ESTIMATE OF GLOBAL EMISSIONS OF HEAVY METALS TO THE ATMOSPHERE FROM INDUSTRIAL AND NATURAL SOURCES

***Venkat Reddy Kandadhi, #Dr. Pardeep Kumar**
**Ph.D. Scholar, JJT University Jhunjhunu (Rajasthan)*
#Associate Professor, HBIT Kanpur (UP)

ABSTRACT

In view of high toxicity, environmental mobility, non-biodegradability and stability of heavy metals, their removal becomes an absolute necessity. It is known that legal standard on environmental control are becoming strict and as a result the discharge of heavy metal into aquatic bodies is being rigorously controlled. So it is necessary to remove heavy metals from wastewater before discharge into the water and onto land. There are several methods used for the removal of heavy metals from waste discharges. In practice, the choice of one type of treatment versus another depends on several factors, including the form and concentration of metals in the wastewater, other constituents present, the extent of removal desired, environmental regulations pertaining to the discharge of the treated wastewater, associated capital and operating costs and the amount of sludges or residues generated and their disposal costs (Beszedits and Netzer, 1986). Now a days, chemical precipitation, membrane separation, electrolysis, ion exchange and adsorption are the widely used methods for the removal of heavy metals from wastewater. A brief discussion of these methods is given in the followingsections.
***Keywords:-** flocculent, sludges, semi permeable, cations*

INTRODUCTION

The use of biological materials as biosorbent for heavy metal adsorption and recovery has received a great deal of attention in the past two decades due to their good performance and low cost (Volesky, 1994; Kratochvil and Volesky, 1998). The passive sorption and/or complexation of metal ions by the biomass were termed "biosorption" (Shumate and Strandberg, 1985). The biosorption process involves a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, metal ions) and a solid phase (sorbent or biosorbent; biological material) on which it is sorbed. Due to higher affinity of the sorbent for the sorbate species, the latter is attracted and bound there by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution. The degree of sorbent affinity for the sorbate determines its distribution between the solid and liquid phases.

The biological materials are capable of removing even trace levels of metal ions. They can also be used to recover rare, precious or strategic metals from waste solutions. Biosorption is caused by a number of different mechanisms, depending on the type of particular binding sites responsible for metal sequestering. The abundant biomass can be obtained inexpensively, as they are waste or byproducts of large-scale industrial processes. Hence, biosorption coupled with desorption may provide an economic and effective alternative for removal and recovery of heavy metal.

Biosorption processes can compete with other processes for the removal of heavy metals from wastewaters (Friis and Meyers-Keidi, 1986) especially, when other processes are ineffective or extremely expensive and the discharge concentrations are required to be very low (Volesky, 1990).

The major advantages of biosorption over conventional treatment methods include (Kratochvil and Volesky, 1998a):

- Low cost
- High efficiency
- Minimization of chemical and biological sludge
- No additional nutrient requirement
- Regeneration of biosorbent
- Possibility of metal recovery

Factors affecting biosorption: There are a number of physical and chemical factors which affect the biosorption of metals.

1. PH is the most important parameter in the biosorptive process because it affects the solution chemistry of the metals, the activity of the functional groups in the biomass and the competition of metallic ions (Friis and Myers-Keith, 1986).
2. Biomass concentration in solution seems to influence the specific uptake: for lower values of biomass concentrations there is an increase in the specific uptake (Fourest and Roux, 1992; Gadd, 1988). Gadd (1988) suggested that an increase in biomass concentration leads to interference between the binding sites. Fourest and Roux (1992) invalidated this hypothesis attributing the responsibility of the specific uptake decrease to metal concentration shortage in solution.
3. Temperature influences the biosorption performances (Aksu et al, 1992).
4. Biosorption is mainly used to treat wastewater where more than one type of metal ions is present; the removal of one metal ion may be influenced by the presence of other metal ions.

The process of biosorption is the most promising technique. The most widely used industrial sorbent is activated carbon; however it is an expensive material. Biosorbents prepared from different types of discarded materials are very convenient material in terms of cost for heavy metal removal from wastewater. A number of materials have been tested as biosorbent for heavy metals removal and a number of studies have been reported using biosorbent like: Soya cake (Daneshwar et al, 2002), Sawdust (Hamadi et al, 2001), Lignocellular substrate (Aoki et al, 1982), Rice husk (Guo et al, 2003), Groundnut husk carbon, Tea leaves, Mango leaves, Coconut (Choy et al, 1999), Fiber pith, Hazel nut carbon etc.

Most of the biosorbents explored so far, have not been fully investigated till their full-scale system application and hence it is difficult to assess their reported efficiency at the user end. Many of the explored biosorbents lack important features like,

- User friendliness in terms of easy availability of raw material and their preparation method, which is important for commercializing the developed process
- Universality in terms of removing heavy metals from multiconstituent wastewater
- High efficiency in terms of volume treated within the permissible limits
- Cost effectiveness

Present investigations were intended to explore the above-defined problems with the objective of developing of biosorption process with biosorbents having the above-mentioned features. Natural materials that are available in large quantity or certain waste from agricultural and forestry practices could be potential low cost biosorbents.

MATERIALS & METHODS

OBJECTIVES OF THE STUDY

In this study Agriculture waste (Rice husk) and timber industry waste (Saw dust) were selected for the making of adsorbent. Because of their easily availability, low cost, easy preparation, handing and storage make them suitable low cost biosorbents. The removal of three metal pollutants commonly encountered in electroplating effluents namely- Chromium, Nickel and Copper has been investigated.

The objectives of this study were:

1. Preparation and characterization of biosorbents using rice husk and saw dust.
2. To explore the adsorption efficiency of different biosorbents under different experimental conditions including pH, biosorbents dose, initial metal ion concentration, contact time and temperature in batch mode experiments and in mono, binary and multi-metal systems.
3. Application of different isotherms to the generated data.
4. Desorption studies to explore the reusability of the biosorbents.
5. Removal of heavy metals from industrial effluent under optimum experimental conditions.

The experiments were carried out in batch mode to explore the biosorption properties of selected biosorbents. The various steps performed to achieve the objectives of the present study are given below:

1. Collection of raw material and preparation of biosorbents
2. Characterization of biosorbents
3. Preparation of glassware and synthetic metals solutions
4. Biosorption studies

5. Collection, characterization and bioremediation of industrial effluent
6. Application of mathematical equations and models used to generated data

Collection of raw material and preparation of biosorbents

Two biomaterials, namely: Rice husk, an agriculture waste and Saw dust, a timber industry waste were used for the making the biosorbents. Rice husk and saw dust were procured from local rice mill and saw mill, respectively located at Kurukshetra (Haryana). These two raw materials were converted into six different biosorbents as described below:

Preparation of boiled Rice husk (BRH) and boiled Sawdust (BSD)

The collected rice husk and sawdust were dried under sun and impurities were separated manually. The materials were grinded and sieved through the sieves of 300 micron size. Then they were boiled with distilled water for 5h to make them free from colored compounds and filtered. The residual materials so obtained were washed several times with distilled water till the filtrates were colourless. These materials were dried at 60^oC in hot air oven for 24h, and stored in airtight plastic containers for further use.

Preparation of formaldehyde treated Rice husk (FRH) and formaldehyde treated Sawdust (FSD)

To immobilize the color and water-soluble substances the ground rice husk and saw dust were treated with 1% formaldehyde in the ratio of 1:5 (rice husk/saw dust: formaldehyde, w/v) at room temperature (25 ± 1^oC) for 24h. The rice husk and saw dust were filtered, washed with distilled water to remove free formaldehyde and dried at 60^oC in a hot air oven for 24h. The resulting materials were ground sieved through the sieves of 300 microns size. The materials were stored in airtight plastic containers for further use.

Preparation of Sulphuric acid treated Rice husk (RHC) and Sulphuric acid treated Sawdust (SDC)

Dried rice husk and saw dust were washed with deionized water until all leachable impurities were removed. The samples were then treated with concentrated H_2SO_4 (50%) in a ratio of 2:1 (acid volume: weight of rice husk/saw dust) and allowed to get carbonized at 150^oC in hot air oven for 24h and soaked with deionized water until solution pH was stable. Afterwards, the carbon so obtained was soaked in 2% $NaHCO_3$ (w/v) till any residual acid left was removed. Finally, the samples were dried in hot air oven at 110^oC, cooled, ground and sieved in the size of 300 microns and stored in airtight containers for further use.

Characterization of biosorbents

Various equipments and instruments were used during characterization of biosorbents and batch experiments. Details are given below:

RESULTS & DISCUSSIONS

The present study mainly focused on the develop of inexpensive and effective biosorbents for removing and recovering Cr(VI), Ni(II) and Cu(II).

The optimum pH, biosorbents dose, contact time and temperature for the removal of Cr(VI) from aqueous solutions were 2.0, 4 g L^{-1}, 120 min and 25^0C respectively for all the studied biosorbents at low metal ion concentration. The efficiency of the studied biosorbents for Cr(VI) removal was in the order

SDC>RHC>FSD>FRH>BSD>BRH

The optimum pH, biosorbents dose, contact time and temperature for the removal of Ni(II) from aqueous solutions were 6.0, 20 g L^{-1}, 120 min and 25^0C respectively for all the studied biosorbents at low metal ion concentration. The efficiency of the studied biosorbents for Ni(II) removal was in the order

RHC>SDC>FSD>BSD>FRH>BRH

The optimum pH, biosorbents dose, contact time and temperature for the removal of Cu(II) from aqueous solutions were 5.0, 20 g L^{-1}, 120 min and 25^0C respectively for all the studied biosorbents at low metal ion concentration. The efficiency of the studied biosorbents for Cu(II) removal was in the order

SDC>RHC>FSD>BSD>FRH>BRH

The maximum desorption of Cr(VI), Ni(II) and Cu(II) was recorded for BRH. The desorption of the studied metal ion from the exhausted biosorbents was in the order

Cu(II)> Cr(VI)>Ni(II)

The presence of other metals had antagonistic effect on the biosorption efficiency of the biosorbents. Further the metal removal efficiency of each biosorbent was lesser in actual effluent than aqueous solutions.

The biosorption pattern of all studied biosorbents studied followed the Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm for biosorption of Cr(VI), Ni(II) and Cu(II). Kinetics results showed that all studied biosorbents for Cr(VI), Ni(II) and Cu(II) followed pseudo-second order model with determination coefficient (R^2) > 0.98.

Finally it was concluded that RHC and SDC were best biosorbents for the biosorption of studied metal ions. So rice husk and saw dust biosorbents can be attractive options for the small scale industries located in countryside. Rice husk and sawdust are readily available in developing nations, so this data can be used by small scale industries having low concentrations of Cr(VI), Ni(II) and Cu(II) in wastewater using batch or stirred-tank flow reactors where standard material, such as activated carbon, is not available.

REFERENCES

1. American Public Health Association, Standards method for the examination of water andwastewater. APHA, 1998.

2. Anandkumar, J. and Mandal, B. 2009. Removal of Cr(VI) from aqueous solution using Bael fruit(*Aegle marmelos correa*) shell as an adsorbent. *J. Hazard. Mater.* 168(2-3) 633-640.

3. Anderson, A.R., Polansky, M.M., Roginski, E.E. and Mertz, W., 1987. Factors affecting retention and extraction of chromium by yeast. *J. Agri. Food. Chem.* 26, 838-861.

4. Annadurai, A., Juang, R.S. and Lee, D.J., 2002. Adsorption of heavy metals from water usingbanana and orange peels. *Water. Sci. Technol*. 47(1),185 –190.

5. Anon, 1978. Heavy metals removal by starch Xanthate. *Prod. Finish.* 31, 72-74.

6. Aoki, T. and Munemori, M., 1982. Recovery of Chromium (VI) from wastewaters with iron (III)hydroxide-I. Adsorption mechanism of Chromium (VI) on Fe (II) hydroxide. *Water Res*. 16, 793-796.

7. Aoyama, M., Sugiyama, T., Doi, S., Cho, N.S. and Kim, H.E., 1999. Removal of hexavalent chromium from dilute aqueous solution by coniferous leaves. *Holzforschung* 53, 365– 368.

8. Aravindhan, R., Madhan, B., Rao, J.R., Nair, B.U. and Ramasami, T., 2004. Bioaccumulation of chromium from tannery wastewater: an approach for chrome recovery and reuse. *Environ. Sci. Technol*. 38 (1), 300–306.

9. Argun, M.E., 2008. Use of clinoptilolite for the removal of nickel ions from water: Kinetics and thermodynamics. *J. Hazard. Mater. 150, 587–595.*

10. Arıca, M.Y.I., Tuzun, E., Yalcın, O., Ince, G. and Bayramoglu, 2005. Utilisation of native, heat and acid-treated microalgae *Chlamydomonas reinhardtii* preparations for biosorption of Cr(VI) ions. *Process Biochem*. 40 (7), 2351–2358.

11. Armienta, M.A., Morton, O., Rodriyuez, R., Cruz, O., Aguayo, A. and Ceniceros, N., 2001. Chromium in a Tannery Wastewater Irrigated Area, Leon Valley, Mexico. *Bull. Env. Contam. Toxicol*. 66, 189-195.

12. Arslan, G. and Pehlivan, E., 2007. Batch removal of chromium(VI) from aqueous solution by Turkish brown coals. *Biores. Technol*. 98, 2836–2845.

13. Artola, A., Balaguer, M.D. and Rigola, M., 1997. Heavy Metal binding to anaerobic sludge. *Water Res*. 31, 997- 1004.

14. Athar, M. and Vohra, B.S., 1995. Heavy metal and environment, Willey Eastern Limited, New Delhi.

15. Atkinson, B.W., Bux, F. and Kasan, H.C., 1998. Considerations for application of biosorption a technology to remediate metal-contaminated industriai effluents. *Water Sci. Ass*. 24, 129- 135.

16. Aydın, H., Bulut, Y. and Yerlikaya, C., 2008. Removal of copper (II) from aqueous solution by adsorption onto low-cost adsorbents. *J. Environ. Mgmt.* 87, 37–45.

17. Bai, S.R. and Abraham, E.T., 2001. Biosorption of Cr (VI) from aqueous solution by *Rhizopus nigricans*. *Biores. Technol*. 79, 73-81.

18. Bai, R.S. and Abraham, T.E., 2002. Studies on enhancement of Cr(VI) biosorption by chemicallymodified biomass of *Rhizopus nigricans*. *Water Res*. 36(5), 1224–1236.

19. Baldry, M.G.C. and Dean, A.C.R., 1980. Copper accumulation by *Escherichia coli* strain FE12/5. 1 Uptake during batch culture. *Microb. Let.* 15, 83-87.

20. Baruhart, J., 1997. Occurences, uses and properties of chromium. *Regal Toxicol. Pharm.* 26, 3-7.

21. Basha, S., Murthy, Z.V.P. and Jha, B., 2008. Biosorption of hexavalent chromium by chemicallymodified seaweed, *Cystoseira indica. Chem. Engg. J.* 137, 480–488.

22. Bayat, B., 2002. Comparative study of adsorption properties of Turkish fly ashes. I. The case ofnickel(II), copper(II) and zinc(II). *J. Hazard. Mater*. 95, 251–273.

23. Becquer, T. Quantin, C. Sicot, M. and Boudot, J.P., 2003. Chromium ability in ultramafic soilsfrom New Caledonia. *Sci. Total Environ.* 306, 251-261.

24. Benaıssa, H. and Elouchdi, M.A., 2007. Removal of copper ions from aqueous solutions by driedsunflower leaves. *Chem. Engg. and Process.* 46, 614–622.

25. Beszedits, S. and Netzer, A., 1986. Removal of heavy metals from wastewaters. B & LInformation Service, Report, 1-29.

26. Bhainsa, K.C. and D'Souza, S.F. 2008. Removal of copper ions by the filamentous fungus, *Rhizopus oryzae* from aqueous solution. *Biores. Technol.* 99(9), 3829-3835.

27. Bhattacharya, A.K., Naiya, T.K., Mandal, S.N. and Das, S.K., 2008. Adsorption, kinetics and equilibrium studies on removal of Cr(VI) from aqueous solutions using different low-costadsorbents. *Chem. Engg. and Process.* 137, 529–541.

28. Bishop, P.L., 2002. Pollution prevention: fundamentals and practice. Beijing, Tsinghua University Press.

29. Boddu, V.M., Abburi, K., Talbott, J.L. and Smith, E.D., 2003. Removal of hexavalent chromium from wastewater using a new composite chitosan biosorbents. *Environ. Sci. Technol*. 37 (19), 4449–4456.

30. Brady, D. and Duncan, J.R., 1994. Bioaccumulation of metal cations by Saccharomyes cerevisiae. *Appl. Microbiol. Biotechnol*. 41, 149–154.

31. Brown, P, Jefcoat, I.A., Parrish, D., Gill, S. and Graham, S., 2000. Evaluation of the adsorptive capacity of peanut hull pellets for heavy metals in solution. *Adv. Environ. Res.* 4, 19–29.

32. Browning, E., 1969. *Toxicity of industrial metals.* Chapter 12, 2nd ed. Butterworths, London.,UK.Bueno, B.Y.M., Torem M.L., Molina, F. and de Mesquita, L.M.S., 2008. Biosorption of lead(II),chromium(III) and copper(II) by *R. opacus*: Equilibrium an kinetic studies. *Minerals Engg.* 21, 65-75.

33. Burnett, P.G.G., Handley, K., Peak, D. and Daughney, C.J., 2007. Divalent metal adsorption by the thermophile, *Anoxybacillus flavithermus* in the single and multi metal. *Chem. Geo.* 244, 493-506.

34. Cainelli, G. and Cardillo, G., 1984. Chromium oxidation in organic chemistry. Published by Springer-Verlag (New York) 19, 264.

35. Carvalho, D.R.P., Chong, K.H. and Volesky, B., 1995. Evaluation of the Cd, Cu and Zn biosorption in two-metal systems using algal biosorbents. *Biotechnol. Prog*. 11, 39–44.