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Adsorption of Heavy Metal (Cd^{2+} , Cr^{6+} and Pb^{2+}) from Synthetic Waste Water by Rice husk Adsorbent

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Industrial waste constitutes the major source of various kinds of metal pollution in natural water. There are at least 20 metals which cannot be degraded or destroyed. The important toxic metals are Cd^{2+} , Cr^{6+} and Pb^{2+} . There are numerous methods currently employed to remove and recover the metals from our environment and many physico-chemical methods have been proposed for their removal from wastewater. Adsorption is one of the alternatives for such cases and is an effective purification and separation technique used in industry especially in water and wastewater treatments. Cost is an important parameter for comparing the adsorbent materials. Therefore, there is increasing research interest in using alternative low-cost adsorbents. The use of rice husk as the low-cost adsorbents was investigated as a replacement for current costly methods of removing heavy metal ions from aqueous solutions. The experiment results showed that maximum removal of Cadmium ion by rice husk adsorbent is 92%, Chromium ion is 83% and Lead ion are 93% at optimum condition.

Keyword: Heavy Metal, Aqueous Solution, Rice husk, Adsorption.

1. Introduction

Heavy metal can include elements lighter than carbon and can exclude some of the heaviest metals. "Heavy metals" are chemical elements with a specific gravity at least 5 times that of water. The specific gravity of water is 1 at 4 °C (39 °F). Specific gravity is a measure of density of a given amount of a solid substance when it is compared to an equal amount of water. Some well-known toxic metals with a specific gravity 5 or more times that of water is arsenic (5.7), cadmium (8.65), iron (7.9), lead (11.34), and mercury (13.546)^[1]. Many different definitions have been proposed some based on density, some on atomic number or atomic weight, and some on chemical properties or toxicity^[8]. The main

threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury, chromium and arsenic^[1, 2, 3]. In the right concentrations, many metals are essential to life. In excess, though, these same chemicals can be poisonous. Even chronic, low exposures can have serious health effects. Because heavy metals cannot be degraded or destroyed, they are not broken down and accumulate in the human body—concentrating in the liver, kidneys, brain, skeleton, and keratinized tissue such as hair and nails. Exposure to heavy metals has been linked with developmental disability, various cancers, kidney damage, and even death in some instances. The heavy metals most threatening to human health are lead, cadmium, and chromium.

Several processing techniques are available to reduce the concentrations of heavy metals in wastewater, including precipitation, flotation, ion exchange, solvent extraction, adsorption, cementation onto iron, membrane processing and electrolytic methods. Adsorption is one of the alternatives for such causes the tendency of molecules from an ambient fluid phase to adhere to the surface of a solid. It has advantages over other methods are the simple design, sludge-free and can involve low investment in terms of both the initial costs and land. Adsorption onto activated carbon is a well-known method for removing toxic metal ions, but the high cost of activated carbon restricts its use in developing countries. The adsorption abilities of a number of low-cost adsorbents (e.g., cheap zeolites, clay, coal fly ash, sewage sludge, agriculture waste and biomass) have been determined for the removal of heavy metals from water^{4, 5}. Therefore, there is a need to look into alternatives to investigate a low-cost adsorbent which is effective and economic, for potential approach is the use of heavy metals removal, Rice husk is one of the most popular adsorbent⁹.

In this investigation experiment perform to evaluate the effectiveness of employing a rice husk for the adsorptive removal of Cd^{2+} , Cr^{6+} and Pb^{2+} from synthetic wastewater, using batch experiment and isotherm studies to determine the adsorption capacities.

Table1: Table shown the MCL standards for heavy metals, established by USEPA, WHO, OSHA ^[CPCB]

Heavy metal	WHO (ppm)	USEPA (ppm)	CPCB (ppm)	OSHA (ppm)
Cadmium	0.005	0.005	0.2	0.01
Chromium	0.1	0.1	0.1	0.5
Lead	5.0 ppb	0.06	0.1	0.05

1.1 Cadmium

Cadmium is a natural element in the earth's crust. It is usually found as a mineral combined with other elements such as oxygen (cadmium oxide), chlorine (cadmium chloride), or sulfur (cadmium sulfate, cadmium sulfide). It doesn't have a definite taste or odor. The cadmium that industry uses is extracted during the production of other

metals like zinc, lead, and copper. Cadmium enters air from mining, industry, and burning coal and household wastes. Cadmium¹³ particles in air can travel long distances before falling to the ground or water. It enters water and soil from waste disposal and spills or leaks at hazardous waste sites. It binds strongly to soil particles. Some cadmium dissolves in water. It doesn't break down in the environment, but can change forms. Fish, plants, and animals take up cadmium from the environment. Environmental Protection Agency (EPA) decides drinking water limit for Cd is 5 ppb. Acute effects of cadmium occur by breathing high levels dust or fumes and may cause throat dryness, cough, headache, vomiting, chest pain, extreme restlessness and irritability, pneumonitis, possibly bronchopneumonia and can cause death due to severe lung damage. Eating food or drinking water with very high levels (metal and compounds) increases salivation, severely irritates the stomach, leading to vomiting and diarrhea. Skin contact with cadmium is not known to cause health effects in humans or animals. Long term exposure to lower levels of cadmium in air, food, or water leads to a buildup of cadmium in the kidneys and possible kidney disease. Other potential long term effects are lung damage and fragile bones, abdominal pain, choking and tenesmus¹⁸.

1.2 Chromium

Chromium has three main forms chromium (0), chromium (III), and chromium (VI). Chromium (III) compounds are stable and occur naturally, in the environment. Chromium (0) does not occur naturally and chromium (VI) occurs only rarely. Chromium compounds have no taste or odor. Chromium (III) is an essential nutrient in our diet, but we need only a very small amount. Other forms of chromium are not needed by our bodies. Chromium is used in manufacturing chrome-steel or chrome-nickel-steel alloys (stainless steel) and other alloys, bricks in furnaces, and dyes and pigments, for greatly increasing resistance and durability of metals and chrome plating, leather tanning, and wood preserving^{2, 13}. Very small amounts of chromium (III) are in everyday foods. All forms of chromium can be toxic at high

levels, but chromium (VI) is more toxic than chromium (III). Acute toxic effects occur when very high levels of chromium (VI) in air that can damage and irritate your nose, lungs, stomach, and intestines. People who are allergic to chromium may also have asthma attacks after breathing high levels of either chromium (VI) or (III). Long term exposures to high or moderate levels of chromium (VI) cause damage to the nose (bleeding, itching, sores) and lungs, and can increase your risk of non-cancer lung diseases. Ingesting very large amounts of chromium can cause stomach upsets and ulcers, convulsions, kidney and liver damage, and even death^[8].

1.3 Lead

Lead poisoning is one of the commonest occupational diseases, although in recent years there has been a decline in both the number of reported cases and the severity of the symptoms presented, hence lead poisoning has shifted from an industrial hazard to an environmental one. Inorganic lead is not significantly absorbed through the skin, but is absorbed in small amounts from the gastrointestinal tract, which it may enter through the swallowing of inhaled particles or via tobacco, food etc. Lead dust, fumes or vapors are more easily absorbed from the respiratory tract, once absorbed it is distributed particularly to the liver and kidneys, and is then stored in the bones. Lead affects the red blood cells (anemia and other effects on the hemopoietic system are the commonest effects) and causes damage to organs including the liver, kidneys, heart, and male gonads, as well as causes effects to the immune system^[8].

2. Materials and methods:

2.1 Chemicals

Analytical grade reagents were used for heavy metal solution; ACS reagent grade concentrated sulfuric acid and NaOH were used to adjust pH values of samples. In all experimental work, distilled de-mineralized water was used.

2.2 Adsorbent

Rice husk: Rice husk was obtained from a local

mill in near the city. The rice husk was screened and washed with de-ionized water to remove dirt and metallic impurities after which it was dried in the oven at about 105 °C for 2 hours. The dried rice husk was grounded and sieved in the mesh in the range between 250 µm and 150 µm in order to increase its surface area. The purpose of this work was to improve textural parameters of carbons obtained from rice husk 100 gm of carbonized rice husks were soaked in 0.6 M of citric acid for 2 hours at 20 °C. Acid husk slurry is dried overnight at 50 °C and the dried husks are heated to 120 °C under aerobic conditions. The reacted product was washed repeatedly with distilled water (200 ml/g). Finally the cleaned rice husk was oven dried overnight at 100 °C. It was reported that modified rice husk is a potentially useful material for the removal of Cr, Cd and Pb from aqueous solutions. The adsorbents were prepared as described^[19, 12].

2.3 Adsorbate

Pb(NO₃)₂, Cd(NO₃)₂ and K₂Cr₂O₇ were obtained in analytical grade (Merck Co.) and used without further purification synthetic 1000 ppm stock solution prepared for each metal^[20].

1) Stock solution of Cd (1000 mg/l)

2.21 grams of Cd(NO₃)₂ was added in 100 ml of distilled water in 1000 ml volumetric flask. It was dissolved by shaking and the volume was made up to the mark. Lead solution concentration of this solution was 1000 mg/l.

2) Stock solution of Cr (1000 mg/l)

2.82 grams of K₂Cr₂O₇ was added in 100 ml of distilled water in 1000 ml volumetric flask. It was dissolved by shaking and the volume was made up to the mark. Lead solution concentration of this solution was 1000 mg/l.

3) Stock solution of Pb (1000 mg/l)

1.6 grams of Pb(NO₃)₂ was added in 100 ml of distilled water in 1000 ml volumetric flask. It was dissolved by shaking and the volume was made up to the mark. Lead solution concentration of this solution was 1000 mg/l.

2.4 Glassware and Apparatus Used

All glass wares (Conical flasks, Pipette, Measuring cylinders, Beakers, Petri plates and Test tubes etc.) used are of Borosil/Rankem. The instruments and apparatus used throughout the experiment are listed in table below:

Table 2: List of Instruments used during the whole experiment

S. No.	Instrument	Make
1.	UV-Visible spectrophotometer	Systronics spectrophotometer 118
2.	Digital Weight Balance	Atco Company
3.	What man filter paper no.1	-
4.	Orbital shaker	Remy
5.	pH meter	Adair dutt (AOP- Series)

Analysis of adsorbate: Estimation of metals: The metals were estimated using standard methods as described by Al- Asheh(1). Wavelength of adsorption of Pb, Cd, Cr from aqueous solution is 520 nm, 326 nm, 324 nm respectively^[7, 11].

2.5 Batch mode adsorption studies

The adsorption of heavy metals on coconut husk was studied by batch technique. The general method used for this study is described as below: Isotherm experiments were conducted to investigate the relationship between the solid phase concentrations of an adsorbate, the amount of adsorbate adsorbed per unit mass of adsorbent and the solution phase concentration of the adsorbent at an equilibrium condition under constant temperature. Six solutions with different initial concentrations of (2, 4, 6, 8 and 10 ppm) of each heavy metals solution (namely Cd, Cr, Pb) were prepared. The required pH was adjusted by drop wise addition of 0.1 N H₂SO₄, 0.1 N NaOH, depending on the acidity of the sample. All experiments were carried out at 25 °C by adding different amounts of adsorbents to different concentrations of 100 ml of heavy metal ions solution. The agitation rate for all experiments was 180 rpm and the residence time was (20, 40, 60, 80... 180 minutes).

In each experiment we added known quantity of adsorbent in 100 ml of heavy metal solution after a certain time adsorbents were then separated from the solution by using filter paper (Whatman No. 41) and the residual heavy metals ions concentration in the solution was then determined by UV-visible spectrophotometer with the help of calibration curve.

The concentration of heavy metal ions remaining in solution was measured by UV-visible spectrophotometer (Systronic 118). The effect of several parameters, such as pH, concentrations, contact time and adsorbent dose on the adsorption was studied. The pH of the adsorptive solutions was adjusted using sulfuric acid, sodium hydroxide and buffer solutions when required adsorption of metal ions on the walls of glass flasks determined by running the blank experiments was found negligible.

The results of these studies were used to obtain the optimum conditions for maximum heavy metals removal from aqueous solution. The percent heavy metal removal was calculated using Eq.

$$\text{Metal ion removal (\%)} = [(C_0 - C_e) / C_0] \times 100 \dots\dots\dots (1)$$

Where C₀: initial metal ion concentration of test solution, mg/l; C_e: final equilibrium concentration of test solution, mg/l^[3].

3. Results and discussion

3.1 Effect of contact time

Fig. 1, 2 and 3 shows the variation in the percentage removal of heavy metals with contact time using 1 gm /100 ml of treated rice husk adsorbent at 6 pH. It is observed that for Cd²⁺ the percentage removal is 92%, Cr⁶⁺ the percentage removal is 83% and Pb²⁺ ions, the percentage removal is nearly 93% at, 4 ppm even throughout the 120 min. contact times. It is observed that in all cases the percentage removal is comparatively lower for 20 min. contact time, with increasing removal efficiencies at higher contact time up to 120 min and then gradually decrease at 180 minutes. The maximum removal obtained at 120 minutes. It is evident from the results that the contact time required to attain equilibrium is dependent on the initial concentration of heavy

metals. For the same concentration, the percentage removal of heavy metal increases with increase of contact time till equilibrium is

attained. The optimal contact time to attain equilibrium with coconut husk adsorbent is 120 minutes.

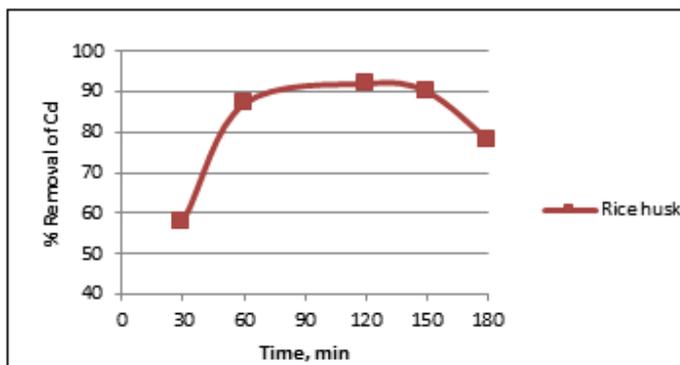


Fig 1: Effect of contact time on cadmium (Parameter- 6 pH, Concentration 4 ppm and Dose Amount 3 gm)

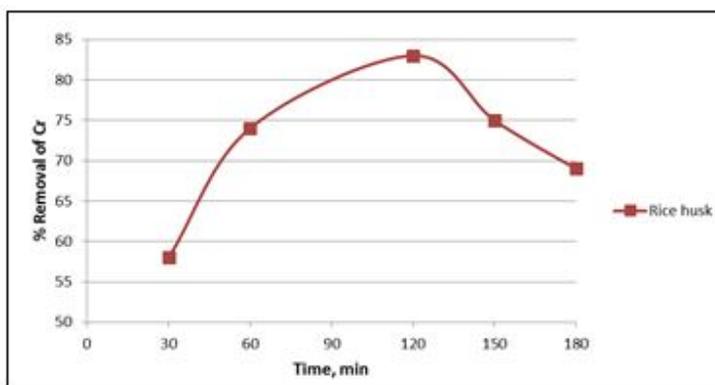


Fig 2: Effect of contact time on chromium (Parameter- 6 pH, concentration 4 ppm and dose amount 3gm)

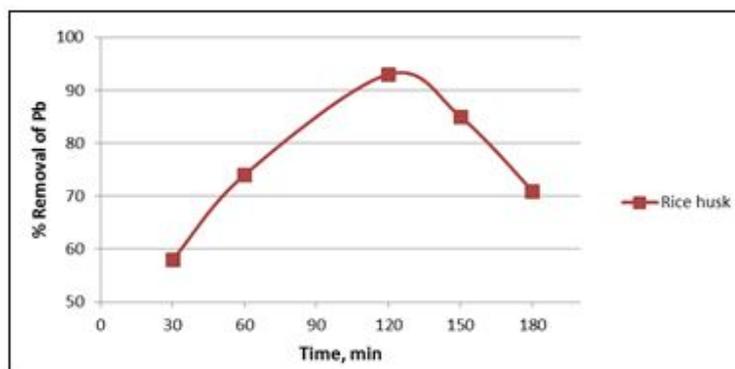


Fig 3: Effect of contact time on lead (Parameter- 6 pH, Concentration 4 ppm and Dose Amount 3 gm)

3.2 Effect of pH

pH variation is one of the most important parameters controlling uptake of heavy metals from wastewater and aqueous solutions. Fig. 4, 5 and 6 shows the effect of pH on heavy metals removal efficiencies of rice husk adsorbent.

These studies were conducted at an initial metal ions concentration of 4 ppm in 100 ml solution, at constant adsorbent dose 4 gm /100 ml solution, 120 minutes agitation period by varying the pH in each solution.

The percentage adsorption increases with pH to attain a maximum at 6 pH for Cd^{2+} and Pb^{2+} and thereafter it decreases with further increase in pH. The percentage adsorption increases with 2 pH for Cr^{6+} thereafter, it decreases with further increase in pH. The maximum removals of Cd^{2+} and Pb^{2+} at 6 pH and Cr^{6+} at 2 pH were found to be nearly 92%, 93% and 83%, respectively. The maximum

adsorption at 6 pH may be attributed to the partial hydrolysis of M^+ , resulting in the formation of MOH^+ and $\text{M}(\text{OH})_2$ would be adsorbed to a greater extent on the non-polar adsorbent surface compared to MOH^+ . With increase of pH from 2 to 6, the metal exists as $\text{M}(\text{OH})_2$ in the medium and surface protonation of adsorbent is minimum, leading to the enhancement of metal adsorption^[6].

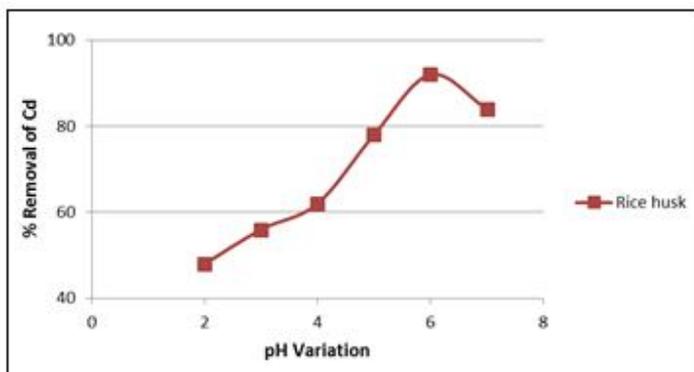


Fig 4: Effect of pH on cadmium (Parameter- Concentration 4 ppm, Dose Amount 3 gm and Contact Time 120 minutes with agitation)

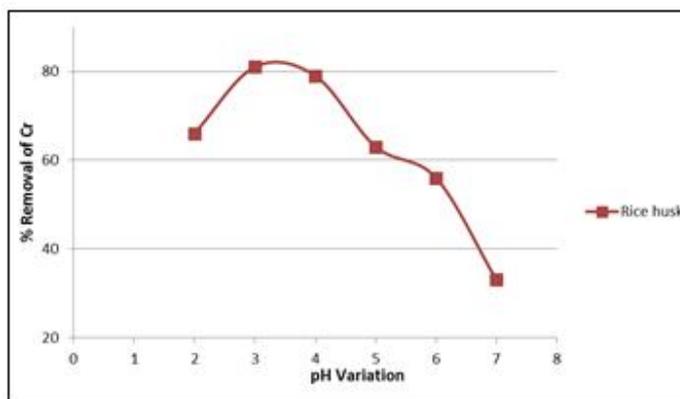


Fig 5: Effect of pH on chromium (Parameter- Concentration 4 ppm, Dose Amount 3 gm and Contact Time 120 minutes with agitation)

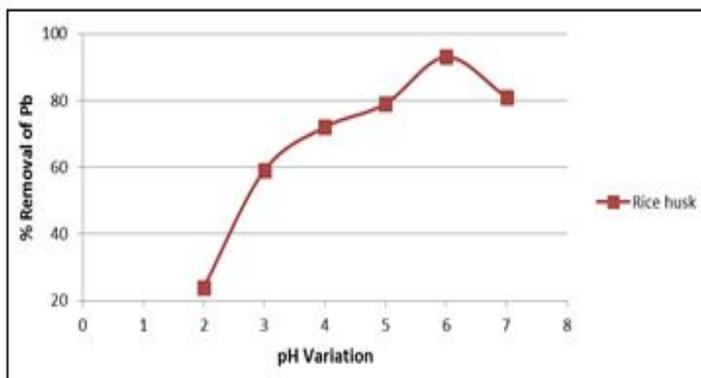


Fig 6: Effect of pH on chromium (Parameter- Concentration 4 ppm, Dose Amount 3 gm and Contact Time 120 minutes with agitation)

3.3 Effect of adsorbent dose

The results for adsorptive removal of heavy metals with respect to adsorbent dose are shown in Fig. 7, 8 and 9 over the range 1 to 5 gm/100 ml, at pH 6 and 120 minutes contact time. The percentage removal of heavy metals is seen to increase with adsorbent dose. From fig. 7, 8 and 9, it is observed that there is a sharp increase in percentage removal with adsorbent dose for Cd^{2+} , Cr^{6+} and Pb^{2+} ions. The maximum removal of Cr^{6+} , Pb^{2+} are 83% and 93% respectively at 4

gram dose amount of rice husk adsorbent and from fig. 7 maximum removal Cd^{2+} is 92% at 3 gram adsorbent dose.

It is apparent that the percent removal of heavy metals increases rapidly with increase in the dose of the adsorbents due to the greater availability of the exchangeable sites or surface area. Moreover, the percentage of metal ion adsorption on adsorbent is determined by the adsorption capacity of the adsorbent for various metal ions.

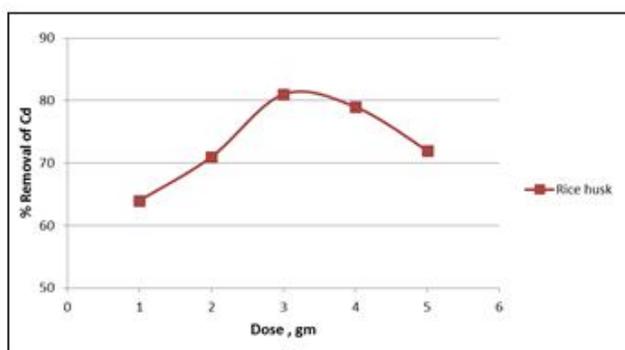


Fig 7: Effect of adsorbent dose on cadmium (Parameter- pH 6, Concentration 4 ppm, Contact Time 120 min. with agitation)

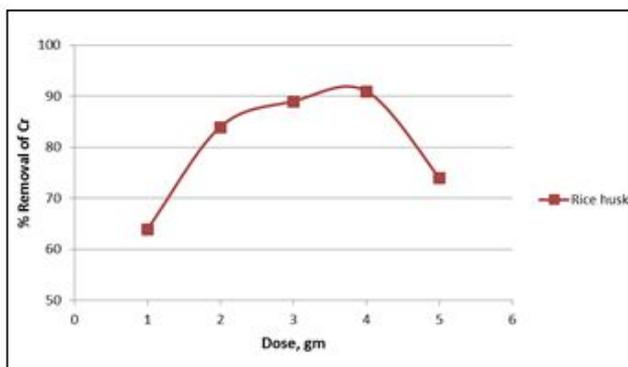


Fig 8: Effect of adsorbent dose on chromium (Parameter- pH 6, Concentration 4 ppm, Contact time 120 min. with agitation)

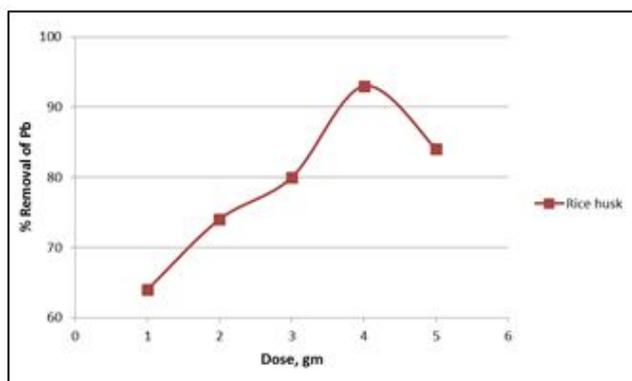


Fig 9: Effect of adsorbent dose on lead (Parameter- pH 6, Concentration 4 ppm, Contact Time 120 min. with agitation)

3.4 Effect of initial concentration of heavy metal

The effect of concentration at 1 gm/100 ml adsorbent dose, 6 pH, 180 rpm and 120 contact time were observed. The effect of initial concentration on the percentage removal of heavy metals by rice husk is shown in fig. 10. It can be seen from the figure that the percentage removal decreases with the increase in initial heavy metal concentration for Cr⁶⁺, Pb²⁺ and Cd²⁺. The percentage removal is highly effective on the 4 ppm initial concentration after which percentage removal decreases gradually to below 70%. At

higher initial concentrations (4 ppm) for Pb²⁺ shows greater percentage removal than Cr⁶⁺ and Cd²⁺. At lower initial metal ion concentrations, sufficient adsorption sites are available for adsorption of the heavy metals ions. Therefore, the fractional adsorption is independent of initial metal ion concentration. However, at higher concentrations the numbers of heavy metal ions are relatively higher compared to availability of adsorption sites. The maximum removal of cadmium, chromium and lead ion are 92%, 83% and 93% respectively at 4 ppm concentration.

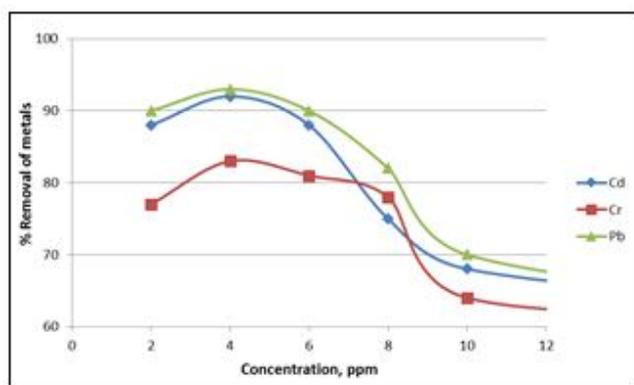


Fig 10: Effect on concentration by rice husk (Parameter- pH 6, Dose Amount 4 gm, Contact Time 120 minutes with agitation)

3.5 Adsorption Isotherm

In order to model the sorption behavior, adsorption isotherms have been studied. Since maximum reduction of Cd²⁺, Cr⁶⁺ and Pb²⁺ adsorption are observed at nearly 6 pH, the isotherm experiments have been conducted at this pH to full saturation potential of rice husk. The initial concentration of metal solution fixed at optimum adsorption. The adsorption process of Cd²⁺, Cr⁶⁺ and Pb²⁺ are tested by Langmuir and Freundlich isotherm models. Langmuir equation is given below^[17]:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e$$

Where C_e is the equilibrium concentration (mg/l) of Cd in the solution q_e , the amount of cadmium sorbed per unit weight of sorbent (mg/g); q_m the maximum adsorption capacity; and b , the energy of adsorption.

Freundlich isotherm model is given by the following equation^[14]

$$\log q_e = \log K_f + \frac{\log C_e}{n}$$

The fit of the data imply that the intercept (K_f) is the sorption capacity and the slope ($1/n$) of the sorption intensity, the constants incorporating the entire factor affecting the adsorption process. Further, the essential characteristics of the Langmuir isotherm can be described by a separation factor R_L , which is defined by the following equation

$$R_L = \frac{1}{1 + b \cdot C_0}$$

Where C_0 is the optimum initial concentration (ppm) of metal ions and b is Langmuir constant. The value of R_L indicates the shape of the isotherms to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($R_L < 1$) or irreversible ($R_L = 0$). Isotherm is determined by the plotting total metal ions bound to the adsorbed (mg/g) to the residual

concentration (mg/L). It is shown that the adsorption capacity of rice husk increases rapidly 0.94 to 2.231 mg/g for the equilibrium concentration 4 mg/L

3.6 Adsorption Kinetics

Two simplified kinetic models were adopted to examine the mechanism of the adsorption process. First, the kinetics of adsorption was analyzed by the Lagergren pseudo-first-order equation as depicted in Equation^[15].

$$\log(q_e - q_t) = \log q_e - \left(\frac{K}{2.303}\right)t$$

Here q_e and q_t , the amount adsorbed at equilibrium time and time t (min) and K the first order rate constant for adsorption (min^{-1}). Values of K at ambient temperature were calculated from the plots of $\log(q_e - q_t)$ versus t for a

concentration of 4 ppm for Cd^{2+} , Cr^{6+} and Pb^{2+} ions.

On the other hand, the pseudo-second-order equation based on equilibrium adsorption is expressed by Equation^[16].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e t}$$

However, the correlation coefficient R^2 showed that the pseudo-second order model, fits better the experimental data ($R^2 > 0.990$) than the pseudo-first order model (R^2 in the range of 0.888-0.964). The kinetic parameters have been found that the equilibrium sorption capacities determined using second-order model were in agreement with the experimentally determined equilibrium sorption capacities.

Table 3: Langmuir and Freundlich isotherm constants and correlation coefficients for the adsorption by rice husk adsorbent.

Metals	C_o (ppm)	Langmuir isotherm constants				Freundlich isotherm		
		q_m , mg/g	b (l/g)	(R^2)	(R_L)	Sorbition Capacity (K_f) (l/g)	(n)	(R^2)
Cd	4	2.0	0.658	0.943	0.875	49.40	1.036	0.813
Cr	4	0.851	5.432	0.083	0.972	15.37	0.856	0.813
Pb	4	1.416	0.994	0.996	0.652	66.31	1.218	0.920

Table 4: Comparison of the pseudo-first-order and pseudo-second-order adsorption rate constants and the calculated and experimental q_e values obtained for an initial concentration of 4 ppm of metal ions.

Metals	C_o (ppm)	q_e exp. (mg/g)	Pseudo I st order kinetic model			Pseudo II nd order kinetic model		
			K_1	q_e	R^2	K_2	q_e	R^2
Cd	4	4.13	0.414	0.898	0.974	0.892	2.94	0.972
Cr	4	1.89	0.276	3.391	0.893	0.184	1.89	0.812
Pb	4	3.75	0.322	0.927	0.969	0.571	2.86	0.991

4. Conclusions

For the past few years, there is increasing interest in the preparation of low-cost adsorbent as an alternative to biosorption of Cd^{2+} , Cr^{6+} and Pb^{2+} ions. In this research, rice husk has shown its potential to be an active bio-adsorbent material in solving wastewater pollution as a cost-effective adsorbent. The usage of the rice husk might help to overcome part of the excessive agricultural wastes in some part of the world. The experiment results showed that maximum removal of Chromium ion by rice husk adsorbent is 83% and

for Cadmium & Lead ion are nearly 93% at optimum condition at optimum condition (6 pH, 120 min. contact time, 3 gm adsorbent dose and 4 ppm concentration). The adsorption process of metal solution can be described by Langmuir isotherm and Freundlich isotherm models. However Langmuir shows a good agreement with the equilibrium data. The adsorption of cadmium (Cd^{2+}), lead (Pb^{2+}) onto adsorbents (coconut husk) followed the pseudo second order reaction while chromium (Cr^{6+}) followed the pseudo first order reaction.

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