Application of Vetiver Grass Root for Removal of Chromium and Lead from Aqueous Solution

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Abstract- Heavy metals are one among the maximum poisonous causing substances to the surroundings. Process of adsorption find a use in removing heavy metals from wastewater. Many scrutinies have been performed for removal of heavy metals by using distinct materials. Numerous adsorbents were used to isolate different kinds of metal ions present in wastewater particularly the ones which might be harmful to mankind. In this project, Vetiveria zizanioide root powder is used as adsorbent to remove chromium and lead from aqueous solutions. The adsorbent is good at removal of heavy metals. Batch studies were carried out to reap the most optimum values for chromium and lead. Influence of variables like contact time, adsorbent dose, pH and initial metal ion concentration were also ascertained. The optimum values obtained were 120 mins contact time, 1.5g of adsorbent dose and pH 6 for chromium and 90 mins contact time, 1.5g adsorbent dosage and pH 7 for lead, using vetiver root powder adsorbent. Langmuir and Freundlich isotherm models are used to define the adsorption performance. Adsorption values well suited to Freundlich isotherm model. The greatest removal ability of adsorption was found to be 92% for chromium and 86% for lead using vetiver root powder..

Keywords- Chromium, Freundlich isotherm, Heavy metals, Langmuir isotherm, Lead, Vetiveria zizanioide

I. INTRODUCTION

Mainly pollution is due to the increased poisoning effect of heavy metals that is increasing with the increased use of chemicals in the various fields like industries, agriculture, etc. The main cause of various types of metal pollution in natural water is wastes from the industries. Hence, it has to be solved out by effective measures like immediate introduction of cleaner technologies which can reduce the pollution and degradation of the environment. Zero waste discharge is not achievable but it is necessary to reduce the waste (Chaudhari U E, 2009). Discharge of excess amounts of metal poisoned waste water from the industries that are concerned with heavy metals like Ni, As, Cu, Zn, Cr, Pb and Cd has made them malignant than other chemical-intensive industries. Increased solubility of these metals in the water bodies is resulting in increased deposition of these heavy metals in the living beings (Barakat M A, 2011). When they enter the food chain there is accumulation of higher concentrations of the heavy metals in the human beings which results in the severe damage to the health.

Various processes like coagulation, ion exchange, chemical precipitation and electrochemical removal are adapted in traditional treatment of inorganic effluent in order to make it free from heavy metals. But these processes are disadvantageous as they require great energy, produce virulent sludge and incomplete removal of heavy metals (Barakat M A, 2011). Nowadays development of inexpensive adsorbents with metal binding power is emphasized. Adsorption can be defined as a surface phenomenon which involves conglomeration of atoms/molecules on the material surface (solid or liquid phase). This phenomenon involves two parts adsorbate and adsorbent. Adsorbate is a material which agglomerate on the surface whereas adsorbent is an element on whose surface adsorption take place (liquid, solid or gas phase). There are different types of adsorbents that may be of mineral, biological or organic origin, zeolite, biomass, agricultural wastes, polymer and industrial byproducts. This work is focused on removal of chromium and lead by using powder of vetiver root as adsorbent under various conditions.

METALS:

Chromium has gained recognition by its hazardous property. The major forms of chromium are: Chromium (0), Trivalent Chromium-Cr(III) and Hexavalent Chromium-Cr(VI). Hexavalent chromium is artificial (by human activities) and more toxic whereas trivalent is naturally occurring and is needed in small amounts in the diet for metabolism of lipid and sugar, absence of which causes chromium deficiency (Amaresh and Hoolikantimath, 2015). Mainly chromium (VI) pollution is due to; Mining industry, Leather tanning industry, Cement industry, Electroplating industry, Textile industries, etc. Chromium (VI) is toxic to human, animals, plants and microbes about 500 times more than trivalent. Respiratory tract is the major targeted organ of inhalation of chromium in humans.

Lead occurs in three oxidation form: Pb (0), the metal; Pb (II) and Pb (IV). Among which Pb(II) is the most

available form in the environment, Pb(IV) obtained only in the presence of highly oxidizing conditions and lastly existence of Pb(0) (metallic lead) in nature is rare. Maximum amount of lead in the environment is added up due to its notable utilize in paint and gasoline and also due to ongoing and/or historic mining and commercial activities rather than occurring naturally. But high levels of lead is due to various human activities viz., smelting, mining, informal recycling and refining of lead; electronic wastes and its use in water pipe and solder, etc. It is venomous for human body systems mainly nervous, digestive and skeletal systems even in low concentrations. The major focus of lead is on the nervous system both in adults and children. Table 1 shows ISI tolerance limit for discharge of chromium and lead.

		Limits for Discharged to-	Tolerance limits for inland surface		
Parameter and Unit	Inland Surface Water (IS:2490- 1974)	Public Sewers (IS:3306- 1974)	water, when used as raw water for public water supplies (IS:2296-1974)		
Lead (mg/L)	0.1	1	0.1		
Chromium (VI) (mg/L)	0.1	2	0.05		
Chromium Total (mg/L)	2	2	-		

Table 1: ISI	Tolerance	Limit for	Discharge	of Effluents

VETIVERIA ZIZANIOIDE:

Being native to India, vetiver has been widely used traditionally for the extraction of perfumery oil from its roots since ancient days. Since centuries, its hedges are used for contour protection. Usually, it is recognized as vetiver grass, which is a cluster of grass rising from South India. Vetiver, shown in Figure 1, is a member of the family of grasses such as Maize, Sugarcane, Sorghum & lemon grass. Cultivars of vetiver in south India are sterile & non invasive. Vetiver grass (Vetiveria zizaniodides L. Nash) is a perennial with high speed growth, high biomass production which possesses deep root system (Kanokporn and Monchai, 2008). This stem is coupled with a finely sized and highly dense root system extending 3-4 meters below ground as shown in Figure 2.

In 1995, it was recognized that vetiver grass possess "super adsorbent" property that is appropriate for discarding effluent and leachate produced from wastewater treatment plants and landfill.



Figure 1: Vetiveria zizanioide (Source: The Vetiver Network International, TVNI)



Figure 2: One Year Old Vetiver with 3.3m Deep Root System (Source: The Vetiver Network International, TVNI)

Vetiver has become an important means of earning. Leaves are used in the manufacturing of high quality handicrafts. Due to the documented calming effect of vetiver oil it is majorly used by healing arts practitioners in aromatherapy applications, in regions like India and Thailand. Different ailments like mouth ulcers, fever, boils, epilepsy, burns, snake bite, scorpion sting, rheumatism, head ache etc are treated by using different parts of grass by various tribes. Oil from vetiver roots are anti-oxidant in nature which are used in reduction/prevention of cancer. In India, Vetiver grass is also used as:

- Dried roots for scenting clothes and as water flavoring agent.
- Eco-friendly soil binders and pulp of plant for paper and straw board.

- In preparation of sharbhat or soft drink during summer in North India.
- Dried culms as brooms and for roof thatching.
- Root mats for door and window screen that provide cooling effect in summer.

Taxonomic position of Vetiveria zizanioide is as follows:

Domain	:	Poaceae
Kingdom	:	Plantae (Plants)
Subkingdom	:	Tracheobionta
Super division	:	Spermatophyta
Division	:	Magnoliophyta
Class	:	Liliopsida
Subclass	:	Commelinidae
Order	:	Cyperales
Family	:	Poaceae (Grass family)
Genus	:	Vetiveria Bory
Species	:	Vetiveria zizanioides (L.)

Vernacular Names is as follows:

English	:	Vetiver
Kannada	:	Laamancha, Kaddu
Sanskrit	:	Ushira
Hindi	:	Khas, Khus
Malayalam	:	Ramaccham, Vettiveru
Marathi	:	Vala
Tamil	:	Vattiver
Telugu	:	Kuruveeru, Vettiveellu

II. MATERIALS AND METHODOLOGY

PREPARATION OF ADSORBENT

Vetiver grass roots purchased from the local market in ayurvedic shop were initially washed with distilled water in order to eliminate foreign matter like sand, dirt, soluble and coloured components. Then the roots were dried in the sunlight for 2 to 3 days and then crushed by domestic grinder. Later the powder was sieved to obtain the particle size in the range of 150 microns to 300 microns, which was later used in adsorption experiments, Figure 3. Then the adsorbent were placed in an oven maintained at the temperature of 30°C for about 30 minutes in order to erase the adhering moisture content and then it is preserved in air tight plastic covers. No chemical modification was made.

PREPARATION OF AQUEOUS SOLUTIONS

Analytical reagents and distilled water were used in preparing all the required solutions. Preparation of stock solution of chromium (1000mg/L) was done by dissolving 2.828g of 99.9% analytical grade $K_2Cr_2O_7$ in 1000ml of

distilled water. Similarly solution of lead (1000mg/L) by dissolving 1.615g of 99% of Pb(NO₃)₂ in 1000ml distilled water in 1L volumetric flask up to the mark, to obtain the required concentration of solution. Different concentrations of synthetic sample of chromium and lead are prepared from the stock solutions by suitable dilutions. Desired value of pH is obtained by addition of 0.1N H₂SO₄ or 0.1N NaOH.

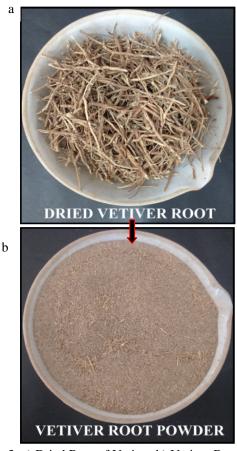


Figure 3: a) Dried Root of Vetiver b) Vetiver Root Powder

EXPERIMENTAL PROCEDURE

At different pH, adsorbent dose, contact time and initial concentration, batch experiments were carried out. 500ml of metal ion solution (chromium or lead) of particular concentration was used for each batch experiments. The mixture was agitated at desired amount of adsorbent and pH for a required duration on mechanical shaker. Then the adsorbent was differentiated from the supernatant by filtration. Table 2 shows the variables studied. By Atomic Absorption Spectrometer (AAS), the final concentration of ions was evaluated. The removal percentage (R %) was calculated by the following formula:

$$R(\%) = \frac{C_{i} - C_{e}}{C_{i}} \times 100$$
 (1)

Where;

- C_i = Initial concentration of solution
- C_e = Equilibrium concentration of solution

Table 2: Experimental	Conditions	Investigated
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Parameters	Values Investigated	
Agitation time, t, mins	30, 60, 90, 120, 150 &180	
Adsorbent dosage, M, g	0.5, 1, 1.5, 2, 2.5 & 3	
pH of the aqueous solution	4, 5, 6, 7, 8 & 9	
Initial concentration of	10, 20, 30, 40 & 50	
aqueous solution, C _i , mg/L	10, 20, 30, 40 & 30	
Rotation Speed, RPM	100	

ADSORPTION ISOTHERM STUDY

It is the graphical representation (mathematical expression) that correlates amount of adsorbed gas on adsorbent at equilibrium pressure and constant temperature. Relation between the amount of metal ions adsorbed on the solid phase and concentration of metal ions in solution is given by isotherm, at equilibrium of two phases. Adsorption on surface sites of the solid for low metal ion concentration induces metal ion removal from aqueous solutions whereas adsorption and internal exchange occur at high concentrations.

Langmuir Isotherm

This isotherm can be applied on various types of natural adsorbent to analyze which adsorbate is most efficient to deal with known contaminants. Each and every contaminant molecule is not removed by adsorption. Rather the process reaches equilibrium after certain amount of contaminant has been adsorbed on adsorbent surface. After this point, increasing contact time will not increase the adsorption. Using Langmuir isotherm equation, desired dose of adsorbent to get required equilibrium concentration of contaminant may be calculated.

The Langmuir equation is given by:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e}$$
(2)

The linearization form of Langmuir equation (2) is:

$$\frac{M}{X} = \frac{1}{q_e} = \frac{1}{K_a q_m} \times \frac{1}{C_e} + \frac{1}{q_m}$$
(3)

When $\frac{M}{x}$ is plotted against $\frac{1}{C_e}$, that has a straight line with slope as $\frac{1}{K_a q_m}$ and $\frac{1}{q_m}$ as an intercept.

Where,

 C_e = Equilibrium metal concentration, mg/L X = Concentration of pollutant adsorbed, mg/L, (C_i - C_e)

- M = Adsorbent Concentration, g/L
- $q_m = Maximum$ adsorption capacity for forming monolayer, (mg/g), from graph
- K_a = Relative energy of adsorption, (L/mg), from graph

Freundlich Isotherm

An empirical bisorption isotherm for non ideal system was presented in 1906 by a German physical chemist Herbert Max Finley Freundlich. It describes the heterogeneous surface energy application in bisorption process. In 1909, he gave an empirical expression representing isothermal variation of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure.

Empirical equation is given by:

$$q_e = \frac{X}{m} = K C_e^{1/n}$$
(4)

The linearization form of equation (4) is: $\log q_e = \log K + \frac{1}{n} \log C_e$ (5)

When $\log q_e$ plotted against $\log C_e$, it has straight line with $\frac{1}{n}$ as slope and log K as an intercept. K and $\frac{1}{n}$ are Freundlich empirical constants, dependent on number of environmental factors.

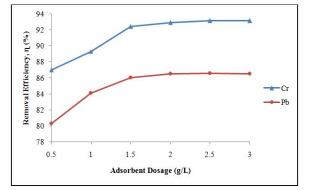
Where,

K =Indication of adsorption capacity, from graph

 $\frac{1}{2}$ = Measure of intensity of adsorption, from graph

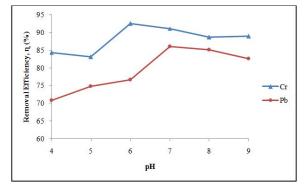
III. RESULTS AND DISCUSSIONS

Effect of Adsorbent Dosage - It is observed that Cr and Pb removing efficiency generally increased by increase in the dose of adsorbent. It may take place because of adsorbent which are in high dosage that provides ions with greater exchangeable sites. From graph 1, the maximum removal percentage of Cr was about 92% and Pb was about 86% at the dosage of 1.5g by vetiver root powder. Equilibrium condition is achieved at certain adsorbent dosage. So, 1.5g of vetiver root powder is taken as optimum dosage and is used for future experiments.



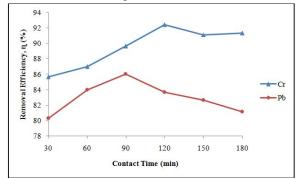
Graph 1: Effect of Vetiver Root Powder Dosage on Cr and Pb Removal

Effect of pH - It is seen that the adsorption gradually increases as the pH rises from 4 to 9. Graph 2, shows percentage of Cr and Pb ions removal by by vetiver root powder, the maximum percentage efficiency achieved was 92% at pH 6 for Cr and 86% at pH 7 for Pb. These values are considered optimum for further studies.



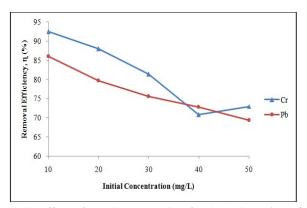
Graph 2: Effect of pH for the Adsorption of Cr and Pb onto Vetiver Root Powder

Effect of Contact Time - It was found that rapid adsorption of Cr and Pb took place initially within 30 mins as shown in graph 3. The metal ion removal capacity increased with rise in contact time prior it reaches a stable state. The adsorption percentage did not vary significantly after 120 mins and 90 mins for Cr and Pb respectively by vetiver root powder. Hence these values are taken as optimum contact time.



Graph 3: Effect of Contact Time for the Adsorption of Cr and Pb onto Vetiver Root Powder

Effect of Initial Concentration - From graph 4 it was clear that by increasing initial metal ion concentration, there was reduction in its percentage of removal. Higher ratio of initial number of moles of ions to the empty sites present may be the reason for low level uptake at high concentration of metal. Number of adsorbent sites available was fixed for a certain amount of adsorbent as a result equal amount of adsorbing takes place, resulting in reduced removal of adsorbate, ensuing to a high initial concentration.

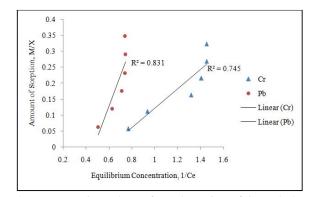


Graph 4: Effect of Ion Concentration for the Adsorption of Cr and Pb onto Vetiver Root Powder

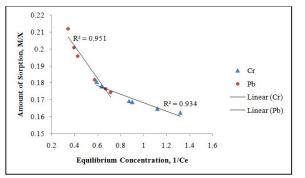
ADSORPTION ISOTHERM

The various constant values of Langmuir and Freundlich isotherm models are calculated and given in Table 3. Langmuir and Freundlich isotherms for Cr and Pb are presented in graph 5 to 10 respectively. It shows that the data obtained from experiment fitted to both the isotherms. By comparing the regression coefficient R^2 , it was seen that Langmuir R^2 values are very poor than Freundlich. Therefore, Freundlich model equation fitted better for adsorption, which is dependent on heterogeneous surfaces with the interaction between adsorbed molecules.

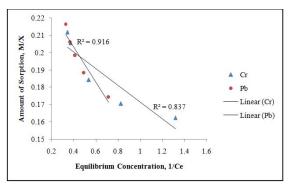
Langmuir Isotherm:

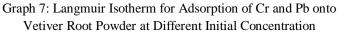


Graph 5: Langmuir Isotherm for Adsorption of Cr and Pb onto Vetiver Root Powder at Different Adsorbent Dosage

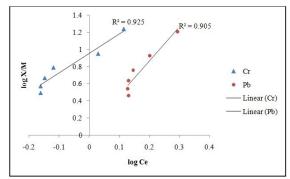


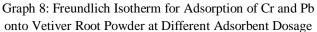
Graph 6: Langmuir Isotherm for Adsorption of Cr and Pb onto Vetiver Root Powder at Different pH

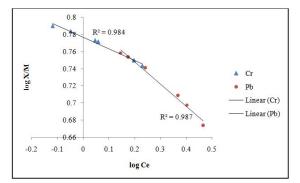




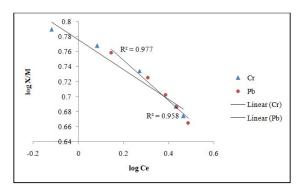
Freundlich Isotherm:

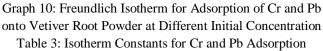






Graph 9: Freundlich Isotherm for Adsorption of Cr and Pb onto Vetiver Root Powder at Different pH





Chromium							
Parameter	Langmuir Isotherm			Freundlich Isotherm			
	Ka	q _m	\mathbf{R}^2	K	1/n	\mathbf{R}^2	
Adsorbent Dosage	0.469	2.197	0.745	8.974	0.443	0.925	
pН	7.721	5.181	0.934	5.970	7.462	0.984	
Initial Conc.	4.562	4.566	0.837	5.956	5.051	0.958	
	Lead						
Parameter	Langmuir Isotherm			Freundlich Isotherm			
1 al aniciel	Ka	$q_{\rm m}$	\mathbb{R}^2	K	1/n	R ²	
Adsorbent Dosage	0.598	5.494	0.831	1.180	0.252	0.905	
pН	2.515	4.184	0.951	6.295	3.876	0.987	
Initial Conc.	2.430	4.115	0.916	6.338	3.731	0.977	

IV. CONCLUSIONS

- 1. More than 90% efficiency can be achieved on selecting precise amount of adsorbent dosage.
- 2. Metal absorbing capacity of adsorbents increased with higher values adsorbent dosage, increased contact time and pH.
- 3. Results show that removal efficiency of chromium was 92% and lead was 86% by vetiver root powder.
- 4. Chromium removal efficiency was greater as compared to lead.
- 5. As low cost adsorbent vetiver root powder can be effectively used for Cr and Pb removal without giving any chemical treatment for adsorbents.
- Here correlation coefficient R² of Freundlich equation showed higher values compared to that of R² values of Langmuir equation. On comparing the correlation coefficient (R²), Freundlich isotherm was good model for adsorption system for both the metals.

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