REMOVAL OF CADMIUM IONS FROM AQUEOUS SOLUTIONS BY TWO LOW-COST MATERIALS

H. BENAISSA* and M.A. ELOUCHDI

* Laboratory of Sorbent Materials and Water Treatment, Department of Chemistry
Faculty of Sciences, University of Tlemcen, P.O. Box 119
13 000 Tlemcen - Algeria
E-mail: ho_benaissa@ yahoo.fr

ABSTRACT

This study compared the abilities of two low-cost materials: a dried activated sludge and sunflower leaves to remove cadmium from aqueous solutions. Kinetic data and equilibrium sorption isotherms were measured in batch conditions. Kinetics of cadmium sorption was time contact and initial cadmium concentration dependent. The cadmium uptake of these two low-cost materials was quantitatively evaluated using sorption isotherms. Results indicated that the Langmuir model gave a better fit to the experimental data than the Freundlich equation. A high cadmium sorption was observed by both these materials. The sunflower leaves, were the most effective to uptake cadmium ions with a maximum sorption capacity about 147.06 mg/g compared to that of activated sludge 103.03 mg/g.

KEY WORDS: removal; cadmium; activated sludge; sunflowers leaves.

INTRODUCTION

It is well recognised that the presence of heavy metals in the environment can be detrimental to a variety of living species, including man. Metals can be distinguished from other toxic pollutants, since they are non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain. For example, cadmium, which is widely used and extremely toxic in relatively low dosages, is one of the principle heavy metals responsible for causing these problems (Hutton & Symon [1], Nriagu [2]). A variety of industries such as: the non-ferrous metal industry, mining and mineral processing, pigment manufacture, battery manufacture, the printing and photographic industries and metal working and finishing processes, etc..., are responsible for the release of cadmium into the environment through their wastewaters (Holan et al. [3], Volesky et al. [4], Chong & Volesky [5]). In addition, considerable quantities of heavy metals can be released into the environment through routes other than in wastewaters. The main techniques which have been utilised to reduce the heavy metal ion content of effluents, have been found to be limited, since they often involve high capital and operational costs and may also be associated with the generation of secondary wastes which present treatment problems, such as the large quantity of sludges generated by precipitation processes (Singh et al. [6], Yin & Blanch [7], Sadowski et al. [8]).

Therefore, there is a need to develop low cost, naturally occurring, abundant materials that can remove heavy metals efficiently. Several such sorbent materials have been reported in the literature. Because plants as waste materials from agriculture and dried activated sludge from many waste water treatment plants are broadly available and relatively inexpensive, an investigation of their uses as sorbent materials seems most appropriate. Very little informations (Gourdon et al. [9,10], Tien & Huang [11,12], Kasan [13], Imai & Gloyna [14], Shi et al. [15]) are available for heavy metals sorption from aqueous solutions by activated sludges and sunflower leaves in the literature. These low-cost materials may be particularly suitable for application in small industries and developing countries.

In the present study, a comparison of the performances of two waste by-product materials: dried activated sludge and sunflower leaves to remove cadmium from aqueous solutions was carried out. During this investigation, the kinetics and equilibrium of cadmium removal were studied in batch conditions. In order to describe the isotherm mathematically and to obtain information about their maximum sorption capacity for comparison, the experimental sorption equilibrium data were correlated by either the Langmuir or Freundlich equations.

MATERIALS AND METHODS

In this study, two waste by-product materials were used to remove cadmium from aqueous solutions.

- Dried Activated sludge (a mixed microbial community) from a conventional biological wastewater treatment plant in our region (Maghnia - Algeria -), in the form of large flakes having a 0.2-5.0 mm particle size, was used throughout this work without any preliminary purification.

- Sunflower leaves as an agricultural by-product waste, collected from our region of Tlemcen - Algeria - in the form of large flakes, were used as adsorbent after the following treatment: 5g of dried sunflower sheets were contacted with 1 L of distilled water in a beaker agitated vigorously by a magnetic stirrer at ambient temperature of 25°C during 4 hours, then continuously washed with distilled water to remove the surface adhered particles and water soluble materials, and oven-dried overnight at 60-80°C for 24 hours after filtration. This material was crushed and sieved to have particles of size 0.5 - 3.15 mm for further batch sorption experiments.

Cadmium solutions of desired concentration were prepared from $Cd(NO_3)_2.4H_2O$ (Windor Laboratories Limited), by dissolving the exact quantities of cadmium salts in distilled water. All chemicals were commercial products used without purification.

1- Uptake kinetics of metal

The initial solution metal concentration was 100 mg/L for all experiments except for that carried out to examine the effect of the initial concentration of cadmium. For metal removal kinetics studies, 0.6 g of dried activated sludge or sunflower leaves was contacted with 300 mL of metal solutions in a beaker agitated vigorously by a magnetic stirrer using a water bath maintained at a constant temperature of 25°C. In all cases, the working pH was that of the solution and was not controlled. The residual cadmium concentration in the aqueous solution at appropriate time intervals, was obtained by using a Cd^{2+}- ion selective electrode technique. The electrode used for measurement of cadmium was Orion Model 9448 and was used in conjunction with Orion Model reference electrode and an Orion Model 710A meter, which provided readings accurate to ± 0.1 mV. For the measurement of pH, an Orion Model 9107 combination electrode, with the aforementioned meter, was used. pH readings were monitored to + 0.01 unit. For certain experiments, this cadmium concentration was also done using a Perkin Elmer Model 2280 atomic absorption spectrophotometer. No differences in the results obtained by these two methods of analysis were observed in the experimental error. The metal uptake q (mg ion metal/g dried activated sludge) was determined as follows:

$$q = (C_0 - C_t) \text{ x } V/m$$

where C_0 and C_t are the initial and final metal ion concentration (mg/L), respectively, V is the volume of solution (mL), and m is activated sludge or sunflower leaves weight (g) in dry form.

Preliminary experiments had shown that cadmium adsorption losses to the container walls and to the filter paper were negligible.

2- Uptake isotherm of metal.

The equilibrium isotherms were determined by contacting a constant mass (0.200g) of activated sludge or sunflower leaves with a range of different concentrations of cadmium solutions. Activated sludge or sunflower leaves and cadmium solution were agitated in a series of 250 ml conical flasks with equal volumes of solution (100 ml) for a period of 24 hours at room temperature. The contact time was previously determined by kinetics tests using the same conditions. The reaction mixture pH was not controlled after the initiation of experiments. After shaking the flasks for 24h, the final pH was measured. The final concentration of unbound cadmium was obtained by using a Cd^{2+}- ion-selective electrode technique and the cadmium loading by activated sludge or sunflower leaves calculated.

RESULTS AND DISCUSSION

All batch sorption experiments reported here were investigated at initial pH value < 7, because insoluble cadmium hydroxide starts precipitating from the solution at higher pH values, making true sorption studies impossible.

1 - Uptake kinetics of metal

According to the Figure1, the kinetics of cadmium removal by a dried activated sludge and sunflower leaves, respectively, present a same shape characterized by a strong increase of the capacity of cadmium sorption during the first minutes of contact solution - sorbent, follow-up of a slow increase until to reach a state of equilibrium. The necessary time to reach this equilibrium is about 6-7 hours and an increase of sorption time to 24 hours doesn't show notable effects. The capacities of cadmium sorption at equilibrium are: 43.54 and 39.10 mg/g for sunflower leaves and dried activated sludge, respectively, at initial cadmium concentration of 100 mg/L.

During the course of cadmium removal by activated sludge or sunflower leaves, we noticed an evolution in the value of the initial pH of the solution presented in Figure 2. This can be interpreted by a competition between cadmium ions and H_3O^+ for binding sites. As a result of this competition, only some of superficial groups become available to cadmium ions for sorption.

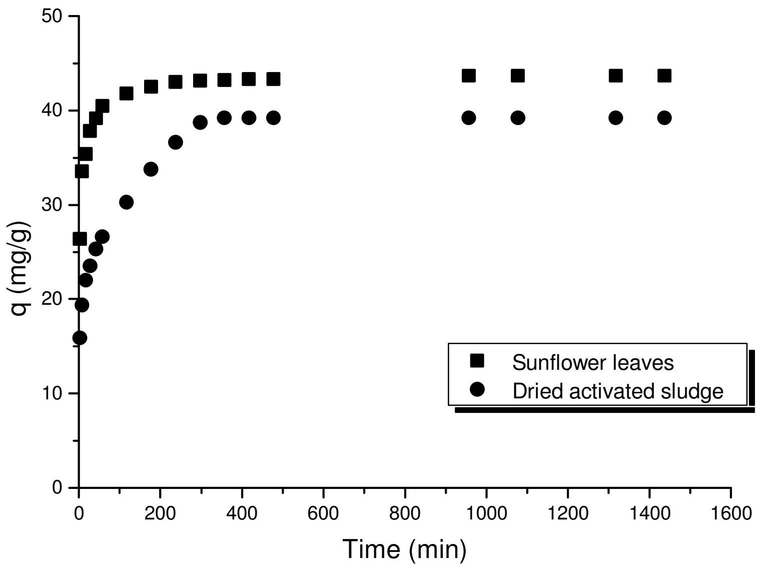

Figure 1: Kinetics of cadmium sorption by a dried activated sludge and sunflower leaves.

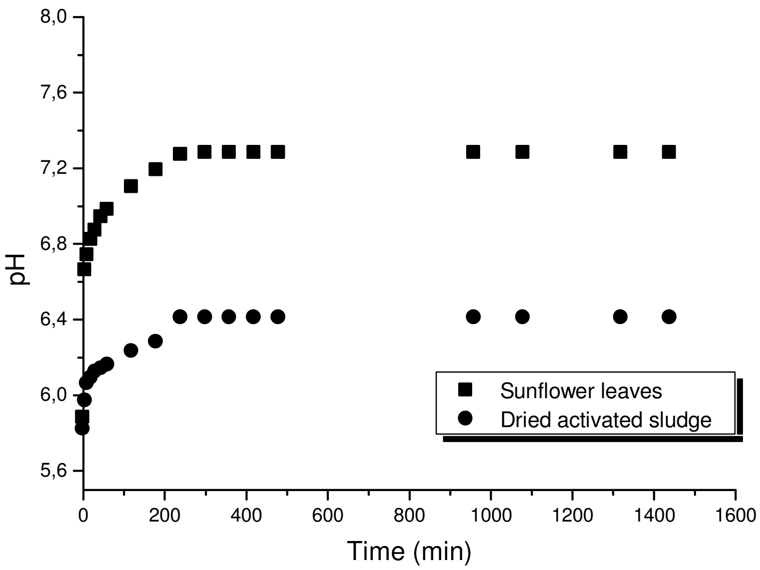

Figure 2: pH profiles of cadmium sorption by a dried activated sludge and sunflower leaves

Several experiments were also undertaken to study the effect of varying the initial cadmium concentration on the cadmium sorption kinetics from solution. The results obtained are shown in Figures 3-4, and indicate that the obtained curves have the same shape. The necessary average time to reach equilibrium is about 6-7 hours for all concentrations tested with both these materials. We also notice that the capacity of cadmium removal by these materials at the equilibrium increases with the initial concentration in cadmium.

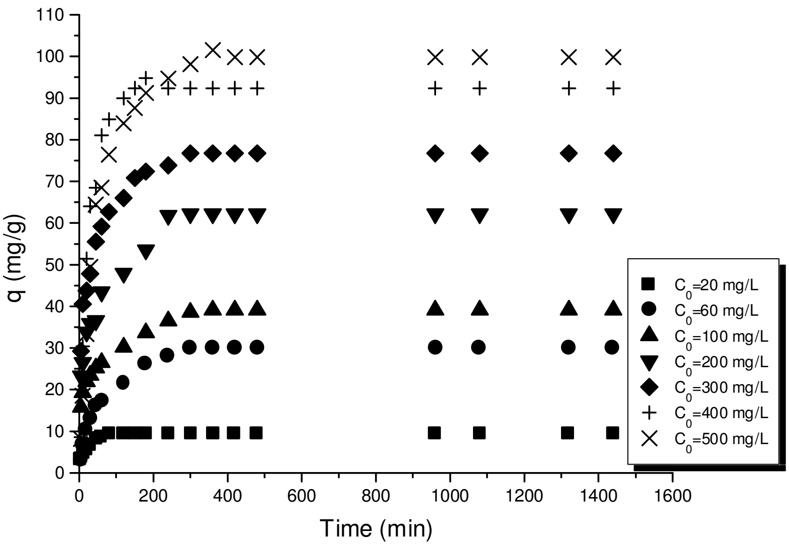

Figure 3: Effect of initial cadmium concentration on the kinetics of cadmium sorption by a dried activated sludge.

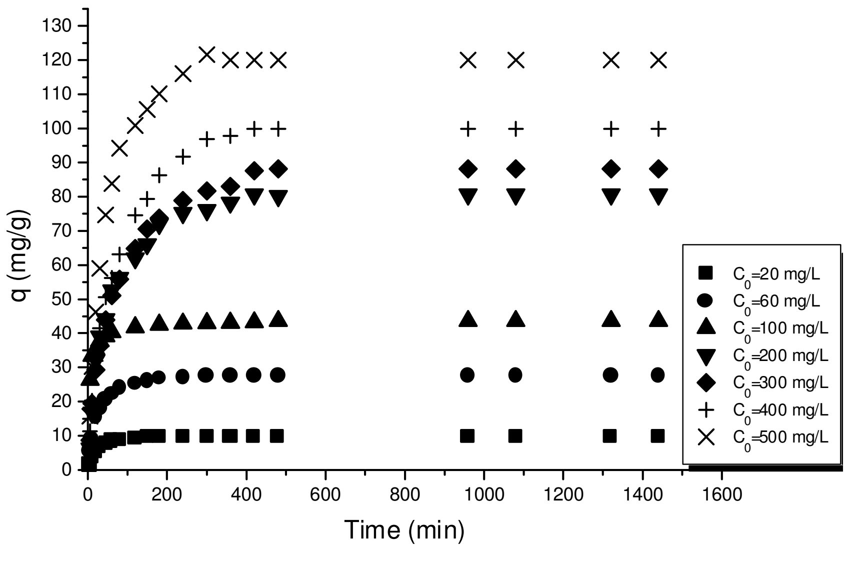

Figure 4: Effect of initial cadmium concentration on the kinetics of cadmium sorption by sunflower leaves.

During the phenomenon of cadmium removal, we also noticed an increase of the initial pH of the solution for all studied concentrations (figures are not shown here), without reaching the pH value of cadmium precipitation.

2- Equilibrium of sorption

To study equilibrium of cadmium removal by activated sludge and sunflower leaves, the isotherms of sorption with no initial pH control of solution were measured. As shown in Figure 5, the isotherms obtained for cadmium sorption are of Langmuir's type according to the classification of Brunauer [16] and of L type according to the classification of Giles et al. [17].

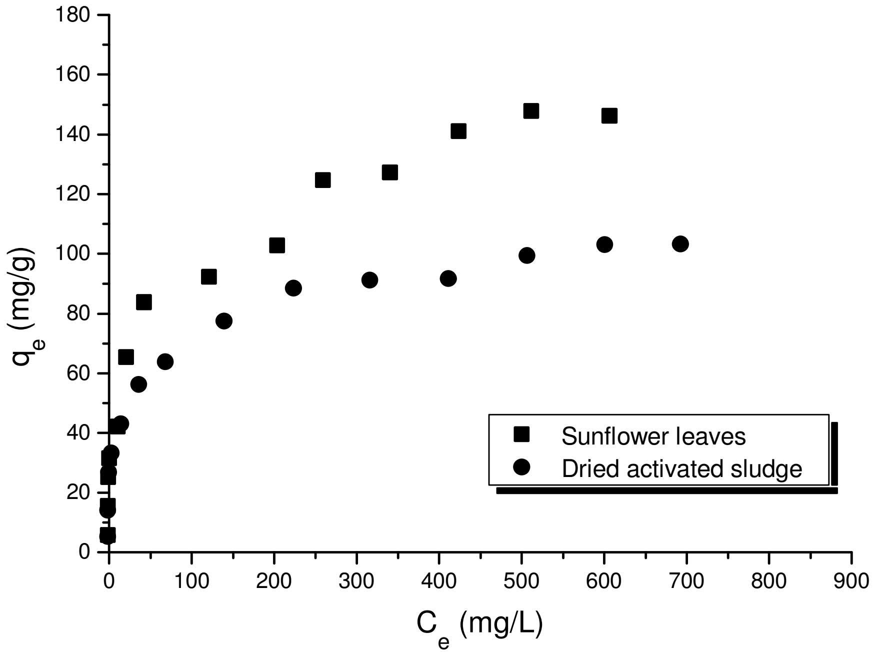

Figure 5: Isotherms of cadmium sorption by a dried activated sludge and sunflower leaves at 25 °C

During experiments of sorption equilibrium, it was observed that the initial pH of the solution increased slightly and equilibrium pH varied with the initial concentration. To describe sorption isotherms of ions from aqueous solutions, there are few models in the literature. The use of biological materials, in particular, activated sludge and sunflower sludge, is an enormous complicating factor i.e the uptake process is a complex one. The utilization of a model has value in comparing different biomaterials under different operating conditions and rests solely on the adequacy between the observed experimentally tendencies and the shape of the mathematical laws associated to this model. Among the models available, the Langmuir [18] and Freundlich [19] sorption models are commonly used to fit experimental data when solute uptake occurs by a monolayer sorption. These models were tested in the present work. The Langmuir model has the form:

$$q = q_m\, b\, C_e/1+bC_e \tag{1}$$

and the Freundlich model has the form:

$$q = KC_e^{\,n} \tag{2}$$

where: q is the amount of metal ion sorbed at equilibrium per g of sorbent (mg/g); C_e the equilibrium concentration of metal ion in the solution (mg/L); q_m , b are the Langmuir model constants; K, n the Freundlich model constants. If the equation of Langmuir is valid to describe our experimental results, it must verify the linearized shape of the basis equation, in system of coordinates C_e/q vs. C_e, that will permit us to obtain the constants q_m and b from the intercept and slope. If the equation of Freundlich is also verified, we must obtain a right in the system of coordinates Ln q vs. Ln C_e, the slope and the intercepts to the origin give n and k respectively. Results of the modelling of isotherms of cadmium sorption by activated sludge and sunflower leaves respectively, according to these models, are represented in Figures 6-7.

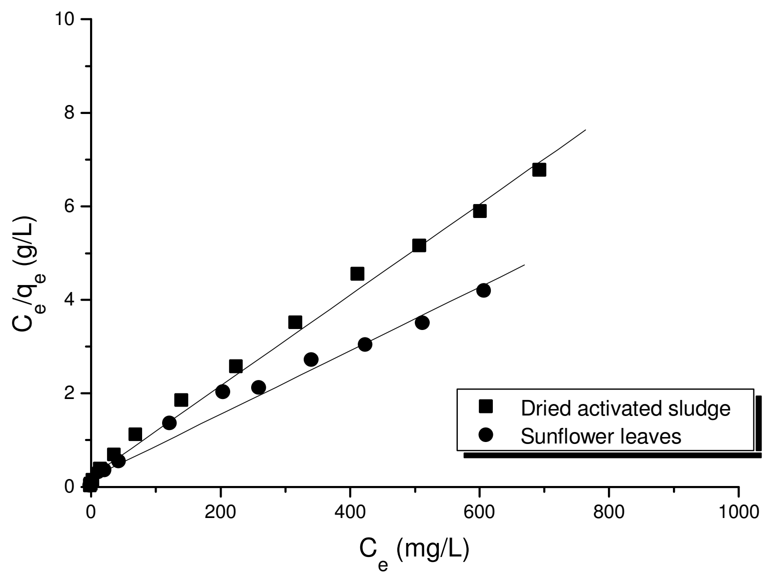

Figure 6: Linearized plot of Langmuir isotherm for cadmium sorption by an dried activated sludge and sunflower leaves

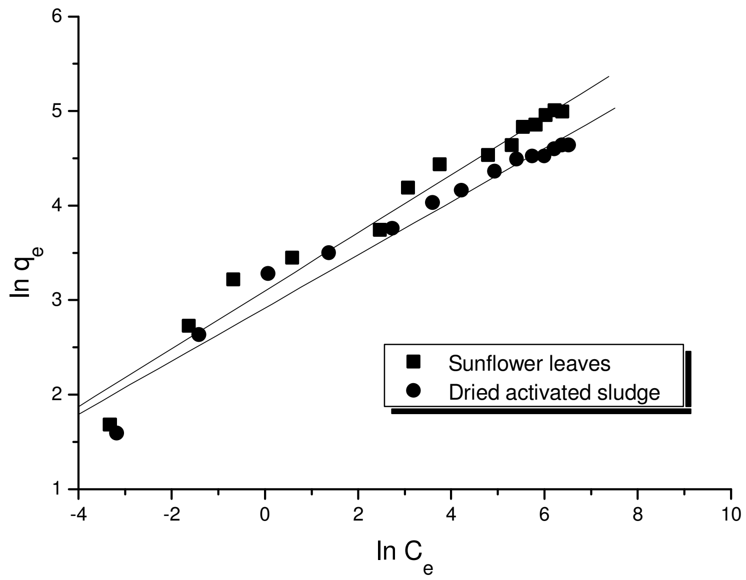

Figure 7: Linearized plot of Freundlich isotherm for cadmium sorption by a dried activated sludge and sunflower sludge

It appears that the Langmuir model best fits the experimental results over the experimental range with good coefficients of correlation. The model parameters determined by least squares fit of the experimental sorption data are: q_m = 103.09 mg/g, b = 0.044 L/mg (R = 0.996) for activated sludge and q_m = 147.06 mg/g, b = 0,036 L/mg (R = 0.991) for sunflower leaves. According to coefficients of correlation: k = 1.075, n = 0,306 (R = 0.985) for sunflower leaves and k = 18.47, n = 0.281 (R = 0.980) for activated sludge obtained, we deduct that the model of Freundlich is not adequate for modelling isotherms in all the studied concentrations domain, what is besides our objective. The applicability of these models should be considered as a mathematical representation of the sorption equilibrium over a given metal-ion concentration range. The mechanistic conclusions from the good fit of the models alone should be avoided. In spite of the above limitations, these models can provide information on metal-uptake capacities and differences in metal uptake between various species [20]. From these results, a high cadmium sorption is observed by both these materials. The highest removal of cadmium ions is obtained with sunflower leaves.

CONCLUSION

The results obtained confirm that dried activated sludge and sunflower leaves can remove cadmium ion from aqueous solution. The sorption performances are strongly affected by parameters such as: contact time and initial cadmium concentration. The amount of cadmium removed by these materials used increased with the increase of these parameters at a specific time. A good fitting of cadmium sorption equilibrium data is obtained with Langmuir model in all the range of concentrations studied. From these results, a high cadmium sorption is observed by both these materials. The highest removal of cadmium ions is obtained with sunflower leaves.

REFERENCES

1. Hutton, M. and Symon, C., Quantities of cadmium, lead, mercury, and arsenic entering the environment from human activities, Sciences Total Environmental., Vol. 57, pp. 129-150, 1986.
2. Nriagu, J.O., A silent epidemic of environmental metal poisoning?, Environmental Pollution, Vol. 50, pp. 139-161, 1988.
3. Holan, Z.R., Volesky, B. and Prasetyo, I., Biosorption of cadmium by biomass marine algae, Biotechnology and Bioengineering, Vol. 41, pp. 819-825, 1993.
4. Volesky, B., May, H. and Holan, Z.R., Cadmium biosorption by saccharomyces cerevisiae, Biotechnology and Bioengineering, Vol. 41, pp. 826-829, 1993.
5. Chong, K.H. and Volesky B., Description of two metal biosorption equilibria by Langmuir - type models, Biotechnology and Bioengineering, Vol. 47, pp. 451-460, 1995.
6. Singh, D.B., Prasad, G., Rupainwar, D.C. and Singh, V.N., As(III) Removal from aqueous solution by adsorption, Water, Air and Soil Pollution, Vol. 42, pp. 373-386, 1988.
7. Yin, J. and Blanch, H.W., A bio-mimetic cadmium adsorbent: design, synthesis, and characterization, Biotechnology and Bioengineering, Vol. 34, PP. 180-188, 1989.
8. Sadowski, Z., Golab, Z. and Smith, R.W., Flotation of streptomyces pilosus after lead accumulation, Biotechnology and Bioengineering, Vol. 37, pp. 955-959, 1991.
9. Gourdon, R., Bhende, S., Rus, E. and Sofer, S.S., Comparison of cadmium biosorption by Gram-Positive and Gram-Negative bacteria from activated sludge, Biotechnology Letters, Vol. 12, part 11, pp. 839-842, 1990.
10. Gourdon, R., Rus, E., Bhende, S. and Sofer, S.S., Mechanism of cadmium uptake by activated sludge, Applied Microbiology and Biotechnology, Vol. 34, pp. 274-278, 1990.
11. Tien, C-T. and Huang, C.P., Formation of surface complexes between heavy metals and sludge particles, In. Heavy Metals in the Environment: Trace Metals in the Environment 1, Ed. Vernet J.-P.), Elsevier, pp. 295-311, 1991.

12. Tien, C-T. and Huang, C.P., Kinetics of heavy metal adsorption on sludge particulate, In. Heavy Metals in the Environment: Trace Metals in the Environment 1 (Ed. Vernet, J.-P.), Elsevier, pp. 313-328, 1991.
13. Kasan, H.C., The role of waste activated sludge and bacteria in metal-ion removal from solution, Critical Review, Environment Science and Technology, Vol. 23, part 1, pp. 79-117, 1993.
14. Imai, A. and Gloyna, E.F., Speciation of chromium (III) in activated sludge, Water Environmental Ressource, Vol. 68, part 3, pp. 301-310, 1996.
15. Shi, W., Xu, X. and Sun, G., Chemically modified sunflower stalks as adsorbents for color removal from textile wastewater, Journal of Applied Polymer Sciences, Vol. 71, pp. 1851-1861, 1999.
16. Brunauer, S., The adsorption of gases and vapors, Princeton, New York, 1945.
17. Giles, C. H., Mac Ewan, T. H., Nakhwa, S. N. and Smith, D. J., Studies in adsorption. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and measurements of specific areas of solids. Chemical Society, pp. 3973-3993, 1960.
18. Langmuir, L., The adsorption of gass, mica and platinium, Journal of American Chemical Society, Vol. 40, pp. 1361, 1918.
19. Freundlich, H., Colloid and capillary Chemistry. Metheum, London, 883, 1926.
20. Kapoor, A. and Viraraghavan, T., Fungal biosorption- An alternative treatment option for heavy metal bearing wastewaters: A review, Bioresource Technology, Vol. 53, pp. 195-206, 1995.