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REMOVAL OF HEAVY METALS FROM WASTE WATER BY THE TREATMENT OF LOW COST NATURAL ADSORBENT

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ABSTRACT

The study of removal of heavy metals Cr(II), Cu(II) and Zn(II) from stimulated waste water by batch adsorption experiments with low cost natural adsorbent Castor seed husk(CSH) use as a natural adsorbent for effective removal of Cr(II), Cu(II) and Zn(II) ions. The main parameters influenced the Cr(II), Cu(II) and Zn(II) adsorption process such as percentage recovery, initial metal concentration, effect of adsorbent dosage, metal ion concentration, effect of contact time & effect of pH was studied in batch experiments. The experimental results were analyzed by using Langmuir adsorption isothermal, & Freundlich adsorption isothermal model. The kinetic data well described by the pseudo first order kinetic model. The thermodynamic parameters such as ΔH, ΔG and ΔS also determined. Castor seed husk (CSH) was successfully employed for removal of Cr(II), Cu(II) and Zn(II) ions from waste water and the techniques will be appears industrially applicable & feasible.

Keywords: Adsorption, Castor seed husk (CSH), Cr(II), Cu(II) and Zn(II), kinetics, Thermodynamics, Adsorption isotherm.

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INTRODUCTION

Environmental pollution due to development in modern industrialpractice is one of the most significant problems of this century. Of this thecontamination of water resources by hazardous pollutants has attracted muchserious attention in the last few decades. This is particularly due to their toxic,acute and chronic health effects.Heavy metals are major toxic pollutants with severe health effects on humans. They are released into the environment from a variety of industrial activities.Heavy metals are chemical elements with a specific gravity that is at least 5 times the specific gravity of water and is toxic or poisonous even at low concentrations. Some well-known toxic metallic elements are arsenic(sp.gravity 5.7) iron(7.9) chromium (7.19)cadmium (8.65) lead (11.34) and mercury (13.54). Heavy metal ions are discharged into water system from various industrial activities such as electroplating industries, electronic equipment manufacturing, and chemical processing plants. Due to rapid development of industrial activities, the levels of heavy metals in water systems have substantially increased. Heavy metals can easily enter the food chain because of their high solubility in water. Cadmium, copper, chromium, lead and zinc are extremely toxic heavy metals of widespread use in many industries. The heavy metals pollution represents an important problem with human health concerns and serious ecological consequences. It is therefore essential to remove heavy metals from industrial waste waters and drinking water. Plant materials are mainly comprised of cellulose materials that can adsorb heavy metal cations in aqueous solution. Numerous waste biomass sources are available in nature in which adsorption properties have been reported e.g rice husk, saw dust, tea and coffee waste, orange peel peanut shells, activated carbon, dry tree leaves and barks[1].

Heavy metals are associated with myriad adverse health effects including allergic reactions (beryllium, chromium), neurotoxicity (lead), nephrotoxicity (mercuric chloride, cadmium chloride), and cancer (arsenic, hexavalent chromium). Humans are often exposed to heavy metals in various ways mainly through the inhalation of metals in the workplace or polluted neighborhoods or through the ingestion of food (particularly seafood) that contains high levels of heavy metals or paint chips that contain lead[2]. Adsorption is powerful technique for determining the rate parameters involved in an adsorption. Adsorption can be a potential alternative to traditional treatment processes of metal ions removal [3-5].The phenomenon of adsorption has been described in a wide range of non-living biomass like potato peel waste[6], untreated cocos nucifara [7], orange peel [8], crab shell [9], untreated coffee grounds [10], as well as of living biomass like, microbial cell [11], moss [12], yeast[13], fungi [14], algae [15-18]. Adsorption has been proved to be an excellent way to treat industrial waste effluents, offering significant advantages like the low-cost, availability, profitability, easy of operation and efficiency [19].

Numerous waste biomass sources are available in nature in which some experimental adsorption properties have been reported e.g rice husk [20], saw dust [21-23], tea and coffee waste [24-25], peanut shells[26], activated carbon [27-28]dry tree leaves and barks [29-31]. In literatures, studies were conducted usingbanana peelfor As(III) [32] and watermelon rind for Ni(II) and Co(II)[33-34]. studied the effect of various parameters on adsorption capacity using untreated coffee grounds as adsorbent[35].examined the role of low cost adsorbents on lead and zinc ions removal from waste water[36]. carried out investigations on *Azadirachta indica* (neem) leaf powder as an adsorbent on chromium removal from aqueous solution. The results indicated that the adsorption capacity is strongly depends on equilibrium pH [37] used the untreated coffee husks as adsorbents for the removal of heavy metal ions such as Cd(II), Cu(II) and Zn(II) from aqueous solution [38] carried out batch adsorption studies using mango biomass for Pb(II), Zn(II), Ni(II) and Cu(II) ions[39]investigated the potential of mango leaves powder for removal of Grey BL dye from aqueous solution.The comparison of adsorption capacities of guava and mango leaves powder for adsorption of methylene blue dye was studied [40]. Mango peel waste was evaluated as a new sorbent for adsorption of Cd(II) and Pb(II) ions from aqueous solution by [41]. In the present work, we have studied the potential of Cr(II), Cu(II) and Zn(II) biosorption on a agro material which is a waste material of castor seed husk. Results from this study can be used to assess the Cr(II), Cu(II) and Zn(II) removal from waste water.

MATERIALS AND METHODS

Adsorbent

The castor seed husk (CSH) is the waste was thoroughly rinsed with water to remove dust and soluble material. Then it was allowed to dry at room temperature. The dried castor seed husk was grounded to a fine powder in a grinding mill and sieved to get fine powder. The fine powder was then treated with sodium hydroxide (0.2 mol/L0 to improve the biosorption capacities to Cr(II), Cu(II) and Zn(II) ions. For this purpose 100 gms of dried castor seed husk powder soaked in solution of 500ml NaOH (0.2 mol/L) for 20 hrs. Then filter it and washed with de-ionized water until the pH value of the solution reached 7.0, then castor seed husk powder was dried at 110^0c in an oven for 14 hrs and was then stored in desiccators for final study.

Materials

All the chemicals used were of analytical reagent (AR) grade. Stock solution of 1000mg/L of Cr(II), Cu(II) and Zn(II) was prepared from Chromium sulphate,copper sulphate and Zinc sulphate by distilled water. Desiredtest solutions of Cr(II), Cu(II) and Zn(II) ions were prepared using appropriate subsequent dilution of the stock solution. The range of concentrations of Cr(II), Cu(II) and Zn(II) ions prepared from standard solution varies between 10 and 100 mg/L. Before mixing the adsorbent, the pH of solution was adjusted to the required values with 0.1 m NaOH.

Adsorption Study (Batch Process)

The dried 200 mg of castor seed husk (CSH) powder was taken in a stoppered bottle and standard solution 200 ml containing various concentration of Cr(II), Cu(II) and Zn(II) was added in the bottle and shake well. The equilibrium by shaking the contents of the solution at room temperature. The content was filtered. The adsorbate and adsorbent were separated by filtration. The filtrate was determine by spectrophotometrically. It measures the concentration of Cr(II), Cu(II) and Zn(II). Effect of pH of the Cr(II), Cu(II) and Zn(II) solution having 40 mg/L initial concentration. Effect of initial concentration of Cr(II), Cu(II) and Zn(II), agitating time and the adsorbent dose was also studied.

RESULTS AND DISCUSSION

Effect of pH

Effect of pH o solution is very important in adsorption process of metal ions. pH of solution affect on surface of adsorbent, solubility of metal and also the speciation of metal ions. The effect of pH on the removal of Cr(II), Cu(II) and Zn(II) ion using castor seed husk powder as an adsorbent. It was studied with the initial pH range from 2 to 9 it relates the initial pH of the solution and the percentage of Cr(II), Cu(II) and Zn(II) ions. With increasing pH from 5 to 7 the percentage of Cr(II), Cu(II) and Zn(II) increases.

Effect of Adsorbent Dose

The effect of adsorbent on Cr(II), Cu(II) and Zn(II) removal was studied by batch adsorption process. The percentage of removal of Cr(II), Cu(II) and Zn(II) reaches about 77% to 95 % each. The dose required is near about 200mg/25 ml for the initial concentration of 25 mg/L at pH 5.

Effect of contact time

The rate of removal of Cr(II), Cu(II) and Zn(II)ion the effect of contact of Cr(II), Cu(II) and Zn(II) adsorption on castor seed husk powder was studied. The percentage removal of Cr(II), Cu(II) and Zn(II) ions at different initial values Cr(II), Cu(II) and Zn(II) ions, concentration of solution varies from 5,10,15,20,25,30,35,40,45,50 mg/L and batch experiments were carried out by taking 200 ml of this solution with dried 200 mg ofadsorbent and the system is equilibrium by shaking the solution content at room temperature . The equilibrium of solution reaches in 7 hours. Final concentration of Cr(II), Cu(II) and Zn(II) was determined by spectrophotometrically. The removal of Cr(II), Cu(II) and Zn(II) was 72 5, 84 % and 86 % respectively. The adsorption of Cr(II), Cu(II) and Zn(II) on castor seed husk (CSH) powder adsorbent was a function of time was studied.As the concentration of metal ion increases

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surface area of adsorbate was covered more & more and hence at the higher concentration of Cr(II), Cu(II) and Zn(II) ions capacity of metal ions adsorbed in the surface of adsobate is decreased due to unavailability of the surface area of adsorbate. It conclude that at lower concentration of Cr(II), Cu(II) and Zn(II) ions the percentage of adsorption is high because of the moreactive site of adsorbate is available for the adsorption.

Freundlich Adsorption Isotherm

Freundlich plot for the adsorption of Cr(II), Cu(II) and Zn(II) ions with castor seed husk powder shows that the values of adsorption intensity 1/n is less than 1, indicates the applicability of Freundlich adsorption **Table 2.**

Langmuir Adsorption Isotherm

The value of Q_0 of Langmuir adsorption isotherm found to be comparable with commercial activated carbon. Value of b lies between 0 to 1 it indicate that the adsorption is favourable. It indicate that the applicability of Langmuir adsorption isotherm **Table 3**

Adsorption Kinetics

Adsorption rate ofCr(II), Cu(II) and Zn(II) ions on castor seed husk powder was studied by first order kinetic rate equation. It is found that the initial concentration of Cr(II), Cu(II) and Zn(II) ions increases rate constant decreases it indicate that the adsorption does not follow the first order kinetics **Table 4**

Thermodynamics Parameters

Adsorption rate depends on temperature was investigated at 298K,303K 308k and 315 K. it conclude that increasing temperature mass of Cr(II), Cu(II) and Zn(II) ions per unit mass of the adsorbent was increased. At above temperature the change in Gibb's free energy, Change in enthalpy and Change in entropy was calculated. Change in Gibb's free energy shows negative value indicate that the adsorption of Cr(II), Cu(II) and Zn(II) ions on castor seed husk powder is spontaneous and feasibility. The change in enthalpy value indicates

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endothermic nature of Cr(II), Cu(II) and Zn(II) ions on castor seed husk powder. The change in entropy shows positive value indicates increase randomness during the adsorption process of Cr(II), Cu(II) and Zn(II) ions on castor seed husk powder. **Table 5**

Table 1. Summary of % Recovery & Adsorbent Capacity of adsorbent,Initial concentration25 mg/L. Adsorbent dose 1 gm/L

Sr.No.	Adsorbent	Heavy Metal	Final Conc (mg/L)	% Recovery	Q(mg/L)
1	Castor seed husk (CSH)	Cr(II)	33.55	51.85	17.50
2		Cu(II)	49.68	87.46	23.63
3		Zn(II)	54.25	36.44	12.90

Table 2. Freundlich Adsorption isotherm of Cr(II), Cu(II) and Zn(II) on (CSH)

Sr.No.	Heavy Metal	Concentration	Freundlich Constant	
			K	1/n
1	Cr(II)	10 mg/L	3.3540	1.021
		20 mg/L	5.1837	1.354
		30 mg/L	6.8894	1.556
		40 mg/L	7.3813	2.014
2	Cu(II)	10 mg/L	4.8868	1.433
		20 mg/L	7.1537	1.982
		30 mg/L	9.3840	1.993
		40 mg/L	7.0024	2.631
3	Zn(II)	10 mg/L	3.4402	2.013
		20 mg/L	8.8241	3.286
		30 mg/L	9.3518	5.351
		40 mg/L	7.6329	2.574

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Table 3. Langmuir Adsorption isotherm of Cr(II), Cu(II) and Zn(II) on (CSH)

Sr.No.	Heavy Metal	Concentration	Langmuir Constant	
			Q_0	b
1	Cr(II)	10 mg/L	35.47	0.033
		20 mg/L	41.05	0.048
		30 mg/L	43.58	0.051
		40 mg/L	50.61	0.084
2	Cu(II)	10 mg/L	55.32	0.074
		20 mg/L	58.67	0.082
		30 mg/L	63.97	0.094
		40 mg/L	57.14	0.099
3	Zn(II)	10 mg/L	48.54	0.006
		20 mg/L	51.36	0.032
		30 mg/L	53.82	0.052
		40 mg/L	61.79	0.087

Table 4. Adsorption Kinetics of Cr(II), Cu(II) and Zn(II) on (CSH)

Sr.No.	Heavy Metal	Concentration	First order rate constant (K_1)
1	Cr(II)	10 mg/L	3.8894×10^{-3}
		20 mg/L	4.1158×10^{-3}
		30 mg/L	5.2025×10^{-3}
		40 mg/L	7.3476×10^{-3}
2	Cu(II)	10 mg/L	5.4021×10^{-3}
		20 mg/L	9.3864×10^{-3}
		30 mg/L	8.8521×10^{-3}
		40 mg/L	8.2143×10^{-3}
3	Zn(II)	10 mg/L	3.3188×10^{-3}
		20 mg/L	4.9931×10^{-3}
		30 mg/L	8.4282×10^{-3}
		40 mg/L	9.0091×10^{-3}

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Table5. Thermodynamic parameters for the adsorption ofCr(II), Cu(II) and Zn(II) on CSH at various temperatures(CSH)

Sr.No	Heavy Metal	T(^{0}K)	ΔG (KJ/mol)	ΔH(KJ/mol)	ΔS (KJ/mol)	R^2
1	Cr(II)	298	-27.32	45.38	0.3411	0.0874
		303	-30.61			
		315	-34.28			
		340	-40.26			
2	Cu(II)	298	-28.38	50.68	0.4399	0.9112
		303	-39.12			
		315	-43.53			
		340	-42.66			
3	Zn(II)	298	-29.68	46.56	0.2894	0.7432
		303	-38.16			
		315	-49.40			
		340	-53.55			

CONCLUSION

- CSH was used as adsorbent for Cr(II), Cu(II) and Zn(II) , It is good adsorbent for the removal of Cr(II), Cu(II) and Zn(II), Adsorption process is rapid at the starting and it becomes slow at the saturated stage. It dependent on an initial concentration of adsorbate and also time for adsorption.
- CSH does increased percentage of adsorption also increased.
- This adsorption is good agreement with Freundlich adsorption isotherm and also for Langmuir adsorption isotherm it indicate monolayer adsorption of Cr(II), Cu(II) and Zn(II) on CSH.
- Adsorption process is good at pH 5, The uptake capacity of Cr(II), Cu(II) and Zn(II) is better for CSH.

- Temperature effect shows that with increasing temperature capacity of adsorption increases.
- CSH could be exploited for commercial applicable.
- The cost of adsorbent CSH is very low is easily available.
- The adsorbent CSH can be deposed safely.

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