Journal of Scientific Research
Vol. XXXIX No. 2, December, 2009

ISSN 0555-7674

"BIOSORPTION OF CHROMIUM (VI) A LOW COST MILLING AGRO WASTE BLACK GRAM(CICER ARIENTENUM) HUSK BY FLASH COLUMN PROCESS."

Dania Ahmad *, Mukhtar-ul-Hassan , , Hafiza Naila Khalid , Sara Khatoon, Nadia Jamil, Hafza Bushra Fatima.
Institute of Chemistry, University of the Punjab, Lahore Pakistan.

Abstract: Black Gram husk, a very common milliing agro-waste proved to be the best adsorbent for the removal of Chromium (VI).Cr(VI) removal was studied on Black gram husk bgh by Flash Column process. Different parameters i.e. particle size of (bgh), column length, column width, and concentration of metal solution were studied. A comparative study of modification of adsorbent was also done for which bgh was modified with EDTA, acids, bases, and volatile organic solvents. Modified adsorbents showed a decrease in adsorption capacity. EDTA modified, base modified and ash of adsorbent (bgh) proved to be the poor adsorbents for metal ions. Polar volatile organic solvent modified adsorbent showed a greater adsorption efficiency for Cr (VI). Acid modified adsorbent also proved good adsorption efficiency. The black gram husk (bgh), which is a readily available low cost milling agro waste, proved to be suitable for biosorption of Cr (VI) in aqueous solution The biosorption characteristics fit well with Langmuir and Freundlich isotherm.

KEYWORDS: Black gram husk (bgh), Chromium(VI), Adsorption. agrowaste Langmuir isotherm, Freundlich isotherm

Introduction:

The discharge of heavy metals into surface waters has become a matter of concern in Pakistan over the last two decades. These contaminants are introduced into surface waters through various industrial operations [1]. The pollutants of concern include lead, chromium, zinc, and copper. Heavy metals such as zinc, lead and chromium have number of applications in basic engineering works, paper and pulp industries, leather tanning, petrochemicals fertilizers, etc. The hexavalent and trivalent chromium is often present in electroplating wastewater [2].

Heavy metal remediation of aqueous streams is of special concern due to recalcitrant and persistency of heavy metals in environment. Heavy metals are natural components present in earth's crust. Heavy metals are the elements that exhibit metallic properties, which would mainly include the transition metals, some metalloids, lanthanides, and actinides. They can not be degraded or destroyed. Some heavy metals are might be essential for body as micronutrients i.e. copper, zinc, selenium, manganese, cobalt, etc. but most of them are hazardous, as they can lead to poisoning**.** These heavy metals are of much concerned for their hazardous effects which tend to bioaccumulate, which means the increase in the concentration of chemical in the body of the organisms as compared to the environment.

Chromium exists primarily in Trivalent [Cr (III)] or Hexavalent [Cr (VI)] oxidation states**.** It is a toxic compound, in particularly in its h6xavalente form, it constitutes a major pollutant of various industrial effluents. It results from its

1-For Proof and Correspondence: **Dania Ahmad**

various uses a harmful significant polluting load for both human and environment. The over-exposure with chromium dust leads to irritations with the deterioration of the skin and possibly to a wide breathing and probably with the cancer of the fabric epithelium of the lungs [3]

Chromium has number of applications in basic engineering works, paper and pulp industries, leather tanning, petrochemicals fertilizers, etc. The hexavalent and trivalent chromium is often present in electroplating wastewater .Other sources of chromium pollution are leather tanning, textile, metal processing, paint and pigments, dyeing and steel fabrication. Lead is used as industrial raw material in the manufacture of storage batteries, pigments, leaded glass, fuels, photographic materials, matches and explosives [4]

The conventional methods for treatment of lead and chromium wastes include: lime and soda ash precipitation, adsorption with activated carbon, ion exchange, oxidation and reduction, fixation or cementation. These methods are economically unfavorable or technically complicated, and are used only in special cases of wastewater treatment [5]

Biosorption of heavy metals from aqueous solutions is a relatively new technology for the treatment of industrial wastewater. Adsorbent materials derived from low cost agricultural wastes can be used for the effective removal and recovery of heavy metal ions from wastewater streams. The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials.[6] [7]

Natural low cost material that have been studied for the removal of Chromium(VI) by adsorption include rice straws [8], eucalyptus bark, black gram husk[9], sugarcane bagasse[10] The functional groups present in agricultural waste biomass viz. acetamido, alcoholic, carbonyl, phenolic, amido, amino, sulphydryl groups etc. have affinity for heavy metal ions to form metal complexes or chelates. Elucidation of mechanisms active in metal biosorption is essential for successful exploitation of the phenomenon and for regeneration of biosorbent materials in multiple reuse cycles. [11]

Materials and methodology

Process involved is column type-continuous flow adsorption operation. Experiments were carried out to investigate the parameters for the optimization of the extraction of Pb(II) from the sample solution by using Balance ER-120A (AND), Perkin Elmer Analyst 100 Atomic Absorption Spectrometer, Electrical crusher 8800 rpm Jimo disc mill model15, Mechanical Stirrer , Suction pump two stage by EDWARDS. Ac motor BS 5000-Electric Grinder.

Preparation of Adsorbent

Adsorbent used in this experiment work was Black Gram (Cicer *arientenum)* husk, which was taken; cleaned and dried. It was then grinded in an electric crusher to obtain homogeneous grinding. Ground husk was passed through fine sieves to obtain fine mesh size particles.

Preparation of solutions

2.82 g of $K_2Cr_2O_7$ was dissolved in small amount of distilled water and the volume was reused up to mark in a 1000 ml measuring flask with distilled water. This was the 1000ppm solution of Potassium dichromate that was used as a stock solution . successive dilutions were made to obtain standards.

General procedure:

Column was filled with adsorbent up to 15 cm of height , a suction was applied to the vacuum flask in which column was fixed. 200 ml standard solution of 50 ppm concentration was passed through the column, elution time was 2 hrs .and drawn into the vacuum flask. Percentage adsorption of Cr(VI) was measured by estimating remaining amount of Chromium(VI) in the sample by Atomic Absorption Spectroscopy (AAS). Experiment was performed for various parameters and for modified adsorbent under same conditions.

Selection of best adsorbent

Different adsorbents i.e. rice straw, eucalyptus bark, black gram husk, wheat bran, sumble shells were filled to the column up to same height i.e. 15 cm. All the adsorbents were taken in the size range of 30-40 mesh. 200 ppm solution of potassium dichromate was passed through the column containing adsorbent. The suction was applied through a suction pump to the vacuum flask to draw all the solution from the column. Percentage adsorption was calculated for each adsorbent by estimating remaining concentration of Cr (VI) in filtrate by AAS

Selection for mesh size of adsorbent

Black gram husk was ground for particle sizes 50-80 mesh, 40-50 mesh, 30-40 mesh, & 16-30 mesh. The adsorbent was cleaned and dried. The column was filled up to 15 cm with each mesh size. The solution was passed through the column and drawn into the vacuum flask by applying suction to the flask. The process was done for each mesh size The percentage adsorption was calculated by estimating the amount of Cr(VI) remaining in the filtrate by Atomic Absorption Spectroscopy(AAS).

Concentration of adsorbate:

Standard solutions of Potassium dichromate $K_2Cr_2O_7$ was prepared in the concentration range of 10 ppm 70 ppm . 200ml of each concentration was taken for sample preparation. Column was filled with the adsorbent of size 30-40 mesh up to 15 cm . Solution was passed through the column and drawn to the vacuum flask by applying a suction t o the flask. The elution time was kept same by suction pump. The percentage adsorption was calculated by estimating the amount of Cr(VI) remaining in the filtrate by Atomic Absorption Spectroscopy

Study of Acid modification of adsorbent:

To study the effect of acid modification on black gram husk it was treated with same conc.of different acids. Standard solutions of different acids of 1M concentrations were prepared (i.e. HNO_3, H_2SO_4, Citric acid). Equal amounts of adsorbent were soaked into each of these acid solutions for 3 hours. Then these adsorbents were filtered and dried at room temperature. After drying these adsorbents were washed thoroughly with distilled water maintaining the pH their filtrate equal to normal. Then they were dried at room temperature. The adsorbents were filled into the column up to 15 cm .Samples were obtained for each of them by passing 200 ml of $K_2Cr_2O_7$ of 50ppm concentration through column fixed in a vacuum flask with an attached suction. The %age adsorption was calculated by estimating the remaining amount of Cr(VI) into the filtrate by Atomic Absorption Spectroscopy.

Study of Base modification of adsorbent;

To study the effect of base modification on adsorption capacity of bgh, it was treated with same conc. of different bases. Standard solutions of 1 M concentration of different bases (i.e., NaOH, KOH, and NH4OH) were prepared. The adsorbents were soaked in 500ml of each base separately for 3 hours. After soaking filtered and dried at room temperature. Then these dried adsorbents were washed thoroughly with distilled water to maintain the pH of filtrate equal to normal, and dried at room temperature. These base modified adsorbents were filled separately in the column up to 15cm height, and 200 ml solution of 50ppm concentration of $K_2Cr_2O_7$ was passed through the column which was fixed in a vacuum flask with an attached suction pump. The %age adsorption was calculated by estimating the remaining concentration of Cr(VI) in the filtrate by Atomic Absorption Spectroscopy.

Study of modification of adsorbent with volatile organic solvents:

To study the adsorption capacity change in bgh by modification with volatile organic solvent, it was treated with different organic solvents. Organic solvents like $CCl_{4,}$ n-hexane, 50% V/V ethyl alcohol and methyl alcohol, acetone, ethyl acetate were used for the modification. The adsorbents of equal amounts were soaked in the solvents in the beaker and covered them with Aluminum foil for 3 hours. Solvents were evaporated at room temperature, and then filled in the column to check the adsorption of metal. The column was filled up to a height of 15cm fitted in a vacuum flask with an attached suction pump. 200 ml of 50ppm conc. Solution of $K_2Cr_2O_7$ was passed through the column, and the %age adsorption was calculated by estimating Cr(VI) amount in filtrate by Atomic Absorption Spectroscopy.

Study of Modification of Adsorbent with EDTA:

To study the effect on the adsorption capacity of bgh by modification with a comlexing agen it was treated with with EDTA.0.1M solution of EDTA was prepared by dissolving 37.2 g /1000ml of water. Adsorbent (bgh) was soaked into 500 ml of this EDTA solution for 24 hrs. Then filtered and dried at room temperature. This modified adsorbent was filled into the column up to 15 cm. 200 ml of standard solution of $K_2Cr_2O_7$ of concentration 50 ppm was passed through the column and drawn into the vacuum flask with which a suction was attached. %age adsorption was calculated by estimating the remaining concentration of Cr(VI) in the filtrate by atomic Absorption Spectroscopy (AAS).

Results and Discussion

The graph between concentration of Cr(VI) and the absorbance showed that there was gradual increase in the absorbance of the solution with increasing concentration of CR(VI) ions in the solution.

The results revealed that straight line graph verified Beer-Lambert law as shown in fig are 1.

Among five different adsorbents black gram husk proved to be the best biosorbent for Cr (VI) showing 85.01% adsorption as shown in fig-2.The fact involved is that Cr (VI) ions showed greatest affinity towards the binding sites of black gram husk as compared to active sites of other adsorbents used .

The minimum mesh size showed the best results i.e. the maximum adsorption of the metal from the sample solution. It may be so because the equal quantity of different mesh size provides different number of particles and thus different surface area and binding sites. Larger particles provide minimum number of binding sites exposed to the solution molecules and the smallest particle size provides largest surface area and more binding sites are available for metal ions to get bind. This can be shown in the fig 3.

Initial conc. of metal ion conc. trend revealed that sorption capacity of Black gram husk increases by increasing initial metal ion concentration. This is due to the fact that in case of low concentration of metal ion solution there are, no doubt, more activated sites available for metal ions to adsorb on it but the equilibrium b/w the metal ions and the adsorbent's active sites sets up very soon and metal solution do not release more dichromate ions $(Cr_2O_7)^{-2}$ to adsorb on metal surface. As we increase metal ion concentration there are metal ions available to adsorb on the surface the %age adsorption increases in this way up to a certain concentration where all the active sites are saturated with adsorbed metal ions i.e. at 50 ppm concentration maximum adsorption efficiency was observed.

When the concentration was further increased there is a trend of decreasing adsorption. The reason for this is at high concentration of metal ions there is a competition between the metal ions to adsorb on the active sites of the adsorbent because less number of active sites is available as compared to the metal ions so there is a decrease in adsorption efficiency at higher concentrations of metal ions.

The results of acid modification of bgh showed that adsorption was affected by the presence of anions of acid i.e. NO_3^-, SO_4^{-2}, Cl^-, maximum adsorption among these modified adsorbents was adsorbed in nitric acid modified adsorbent and very less in citric acid it means that when these are modified with the acid the adsorbent surface become protonated and when metal solution was passed to adsorb it should be adsorbed more rapidly because Cr(VI) adsorbs on the adsorbent surface as dichromate $(Cr_2O_7)^{-2}$ ions but there is also a competition between metal ions and anions of acid so there are less number of active site for metal ions to bind with as compared to simple adsorbent (not modified) .

Results showed that base modified adsorbents showed zero efficiency to adsorb Cr(VI) on their surface. The functional groups present on the adsorbent surface highly favour the attachments of anions on its surface. When the adsorbent is treated with base Hydroxyl groups OH^- are attached to the active sites and saturate them leaving no binding sites available for metal ions attachment. When metal solution is passed through it OH^- ions are more competitive to remain attached with the surface of adsorbent and there is almost no attachment of metal ions to the surface of base modified adsorbent All three bases which were used to modify the adsorbent showed same behaviour where NH_4OH is a weak base but it also showed the same behaviour as other two strong bases showed .So there is a negative effect on %age adsorption of metal Cr(VI) on the base modified Black gram husk. Base modified Black gram husk showed zero adsorption efficiency for Cr(VI) due to high binding affinity with OH^- ions.

Results showed that nonpolar solvents showed no effect on the adsorption efficiency of metal ions on the surface of adsorbent. The reason is non-polar solvents do not affect the binding sites of the adsorbent and the %age adsorption was same as for the non modified adsorbent. But as the solvent tends to be polar it increases the adsorption efficiency of metal on the surface of adsorbent. This is not in the case of other metals because most of the other metals tend to adsorb on the surface as cations while Chromium (VI attaches to the surface of the adsorbent as anionic form i.e. in dichromate $(Cr_2O_7)^{-2}$ form. So ester group favors the attachment of Cr(VI) on the surface of adsorbent , hence shows a positive adsorption effect for %age adsorption of Cr(VI) on the surface of Black gram husk.

Conclusions

Fig-1: Verification of Beer- Lambert law

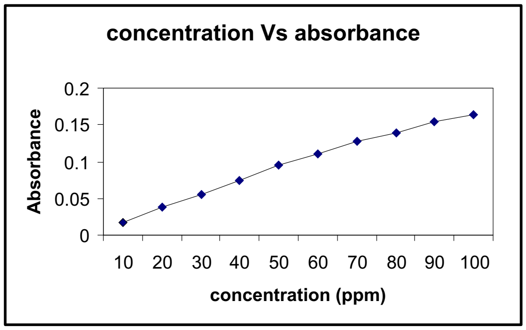


Fig-2: Selection of adsorbent

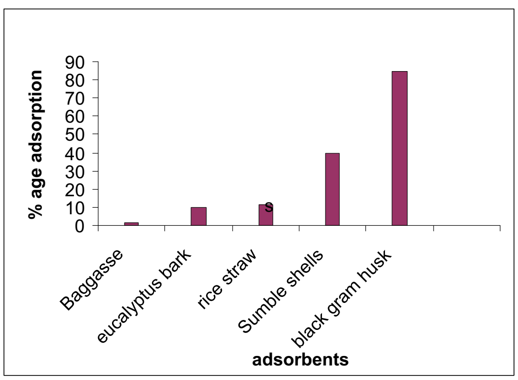


Fig-3: Effect of particle size of Adsorbent (Black gram husk);

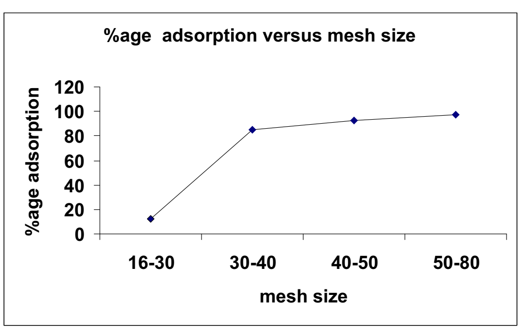


Fig-4: Effect of concentration of metal ions:

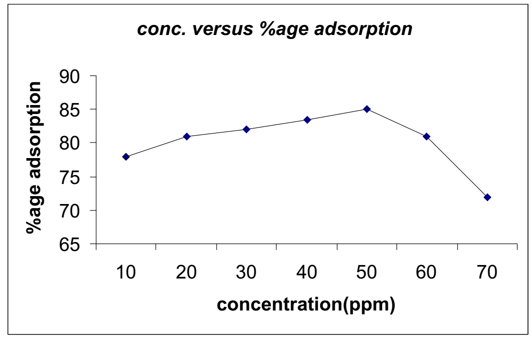


Fig.5: Effect of Acid modification on Adsorption:

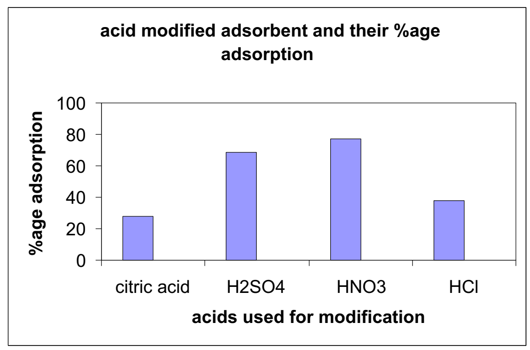
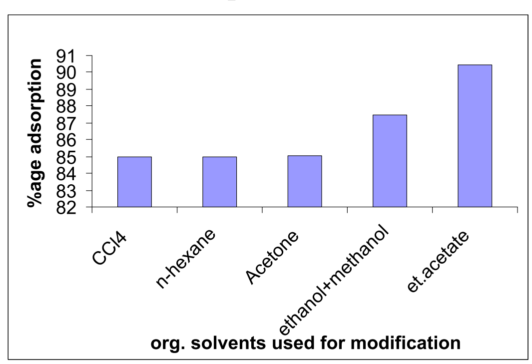


Fig. 6: Effect of base modification on Adsorption:

Sr. no.	Base for modification	%age adsorption
1	NaOH	0
2	KOH	0
3	NH_4OH	0

Fig-7: Effect of modification by organic solvents on adsorption



Adsorption isotherms:

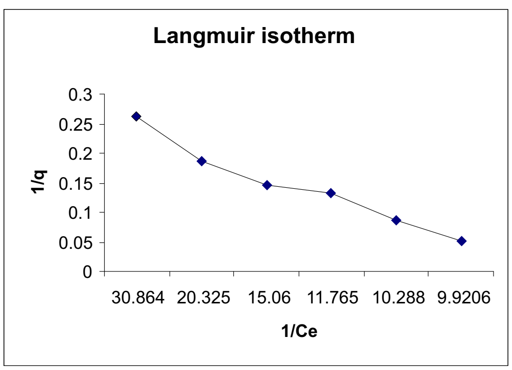
The Langmuir and freundlich isotherms were plotted according to equations 1 and 2

$$q = Q_{max}\ bCe\ /1+bCe \qquad (1)$$

$$q = K_f\ (Ce)^{1/n} \qquad (2)$$

Where q (mg/g) is the amount of metal adsorbed per unit mass of adsorbent and Ce (mg/L)is the equilibrium concentration of adsorbate in solution after adsorption .Qmax (mg Cr/g black gram husk) and b (Langmuir adsorption coefficient, a constant) are Langmuir parameters. K_f is the Freundlich adsorption coefficient.

The Langmuir and Freundlich isotherms are shown below respectively and the corresponding parameters are given in following table.



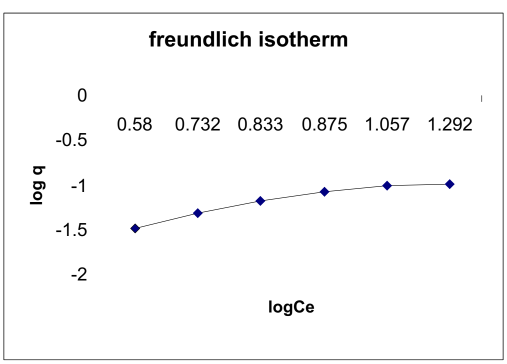


Table :

Langmuir and Freudlich adsorption isotherm parameters

Langmuir parameters			Freundlich parameters		
Q_{max} (mg Cr /g black gram husk)	b	R^2	1/n	Kf	R^2
1666.6	0.068	0.91	0 .098	0.03	0.91

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