



## Studies on Adsorbent Dosage, Particle Sizes and Ph Constraints on Biosorption of Pb(II) and Cd(II) Ions from Aqueous Solution Using Modified and Unmodified Crasstrotrea Gasar (Bivalve) Biomass

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### ABSTRACT

*Biosorption of Pb(II) and Cd(II) ions from aqueous solution did not improve by chemical modification of Crasstrotrea Gasar biomass with oxalic acid and ethanol. Unmodified Crasstrotrea Gasar biomass was proved to be very effective adsorbent for the removal of Pb (II) and Cd(II) ions from aqueous solution. As the particle sizes increases from 106-500 $\mu$ m, the percentage removed increases. The particle size of 500 $\mu$ m showed the highest removal. Also the percentage metal ions sorbed increases, as the dosage of the adsorbent increases from 0.2g to 1.0g and further increase of the adsorbent did not provide more increment in the percentage removal of the metal ions. The present study was found to be highly pH dependent process. The percentage removal of Pb(II) and Cd(II) ions was at maximal at pH 10. Since the Crasstrotrea Gasar biomass is cheap, abundantly available and environment friendly, so it can be used for metal ion removal from aqueous solution using a simple and cost effective treatment procedure.*

**KEY WORDS:** Biosorption, heavy metals, agricultural by-product

### INTRODUCTION

The concentration levels of heavy metals in the environment are continually changing due to man's activities. These have generated a lot of interest in pollution studies. Major natural sources of these metals are rock-weathering, releases from terrestrial and submarine sediments. Heavy metals are often found in crude oils in small quantities are removed during the refining process [10].

Heavy toxic metals entered into the environment through waste water from metal plating industries and industries of Pb, Cd – Ni batteries, phosphate fertilizer, mining, pigments electroplating, Corrosion, and other industrial waste [4]. The discharge of heavy metals into the environment has become a matter of concern because of their hazardous nature. Heavy metals are toxic and pose a threat to man and the environment [37].

Adsorption has now been recognized as an effective and economic method for the removal of pollutants from the environment [33,26]. Adsorption is operative in most natural, physical, biological and chemical system, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification [9]. Similar to surface tension, adsorption is a consequence of surface energy [32, 29].

Many adsorbents, which include, pillared clay [34]; Cassava waste [3], Caladium bicolor [16,17], Maize cob and husk [18] have been reported.

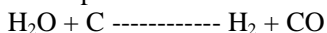
In this present study, Pb(II) and Cd(II) ions removal from aqueous solution using modified and unmodified Crasstrotrea Gasar biomass were examined. The constraints of pH, particle sizes and dosage of the adsorbent were also studied.

### MATERIALS AND METHODS

#### Collection and Preparation of Samples

The marine animal shells was collected from Okirika village of Rivers state of Nigeria and was washed thoroughly, clean of adhering dirt, rinsed thoroughly with de-ionized water and dried in the oven at 105°C for two days. The process helped to remove moisture present in the material, which was different from the chemisorbed water normally, released during carbonization reactions of

elevated temperature. Higher temperature of 150 °C was used to ensure complete dehydration. The purpose of dehydration was to effect de-sorption of physically absorbed water which may catalyze the decomposition of the char carbon thereby producing a very low carbon.



After oven drying, the sample was macerated into powdered form. The powdered form of the sample obtained was first sieved through a 1000 µm mesh and then through 500 µm, 250 µm, and 106-µm meshes.

#### **Chemical Activation of the Adsorbent**

The sieved sample was soaked in 0.3 M HNO<sub>3</sub> for 24 hours at room temperature. The adsorbents was then filtered through What man no. 41 filter paper and rinsed thoroughly with de-ionized water to maintain a pH of 7.4. The rinsed adsorbent was kept in an oven at 100°C for 12 hours for the moisture and finally stored in a tight plastic container.

The treatment of the adsorbent with 0.3 M HNO<sub>3</sub> aids to oxidize the adhering organic material, removal of any debris or soluble bio-molecules that might interact with the metal ions during the sorption. This process is called chemical activation.

#### **Chemical Modification of the Adsorbent.**

The oven dried chemical activated sample was weighed and divided into two parts. 200g of first part was left untreated was labeled the unmodified sea animal shell A (USASA) where A is shell of *Crasstrotrea Gasar* (*Bivalve*). 400g of second part was treated with 5 dm<sup>3</sup> of 3 M Oxalic acid solution for 24 hours at 28° C in a well ventilated place according to the method<sup>30</sup>. The biosorbent was then esterified [23,11] by suspending the adsorbent in 1.6 L of ethanol and 240 MI of concentrated hydrochloric acid. The mixture was shaken for 5 hours at 150 rpm, filtered and the residue was washed thoroughly with distilled water to maintain pH of 6.9 and finally oven dried at 100° C, stored and was labeled modified sea animal shell A (MSASA). Surface functional group can be introduced via chemical modification [30, 23, 11].

All reagents used were analytical grades, purchased and used without further purification.

#### **Effect of Particles Size of the Adsorbents.**

Initial concentration of 4 Mg/L of the metal ions (Pb<sup>2+</sup> and Cd<sup>2+</sup> ) solution were prepared. 50 MI of each these metal ions solution were mixed and put in a conical flask containing 1 g of each of the 850 µm, 500 µm, 250 µm, and 160 µm particles sizes of modified and unmodified adsorbent. They were corked and left to stand for 10 minutes in a rotary shaker at a constant speed of 150 rpm, temperature of 29° C and optimum pH of 7.4. At the end of the time, the mixtures were filtered. The various metal ions content of the filtrates were determined by an air acetylene flame atomic absorption spectrophotometer (UNICAM SOLAAR 32).

#### **Effect of pH**

The pH of 50 MI of metal ions solutions with initial concentration 4 Mg/ L were adjusted to values 2, 4, 7, 10 and 12 by adding 0.1 M HCl or 0.1 M NaOH solutions. Then 1 g of each of the adsorbent (Both modified and unmodified) with particle size 500 µm was added and agitated in a shaker for 60 minutes at 29°C. Then, the suspensions were filtered and the metal ions content of the filtrates were determined using an air acetylene atomic absorption spectrophotometer (UNICAM SOLAAR 32).

#### **Effect of Adsorbent Dosage**

Initial concentration of 4 Mg/L of the two metal ions (Pb<sup>2+</sup> and Cd<sup>2+</sup>) solution was prepared. 50 MI of each these metal ions solution were mixed and put in a conical flask containing 0.2 g, 0.4 g, 0.6 g, 0.8 g, 1.0 g, and 1.2 g respectively of the 500 µm, particles size of modified and unmodified adsorbent. The mixtures was corked and left to stand for 10 minutes in a rotary shaker at a constant speed of 150 rpm at a temperature of 29° C and optimum pH of 7.4. At the end of the time, the mixtures filtered. The various metal ions content of the filtrates were determined by an air acetylene flame atomic absorption spectrophotometer (UNICAM SOLAAR 32).

## **RESULTS AND DISCUSSION**

The experimental results for the adsorption of Pb(II) and Cd(II) ions on the unmodified and modified adsorbent with different particle sizes were plotted and reported above. Figure 1 show the plot of the percentage of the metal ions removed against the particle sizes of the adsorbent. From the plots, it was observed that as the particle size increases from 106 - 500µm, the percentage removed increases and went down at particle size 850 µm. Although, one would expect that the smaller particle size should

give a greater percentage removal because of the surface area, but as the particle size increased, the number of micro pores also increases.

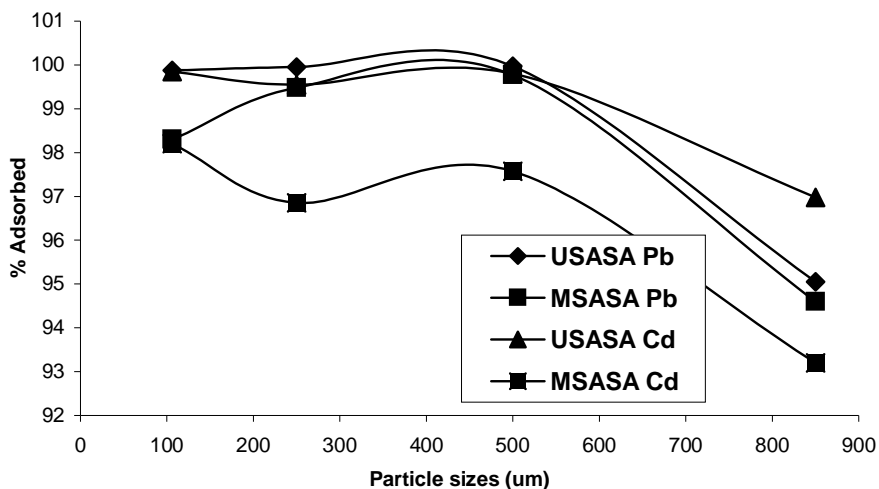


Figure 1: Effect of Particle Sizes of the Adsorbent for the Removal of Pb(II) and Cd(II) Ions from Aqueous Solution

The increase in micro pores increases the number of the accessible sites, hence increases the percentage adsorbed. This is similar to the results of [12], reported that there was no influence of bio-sorbent size on adsorption capacity. They reasoned that the two particle sizes of adsorbent they tested were actually of the same thickness (dimension which determines the diffusion distance). This is so because size grading of ground biomass particle by standard sieves works on the length and width dimensions.[24] ,showed that larger biomass particles of *Sargassum fluitans* and *Ascophyllum nodosum*, had higher metal uptake than smaller particles. [19], showed that as the particle size increase from 0.15 mm to 0.85 mm, the amount adsorbed also increased, but from particle size 0.85 mm to 1.00 mm, the amount adsorbed decreased.

From the results of this study, the percentages of metal ion removed on unmodified sorbent were higher than modified sorbent. This means that modification of the adsorbent did not improve the adsorptive capacity of the adsorbent used. In this study, ethanol in the presence of concentrated HCl was used for the esterification of the carboxylic acids present on the cell wall. Thus, the introduction of ester groups such as  $\text{RCOOCH}_2\text{CH}_3$  alters the surface characteristics of the adsorbents; hence affect the percentage of metal ion removed [27, 23].

Metal uptake by bio-sorption is reported to occur through interactions with functional groups native to the biomass cell wall [15]. It is metabolism-independent and proceeds rapidly within some minutes by any one or combination of the following metal binding mechanisms; coordination, complexation, ion exchange, physical adsorption (e.g. electrostatic) or inorganic micro-precipitation. The mechanism of metal bio-sorption is complicated, the status of biomass (living and non-living), types of biomaterials, properties of metal-solution chemistry, ambient/environmental condition such as pH, will all influence the mechanism of metal bio-sorption [35].

The decrease in the percentage adsorbed on modification is probably as a result of steric hindrance caused by the attachment of the ester group on the adsorbent surface [20]. Therefore, this reduces the ease with which the hydrogen ions were lost, hence, decreasing the contribution by columbic interaction of the metal ions with the surface groups to the adsorption capacity. This was similar with the work of [7, 21, 8] but not similar to the work carried out by [31].

The adsorption trend is  $\text{Pb}^{2+}$  (99.99 ± 0.004 %) >  $\text{Cd}^{2+}$  (99.50 ± 0.006). Thus, the influence of bio-sorbent size on the metal uptake seems to be a function of both the type of biomass and metal ion. Other researches have also reported the influence of particle size on the biomass adsorption [36,18].

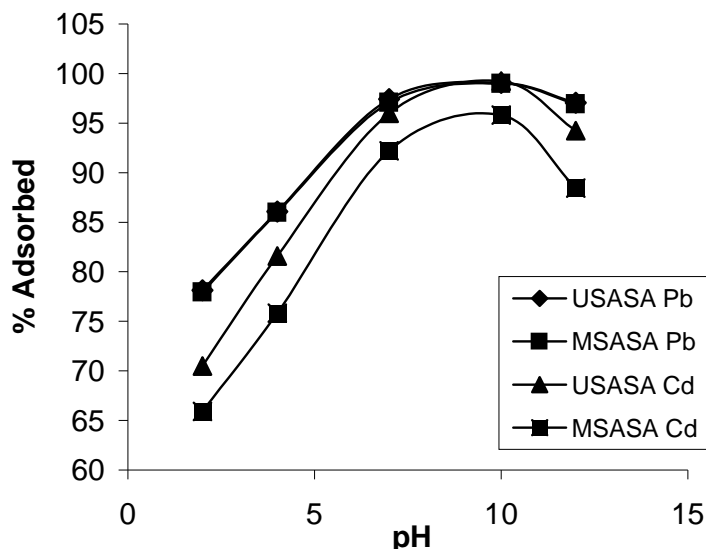


Figure 2: Effect of pH on the Biosorption of Pb(II) and Cd(II) ions from Aqueous Solution on USASA and MSASA

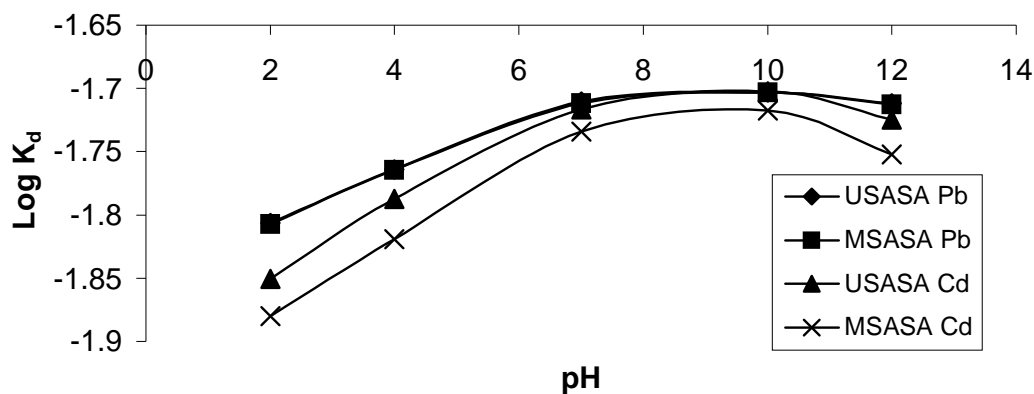


Figure 3 : Coefficient of Distribution for the Removal of Pb(II) and Cd(II) ions from Aqueous Solution on USASA and MSASA

The adsorption of Pb(II) and Cd(II) ions from aqueous solution on modified and unmodified sea animal shells in this research were found to be a highly pH dependent process. pH of the solution, in fact determines the chemistry, degree of ionization and speciation of metal ions and also affects the surface charge of the adsorbent. In this experiment, the adsorption behaviors of the aforementioned metal ions were studied at different pH values. The results obtained are shown in figure 2. From the plots, it was observed that the percentage of metal ion removed had a characteristic change as pH changes. The percentage of metal ion removed increases as pH increase from 2 – 7 and increased to maximum at pH 10, then decreased at pH 12 for the metal ions. This is similar to work carried out by<sup>2</sup>. At low pH, the cell surface sites are closely linked to the H<sup>+</sup> ions, thereby making these unavailable for other cations. However, with an increase in pH, there is an increase in ligands with negative charges which results in increase binding of cations [23].

pH is an important parameter for adsorption of metal ions from aqueous solution because it affects the solubility of the metal ions concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction. It is now established that heavy metals are taken up from water predominantly by ion exchange and complexation reactions [12].

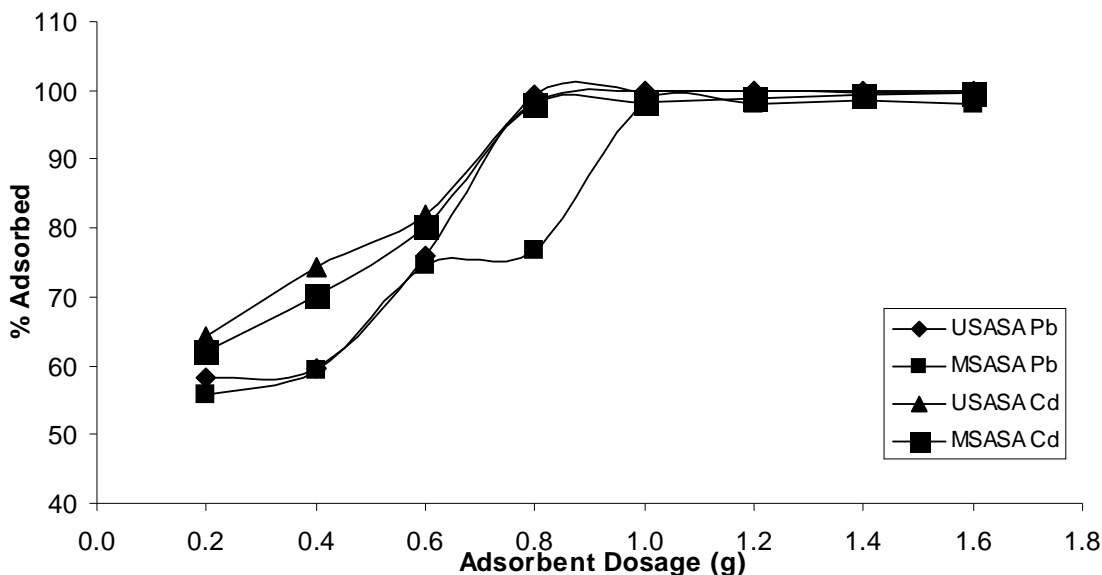
According to [13], pH dependent binding suggests that metal ions are adsorbed by biomass through carboxyl, carbonyl or hydroxyl ligands. This is similar to the findings with the adsorbents used. The addition of NaOH raises the pH before equilibration, enhanced sorption of metal ions by the biomass. NaOH hydrolysis further showed that metal ion adsorption occur through carboxylic or hydroxylic ligands of the adsorbent [14].

At higher pH, the coordinating ligands may be deprotonated and available to adsorb positively charged ions such as Pb(II) and Cd(II) ions through an ion exchange mechanism. At lower pH, the hydroxyl groups may become protonated and can no longer attract the positively charged ions.

The effect of pH on metal bio-sorption has been studied by many researches and the results demonstrated the increasing pH values, as algae biomass [22], as coconut fiber and sawdust (Igwe et al., 2005), as maize cob [18], as activated carbon [6].

<sup>20</sup> reported that the extent of hydrogen ion exchange would depend on the relative concentrations of the exchangeable hydrogen and hydrogen ion concentration of the medium. According to [25], at low pH values, the surface of the adsorbent would be closely associated with hydronium ions, which hinder the access of the metal ions to the surface functional groups. Consequently, the percentage of metal ion removed decrease at low pH.

Figures 3 showed the variation of distribution coefficients ( $K_d$ ) of Pb(II) and Cd(II) sorption between unmodified and modified adsorbents as a function of pH. It was further observed that as the pH increased the distribution coefficient,  $K_d$ , which indicates the amount of metal bound to the biomass, also increases with or without modification, with higher binding of the metal ions occurring between pH 8 – 10.



**Figure 4: Effect of Adsorbent Dosage for the Biosorption of Pb(II) and Cd(II) Ions from Aqueous Solutions**

The effect of dosage of the adsorbents for the adsorption of metal ions studied was shown on figures 4. From the figure, it was observed that the percentage removal of the metal ions increases with increasing the adsorbents doses from 0.2 g to 1.0 g and further increase of the adsorbent doses did not provide more increment in the Percentage of the metal ion removed. Therefore, 1.0 g dose of the adsorbents were used in all the studies.

The increase in the percentage of the metal ion removal with increase in adsorbent dose is due to the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent. Non-significant increase observed when the adsorbent doses were increased from 1.0 g to 1.6 g, suggests that after a certain dose of adsorbent, the maximum adsorption is attained and the amount of

ions bound to the adsorbent and the amount of free ions remains constant even with further addition of the dose of adsorbent. This is similar to studies reported by [1,28,5].

## CONCLUSION

Bio-sorption of Pb(II) and Cd(II) ions from aqueous solutions depend significantly on pH, particle size and dosage of the adsorbent used. Crasstrotrea Gasar biomass, cost effective and environment friendly adsorbent was proved to be a very good adsorbent for the removal of Pb(II) and Cd(II) ions from aqueous solutions. At pH 10, adsorption was at maximal with 500 $\mu$ m particle size and 1.0 g of the adsorbent. Adsorption cannot be improved by chemical modification with oxalic acid and ethanol (esterification).

## REFERENCES

- [1] Abdel-Ghani, N. T., M. Hefray, G. A. F. EL-Chaghaby (2007). Removal of Lead from aqueous solution using low cost abundantly available adsorbent. *Int. J. Environ. Sci. Tech.* 4(1): 67-73.
- [2] Abdul-Ghaffar (2006). Removal and stabilization of Chromium metal ions from industrial effluents. *EJEAFCHE*, 5 (2): 1286-1295.
- [3] Abia, A. A., Horsfall, M. Jnr. And O. Didi (2003). The use of chemically modified and unmodified cassava waste for the removal of Cd, Cu, and Zn ions from aqueous solution. *Bioresour. Tech.*, 90:345-348.
- [4] Ahalya, N., Kanamadi, R. D. and Ramachandra, T. V. (2005). Biosorption of Chromium (VI) from aqueous solutions by the husk of Bengal gram (*Cicer avientinum*). *Electron. Jour. Of Biotechnol.* 8(3): 257-264.
- [5] Alok Mittal (2006). Removal of the dye, Amaranth From waste water using hen feathers as potential adsorbent. *Electron. J. Environment. Agric. Food Chem.* 5(2): 1296-1305.
- [6] Ansari R. and M. Sadegh (2007). Application of Activated Carbon for the removal of arsenic ions from aqueous solution. *E-Journal of Chem.* Vol. 4(1):103-108.
- [7] Beveridge, T. J. and Murray, R. G. E.(1980) Sites of metal deposition in the cell wall of bacillus subtilis. *J. of Bioethcnol.* Vol. 141, no 2: 876 – 887.
- [8] Cohen-Sheol, N. Ilzyer, D. Gilath, I. and Tel-or, E. (2002). The involvement of Pectin in Sir(II) ion biosorption by *Azolla*. *Water Air and Soil Pollution.* Vol. 135(1): 1-4.
- [9] Cussler, E. L. (1997). Diffusion: Mass Transfer in Fluid Systems, 2<sup>nd</sup> ed., 308-330.
- [10] Cutler, J. C. (2007). "Hydrocarbon Chemistry: In: Encyclopedia of Earth. Eds. (Washington, D. C. Environmental Information Coalition, National Council for Science and the Enviornment).
- [11] Drake, Lawrence, R., Lin, Shan., Rayscon, Garry D. and Jackson, Paul J. (1996). Chemical modification and metal binding studies of *Datura innoxia*, *Environmental Science and Toxicol.* Vol. 30 (1): 110-114.
- [12] Eneida, S. C., Celia, R. G. T. and Teresa, M. K. R. (2005). Biosorption Chromium (III) by *Sargassum* sp. Biomass. *Electron. J. Biotechnol.* 5:1-7.
- [13] Gardea-Torresday, J. L., Tongan, D. J. M., Salvador (1996). Copper adsorption by etherified and unesterified fractions of sphagnum peat moss and its different hormic substances. *J. Hazard. Matter* 48:1191-206.
- [14] Gardea-Torresday, J. L., Tiemann, K. J. Dokken, K. and Gamez, G. (1998d). Investigation of metal binding in Alfalfa Biomass through chemical modification of Amino and Sulphydryl ligands. Proceedings of the 11998 Conference of Hazardous Waste Research, Texas, U.S.A.
- [15] Goksungur, Yekta, Uren, Sibel and Guvenc, Ulgar (2005). Biosorption of Cadmium and Lead ions by ethanol treated waste baker's yeast biomass. *Bioresource Technol.* Vol. 96(1): 103-109.
- [16] Horsfall, M. Jnr. And A. I. Spiff (2004). Studies on the effect of pH on the sorption of Pb<sup>2+</sup> and Cd<sup>2+</sup> ions from aqueous solutions by *Caladium bicolor* (Wild Cocoyam) biomass. *Electron J. Biotechnol* 7:310-320.
- [17] Horsfall, M. Jnr. And A. I. Spiff (2005). Effects of Temperature on the Sorption of Pb<sup>2+</sup> and Cd<sup>2+</sup> from aqueous solution by *Caladium bicolor* (Wild Cocoyam) biomass. *Electron J. Biotechnol.* 8:162-169.
- [18] Igwe, J. C. and A. A. Abia (2003). Maize Cob and Husk as adsorbents for removal of cadmium, lead and zinc ions from waste water. *Physical Sci.* 2:83-94.
- [19] Igwe, J. C. and A. A. Abia (2006). Sorption Kinetics and Intraparticulate diffusivity of As(III) bioremediation from aqueous solution, using modified and unmodified coconut fiber *Ecl. Quim., SaO. Paulo*, 31(3): 23-29.
- [20] Igwe, J. C., Ogunewe, D. and Abia A. A. (2005). Competitive adsorption of Zn (II), Cd(II) and Pb(II) ions from aqueous and non-aqueous solution by maize Cob and Husk. *Africa J. of Biotechnol.* Vol. 4(10): 1113-1116.

- [21] Jianlong, Wang (2002). Biosorption of copper (ii) by chemically modified biomass of *Saccharomyces cerevisial*. *Process Biochemistry* vol. 37, no. 8; 847 – 850
- [22] Kratochvil, D. P. Pimentel and B. Volesky (1998) Removal of trivalent chromium by seaweed biosorbent. *Environ. Sci. Technol.*, 32:2693-2698.
- [23] Krishnakuman Parvathi, Ramachandramurthy Nagendran and Redhkrishnan Nreshkumar (2007). Lead biosorption onto waste beer yeast by product a means to decontaminate effluent generated from artery manufacturing industry. *Electron. J. of Biotechnol.* Vol. 10. No. 92-104.
- [24] Leusch, A., Z. R. Holan and B. Volesky, 91995). Biosorption of heavy metals (Cd, Cu, Ni, Pb, Zn) by chemically reinforced biomas of marine algae. *J. Chem. Technol. Biotechol.*, 62: 279- 288.
- [25] Low, K. S., C. K. Lee and A. C. Leo (1995). Removal of Metals from electroplating waste using banana Pith. *Bioresour. Technol.*, 51: 227-231
- [26] Martins, Bruno, L., Curz, Clando, C. V., Luna Aderval S. and Henriques, Cristrane A. (2006). Sorption and desorption of  $Pb^{2+}$  ions by dead sargassum sp. Biomass. *Biochemical Engineering Journal*, VOL. 27 no. 3; 310-314.
- [27] Motoyuki, S. (1990). Adsorption Engineering. Elsevier Sci. Publishers p.5-61.
- [28] Murat Teker and Mustafa Imamoglo and Onger Saltabas (1999). Adsorption of Copper and Cadmium ions by activated carbon from rice Hulls. *Turk. J. Chem.* 23:185-191.
- [29] Narayan, R. L. and T. S. King (1998). Hydrogen adsorption states on Silica-Supported Ru-Ag and Ru-Cu bimetallic catalysts investigated via microcalorimetry. *Thermochimca Acta*, Vol. 312, nos. 1-2; 105-114.
- [30] Okieimen, C. O., Okieimen, F. E. (2001). Enhanced metal sorption by groundnut (*Arachis hypugea*) Husks Modified with thioglycolic Acid. *Bulletin of Pure and Applied Sciences* 20c(i), 13-20.
- [31] Tiemann, K. J., Gardea – torresdey, j. L. Sias, S., Gamez, G., Rodringuez, o., Renner, M. W. and Furenlid, L. R (1999):study of the ligands involve in the metal binding to Alfalfa Biomass. *Environ. Sci. tehncol.* Vol. 31, 182A – 186A
- [32] Vander Wiel, D. P., M. Pruski and T. S. King (1999). A Kinetic Study of the Adsorption and Reaction of Hydrogen on Silica-Supported Ruthenium and Silver-Ruthenium Bimetallic Catalysts during the hydrogenation of Carbon Monoxide. *Journal of Catalysis*, Vol. 188, no. 1, 186-202.
- [33] Veglio, F. and Becolchini, F. (1997). Removal of metals by biosorption: a review. *Hydrometallurgy*, Vol. 44(3); 301-316.
- [34] Vinoid, V. P. and T.S. Anorudhan, (2001). Sorption of Tannic acid on Zirconium Pillard Clay. *J. Chem. Technol. Biotechnol.* 7; 92-101.
- [35] Wang, Jianlong, and Chen, Cann (2006). Biosorption of heavy metal by *Saccharomyces Cerevisiae* A Review. *Biotechnology Advances*, Vol. 24 (5): 427-451.
- [36] Yang, J. and B. Volesky (1999). Biosorption of uranium on Sargassum biomass. *Water Res.* 333:3357-3363.
- [37] Zupanc, C. A. Hornung,, Hornung, O. Hinrichsen and M. Muhler (2002). The Interaction of Hydrogen with Ru/MgO Catalysts, *Journal of Catalysis*, Vol. 209, 501-514.