Application of Cocos nucifera for Removal of Chromium and Lead from Aqueous Solution

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Abstract - *The harmful metals has to be treated before its outlet into the water bodies in order to prevent the adverse effects caused due to its poisoning of water. Process of adsorption find a use in removing heavy metals from wastewater. Numerous adsorbents were used to isolate different kinds of metal ions present in wastewater particularly the ones which might be harmful to mankind. Proficiency of adsorption is essentially dependent on the factors like nature of adsorbent and its dosage, pH, concentration, temperature, agitation time, etc. In this project, adsorbent used is coconut shell powder (Cocos nucifera) to remove chromium and lead from aqueous solutions. Batch studies were carried out to bring in 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 60 mins contact time, 2g adsorbent dosage and pH 6 for chromium and 120 mins contact time, 2g dosage of adsorbent and pH 5 for lead, by using coconut shell powder adsorbent. Langmuir and Freundlich isotherm models are used to define the adsorption performance. Adsorption values were well suited to Freundlich isotherm model. The greatest removal ability of adsorption was found to be 97% for chromium and 93% for lead.*

Key Words: Chromium, Cocos nucifera, Freundlich isotherm, Heavy metals, Langmuir isotherm, Lead

1. INTRODUCTION

Undesirable changes in the environmental aspects influenced by human beings that are dangerous are known as pollution. Pollution has increased its influence since 20th century due to unplanned industrialization, dangerous impact of change in life style, uncontrollable usage of natural resources and unsafe agricultural practices etc. The life on the earth is dependent on the qualitative and quantitative availability of the water. Therefore water acts as an essential fuel to the living beings. Such an essential fuel is available on the earth as surface water and ground water through various mechanisms of purification viz, physical, chemical and microbiological processes occurring in natural bodies. Despite of this, natural water is found very often suitable for the direct consumption. Excessive industrialization and population explosion has posed problem in disposal of the large quantities of wastewater.

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 [4]. 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.

Nowadays researches are undertaken in flourishing cheaper and skillful techniques that can reduce the wastewater production and qualitatively improve the effluent treated. Present days, to the conventional techniques, adsorption has become a substitute. Generally adsorption involves physical/chemical affinity between adsorbate and adsorbent that bound each other. This affinity is the resultant of residual or unbalanced forces on the surface of the adsorbent that retains atoms/species on the surface. Desorption is opposite to this action [1]. Adsorption usually takes place in three ways; continuous, batch and semi-batch. Affinity between the surface of adsorbent and atoms/molecules being adsorbed results in adsorption at molecular level [2].

Biosorption is defined as a physico-chemical process that involves biological material for removal of substances from the solution. Living and dead organisms (including their components) follow this property. Thus, it is recited that metal ions from the aqueous solutions can be removed by different waste biomaterials, yeast, algae, bacteria, microbes and fungi [9]. The biosorption advantages over conventional methods are:

- Inexpensive
- Increased efficiency
- Reduced chemical and biological sludge
- Additional nutrient is not needed
- Biosorbent regeneration
- Metal recovery possibilities

On the whole purpose of present thesis is to check out the heavy metal reducing capacity from aqueous solution using coconut shell powder. Heavy metals of interest in this work are chromium and lead.

1.1 Chromium

Being the first element of group 6, it has the atomic number 24 and Cr as its symbol. It is the 21st most ample element of the earth and 6th mainly eco-rich transition metal. It is found naturally in rivers, seawater, gases, volcanic dust, rocks, soil, animals and plants. It 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 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 [1].

The anthropogenic sources of chromium exhalation in the atmosphere are; leather tanning, fertilizers, combustion of natural fuels, chrome plating, catalysts, dye manufacturing industries, printers, wood preservatives, battery making, metal processing, air condensers, emission from cooling towers and incineration of sewage sludge, municipal refuse and other solid wastes. 40% of total industrial use of chromium with higher influx into the ecosphere is by leather industry [12].

Chromium shows both beneficial and damaging characteristics. Chromium (III) and elemental chromium are innoxious in nature. Its beneficial effects are:

- Required for normal glucose, protein and fat metabolism.
- Reduce blood cholesterol levels by decreasing the “LDLs” levels in the blood, that are contributed by cheese, Brewer’s yeast, cereals, whole grain breads, liver and broccoli.
- Help in muscle development and as dietary supplements reach in chromiumpicolinate to body builders [13].

Chromium (VI) is toxic to human, animals, plants and microbes about 500 times more than trivalent.

- Effects on Respiratory Tracts: It is the major targeted organ of inhalation exposure in humans. Chronic inhalation results in perforations and ulcerations of the septum, pneumonia, reduced pulmonary functions, nasal itching, bronchitis and soreness. It also damage kidney, gastrointestinal, immune system, liver and also blood.
- Dermal exposure results in dermatitis, sensitivity and ulceration of the skin.
- Induces mutations in vitro and in vivo and cause cancer in experimental animals and humans.

1.2 Lead

It is a soft blue-gray metal, belonging to the group 4 with 82 as atomic number and Pb as symbol on periodic table. It is found entombed in the earth crust as insoluble and biologically inoffensive form. It is highly resistant to corrosion in acidic nature. It 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.

Low levels of lead as lead sulfide are present in the earth’s crust. But high levels of lead is due to various human activities viz., smelting, mining, informal recycling and refining of lead; manufacture of lead acid batteries and paints; usage of leaded petrol (gasoline); soldering, goldsmith works, ceramics and informal production of leaded glass and cottage industries; electronic wastes and its use in water pipe and solder. Natural phenomenon like geochemical weathering, remobilization of historic sources like lead in soil, sediment and water from mining areas, sea spray emissions and volcanic eruptions contribute to lead in environment [7].

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. It inhibits hemoglobin synthesis and porphyrin metabolism by forming complexes with the oxo groups of enzymes. Asymptomatic impaired abilities, low memory and learning capacity, reduced IQ levels, reduced spoken capacity, defective speech, Paraplegia, encephalopathy unexpectedly direct to seizures, loss of consciousness and death, lead line (blue-black) on gingival tissue, colic (rigorous abdominal cramps, intermittent) etc, are the signs and symptoms in humans due to various degree of exposure to lead. Table 1 shows ISI tolerance limit for discharge of chromium and lead.

Table -1: ISI Tolerance Limit for Discharge of Effluents

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

1.3 Cocos nucifera

The only preferable species in the genus Cocos is Cocos nucifera (coconut palm), shown in Fig 1. It is widely found in tropics where it is most used by the local people. The term coconut denotes the whole coconut palm, the seeds/fruits which are a drupe not a botanical nut. Exocarp, Mesocarp and Endocarp, are the three layers of the fruit. The mesocarp and exocarp together constitute the coconut husk. The mesocarp is nothing but the fibers known as coir that are traditionally and commercially used in maximum. Coconut shell serves to be the most used adsorbent as it is one among the products of agricultural waste. It is utilized as an adsorbent so as to take out the heavy metals from aqueous solution, as adsorbent are available throughout the year and its profuse in the environment is very high. Due to its advantageous uses for good reason, it is often called as "tree of heaven" and "tree of life" [11].

Fig -1: Coconut Palm Tree (Source: International Coconut Gene Bank, ICG)

Taxonomic Position of Cocos nucifera is as follows:

Domain	:	Eukarya
Kingdom	:	Plantae
Subkingdom	:	Tracheobionta
Super division	:	Spermatophyta
Division	:	Magnoliophyta
Class	:	Liliopsida
Subclass	:	Arecidae
Order	:	Arecales
Family	:	Arecaceae (Palm family)
Genus	:	Cocos L. (Coconut palm)
Species	:	Cocos nucifera L.

Vernacular Names is as follows:

English	:	Coconut
Kannada	:	Thengu
Sanskrit	:	Kalpavriksha
Hindi	:	Narial
Malayalam	:	Thenga
Marathi	:	Naral
Tamil	:	Thennai
Telugu	:	Kobbarikaya

2. MATERIALS AND METHODOLOGY

2.1 Preparation of Adsorbent

The endosperm (copra) was separated from the coconut shells, obtained from the local houses, shops and hotels. Then the coconut shells were drenched for around one hour in water, which were later well scrubbed and cleaned by distilled water in order to remove possible strange materials present on it (dirt and sands). Then the washed shells were dried for 2 to 5 days in the presence of sunlight and next the dried shells positioned on a clean hard surface were crushed into smaller fragments by hammer. These fragments were reduced to particles with rough texture with the help of domestic flour milling machine and then grounded to fine particles by the manual grinder. Adsorbent in the powder form was sieved to have particle size in the range of 150 microns to 300 microns, which is later used in adsorption experiments. The finer dust particles separated are placed in an oven maintained at the temperature of 30^{o}C for about 30 minutes to erase adhering moisture content and later placed in an air tight sample container for the further use. There is no chemical modification done.

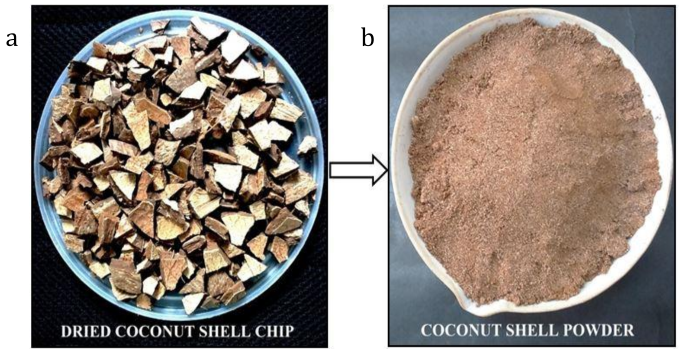

Fig -2: a) Dried Coconut Shell Chip b) Coconut Shell Powder

2.2 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 $Pb(NO_3)_2$ 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 H_2SO_4 or 0.1N NaOH.

2.3 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:

$$R(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

Where; C_i = Initial concentration of solution
C_e = Equilibrium concentration of solution

Table -2: Experimental Conditions Investigated

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 aqueous solution, C_i, mg/L	10, 20, 30, 40 & 50
Rotation Speed, RPM	100

2.4 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:

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

The linearization form of Langmuir equation (2) is:

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

When M/X is plotted against $1/C_e$, that has a straight line with slope as $1/(K_a \cdot q_m)$ and $1/q_m$ 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:

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

The linearization form of equation (4) is:

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (5)$$

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

Where,
K =Indication of adsorption capacity, from graph
1/n = Measure of intensity of adsorption, from graph

3. 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. It is obvious from the chart 1, that the maximum removal percentage of Cr was 97% and that of Pb was 93%, at the dosage of 2g by coconut shell powder. Equilibrium condition is achieved at certain adsorbent dosage. So, 2g of coconut shell powder is taken as optimum dosage and is used for future experiments.

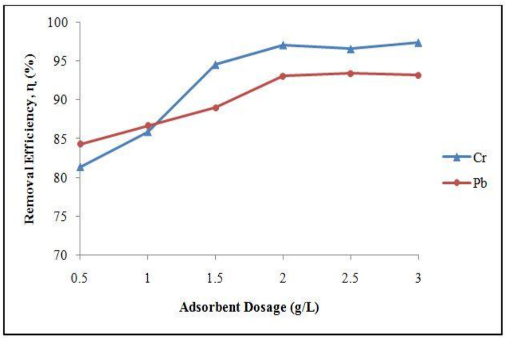

Chart -1: Effect of Coconut Shell Powder Adsorbent Dosage on Cr and Pb Removal

Effect of pH: It is seen that the adsorption gradually increases as the pH rises from 4 to 9. This is interpreted on the fact that decreased contention among proton and metal cation for similar functional groups and decreased positive surface charges result in low electrostatic repulsion between metal ions and surface. Chart 2, shows percentage of Cr and Pb ions removal by coconut shell powder. Maximum percentage efficiency achieved was 97% at pH 6 for Cr ions and 93% at pH 5 for Pb ions. These values are considered optimum for further studies.

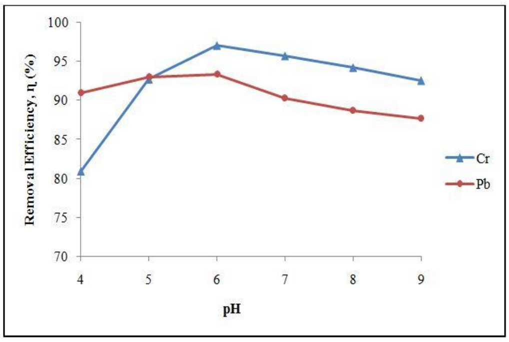

Chart -2: Effect of pH for the Adsorption of Cr and Pb onto Coconut Shell Powder

Effect of Contact Time: It was found that rapid adsorption of Cr and Pb took place initially within 30 mins as shown in chart 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 60 mins and 120 mins for Cr and Pb respectively by coconut shell powder. Hence these values are taken as optimum contact time.

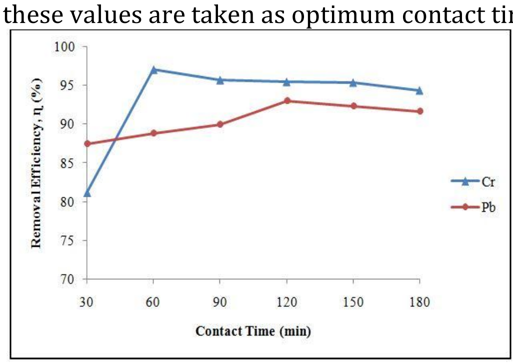

Chart -3: Effect of Contact Time for the Adsorption of Cr and Pb onto Coconut Shell Powder

Effect of Initial Concentration: From chart 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.

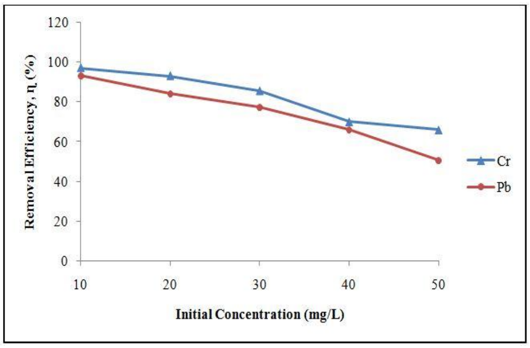

Chart -4: Effect of Initial Metal Ion Concentration for the Adsorption of Cr and Pb onto Coconut Shell Powder

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 chart 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:

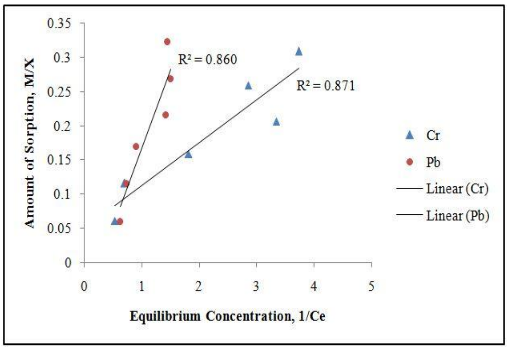

Chart -5: Langmuir Isotherm for Adsorption of Cr and Pb onto Coconut Shell Powder at Different Adsorbent Dosage

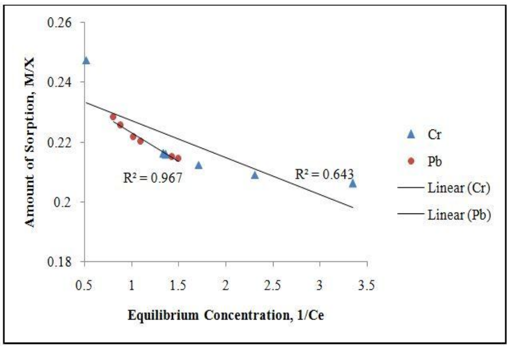

Chart -6: Langmuir Isotherm for Adsorption of Cr and Pb onto Coconut Shell Powder at Different pH

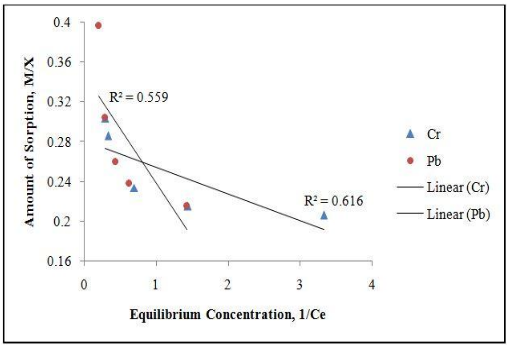

Chart -7: Langmuir Isotherm for Adsorption of Cr and Pb onto Coconut Shell Powder at Different Concentration

Freundlich Isotherm:

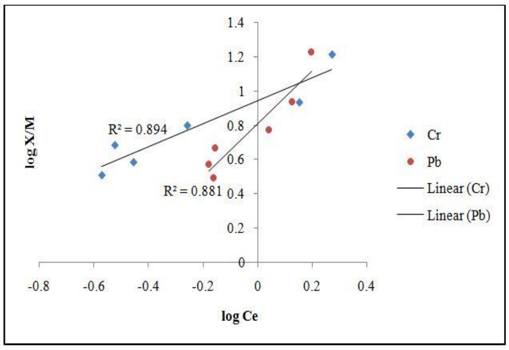

Chart -8: Freundlich Isotherm for Adsorption of Cr and Pb onto Coconut Shell Powder at Different Adsorbent Dosage

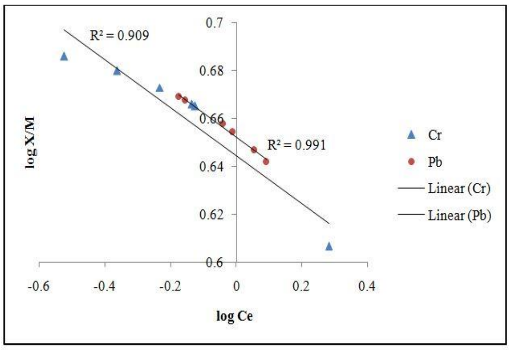

Chart -9: Freundlich Isotherm for Adsorption of Cr and Pb onto Coconut Shell Powder at Different pH

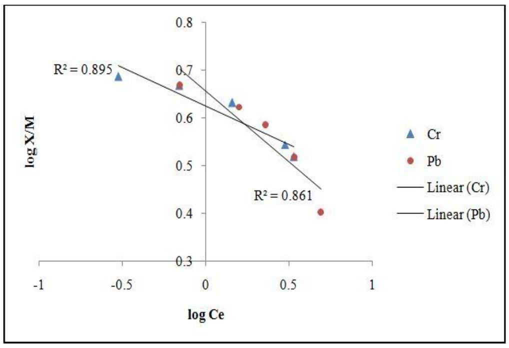

Chart -10: Freundlich Isotherm for Adsorption of Cr and Pb onto Coconut Shell Powder at Different Concentration

Table -3: Isotherm Constants for Cr and Pb Adsorption

Chromium						
Parameter	**Langmuir Isotherm**			**Freundlich Isotherm**		
	K_a	q_m	R^2	K	1/n	R^2
Adsorbent Dosage	0.790	20.408	0.871	8.770	1.493	0.894
pH	19.917	4.184	0.643	4.406	10.101	0.909
Initial Conc.	10.809	3.558	0.616	4.207	6.289	0.895
Lead						
Parameter	**Langmuir Isotherm**			**Freundlich Isotherm**		
	K_a	q_m	R^2	K	1/n	R^2
Adsorbent Dosage	0.275	15.873	0.860	6.486	0.651	0.881
pH	12.737	4.132	0.967	4.487	10.00	0.991
Initial Conc.	3.212	2.882	0.559	4.518	3.401	0.861

4. 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 97% and lead was 93%.
4. Chromium removal efficiency was greater as compared to lead.
5. As low cost adsorbent coconut shell powder can be effectively used for Cr and Pb removal without giving any chemical treatment for adsorbents.
6. Here correlation coefficient R^2 of Freundlich equation showed higher values compared to that of R^2 values of Langmuir equation.
7. On comparing the correlation coefficient (R^2), Freundlich isotherm was good model for adsorption system for both the metals.

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