"Invitro adsorption of Cu (II) on low cost biosorbent using batch reactor and fixed bed column"

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Abstract: *Due to increase in population coupled with mining, extraction and use of various metals as different industrial and household materials, the load of toxic metal pollution in the environment is increasing, so there is a need for the removal of these pollutants. A potential low cost, easily available and environment friendly adsorbent (citrus fruits peel) was used for the removal of Copper (II). Experiments were conducted in batch as a function of temperature, pH, adsorbent dose, initial concentration and time. The removal efficiency of Cu (II) was maximum at 30°c, pH-6, adsorbent dose of 2.5%, contact time 180 minutes from the aqueous solution having initial metal concentration of 100 mg/l. Langmuir and Freundlich adsorption isotherm was employed to evaluate the optimum adsorption capacity of the adsorbent. The adsorption capacity was found to be higher at 18.2mg/g. Kinetic studies showed that first order model was more suitable than the second order model. Adsorption experiment was also conducted in fixed bed column using different metal concentrations, 100% removal was achieved for the concentrations 100mg/l and 150mg/l. From this study it is found that the selected adsorbent is having high potential to remove Cu (II) and needs further study.*
Keywords; *% Removal, Adsorption, Adsorption isotherm, Citrus fruits peel, Copper*

I. Introduction

The tremendous increase in the use of heavy metals in the industries and modern agricultural field over the past few decades has inevitably resulted in an increase flux of metallic substances in aquatic environment. These practices leave persistent toxic heavy metals like chromium, nickel, lead, zinc, cadmium and copper, which tend to bio accumulate and deteriorate the environment (Abbas *et al.,* 2010). Contamination of heavy metals in the environment is a major concern because of their toxicity and threat to human life and environment (Rajendran *et al.,* 2007; Boopathy, 2000). The conventional methods used for the removal of heavy metals are lime precipitation, adsorption into activated carbon, filtration and centrifugation, micro and ultra filtration, crystallization, sedimentation and gravity separation, flotation, precipitation, coagulation, oxidation, solvent extraction, evaporation, distillation, reverse osmosis, ion exchange, electro dialysis, electrolysis, etc. (Volesky *et al.,* 2001).

However, all these methods have disadvantages such as incomplete metal removal, high reagent and energy requirements, and toxic which requires careful disposal (Ahalya *et al.,* 2003). In this context, safe and cost effective methods, such as biosorption using low cost adsorbents and microbial biomass application have been established. Copper toxicity may occur from eating food and drinking water, or breathing air enriched with an excess copper. Acute toxicity of copper may cause anemia, intravascular hemolytic, acute liver failure, and acute renal failure with tubular damage, shock, coma and death and mild conditions may result in vomiting, nausea, and diarrhea (Wyllie, 1957; Spitalny *et al.,* 1984; Knobeloch *et al.,* 1994).

Biosorption is one of the several biological treatment processes for the removal of toxic metals from wastewater and is based on the metal uptake capacity of different biological materials via metabolism or physico-chemical pathways (Fourest and Roux, 1992). Several investigators have studied copper uptake in batch and continuous systems using biosorbents such as brown alga Fucus vesiculosus (Mata *et al.,* 2008), Sargassum fluitans brown seaweed biomass (Naja and Volesky, 2006), raw rice husk (Mohan and Sreelakshmi, 2008) and olive pomace (Pagnanelli *et al.,* 2005), . Traditionally, biosorption studies have focused on batch mode systems; nevertheless, fixed-bed column is the most effective configuration for industrial applications (Volesky, 2003).

The present study was aimed at performing adsorption experiment of Cu (II) by citrus fruits peel waste on batch and fixed bed column reactors and optimization of process parameters such as pH, temperature, contact time, initial metal ion concentration and different adsorbent dosage was carried out for efficient adsorption. Adsorption equilibrium and kinetic works were also carried out to evaluate the Cu (II) removal capacity of citrus fruits peel waste.

II. Materials and Methods

2.1 Biosorbent preparation

Citrus fruit peels such as *Citrus sinensis*; *Citrus Limon* and *Citrus limetta* were collected from fruit juice shop in Thanjavur district and washed thoroughly by distilled water. The washed peels were sun dried for

7 days in order to remove the moisture content of the shells and then they were again washed with distilled water to remove the external dirts and impurities. The washed shells were kept in hot air oven at 50°C for 12 hrs and ground to powder with kitchen grinder and sieved through 0.6mm stainless steel sieve. The obtained 0.6mm sized low cost biosorbent was used for the further study as shown in the Fig. 1.

2.2 Chemicals used
   i.   Metal solution: Synthetic aqueous $CuSo_4$ stock solution was prepared in the concentration of 200mg/l.
   ii. Ammonia solution: 2 drops of ammonia solution was added before taking every absorbance reading using spectrophotometer at 620nm.

2.3 Study of process parameters
The different process parameters such as contact time, adsorbent dose, pH, temperature and initial metal concentration were optimized for better adsorption using batch operating conditions.

2.4 Experimental Procedure for Batch adsorption
From the stock metal solution 100 ml was taken and treated with 1g of adsorbent in 250 ml beaker for 3 hours by agitating with shaker at room temperature. The sample was allowed to settle and then filtered through a whatman filter paper. To the filtrate 2 drops of ammonia solution was added and then it was analyzed using Spectrophotometer at a wavelength of 620nm. The percentage removal of copper (II) was calculated by using the following formula % Removal = ((Co-Ct)/Co) x 100 – (1) where, Co: Initial concentration of copper, Ct: Copper concentration at equilibrium after treatment with adsorbent. The same experimental procedure was repeated for different agitation times. The effects of other parameters were also estimated by following the procedure described above.

2.5 Experimental Procedure for Fixed bed adsorption
The Column biosorption experiments were carried out in Pyrex glass columns of 350mm length and 10mm inner diameter with a capacity of 50ml. The burette was filled with glass beads at the bottom up to 15mm in order to avoid the overflow of adsorbent. The low cost biosorbent was wetted before filling the fixed bed. The pH of the adsorbent was adjusted between 5.8 and 6.0. Then the column was packed with the sorbent up to 150mm length and 20ml of the stock aqueous metal solution was added on to the top of the column, the effluent from the burette was collected and measured for its optical density. The entire column test is conducted at room temperature only. This procedure was done with different metal concentrations such as 100, 150, 200, 250, 300 and 350 mg/l.

2.6 Study of adsorption isotherms and kinetics
Six solutions with concentrations 100, 150, 200, 250, 300 and 350 mg/l were made by proper dilution of stock solutions of copper pH was adjusted to 6. Accurately weighed 2 g of sorbent was added to 100 ml of each metal solution and was agitated for 3 hours. At the end, suspensions were filtered and the filtrate was analyzed for metal ions by spectrophotometry.

2.7 Data evaluation
The amount of Cu (II) adsorbed by the low cost adsorbent was determined using a mass balance equation expressed in the following equation. $q_e = v(C_0-C_e)/m$ – (2) where, qe is metal concentration on the adsorbent (mg/g) at equilibrium, Ce is metal concentration in solution (mg/L) at equilibrium, C0 is initial metal concentration in solution (mg/L), v is volume of initial metal solution used (L), and m is mass of adsorbent used (g).

III.   Results and Discussion
3.1 Effect of agitation time
In order to estimate the adsorption capacity of the adsorbent accurately, it was very much important to allow significant time for the experimental solution to attain equilibrium. As the time increases, copper getting adsorbed by the adsorbent increases, but at a particular point of time, the solution attains equilibrium. Equilibrium agitation time is defined as the time required for the heavy metal concentration to reach a constant value. The equilibrium agitation time is determined by plotting the % removal of copper against agitation time. Results obtained for effect of agitation time are shown in Fig. 2. As the agitation time is increased the % removal increased and at 180 min of agitation time 99.9% removal of copper is observed as shown in Fig. 2.

3.2 Effect of biosorbent dosage

The percentage removal of copper for 180 minutes increased with the increase in adsorbent dosage. The influence of biosorbent on the removal capacity of Cu (II) was depicted in Fig. 3, if we increase the amount of biosorbent the removal of Cu (II) in solution increases, with more biosorption sites of the same, because the amount of added biosorbent determines the number of binding sites available for metal biosorption.

3.3 Effect of initial metal concentration

As the initial concentration of copper increased, the % removal of copper was decreased for the same agitation time of 180 min. The % removal decreased from 99% to 52% with the increase in initial metal concentration from 100 mg/l to 350 mg/l as shown in Fig. 4.

3.4 Effect of Temperature

The percentage removal of copper decreased with increase in temperature, substantiating the fact that the adsorption of copper on low cost adsorbent was physical adsorption. The percentage removal decreased from 97% to 28% as the temperature was increased from 30°C to 50°C as shown in Fig. 5.

3.4 Effect of pH

As can be seen in Fig. 6, this adsorbent can be applied easily in adsorption experiments in acidic medium, because it shows nearly 86% of removal in pH 6. At pH below 6, the main group responsible for metal adsorption, carboxylic acid is protonated due to the high concentration of H+ species. Metal solutions with pH above 6, due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent and ultimately lead to the reduction in sorption capacity. When the pH was increased beyond 6.0, a gradual decrease in the percentage adsorption was observed. This might be due to the competition between (OH-) and copper ions ($CuSo_4^-$). The net positive surface potential of the sorbent decreased with increasing pH resulting in weakening of electrostatic force between adsorbate and adsorbent which ultimately led to the lowering of sorption capacity.

3.5 Fixed bed adsorption

Fixed bed column study was used to evaluate the adsorption capacity of our low cost sorbent using different metal concentrations. 100% removal was achieved for the 100 and 150mg/l Cu (II) concentrations as shown in the Fig. 7. This result reveals that fixed bed column is more efficient than batch adsorption.

3.6 Adsorption Isotherms for Batch experiment

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate specie among liquid and solid phases, based on a set of assumptions that are related to the heterogeneity/homogeneity of the solid surface, the type of coverage, and the possibility of interaction between the adsorbate specie. In this study, equilibrium data were analyzed using the Freundlich and Langmuir isotherms expression.

3.6.1 Freundlich Equation

The Freundlich adsorption isotherm is tried for the adsorption of Cu (II) on low cost adsorbent. The function of Freundlich: $x/m = k_f Ce^n$ - (3) where, x/m = adsorbed substance per gram low cost adsorbent powder, Ce = equilibrium adsorbate concentration, Kf, n = specific constants. The above equation can be written as, $q_e = k_f Ce^n$ – (4). The empirical Freundlich relationship does not indicate a finite uptake capacity. This relationship can be reasonably applied to the low or intermediate concentration ranges. The above equation is linearized as, $log q_e = log k_f + n \, log \, Ce$ – (5). The present data, when plotted shows good linearity for Freundlich relationship (correlation coefficient, $R^2=0.9776$) in case of low cost adsorbent. The slope of isotherm (n) also satisfies the condition of $0<n<1$ for favorable adsorption. The following equation is obtained for low cost adsorbent $log qe = 2.013 + 0.498 \, log \, Ce$ – (6) as shown in Fig 8.

3.6.2 Langmuir adsorption isotherm

The Langmuir adsorption isotherm is given by, $qe = qm \, KL \, Ce / 1 + KL \, Ce$ – (7) which is linearized to, $Ce / qe = 1/qm \, KL + Ce/ qm$ – (8) where, Ce – The equilibrium liquid phase concentration (mg/l), qe – The equilibrium solid phase concentration (mg/l), qm – The maximum adsorption capacity (mg/g), KL – The Langmuir constant. This model assumes that monolayer adsorption take place and that all the available adsorption sites are homogeneous. Furthermore, the model does not consider any interactions among the metal ions that are adsorbed with their neighboring sites. All adsorption energy is constant and does not depend on the level of occupation of the adsorbent active sites. The dimensionless co-efficient (RL) of the model is given by,

$RL = 1 / (1 + KL\ Co) - (9)$ Depending on the values of RL of isotherm can be linear (RL=1), unfavorable (RL>1), favorable (0<RL<1) and irreversible (RL=0). The Langmuir adsorption isotherm is given in Fig. 9.

3.6.3 Comparative Study

The applicability of the two isotherm models was investigated from the coefficient of determination (R^2) values. Based on this, the sorption data were best modeled into Freundlich Isotherm (0.9776) than Langmuir Isotherm Model (0.9765) as shown in Fig. 8 and 9. A high regression correlation coefficient, R2 (0.9776) was shown by the Freundlich model. This indicates that the Freundlich model suited best for describing the sorption process of Cu (II) onto the low cost sorbent.

3.7 Kinetic studies for Batch experiment

In order to analyze the adsorption kinetics of heavy metal ions, the first and second order kinetic models were applied to data. During the present study, the two different kinetic models were applied and showed in Fig. 10a and 10b for Cu (II). Based on linear regression (R2> 0.99) values, the kinetics of Cu (II) adsorption on to the adsorbent can be described well by first-order equation.
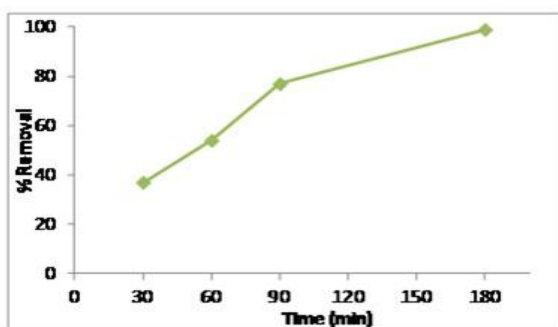
IV   FIGURES

Figure 1: Biosorbent

Figure 2: Effect of Agitation time on the removal of copper using low cost adsorbent
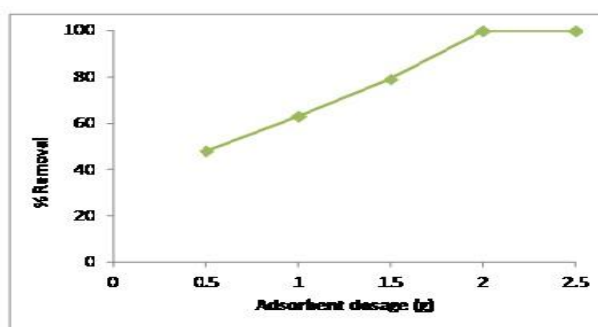

Figure 3: Effect of Adsorbent dosage on the removal of copper using low cost adsorbent
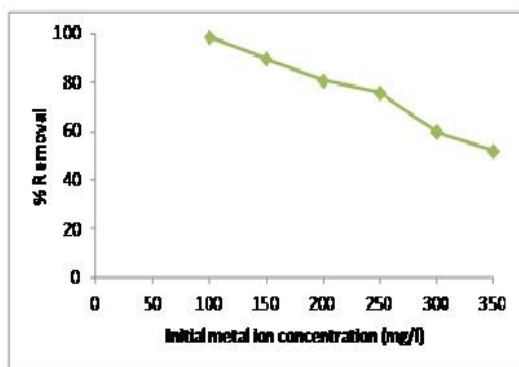

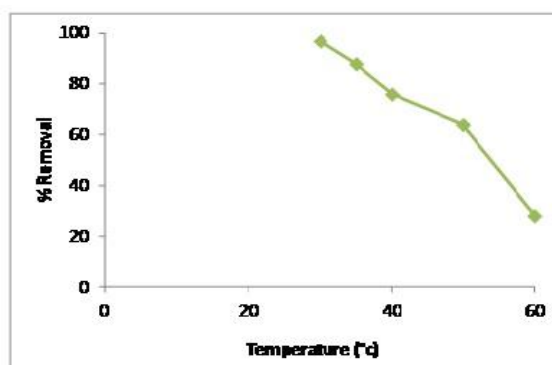Figure 4: Effect of initial metal concentration on the removal of copper using low cost adsorbent

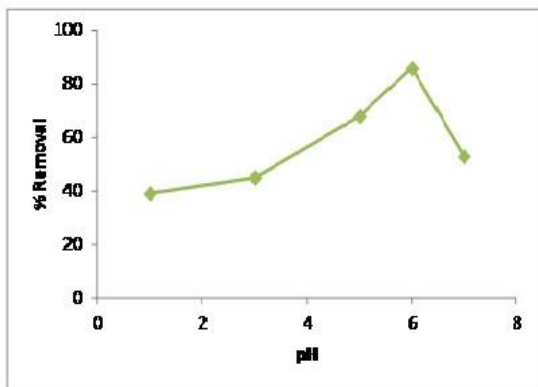Figure 5: Effect of Temperature on the removal of copper using low cost adsorbent

Figure 6: Effect of pH on the removal of copper using low cost adsorbent
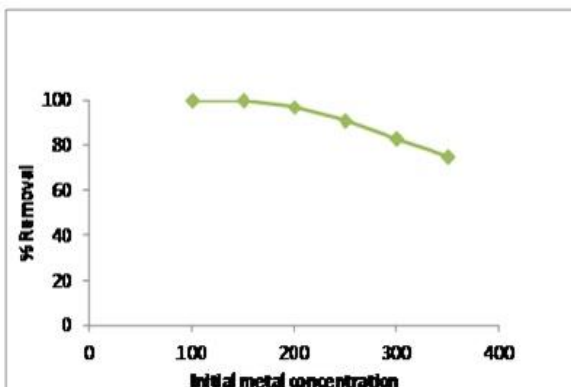

Figure 7: Evaluation of Cu (II) adsorption on low cost adsorbent using fixed bed column
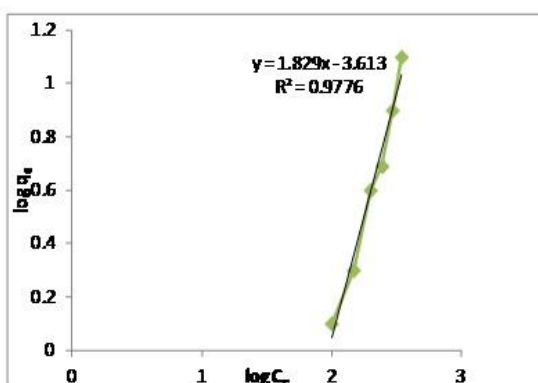

Figure 8: Freundlich Adsorption Isotherm on the Removal of copper using low cost adsorbent
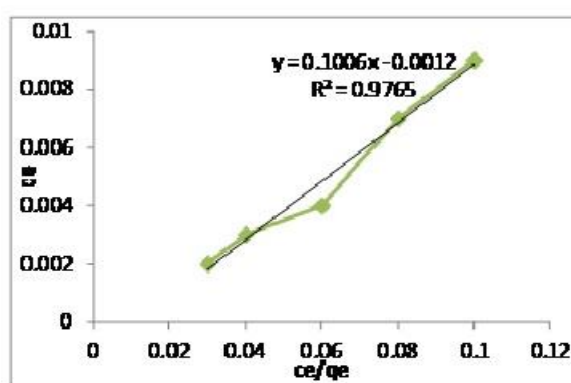

Figure 9: Langmuir Adsorption Isotherm on the Removal of copper using low cost adsorbent
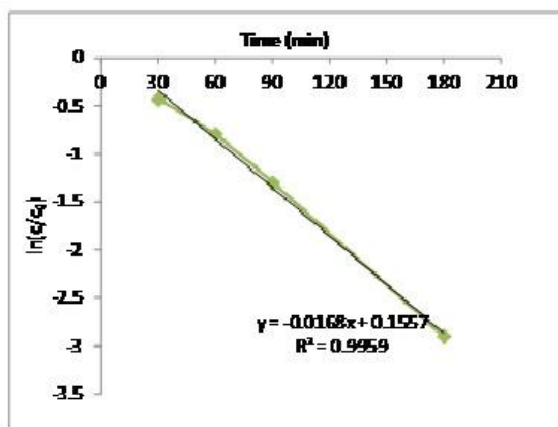

Figure 10a: First order kinetic model for the adsorption of copper on low cost adsorbent
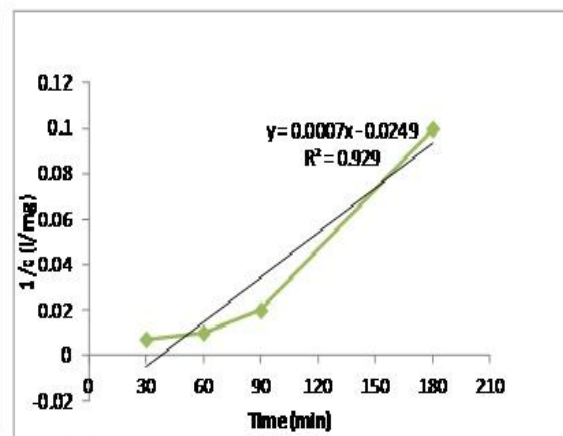

Figure 10b: Second order kinetic model for the adsorption of copper on low cost adsorbent

V Conclusion

This study investigated the feasibility of citrus fruits peel used as a low-cost adsorbent for the removal of Cu (II) from aqueous solution. This adsorbent material is a potential candidate for biosorption and further studies will help to evaluate economical use of this biosorbent. The biosorption was found to be dependent on the solution pH, initial Cu (II) ion concentration, temperature, sorbent dosage and contact time. The maximum removal was observed at 30°c, pH-6, adsorbent dose of 2.5%, contact time 180 minutes from the aqueous solution having initial metal concentration of 100 mg/L. Adsorption experiment was conducted in both batch mode and in fixed bed column, the obtained results reveals that fixed bed column is efficient than batch

adsorption. Langmuir and Freundlich adsorption isotherm was employed to evaluate the optimum adsorption capacity of the adsorbent. The adsorption capacity was found to be higher at 18.2mg/g. Adsorption follows first order kinetic model. Kinetic results showed that both bulk and intra-particle diffusion are effective adsorption mechanisms. As a result of this study, it is concluded that citrus fruits peel adsorbent can be used for removal of heavy metal pollution from wastewater since it is of low-cost, abundant and a locally available.

References

[1]   M. Abbas, Z. Parveen, S. Riazuddin Iqbal, and R. Bhutto, Monitoring of toxic metals (cadmium, lead, arsenic, and mercury) in vegetables of sindh, Pakistan*, Kathmandu university , journal of science, Engineering and Technology, 6,* 2010 , 60-65.
[2]   N. Ahalya, T.V. Ramachandra, and R.D. Kanamadi, Biosorption of heavy metals, *Res. J. Chem. Environ, 7(4),* 2003, 71-79.
[3]   R. Boopathy, *Factors limiting bioremediation technologies, Bioresource* Technology*, 74,* 2000, 63-67.
[4]   E. Fourest , and J.C. Roux, Heavy metal biosorption by fungal mycelia products: Mechanism and influence of pH, *Appl. Microbial. Biotechnology*, 37, 1992, 399-403.
[5]   L. Knobeloch, M. Ziarnik, J. Howard, B. Theis, D. Farmer, H. Anderson, and M. Proctor, Gastrointestinal upsets associated with ingestion of copper – contaminated water, *Environ. Health perspect, 102,* 1994, 958-961.
[6]   Y.N. Mata, M.L. Blazquez, A. Ballester, F. Gonzalez, and J.A. Munoz, Characterization of the biosorption of cadmium, lead, and copper with the brown algae *fucus vesiculus, J.Hazard. Mater, 158,* 2008, 316-323.
[7]   S. Mohan, and G. Sreelakshmi, Fixed bed column study for heavy metal removal using phosphate treated rice husk, *J. Hazard. Mater, 153,* 2008, 75-82.
[8]   G. Naja, and B. Volesky, Multi – metal biosorption in a fixed bed flow – through column, Colloids *surf. A, 281,* 2006, 194-201.
[9]   F. Pagnanelli, S. Mainelli, S. De Angelis, and L. Toro, Biosorption of protons and heavy metals onto olive pomace, *Modelling of competition effects, Water Res. 39,* 2005, 1639-1651.
[10]   P. Rajendran, and P. Gunasekaran, *Microbial Bioremediation* (M.J.P. Publishers, Chennai, 2007), 181-190.
[11]   K.C. Spitanly, J. Brondum, R.L. Vogt, H.E. Sargent, and S. Kappel, Drinking water induced intoxication in a Vermont family, *pediatrics, 74, 1984,* 1103-1106.
[12]   J. Wyllie, Copper poisoning at a cocktail parts, *Am.J.Public Health,* 47, 1957, 617.
[13]   R. Veeraswamy, V. Venkateswaren, and A.R. Kulandaivelu(Ed), *Basic principles of practical chemistry* (S. Chand Publishers, 2007).
[14]   P. Velmurugan, V. Rathina Kumar, and G. Dhinakaran, Dye removal from aqueous solution using low cost adsorbent, *International journal of Environmental Sciences*, *Vol 1, No 7,* 2011.
[15]   B. Volesky, Sorption and Biosorption, Bv sorbex, Quebec, 2003.
[16]   B. Volesky, Detoxification of metal – bearing effluents: Biosorption for the next century. *Hydrometallurgy, 59*, 2001, 203-16.