Koller, F., and Nordgulen, Ø. (2007). "Element concentrations and variations along a 120 km long transect in south Norway-anthropogenic vs. geogenic vs. biogenic element sources and cycles," *Appl. Geochem.* 22(4), 851-871.
- Rho, J.Y. (1997). Taxonomy of Heavy Metal. Resistant streptomycetes Isolated from Old Mines and Characterization of the Metal Binding Protein. Ph.D. Thesis, Dan-Kook University, Korea.
- Ronbanchod, A., Taha, F.M., Suraphong, W. and Prasert, P. (2004). Biosorption of Binary Mixtures of Heavy Metals by Green Macro Alga, *Caulerpa Lentillifera*. *Songklanakarin J. Sci. Technol.*, 24, (1), 199-207.
- Saeed, A. Akhtar, M.W., and Iqbal, M. (2005b). Affinity Relationship of Heavy Metal Biosorption by the Husk of *Cicer arietinum* (Chickpea/black gram) with their atomic weights and structural Features. *Fresenius Environ. Bull.*, 14, 219-223.
- Salano, F., Maurizio, C., Santa, O.C. and Ramirez, S. (2005). Metal Ion Adsorption by *Phomopsis* sp. Biomaterial in Laboratory Experiments and Real Wastewater Treatments. *Water Research*. 39(11), 2273-2280.
- Volesky, B. (1990). Removal and Recovery of Heavy Metals by Biosorption. In: *Biosorption of Heavy Metals*. Volesky, B. (ed), Pp. 7-43. USA: CRC Press, Boca Raton.
- Volesky, B. and Schiewer, S. (1999). Biosorption. Metals. In: *Encyclopedia of Bioprocess Engineering*. Flickinger, M.C., Drew, S.W. (ed), Pp. 433-453. USA: John Wiley and sons publishers.
- Yan, G. and Viraraghavan, T. (2000). Effect of Pretreatment on the Biosorption of Heavy Metals on *Mucor rouxii*. *Water S.A.* 26(1), 119-123.
- Yetis, U., Ozeengiz, G., Dlick, F. B., Ergen, N., Erbay, A. and Dolek, A. (1998). Heavy Metals Biosorption by White Rot Fungi. *Water Sci. Technol.*, 38, 323-330.
- Zheng, G. D., Chen, T. B., Gao, D., and Luo, W. (2004). "Dynamic of lead speciation in sewage sludge composting," *Water Sci. Technol.* 50(9), 75-82.