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"BIOSORPTION OF AQUEOUS LEAD (II) ON RICE STRAWS (ORYZA SATIVA) BY FLASH COLUMN PROCESS."

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Abstract: Biosorption of Pb (II) on rice straws has been studied with the variation in the parameters and on modified rice straws by flash column process. Different parameters like particle size of adsorbent, initial concentration of metal ions, length and width of columns were studied.A comparative study of modification of adsorbent was also done for which rice straws were modified with EDTA ,acids, bases, and volatile organic solvents..Base modified adsorbents have shown an increase in adsorption capacity while acid modified adsorbents proved to be the poor adsorbents for metal ions .similarly ash of rice straws used as adsorbent given higher adsorption and EDTA modified adsorbents have shown least adsorption of metal ions. Polar volatile organic solvents modified adsorbent gave less adsorption efficiency and non polar adsorbent shown no influence on Pb (II) uptake capacity of rice straws. Rice straws proved to be the best biosorbent for Pb(II) in aqueous solution. The biosorption characteristics fit well with Langmuir and Freundlich isotherm.

Key words: Rice straws, Lead (II), Adsorption, Langmuir isotherm, Freundlich isotherm

Introduction:

Our bodies are exposed to the heavy metals which came from the earth's crust. They are introduced in to the biological circle through drinking water, food and air .some of the heavy metals are essential for the metabolism of the human bodies but majority of them are poisonous in greater concentrations. Heavy metals are dangerous as they bio accumulate. Bioaccumulation occurs when an organism absorbs a toxic substance at a rate greater than that at which the substance is lost (metabolize or excreted). Thus, longer the biological half life of the substance, the greater is the risk of chronic poisoning, even if environmental level of the toxins is very low[1]. Lead is considered as one of the top sixteen toxic pollutants because of its carcinogenic characteristics for humans[2].

Lead is a major constituent of the lead-acid battery used extensively in car batteries. Lead is used as a coloring element in ceramic glazes, notably in the colours red and yellow. Lead is used as projectiles for firearms and fishing sinkers because of its density. Lead is used in some candles to treat the wick to ensure a larger, more even burn. Lead is used as shielding from radiations. Molten lead is used as coolent . Lead glass is composed of 12 - 28% lead oxide. It changes the optical characteristics of glass and reduces the transmission of radiation . Lead is the traditional base metal of argon pipes, mixed with varying amounts of tin to control the tone of the pipe. Lead is used as electrodes in the process of electrolysis.[3]

The commonly used procedures for removing metal ions from aqueous streams include chemical precipitations, lime coagulation, ion exchange, reverse osmosis and solvent extraction [4].

The disadvantages like incomplete

removal, high reagent cost and energy requirements, generation of toxic sludge or other waste products that required careful disposal have made it imperative for a cost effective treatment method that is capable of removing heavy metals from aqueous effluents. Adsorption, ion-exchange and chromatography are the sorption processes in which certain adsorptives are selectively transferred from the fluid phase to the surface of particles suspended in a vessel or packed in a column. Similar to surface tension, adsorption is a consequence of surface energy.

Natural low cost material that have been studied for the removal of lead by adsorption include rice straws[5], eucalyptus bark[6], black gram husk[7], sugarcane bagasse[8] and wheat bran.

The toxicity of lead is probably related to its affinity for cell membranes and mitochondria, as a result of which it interferes with mitochondrial oxidative phosphorylation and sodium, potassium, and calcium ATPases. Lead impairs the activity of calcium-dependent intracellular messengers and of brain protein kinase C. In addition, lead stimulates the formation of inclusion bodies that may translocate the metal into cell nuclei and alter gene expression[9]. The present work investigates the possible use of rice straws powder as biosorbent for the industrial effluent treatment.

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 removal 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 model ….15., Mechanical Stirrer , Suction pump two stage by EDWARDS. Ac motor BS 5000- Electric Grinder.

Preparation of Adsorbent:

Biomass collection (Rice straws);

After collecting the straws of rice plant, they were chopped into small pieces, washed with distilled water and dried at room temperature for several days. Dried sample biomass was grinded by electric crusher to obtain homogenous grinding. Grinded rice straws were passed through fine sieves to obtain fine mesh size particles.

Preparation of solutions;

1000 $\mu g.ml^{-1}$ of lead solution was prepared by dissolving 1.oog metallic Lead in 2.5 ml of concentrated nitric acid and diluted the resulting solution to1000 ml with demineralized water. Successive dilutions of stock solutions were carried out to set up standard solutions ranging 10-70 $\mu g.ml^{-1}$.

General procedure used for biosorption studies;

Adsorbent was filled into the column (containing small amount of glass wool at the bottom) up to 18 cm of height, a suction was applied to the vacuum flask (by suction pump) in which column was fixed .300 ml standard solution of 50 $\mu g.ml^{-1}$ concentration was passed through the column, elution time was 2 hrs. and drawn into the vacuum flask. Percentage adsorption of Pb(II) was measured by estimating remaining amount of Lead in the sample by Atomic Absorption Spectroscopy (AAS). Experiment was performed for various parameters and for modified adsorbent keeping the conditions same.

Selection of best adsorbent;

Different adsorbents (Rice straws, Sumbell shells, Eucalyptus bark, Bagasse, Wheat bran, Black gram husk) were grinded by electric crusher and screened out of uniform particle size i.e. 50-80 mesh. Then these adsorbents were filled to the column up to the height of 18 cm. Sample solution of lead nitrate having 50µg.ml^{-1} concentration and 300ml volume was passed through the column and drawn into the vacuum flask by applying suction to the flask. The process was done for each adsorbent. The percentage adsorption was calculated by estimating the amount of Pb(II) remaining in the filtrate by Atomic Absorption Spectroscopy(AAS).

Effect of mesh size of adsorbent;

Rice straws were grinded of particle sizes 50-80 mesh, 40-50 mesh, 30-40 mesh, & 16-30 mesh. The adsorbent of different particle size was filled to the same column length i.e. 18cm. 300ml of 50µg.ml^{-1} solution of lead nitrate was passed through the column and drawn into the vacuum flask by applying suction to the flask. The same process was done for each mesh size. Then all the solutions were subjected to the Atomic absorption spectrometer to measure the absorbance of Pb(II) and % absorption was calculated for each solution using standard solutions. And the 50-80 mesh size was found to be the best among them.

Effect of Concentration of adsorbate;

Standard solutions of Lead nitrate Pb $(NO_3)_2$ was prepared in the concentration range of 10 – 70 µg.ml^{-1}. 300ml of each concentration was taken for sample preparation. Rice straws of 50-80 mesh was used. Column was filled with the adsorbent up to 18 cm. 300ml of each solution was passed through the column and drawn to the vacuum flask by applying a suction to the flask .The elution time was kept same by suction pump. The percentage adsorption was calculated by estimating the amount of Pb(II) remaining in the filtrate by Atomic Absorption Spectroscopy.

Effect of Acid modification of adsorbent;

The adsorbent (Rice straws) was modified with 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 i.e. 16.480g 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 to maintain the pH of their filtrate equal to normal. Then treated adsorbents were again dried at room temperature for two days to remove moisture content completely. These modified adsorbents were filled into the column up to 18 cm .Samples were obtained for each of them by passing 300 ml of Pb $(NO_3)_2$ of 50µg.ml^{-1} concentration through column fixed in a vacuum flask with an attached suction. The time of elution was kept same in each case by the usage of suction pump. The percentage adsorption was calculated by estimating the remaining amount of Pb(II) into the filtrate by Atomic Absorption Spectroscopy.

Effect of Base modification of adsorbent;

The adsorbent (Rice straws) of 50-80 mesh was modified with different bases. Standard solutions of 1 M concentration of different bases (i.e., NaOH, KOH, and NH_4OH) were prepared. The adsorbents were soaked in 500ml of each base separately for 3 hours. After soaking they were filtered and dried at room temperature. Then these dried adsorbents were washed thoroughly with distilled water to maintain the pH of their filtrate equal to normal, and dried at room temperature for two days to remove the moisture content completely. Then these base modified adsorbents were filled separately in the column up to 18cm height, and 300 ml solution of 50µg.ml^{-1} concentration of Pb $(NO_3)_2$ was passed through the column which was fixed in a vacuum flask with an attached suction pump. The elution time was kept same in each case by the usage of suction pump. The percentage adsorption was calculated by estimating the remaining concentration of Pb(II) in the filtrate by Atomic Absorption Spectroscopy.

Effect of modification of adsorbent with volatile organic solvents;

The adsorbent of 50-80 mesh was modified with different volatile organic solvent. 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 . Equal amounts of adsorbent were soaked in each of these solvents separately in the beakers and covered them with Al-foil for 3 hours. Then filtered, 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 18cm fitted in a vacuum flask with an attached suction pump. 300 ml of 50µg.ml^{-1} concentrated solution of $Pb(NO_3)_2$ was passed through the column. The elution time was kept same in each case i.e 2 hours by the usage of suction pump. The percentage adsorption was calculated by estimating Pb(II) amount in filtrate by Atomic Absorption

Results and Discussion

Fig-1: Selection of adsorbent

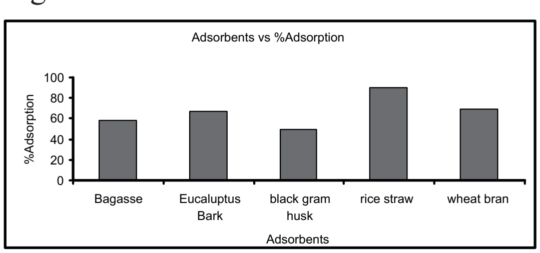


Fig-2: Effect of particle size of Adsorbent (rice straws);

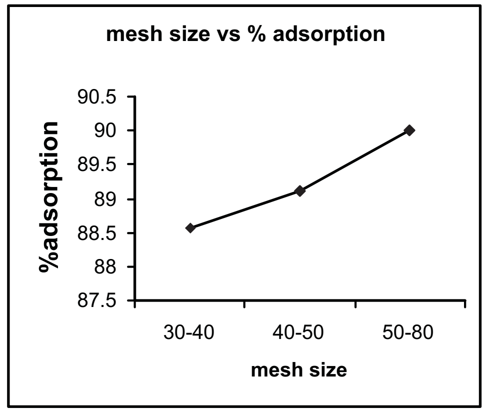


Fig-3: Effect of concentration of metal ions:

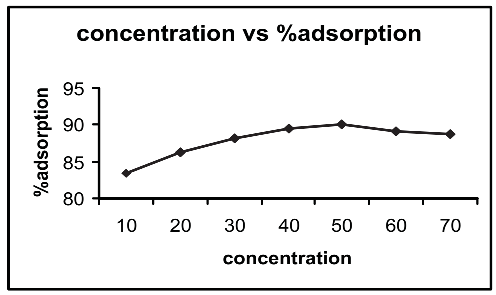


Fig-4: Effect of Acid modification on Adsorption:

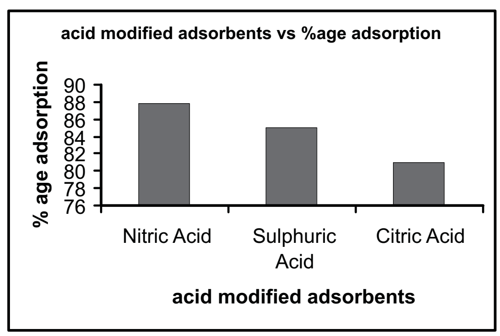


Fig-5: Effect of base modification on Adsorption:

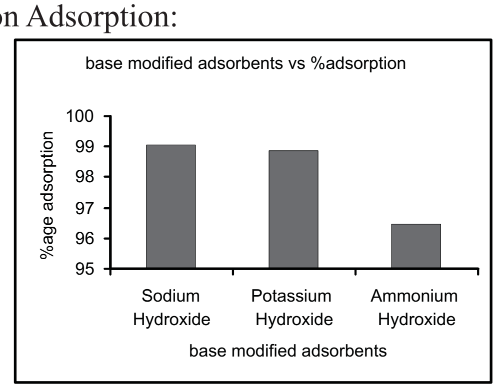
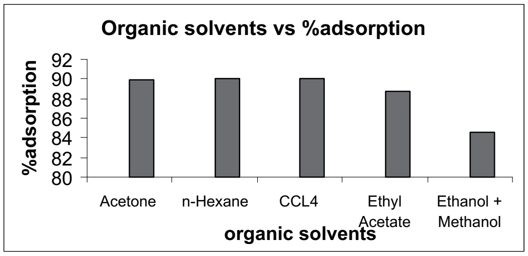


Fig-6: Effect of modification by organic solvents on adsorption:



Spectroscopy.

Adsorption isotherms:

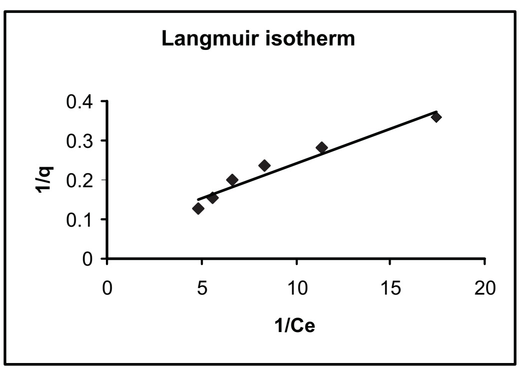
The Langmuir and freundlich isotherms were plotted according to equations 1 and 2.

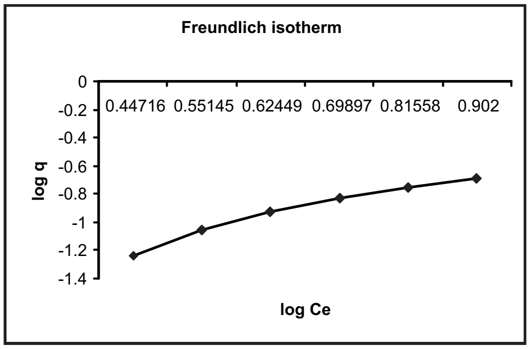
$$q = Q_{max}\, bCe / 1 + bCe \quad (1)$$

$$q = K_f (Ce)\, 1/n \quad (2)$$

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. Q_{max} (mg Pb/g rice straws) 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 Pb /g rice straws)	b	R^2	1/n	Kf	R^2
14.99	3.79	0.94	0 .11	0.05	0.95

Five different adsorbents were used for the adsorption of lead among which rice straws proved to be the best biosorbent for lead showing 90.001 % adsorption as shown in fig one. The fact involved is that Pb^{+2} ions showed greatest affinity towards the binding sites of rice straws 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 two.

From the graph in fig.three it was observed that the %age adsorption increases by increasing metal ion concentration. This increase in the %age adsorption of metal ions continues up to a certain level and then decreases. The fact involved in this regard is that in case of low concentration of metal ion solutions there are, no doubt, more activated sites available for metal ions to adsorb on it but the equilibrium between the metal ions and adsorbent's active sites sets up very soon in metal solution don't release more Pb^{+2} ions to adsorb on adsorbent surface. As we go on increasing initial concentration of metal ions solution's capacity to release ions increases and hence adsorption increases. This trend continues up to a level where all the active sites are saturated with adsorbed metal ions i.e. at 50µg.ml^{-1} concentration maximum adsorption efficiency was observed. By increasing the concentration further a trend of decreasing adsorption was observed. The reason for this is at high concentration of metal ions there is a competition between metal ions to adsorb on the active site of 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 concentration of metal ions.

Result showed that there is a decrease in %age adsorption in case of acid modified adsorbent as compared to the simple adsorbent. Reason is on modifying adsorbent with acids the binding sites are highly protonated but when metal solution was passed to adsorb its strong affinity with binding sites replaced them but all of them are not replaced i.e. there are comparatively less number of active sites for metal ions to bind with and hence it showed relatively less adsorption. However different acids showed different %age adsorption. HNO_3 showed maximum and citric acid showed minimum adsorption among them.

So, at very low pH (below 5) , functional groups of the biomass (hydroxyl group) are protonated and, thus, active sites of biomass for binding of metal ions become less available, so the removal efficiency decreases & hence slightly negative effect on adsorption was observed as compared to adsorption on non modified adsorbent as shown in fig four.

Results showed that base modified adsorbents showed 99.053% efficiency to adsorb Pb(II) on their surface as shown in fig.five.The functional groups present on the adsorbent surface highly favors the attachments of metal ions on its surface. Actually the removal of Pb(II) from their aqueous solutions is due to the functional group i.e. hydroxyl group of polysaccharides present in the cell wall of rice straws and is not due to any metabolic activity of the cells of plants i.e. rice straws.

Rice straw possesses high oxygen; which is largely fixed in hydroxyl group of polysaccharides. These groups help in biosorption process by making a complex between metal ions (present in aqueous solutions) and oxygen of hydroxyl group. The oxygen contains two lone pairs of electrons which it may donate to the metal ions. When the adsorbent is treated with base Hydroxyl groups OH^- of the base do not find any attachment to the active sites and due to the existence of OH^- ions in the cell wall of rice straws thus leaving all binding sites available for metal ions attachment. When metal solution is passed through it Pb^{+2} ions don't face any competition for attachment with the surface of adsorbent and a complex between metal ions and oxygen of hydroxyl group (of cell wall of rice straws) is immediately formed. All three bases which were used to modify the adsorbent shown same behaviors where NH_4OH is a weak base but it showed almost the same behavior as other two strong bases showed.

The results given in fig six showed that there is no effect of non-polar solvent on %age adsorption i.e acetone, CCl_4 , n –hexane even ethyl acetate did not affect % age adsorption . 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 decreases the adsorption efficiency of metal on the surface of adsorbent.

When the carboxylic group on the rice straw surface is esterified they produce a negative effect on adsorption. That's why treatment with ethanol and methanol gave a negative effect on the %age adsorbent.

Conclusion

The biosorption studies of Pb(II) from waste water concludes that rice straws was found to be the best biosorbent of all and it showed appreciable adsorption by increasing column length, initial concentration of metal and decreasing particle size of adsorbent. Modifications produce pronounced effect on adsorption with the exception of non-polar volatile organic solvents.As base modified adsorbent showed excellent adsorption efficiency while in case of acid modified adsorbent adsorption showed a decreasing trend ,due to saturation of binding sites of modified rice straws by protonation.

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