Toxic heavy metal chromium remediation by processed low cost adsorbent-Green coconut shell

Seema Tharannum, Krishna Murthy V, Nandini.V, Shruthi.P.T

Department of Biotechnology, PES Institute of Technology, Bangalore, India
seema@pes.edu

Abstract: In recent years industrialization, consequent urbanization and increasing population, has lead to pollution of basic amenities of life air, water and soil. The major pollutants from the industrial complexes are effluents with heavy metals. Chromium is a highly toxic element and major pollutant present in the environment. Chromium (III) and (VI) are mainly found in chrome plating, dyes and pigments, leather tanning, and wood preserving. Chromium (VI) is mobile and easily soluble into cells of an organism. There are many methods like ion exchange, ultra filtration, reverse osmosis etc by which chromium (VI) can be removed but they are quiet expensive and have many other disadvantages. In our present study, natural products considered to be wastes were used as adsorbents because of its high availability and low-cost. Low cost adsorbent used was Green coconut shell in a processed form in order to compare the efficiency. This study, reports the efficiency of low cost biosorbents in remediation of chromium (VI). It is seen that the biosorbents, green coconut shell has showed high biosorption capacity as it reduced 50% of 100mg/L concentration of chromium in a span of 24 hrs. The obtained results showed that incubation time and size of adsorbent affected the uptake capacity of biosorbent. As the time increased the percentage of adsorption increased till 264 hours. Smaller the size more efficient is the adsorption capacity. Hence, low cost biosorbents can be potential agents of bioremediation of heavy metals which are toxic to all life forms especially to humans.

Key words: Biomass, Waste, Biosorption, Effluent, Industrial, Heavy metals, Toxic.

Introduction

In the wake of industrialization, consequent urbanization and increasing population, the basic amenities of life i.e. air, water and soil are being polluted continuously. Industrial complexes have become the focus of environmental pollution. The major pollutants from the industrial complexes are effluents with heavy metals. Chromium, a highly toxic element is a major pollutant present in the environment, are mainly found in chrome plating, dyes and pigments, leather tanning, and wood preserving (Anyakora et al., 2011). Chromium (Cr) is a heavy metal that can exist in six valence states, 0, II, III, IV, V and VI, which represent the number of bonds an atom is capable of making. Trivalent (Cr-III) and hexavalent (Cr-VI) are the most common chromium species found environmentally. Trivalent is the most stable form and its compounds are often insoluble in water. Hexavalent Chromium is the second most stable form, and the most toxic. Many of its compounds are soluble. Most chromium VI in environment is due to anthropogenic activities. Occupational exposure is via inhalation. Cr (III) is poorly absorbed, whereas Cr (VI) is readily absorbed.. Exposure to chromium leads to nasal irritation, nasal ulcers, and perforation of nasal septum and hypersensitivity reactions and chronic holes of the skin (Holmes et al., 2008). World Health Organization and Indian Standard Institution has the desirable limit for Cr (VI) in drinking water is 0.05mg/L and With reference to Central pollution control board, the allowable chromium concentration in effluents is 2.0-5.0 mg/L. The techniques conventionally used for removal of heavy metals from contaminated sites include: reverse osmosis, electro dialysis, ultra filtration, ion-exchange, chemical precipitation, phytoremediation, etc. Each of these methods has its own merits and demerits (Hima et al., 2007) the methods suggested are being time consuming and needs expertise. Bioremediation is a process of removal of toxic metals using living organisms. Bioaccumulation is the widely used bioremediation technique which involves the accumulation of heavy metals in the organism. Though the technique is widely used, has its own pros and cons. Biosorption is a physicochemical process that occurs naturally in certain biomass which allows it to passively concentrate and bind contaminants onto its cellular structure. The most frequently studied biosorbents are Bacteria, Fungi and Algae. But more recently, the search for new cost effective biosorbents has directed attention and natural sorbents which can effectively remove toxic metals (Senthilkumar et al., 2000). A successful biosorption process requires preparation of good biosorbent. The process starts with selecting various types of biomass. Pretreatment and immobilization are done to increase the efficiency of the metal uptake. The adsorbed metal is removed by desorption process and the biosorbent can be reused for further treatments (Hima et al.,2007). In our study, biomass of Green coconut shell considered as waste and disposed to the environment without any further usage, was used as adsorbent because of its high availability and low-cost.

Materials and Method

Sampling

The adsorbent Green coconut shell waste was collected from coconut vendors , sun dried for 2 days and was blended in a mixer. The blended powder was sieve separated on the basis of particle size of 719 microns and 250 microns and pre treated with 0.1 M NaOH for 3 hours and then washed with distilled water to remove the traces of NaOH(Rosa et al.,2010).The sample was filtered and then dried at 50°c in Hot air oven .

Estimation of Chromium (VI)

Chromium estimation was carried out by spectrophotometric method using Diphenylcarbazide (APHA 2005). Chromium (VI) was determined colorimetrically by reaction with diphenylcarbazide in acid solution. A pink colour complex was formed, absorbance was read at 540nm. Chromium standard of 100mg/L was prepared using potassium di chromate. Optical density of known standard samples was recorded and Graph of absorption versus amount of chromium (µg) was plotted.

Batch Studies

The batch studies were carried in 250ml conical flasks at Room Temperature (RT) by shaking at an interval of two hours. 0.5g of biosorbent Green coconut shell waste was mixed with 100ml of standard chromium solution(100mg/L) in 250ml conical flask. After a known contact period of 24, 48, 72, 96 hours (h), 0.5ml of solution was collected from conical flask and centrifuged at 6000rpm for 5 minutes at 4°c. The supernatant thus collected was estimated for chromium by DPC method (Shankar Congeevaram., 2006). Adsorption studies were conducted in triplicates.

Column Studies

A borosilicate column (21cm X 2.2cm) was filled with adsorbent Green coconut shell waste corresponding to 3cm bed heights. The adsorbent was initially heated with distilled water to 80°C to remove the lipids. The bed was then filled with 10ml of chromium solution (100mg/L). After a known contact period of 24, 48, 72, 96 hours (h), 0.5ml of solution was collected and estimated for chromium by DPC method The amount of chromium before and after adsorption was determined by DPC method.

Results and Discussion

Sampling

The Green coconut shell samples of different sized particles obtained by sieve method were collected processed and stored at room temperature for analysis.

Estimation of Chromium(VI)

The hexavalent chromium was determined calorimetrically by reaction with diphenylcarbazide in acid solution. Absorbance at 540nm was found to increase as the as the chromium concentration increases. The results are as plotted in Figure 1.

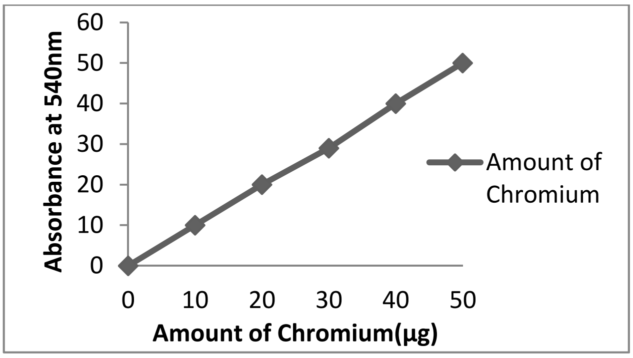

Figure1: Standard Chromium curve by DPC method.

Batch Studies

The amount of chromium decreased from day 1 to day 8. Sample of particle size 719 microns was found to adsorb 90mg of chromium from the solution, whereas, that of particle size 250 microns was found to remove chromium completely from the solution on day 8. Comparisons of amount of chromium in the solution with both the particle sizes are as depicted in Figure 2 (2a and 2b)

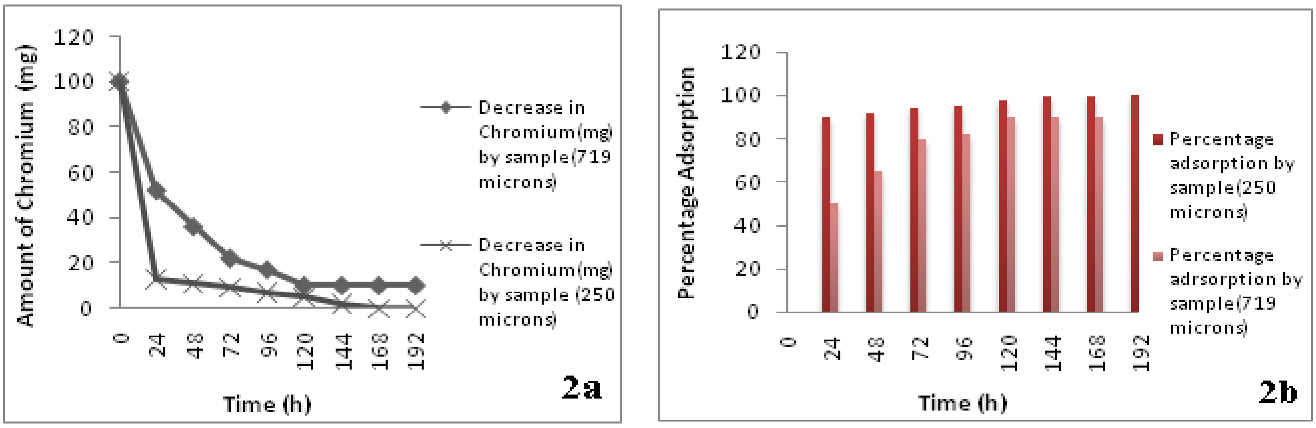

Figure 2: Effect of Particle size on Adsorption in Batch studies 2a: Chromium removal capacity of green coconut shell. 2b: Percentage adsorption of green coconut shell

Column Studies

The amount of chromium was found to reduce gradually and total amount of chromium was to be absorbed in 30h. Sample of particle size 250 microns was found to adsorb chromium completely in a short contact time(42h), whereas, the same of particle size 719 microns showed 100% adsorption by the end of 48h. percentage adsorption by sample of both particle sizes are compared in Figure 3 (3a and 3b).

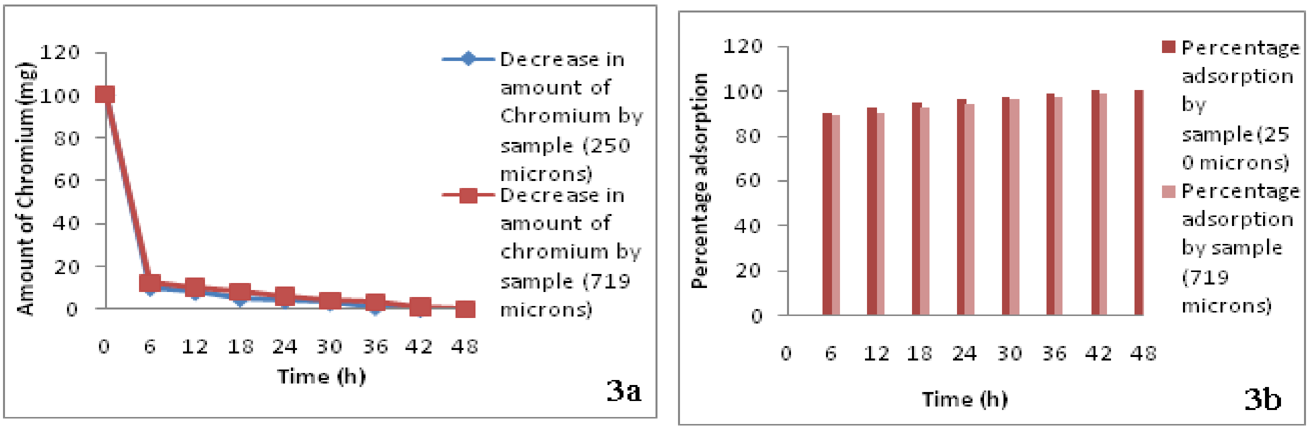

Figure 3: Effect of Particle size on Adsorption in column studies 3a: Chromium removal capacity of green coconut shell. 3b: Percentage adsorption of green coconut shell

SEM and EDS Analysis

Scanning electron microscope evaluated the morphological characteristics of coconut. The micrographs of coconut shell powder before metal uptake and the respective EDS (Energy Dispersive Spectroscopy) analyses are presented in Fig 4a and 5 respectively. Fig 4b and 6 show the same for coconut shell after chromium uptake.

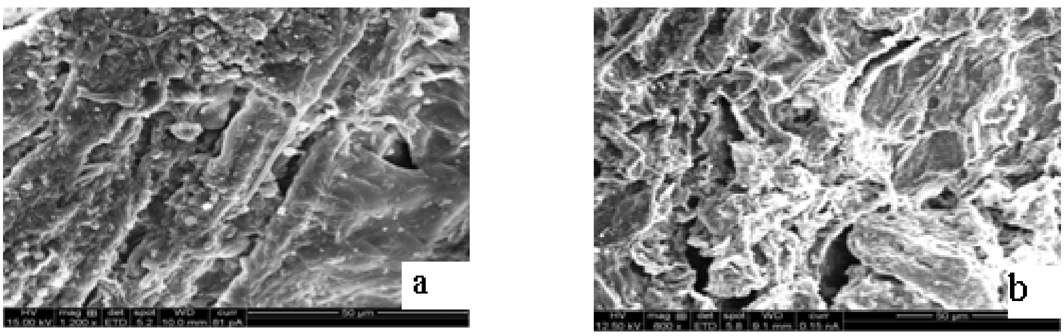

Figure 4: Scanning electron micrograph of coconut shell a) Before and b)after Cr biosorption.

Figure 4 a shows a quite irregular and porous material. This surface characteristic would be substantiating the high adsorption observed for particles of larger size, through mass transport inside the sorbent. Figure 4 b shows no significant difference between the surface of particles loaded with metal ions and the particles that does not suffer the biosorption process .

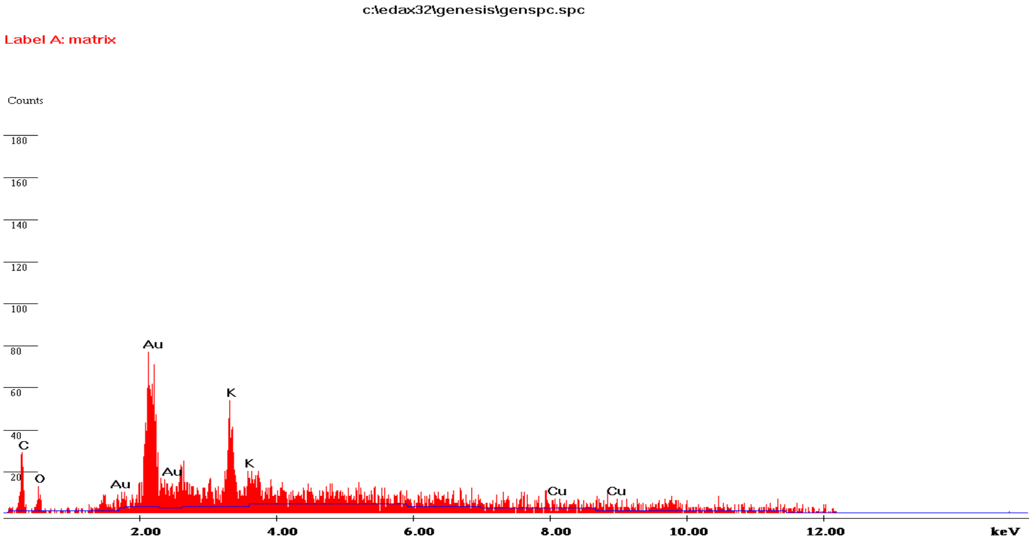

Figure 5: EDS diffractogram of micrographs of coconut shell before Cr uptake.

The EDS analysis presented in Figure 5 shows the presence of Cu, K, O and C as natural species on the coconut shell, as already expected. The presence of these elements could influence on the adsorption mechanism thought ionic exchange interactions.

The EDS analysis in the particle loaded with chromium presented in Figure 6, shows the presence of chromium bands, and the absence of Ca, K, Na, O and Mg bands. This could be indicative of ionic exchange mechanism involvement between these elements and Cr on the surface of particles. The band of Au appears in the EDS, a time that the metalizing of the samples was carried through with this element.

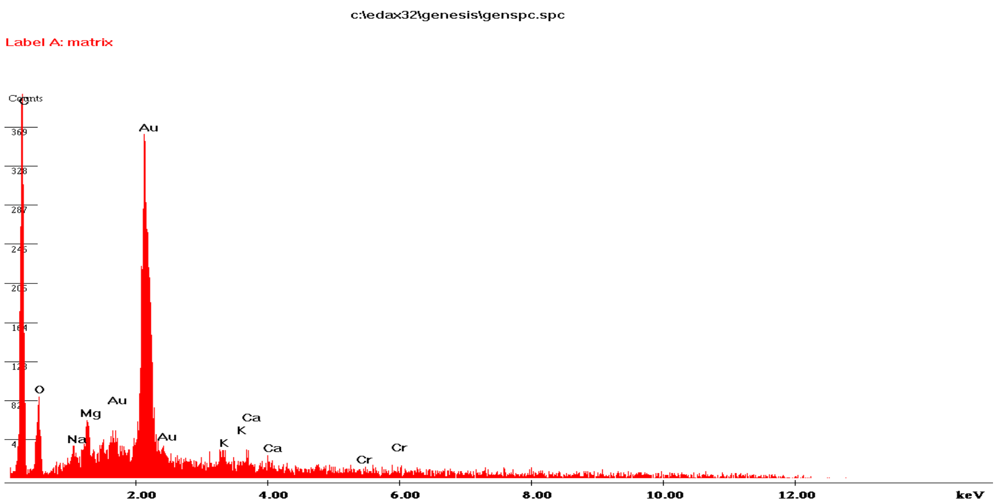

Figure 6:EDS diffractogram of micrographs of coconut shell after Cr biosorption.

Conclusions

The study establishes the role of low cost adsorbent like green coconut shell in biosorption, accumulation and remediation of chromium (VI). Heavy metals can be toxic to all the life forms especially to humans due to their strong affinity to form complexes with the constituents of cell membrane, causing impairment of their functions and loss of integrity. However, low cost adsorbents can be potential agents for bioremediation of heavy metal pollution.
The study when conducted in batch revealed that capacity of green coconut shell to biosorb the heavy metal chromium (VI). Sample G showed to absorb 50% of chromium with an incubation of 24h and 90% adsorption in 144hrs.

The results obtained showed that incubation time affected the uptake capacity of biosorbent. As the time increased the percentage of adsorption increased till 264 hours. Another important parameter was the influence of the particle size (719 and 250 microns) used to uptake chromium. It showed increase in chromium adsorption with decrease of particle size of biomass. Later, a column study was performed in which Sample G and was found to adsorb maximum amount of chromium. So finally, green coconut shell powder of 250 microns showed better results than 719 microns. The analyses accomplished by MEV-EDS proved the presence of chromium in the biomass particles i.e green coconut shell powder after biosorption. The micrographs obtained show a quite irregular and porous material. This surface characteristic would be substantiating the high adsorption observed for particles of larger size, through mass transport inside the sorbent.

Acknowledgements

The authors wish to thank management, PES Institute of Technology, Bangalore for providing research facility to carry out present work.

References

Ahalya N, T.V. Ramachandra, RD Kanamadi(2003). Biosorption of heavy metals: Review. *Research journal of chemistry and environment*, Vol 7(4): 71-79.

Ahmed Ahmed Gaballa, Ranya Amer, Hany Hussein, Hassan Moawad and Soraya Sabry(2003). Heavy metal resistant pattern in moderately halophilic bacteria. *Arab Journal of biotech.*Vol2:267-278

Aksu Z and Acikel U. (2000). Modelling of a single-staged bioseparation process for simultaneous removal of iron (III) and Chromium(VI) by using Chlorella vulgaris. *Biochem Eng. J*, 4:229-238.

Alice Wang and Kevin Lin(2001). Effects of N-Acetylglucosamine and alpha methylglucoside on bacteriophage T4adsorption of E.coli B23.*Journal of Experimental Microbiology and Immunology (JEMI)* .Vol. 1:54-63

Alok Prasad Das and Susmita Mishra(2010). Biodegradation of the metallic carcinogen hexavalent chromium (VI) by an indigenously isolated bacterial strain. *Journal of carcinogenisis*. Vol 9:1-7.

Ansari M I and Mallik A. (2007). Biosorption of nickel and cadmium by metal resistant bacterial isolates from agricultural soil irrigated with industrial wastewater. *Bioresource Technol*, 56(6):3149-3153.

APHA: Standard methods for the examination of water and wastewater. 21st Edn. Washington, D.C. (2005).

Asha Latha Singh(2007).Removal of Chromium from waste water with the help of microbes. e- journal of science and technology.21:361-370.

Bai, R. S., Abraham, T. E., (2001). Biosorption of Cr(VI) from aqueous solution by *Rhizopus nigrificans*. *Bioresources Technology.*, 79: 73-81.

Chimezie Anyakora, Kenneth Nwaeze, Olufunsho Awovedele, Chinwe Nwadike, Mohsen Arbabi and Herbert coker (2011). Concentrations of heavy metals in some pharmaceutical effluents in Lagos, Nigeria. *Journal of Environmental Chemistry and ecotoxicity*, Vol 3, No. 2: 25-31.

Deans J R and Dixon B G. (1998). Uptake of Pb2+and Cu2+ by novel biopolymers. Wat. Res,26:469-472.

Emine Malkov and Yasar Nuhoglu(2007). Potential of tea factory waste for chromium(VI) removal from aqueous solutions:thermodynamic and kinetic studies. *Journal of separation and purification technology*, Vol 54:291-298.

Francisco W.Sousa, Andre G.Oliveira, Jefferson P.Ribeiro, Morsyleide F.Rosa, Denis Keukeleire, Ronaldo F.Nascimento (2010). Green coconut shells applied as adsorbent for removal of toxic metal ions using fixed bed column technology. *Journal of environmental management,* Vol 91:1634-1640.

Gabriela Huama Pino, Luciana Maria Souza de Mesquita,Mauricio Leonardo Torem, Gustavo Adolfo Saavedra Pinto (2006). Biosortion of Cadmium by green cocnut shell powder. *Journal of Mineral engineering*, Vol 19:380-387.

Gadd G M. (1990). Heavy metal accumulation by bacteria and other microorganisms *Experentia. Biochem Eng. J*, 46:834-840.

Guixia Zhao, Xilin Wu, Xiaoli Tan and Xiangke Wang. (2011). Sorption of Heavy metal ions from Aqueous Solutions: A Review. *The Open Colloid Science Journal*, 4: 19-31.

Hima Karnika Alluri, Srinivasa Reddy Ronda, Vijaya Saradhi Settalluri, JayakumarSingh(2007). Biosorption: an ecofriendly alternative for heavy metal removal. *African jounal of biotechnology*, Vol 6, No. 25:2924-2931.

Holmes A.L., Wise S S and Wise J P(2008). Carcinogenicity of hexavalent chromium. *Indian journal of medical research*. Vol 128:353-378.

Jianlong Wang, Can Chen(2008).biosorbents for heavy metals removal and their future. *Journal of biotechnology advances.*Vol 22:196-222.