

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 5, May 2016

Adsorption of Cadmium(II) Ions from Simulated Wastewater Using Raw Luffa Husk: Kinetics, Isotherm and Thermodynamic Studies

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ABSTRACT: Naturally available waste material like raw luffa husk was found to be a low-cost material and also a promising adsorbent for removing cadmium(II) ions from simulated wastewater. A batch adsorption was carried out with various adsorption parameters, such as pH, contact time, initial concentration, dosage and temperature. Kinetics of Cd(II) ions adsorption by RLH is better fit by the pseudo-first order equation. Various thermodynamic parameters such as ΔG° , ΔH° and ΔS° have also been evaluated and it has been found that the adsorption process was spontaneous, endothermic and randomness in nature. The experimental data were analysed using the Langmuir, Freundlich and Temkin isotherm equations. The equilibrium data found to fit well in the Langmuir isotherm, which confirmed the monolayer coverage of Cd(II) ions onto RLH. The result indicate that the RLH can be used to effectively adsorb Cd(II) from wastewater.

KEY WORDS: Adsorption, Heavy metal, Bioadsorbent, Kinetics, Equilibrium, Isotherm

I. INTRODUCTION

Heavy metal pollution in the aquatic system is one the most important environmental problem today[1]. They cause several health risks it affects food chain. The concentration of some of the toxic metals like Cu, Ni, Cd, Cr, As and Zn etc are higher than permissible discharge levels in these effluents[2]. It, therefore, becomes necessary to remove these toxic metals by an appropriate treatment before releasing them into the environment. Cadmium is one of the toxic heavy metal with a greatest potential hazard to humans and environment. Most of the heavy metals cannot be separated by ordinary physical means of separation method. Several convenient methods like coagulation, oxidation process, reverse osmosis, chemical precipitation, ion exchange and the adsorption using activated charcoal. There is a need to develop more effective and economical technologies for the removal of heavy metals from effluent[3]. Adsorption is one of the most favourable techniques applied for water treatment, mainly because it is suitable for low concentration of metal ions and cost effective[4-6]. The current trend is to investigate the possibilities of employing various agro-waste and biological material to remove heavy metals[7]. Several low cost materials such as peanut husk[8], scoria[9], Moringa oleifera bark[10], orange peel[11], cucurbita maxima husk[12], watermelon shell[13] and maize cob[14] have been tested to remove a metal ions from aqueous solutions.

In this study, the potential of the luffa husk as a biosorbent for the removal of Cd(II) from aqueous solution and effluent water was investigated with the influence of experimental parameters such as pH, contact time, initial concentration, adsorbent dosage and temperature. The kinetic data and equilibrium data of adsorption studies were processed to understand the adsorption mechanism of the cadmium ions onto the luffa husk.

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II. MATERIALS AND METHODS

Preparation of adsorbate solution: A stock solution of Cd(II) ion was prepared by dissolving an accurately weighed 2.2818g of cadmium sulphate in 1L of double distilled water.

Preparation of adsorbent material: Luffa husk was collected from the local market. The collected luffa husk was washed with excess tap water to remove soil and dust and finally with double distilled water dried in sunlight. After drying the husk was powdered and sieved to uniform particle sizes and stored in sealed glass bottles. Now the adsorbent is called as RLH (Raw Luffa Husk).

Adsorption experiment: Adsorption experiments were conducted by varying pH, contact time, initial concentration, adsorbent dosage and temperature. The experiments were carried out in 250mL flask using 1g of the adsorbent, the particle size 0.25mm, at room temperature and the total volume of the reaction mixtures was kept at 200mL. The pH of solution was maintained at a desired value by adding 0.1M NaOH or 0.1M HCl. The flasks were shaken for the required time period in a mechanical shaker at 120rpm at predetermined time, the flasks were withdrawn from the shaker and the reaction mixtures were filtered. For the thermodynamic study, the experiments were performed at 301, 307 and 313K. The isotherm study was performed using various concentrations of cadmium solutions (5 to 25mg/L) and different temperatures. All experiments were performed in duplicates. The filtrate samples were analysed using Atomic Absorption Spectrophotometer. The amount adsorbed(q_e) was calculated according to

$$q_e = (C_0 - C_e)XV/M$$

where C_0 and C_e are the initial and equilibrium concentrations (mg/L) of cadmium solution respectively, V is the volume(L), and M is the mass (g) of the adsorbent.

The desorption studies of residual metal ion solution was filtered to separate the adsorbent and generally washed with distilled water to remove any unadsorbed cadmium ion. Solid containing the metal ions was dried under sunlight and stored in a container. About 1g of sample was suspended in 50ml of distilled water. The amount of desorbed cadmium(II) ion was estimated from the filtrate of the reaction mixture. The concentrations of each of these metal ions were estimated from the respective filtrates after the equilibrium studies are conducted.

III. RESULTS AND DISCUSSION

Morphological studies: Studies on an adsorbent's surface topography could provide important information on the degree of interaction between the adsorbent particles and the dry molecules[15]. Scanning electron microscope (SEM) was used to study the surface morphology of RLH. In **figure 1** the textural structure of the adsorbent is presented at x 500 magnification. The SEM image showed the irregular texture and porous nature of the surface of the adsorbent. The rough surface of the adsorbent material as it indicates the high surface area.

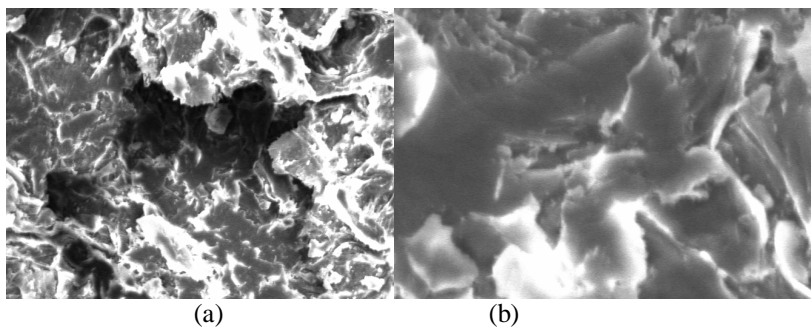


Figure 1 SEM image of (a) raw luffa husk (b) cadmium(II) ion-loaded raw luffa husk.

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Table 1: Characterisation and physical parameters of raw luffa husk

S.no.	Parameters	Values
1	Moisture content (Not more than 9-17%)	13.3%
2	Ash content (not more than 16%)	4.95%
3	Density(g/ml)	0.279
4	pH	5.76
5	Specific gravity (g/ml)	0.711
6	Particle size(mm)	0.250

Effect of pH : The pH of the solution is one of the most important operating parameters that affect the adsorption of metal ions. The pH of the solution affects the competition of metal ions and hydrogen ions for the active sites on the adsorbent surface[16]. The effect of solution pH on the adsorption of Cd(II) ions onto RLH was studied by changing the solution pH range of 5 – 6. The removal of Cd(II) ions increases with the increase in the solution pH and it reaches the maximum value at a pH of 6. At low pH values of the adsorbent was occupied by the H⁺ and H₃O⁺ ions which leads to a reduction of vacancies for Cd(II) ions and consequently causes a decrease in Cd(II) ions adsorption. Although the adsorption of the metal ions was found to be raised by increasing solution pH, further increment of pH caused declining in adsorption due to the formation of metal hydrides. However, a pH value of 6 was chosen as optimum for further experiments to avoid the formation of metal hydroxides.

Effect of contact time: The effect of contact time for the efficient removal of metal ion was studied. In **figure 2** showed a steady rate increase of sorption during the sorbate – sorbent contact time process and the rate of removal became almost insignificant due to a quick exhaustion of the adsorption sites[17-19]. The rate of metal removal is higher in the beginning due to a larger surface area of the adsorbent being available for the adsorption of the metal. In this study cadmium(II) ions amount adsorbed was achieved at 60 minutes. No significant changes were observed in the adsorption of cadmium(II) from solution after 1 hour of equilibration.

Effect of initial concentration: The effect of initial Cd(II) ion concentration in the range of 5 – 25 mg/L on adsorption was investigated and the results are shown in **figure 3**. It was found that the percentage cadmium adsorption increases with increase in initial cadmium concentration, in other words the adsorption capacity increasing from 5 - 25mg/L. This trend is that of the result of the progressive increase in the electrostatic interaction between the cadmium and the adsorbent active sites. Moreover, this can be explained by the fact that more adsorption sites were being covered as the cadmium ions concentration increases. Similar reports by Elaigwu, Hashem and Karaca et al[20-22].

Effect of adsorbate dosage: The effect of adsorbent dosage was studied by varying the adsorbent amounts such as 0.5g and 1g. In **figure 4** shows the adsorption of Cd(II) ions increases rapidly with increase in the amount of RLH due to greater availability of the surface area at higher concentration of the adsorbent. Therefore competition for bonding sites between molecules of the adsorbate should decrease with increase in dosage of the adsorbent[23].

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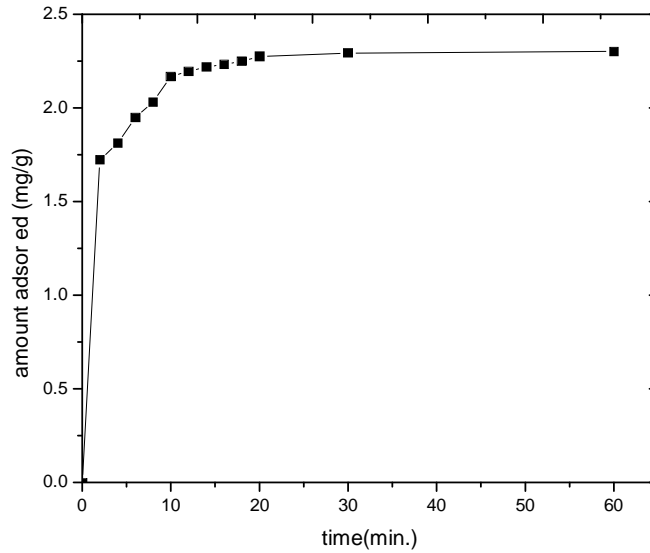


Figure 2: Effect of contact time on adsorption uptake of Cd(II) ion on RLH. Conditions: pH 6, initial concentration 5 mg/L, adsorption dosage 1g, particle size 0.25mm and temperature 301 K.

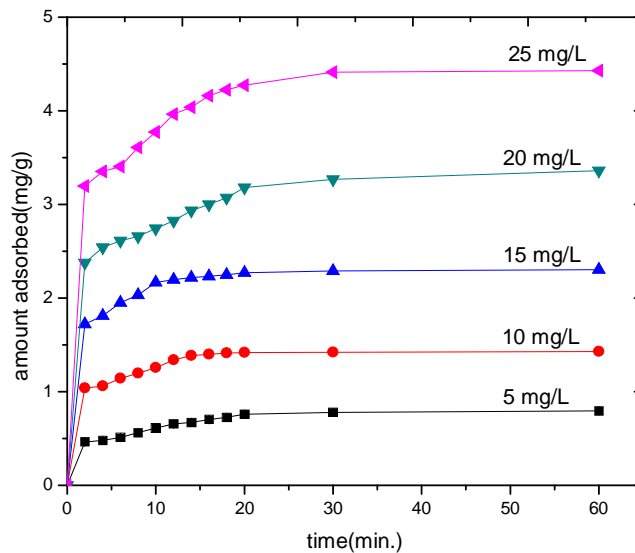


Figure 3: Effect of initial concentration on adsorption uptake of Cd(II) ion on RLH. Conditions: pH 6, adsorption dosage 1g, particle size 0.25mm and temperature 301 K

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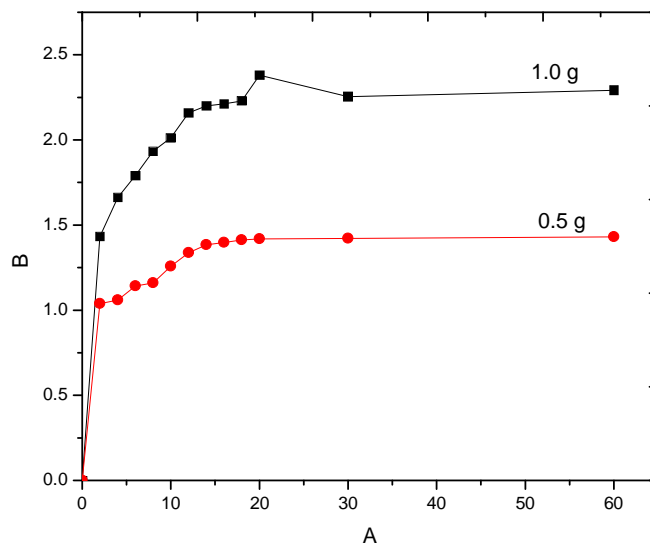


Figure 4: Effect of adsorbent dosage on adsorption uptake of Cd(II) ion on RLH. Conditions: pH 6, particle size 0.25mm, temperature 301 K, and initial concentration 5 mg/L.

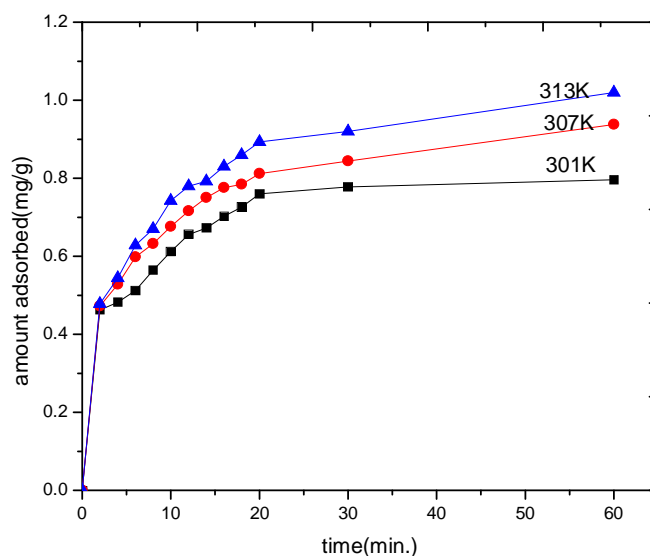


Figure 5: Effect of Temperature on adsorption uptake of Cd(II) ion on RLH. Conditions: pH 6, adsorption dosage 500mg, particle size 0.25mm, and initial concentration 5 mg/L.

Effect of temperature: The adsorption of metal ions has been found to increase with an increase in temperature from 301 to 313 K as shown in **Figure 5**. The increase in adsorption with temperature may be attributed to either increase in the number of active surface sites available for adsorption on the adsorbent or the desolvation of the adsorbing

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species and the decrease in the thickness of the boundary layer surrounding the adsorbent with temperature, so that the mass transfer resistance of adsorbate in the boundary layer decrease[24].

Adsorption thermodynamics: The amount of adsorption of Cd(II) ions decreases with the increase in the temperature. This is mainly due to the decrease in surface activity suggesting that adsorption between Cd(II) ions and RLH is an exothermic process. The maximum removal of Cd(II) ions was obtained at 313 K. To discuss about thermodynamic behavior of the adsorption of Cd(II) ions onto the RLH, thermodynamic parameters such as change in Gibbs free energy (ΔG°), the enthalpy (ΔH°) and the entropy (ΔS°) were estimated from the following equation.

$$\Delta G^\circ = -RT \ln K_c$$

$$\log K_c = \Delta S^\circ / 2.303 R - \Delta H^\circ / 2.303 RT$$

where R is the universal gas constant (8.314 J/mol K), T is the temperature (K) and K_c is the equilibrium constant. The values of the change in enthalpy and entropy were calculated from the slope and intercept of the plots of the $\log K_c$ versus $1/T$. (figure not given) In **table 2** the negative values of change in Gibbs free energy implies that the adsorption of Cd(II) ion onto the RLH was spontaneous and feasible. The negative values of the change in enthalpy suggest the exothermic nature of adsorption and the positive values of change in entropy can be used to describe the randomness at the RLH solution interface the adsorption of Cd(II) ions[25].

Table 2: Thermodynamic parameters and equilibrium constant for adsorption of cadmium(II) ion on raw luffa husk.

Parameter	301 K	307 K	313 K
ΔG° (kJ/mol)	-3.976	-7.095	-7.79
ΔH° (kJ/mol)	-2.489	-2.104	-2.06
ΔS° (kJ/mol)	1.819	2.543	5.362

Adsorption Isotherms: The description of cadmium(II) ion between the adsorbent and aqueous solution, when the system is at equilibrium is important to explain the capacity of the activated adsorbent and the nature of adsorption[26-28]. To determine the adsorption capacity of a new adsorbent material, a study of sorption isotherm is essential and this will help in selecting the adsorbent for the adsorption of metal ions at a particular concentration. Analysis of the isotherm data is important in order to develop an equation, which accurately represents the results of the batch, which could be used for, the design of adsorption system. The data obtained from the adsorption experiment conducted in the present investigation was fitted in different adsorption isotherm equations.

Langmuir isotherm: Langmuir[29] proposed a theory to describe the adsorption of gas molecules onto metal surfaces. The Langmuir adsorption isotherm has found successful applications in many other real adsorption process of monolayer adsorption. Langmuir's model of adsorption depends on the assumption that intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The isotherm equation further assumes that adsorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a Cd(II) molecule occupies a site, no further adsorption can take place at that site. Moreover, the Langmuir equation is based on the assumption of a structurally homogeneous adsorbent where all adsorption sites are identical and energetically equivalent. Theoretically, the sorbent has a finite capacity for the sorbate. Therefore, a saturation value is reached beyond which no further adsorption can take place. The experimental data were fitted to the Langmuir equation

$$C_e / q_e = 1/Q_0 b + C_e / Q_0$$

where C_e (mg/L) is the equilibrium concentration of metal ion, q_e (mg/g) is the adsorption capacity in equilibrium state, Q_0 is the maximum adsorption capacity, and b is the Langmuir constant (equilibrium constant (L/mg)) which reflects quantitatively the affinity between RLH and Cd(II) ions. The linear plot of Langmuir isotherm for metal ion adsorption and the calculated parameters along with regression coefficients are shown in **Figure 6 and Table 3**. The affinity between Cd(II) and RLH adsorbent can be predicted using the Langmuir parameter b from the dimensionless separation factor R_L ;

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$$R_L = 1 / (1 + bC_0)$$

The adsorption process as a function of R_L may be described as follows: $R_L > 1$ unfavourable, $R_L = 1$ linear, $0 < R_L < 1$ favourable, and $R_L = 0$ irreversible. The calculated R_L value for the adsorption of Cd(II) into RLH was found to be 0.558mg/g, which indicates a highly favourable adsorption of Cd(II) onto RLH.

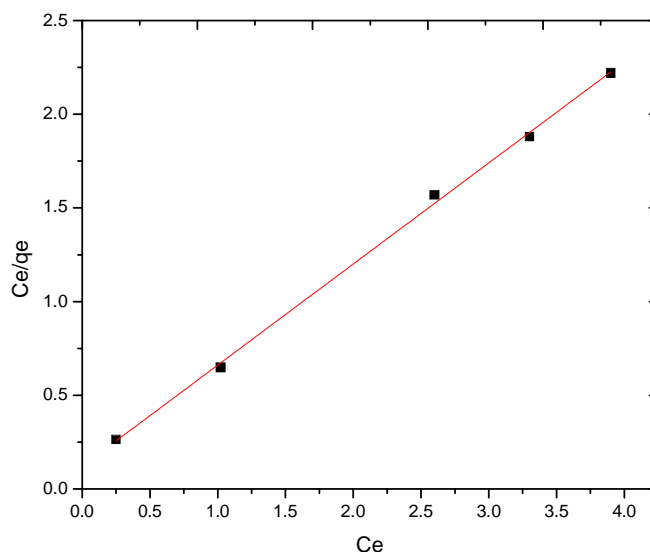


Figure 6: The Langmuir adsorption isotherm for Cd(II) adsorption onto RLH. Conditions: adsorbent dosage 1g, pH 6 and particle size 0.25mm, initial concentrations 5, 10, 15, 20 and 25 mg/L and at room temperature.

Freundlich isotherm: The Freundlich isotherm[30] model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface assumes that different sites with several adsorption energies are involved. Freundlich adsorption isotherm is the relationship between the amounts of cadmium adsorbed per unit mass of adsorbent, q_e and the concentration of cadmium at equilibrium, C_e . The Freundlich adsorption equation has the following general form

$$\log q_e = \log K_F + 1/n \log C_e$$

where K_F and n are the isotherm parameters too be determined. The Freundlich adsorption isotherm represents the relationship between the corresponding adsorption capacity q_e (mg/g) and the concentration of the metal in the solution at equilibrium C_e (mg/L). for this case, the plot of $\log C_e$ vs $\log q_e$ was employed to generate the intercept value of K_F and the slope of 'n' from **figure 7** and **table 3** the Freundlich constant K_F and n were found to be 1.693mg/g and 2.543 respectively.

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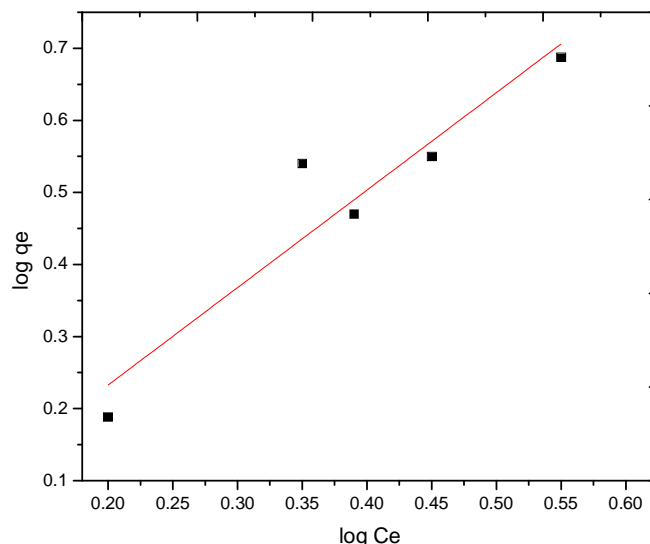


Figure 7: The Freundlich adsorption isotherm for Cd(II) adsorption onto RLH. Conditions: adsorbent dosage 1g, pH 6 and particle size 0.25mm, initial concentrations 5, 10, 15, 20 and 25 mg/L and at room temperature.

The Langmuir and Freundlich adsorption constants calculated from the corresponding isotherms with the correlation coefficients are presented in table 3. The correlation coefficient shows the adsorption process could be described by the both Langmuir and Freundlich model equation. The Langmuir constants values were fit the experimental data. On the other hand, the magnitudes of K_F and n show easy separation of Cd(II) ions from the wastewater and indicated favourable adsorption. As seen from the table 3 the 'n' value was found high enough for separation.

Temkin isotherm: The Temkin isotherm[31] equation assumes that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent – adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum bonding energy. The Temkin isotherm is represented by the following equation.

$$q_e = B_T \ln K_T + B_T \ln C_e$$

where, T is the absolute temperature (K), R is the universal gas constant, K_T is the equilibrium binding constant (L/mg), and b_T is the variation of adsorption energy (KJ/mol). B_T is Temkin constant related to the heat of adsorption (KJ/mol). The Temkin adsorption isotherm model was chose to evaluate the adsorbates[32]. The Temkin isotherm plot of the metal ion is presented in **figure 8** and the isotherm parameter shown in table 3. The Temkin adsorption potential, K_T of RLH of Cd(II) is 1.001(L/mg), the Temkin constant, B_T related to heat of sorption for the metal ion is 2.417kJ/mol.

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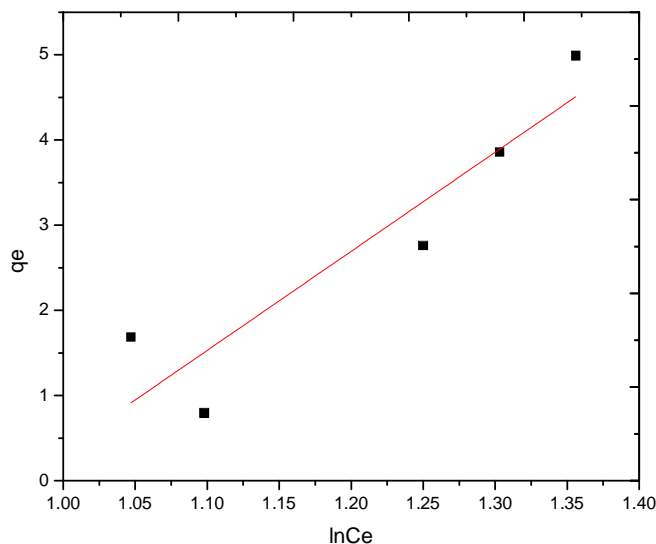


Figure 8: The Temkin adsorption isotherm for Cd(II) adsorption onto RLH. Conditions: adsorbent dosage 1g, pH 6 and particle size 0.25mm, initial concentrations 5, 10, 15, 20 and 25 mg/L.

Adsorption kinetics: The study of adsorption kinetics describes the solute uptake rate, evidently, this control the residence time of adsorbent uptake at the solid-solution interface[33]. Therefore, rate study becomes quite significant for waste water treatment.

$$\log (q_e - q) = \log q_e - k_{ad} t / 2.303$$

where q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g), 'q' the amount of solute adsorbed at any time 't' and ' k_{ad} '. Linear plots of $\log(q_e - q)$ versus t suggest the applicability of the first order kinetics. The rate constants, k_{ad} , were calculated from the slope of the **figure 9**. By regression modelling, experimental curves were found to be the best fit for the data characterized by the regression coefficient ($R^2=0.9908$). The rate constant (K_{ad}) increases with increase in temperature. The findings clearly indicate that higher temperature favours cadmium(II) ion removal by adsorption on adsorbents under study.

Desorption: Desorption studies held to elucidate the nature of adsorption, recovery of metal ions from waste water and recycling adsorbent. Desorption studies were conducted by mixing approximately 1g of metal loaded adsorbent material obtained at the end of the adsorption experiment. Desorption rate was slow and the amount released was also very less. This indicated that the major portion of cadmium(II) ion was, probably, bound to the sorbent through stronger interactions. The amount of desorption around 14%.

Simulated effect by Industrial effluent: To study the application of the adsorbents, industrial effluents were collected from nearby industries and the pH was recorded (pH=8), RLH doses of 1g, BSS 30 and at room temperature. In **figure 10** the amount adsorbed increases from 0.14 mg/L to 5.86 mg/L. From these results it may be concludes that the RLH can also be used in the removal of metal ion like cadmium(II) from effluent water.

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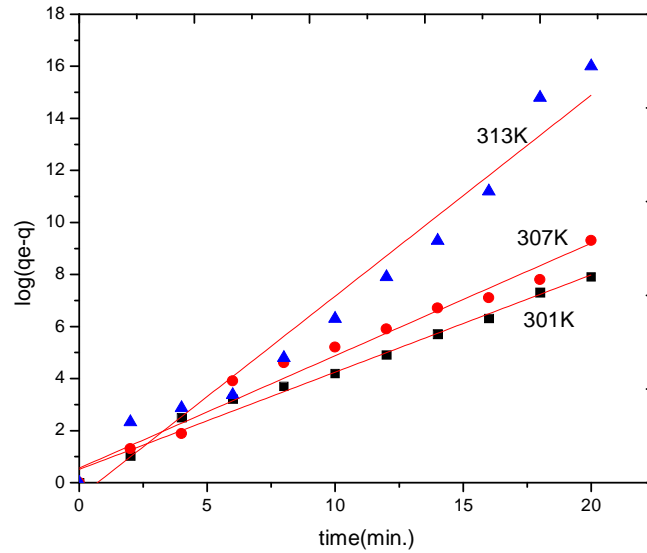


Figure 9 : A typical first order rate plot for adsorption for adsorption of cadmium (II) ion by RLH. Conditions: pH 6, initial concentration 5 mg/L, adsorbent dosage 1g and particle size 0.25mm.

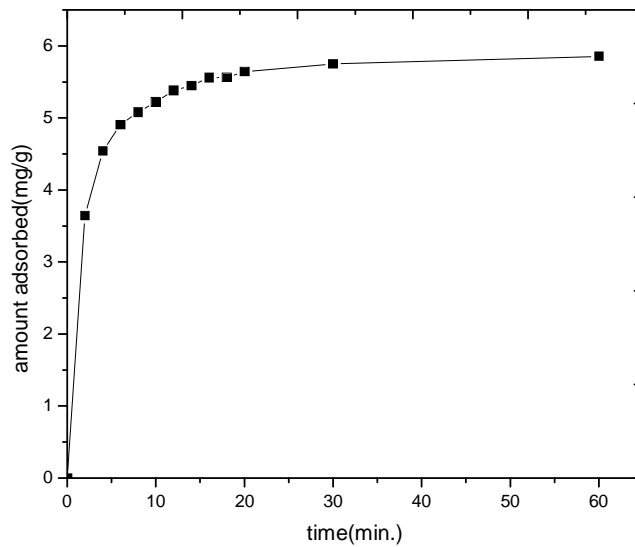


Figure 10 : Industrial effluent for adsorption of cadmium(II) ion by RLH. Conditions: pH 8, initial concentration 5 mg/L, adsorbent dosage 1g, particle size 0.25mm and room temperature.

Table 3. Isotherm models constants and correlation coefficients for adsorption of cadmium from aqueous solutions.

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Isotherm	Parameter	Value
Langmuir	R_L	0.558
	b	4.157
	R^2	0.983
	Q_0	0.190
Freundlich	K_F	1.693
	1/n	0.393
	R^2	0.784
Temkin	B_T	2.417
	K_T	1.001
	R^2	0.805

IV. CONCLUSION

From the overall results of the adsorption of cadmium(II) ion on adsorbent raw luffa husk, the following conclusion were drawn. The adsorption was found to be depended on pH, contact time, metal ion concentration, adsorbent dosage, and temperature. In general, a maximum adsorption was observed at pH 6 for cadmium(II) ion at 313K the isothermal data obey the Langmuir adsorption isotherm for all systems under investigation. The process of uptake of metal ions normally follows pseudo-first order kinetics and the adsorption capacity increase at elevated temperatures. Thermodynamic parameters shows the spontaneous, endothermic and randomness prevailing at the solid-solution interface. Based on the results obtained from these studies, it can be concluded that because the RLH is an easily, locally available, low cost adsorbent and has a considerable high adsorption capacity. The study clearly indicate that the adsorbent is effective for the adsorption of cadmium(II) ion from wastewater.

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