

Biosorption of Pb(II) Ions from Aqueous Solutions Onto Rice Husk and its Ash

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Abstract: The application of low-cost adsorbents obtained from plant wastes as a replacement for costly conventional methods of removing heavy metal ions from waste water has been reviewed. Present study deals with the adsorption of lead (II) from aqueous solution on rice husk and its ash. Rice husk (R.H) is a by-product generally obtained from rice mill. Rice husk ash (R.H.A) is a solid obtained after burning of rice husk. Batch studies were performed to evaluate the influence of various experimental parameters like pH, appropriate equilibrium time, amount of adsorbent, concentration of adsorbate and particle size. Studies showed that pH of aqueous solution affected lead (II) removal as result of removal efficiency increased with increasing solution of pH. The maximum adsorption was about 87.75% and 94.75% for R.H and R.H.A. respectively, at pH 4.6 ± 0.5 , contact time 60 min and initial concentration of 30 mgL^{-1} . Langmuir, Freundlich and Dubinin-Radushkevich (D-R) adsorption isotherms were applicable to the absorption process and their constants were evaluated. The studies showed R.H.A was more favorable than R.H. in removing lead (II) and thus was a better adsorbent. [Journal of American Science. 2010;6(10):143-150]. (ISSN: 1545-1003).

Keywords: Biosorption; Pb(II) Ion; Aqueous Solution; Rice Husk; Ash

1. Introduction

Rapid industrialization has lead to an increased disposal of heavy metals into the environment. The presence of these heavy metals in the environment is of importance concern due to their toxicity and health effects on the human and living creatures. Lead (II) poisoning in human causes severe damage to kidney, nervous system, reproductive system, liver and brain. Severe exposure to lead has been associated with sterility, abortion, still births and neo-natal deaths [1,2]. Process industries, such as battery manufacturing, printing and pigment, metal plating and finishing, ammunition, soldering material, ceramic and glass industries, iron and steel manufacturing units generate large quantities of waste water contaminated with lead (II). In drinking water lead (II) contamination occurs due to the corrosion and leaching of lead pipes and Pb/Sn solder joints associated with copper service lines used in house hold plumbing [3]. The permissible level of lead (II) in drinking water is 0.05 mg/l [4]. The permissible limit of lead in waste water as set by Environment protection Agency [5] is 0.05 mg/l . keeping in view the importance of the situation, specifically toxicity in children, it has diverted the global attention towards understanding its behavioral pattern in ecosystem and metabolism for adopting measures for its effective removal from such industrial and municipal waste effluents. There fore, elimination of toxic heavy metals is attended by many researches. There are various methods to treat the metal contaminated effluent such as precipitation

[6] reverse osmosis, [7], ion exchange [8], coagulation [9] and adsorption [10, 11]. but the selection of the treatment methods differ with respect to costs, complexity and efficiency. Among these technologies adsorption is a user-friendly technique for the removal of heavy metal. This process-seems to be most versatile and effective method for removal of heavy metal if combined with appropriate regeneration steps. This solves the problem of sludge disposal and rendes the system more viable, especially if low cost adsorbents are used. Several recent publication utilized different in expensive and locally abundantly available adsorbents like phaseolus a ureus hulls [12], rice straw [13], rice husk ash [14] and potato peels [15], lemon peel [16] etc. Rice husk are an agricultural waste produced as by-product of the rice milling industry to be about more than 100 million tones, 96% of which is generated in developing countries. Rice husk is mostly used as a fuel in the boiler furnaces of various industries to produce steam. The ash generated after burning the rice husk in the boiler is called rice husk ash. The R.H was collected from the particulate collection equipment attached up stream to the stack of rice-fired boilers. The ash generated got a server disposal problem. The objective of this study was to explore the possibility using R.H and R.H.A. for removing Pb(II) from aqueous solution. The present study has been undertake into report in detail the characteristics of Pb(II) adsorption in the batch process. Various kinetic models as well as

isotherm models have been studied for their usefulness in correlating the experimental data.

2. Material and Methods

2.1. Preparation of adsorbents:

The rice husk (R.H.) was received from a local rice mill, the R.H. were crushed and sieved with 0.180, 0.355 and 0.855 mesh sieve. Then, the husks were thoroughly washed with a stream of distilled water to remove all dirt and then were dried at 100°C to be constant weight. The dried husks were stored in desiccators until used. The R.H.A obtained from burning of R.H husk in electrical oven at 600°C for 3h.

2.2. Preparation of metal-solutions:

The stock solution containing 1000 mg/l of standard Pb(II) were prepared by dissolving 1.59 gm of A.R. $\text{Pb}(\text{NO}_3)_2$ in double distilled water (DDW). In order to prevent precipitation of metals by hydrolyzing, two or three drops of appropriate acid were added to the stock solution. The concentration range of Pb(II) prepared from stock solution varied between 20-100 mgL^{-1} for both rice R.H. and R.H.A. Before mixing the adsorbent, the pH of each last solution was monitored to the required value by adding 0.1M HCl or 0.1 M NaOH solution, respectively. All the chemicals used were of analytical reagent grade and were obtained from Merck (Germany).

2.3. Experimental procedure:

For optimization of pH, contact time, adsorbent dosage and initial concentration, batch experiments were performed at 30°C. Adsorption experiments for the removal of Pb(II) were conducted in the pH range of 2.2–6.8, adsorbent dosage ($1\text{--}5 \text{ gL}^{-1}$) and initial concentration from 20-100 mgL^{-1} and contact time from 0-180 min.

2.4. Analytical techniques:

Metal analyses were performed using "Inductivity coupled plasma", (ICP), 6500 DUO, thermoscientific England atomic absorption spectrophotometer. The amount of adsorbed metal was determined based on the soluble metal concentration measured after and before experiment. The amount of metal adsorbed per unit mass of the adsorbent was calculated as follows:

$$q_e (\text{mg} / \text{g}) = \frac{V}{m} (C_o - C_e) \quad (1)$$

and the percent removal may be calculated as:

$$(C_o - C_e) / C_o \times 100 \quad (2)$$

Where C_o is the initial concentration (mg/l) and C_e is the metal concentration (mg/l) at any time, V is the

volume of the solution (L) and m is the weight of the sorbent used (g). The sorption kinetic data of Pb(II) measured using R.H. and R.H.A. was analyzed in terms of pseudo-first order and pseudo second order sorption and intraparticle diffusion will be calculated. Finally the suitability of the Langmuir, Freundlich and Dubinin-Radushkevich (D.R.) adsorption models to the equilibrium data were investigated for Pb(II) sorbent system.

3. Results and Discussion

The adsorption of Pb (II) in aqueous solution on R.H and R.H.A. were examined by optimizing various physicochemical parameters such as pH, contact time, amount of adsorbent, adsorbent size and adsorbate initial concentration.

3.1. Effect of initial pH:

The pH of the solutions has been identified as the most important variable governing metal adsorption. This is partly due to the fact that hydrogen ion (H^+) themselves are strong competing ions and partly that the solution pH influence the chemical speciation of the functional groups on to the adsorbent surfaces.

In order to evaluate the influence of this parameter on the adsorption, the experiments were carried out at different initial pH values. The pH range was chosen as 2.2–6.8 in order to avoid metal hydroxides, which has been estimated to occur at $\text{pH} > 6.5$ for $\text{Pb}(\text{OH})_2$ [17]. The effect of pH on adsorption efficiencies are shown in Fig.(1). Removal of Pb(II) increase with increasing solution pH and a maximum value was reached at an equilibrium pH of around 4.6 ± 0.5 for rice R.H. and R.H.A. The same trend has also been reported in the removal of Pb(II) ions by other vegetable materials [18-20].

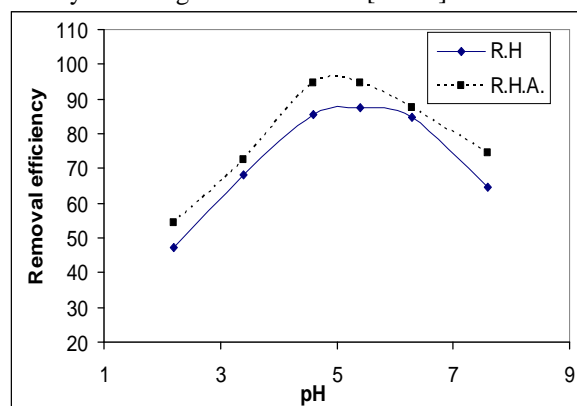
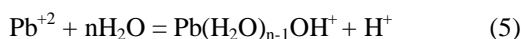
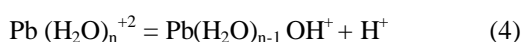
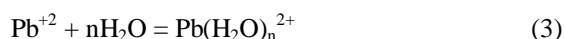


Fig. (1): Effect of pH on biosorption of Pb(II) by selected adsorbents adsorbent dosage 2g/l, initial concentrations 30 mg/l and contact time 2h.

The low degree of adsorption at low pH values can be explained by the fact that at low pH values the $[H^+]$ ion concentration is high and therefore protons can compete with the lead cations for surface sites, since at low pH Pb(II) are present in solution as Pb^{+2} free cations. In addition when pH increases, there is a decrease in positive surface charge (since the deprotonation of the sorbent functional groups could occur), which results in a lower electrostatic repulsion between the positively charged metal ion and the surface of R.H.A, favoring adsorption than its R.H. The process involved for Pb(II) adsorption are the following [21].



Perusal of the literature [22] on Pb(II) speciation shows that the dominant species is $Pb(HO)_2$ at $pH > 6.0$ and Pb^{+2} and $Pb(OH)^+$ at $pH < 6.0$. Maximum removal of Pb(II) was observed at 4.6 ± 0.5 for R.H. and R.H.A.

3.2. Effect of adsorbent concentration:

Dosage study is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of metal ion solution. The effect of adsorbent dosage on the removal of Pb(II) ion at $C_0 = 30\text{mg/l}$ was studied and results are represented in Fig.(2). The removal of metal ion was found to increase with an increase in adsorbent dosage from 0.5-2g/l. The metal ion removed almost remain unchanged after adsorbent dosage g/l. Increase in adsorption with increase in adsorbent dosage attributed to the availability of larger surface area and more adsorption sites. At very low adsorbent concentration, the adsorbent surface becomes saturated with the metal ions and the residual metal ion concentration in the solution to large.

The data clearly shows that the R.H.A is more effective than R.H. for removal of Pb(II) from aqueous solution. The results also clearly indicate that the removal efficiency increases up to the optimum dose beyond which the removal efficiency is negligible (especially about ash).

3.3. Effect of mesh sizes:

The pellet diameter was important factor, the effective surface area increased as the particle sizes decreased and as a consequence, the results indicate that the ion removal enhanced with decreasing the adsorbent particle size. By assuming spherical shape

for particles, it can be shown that the surface area per volume is higher for smaller particles. Importing surface area would increase binding sites and contact surfaces, which results in higher mass transfer and more rapid sorption than when larger particles are used. As shown in Table (1) the maximum uptake of ions was obtained when the pellet diameter was 0.35 mm for R.H. and R.H.A.

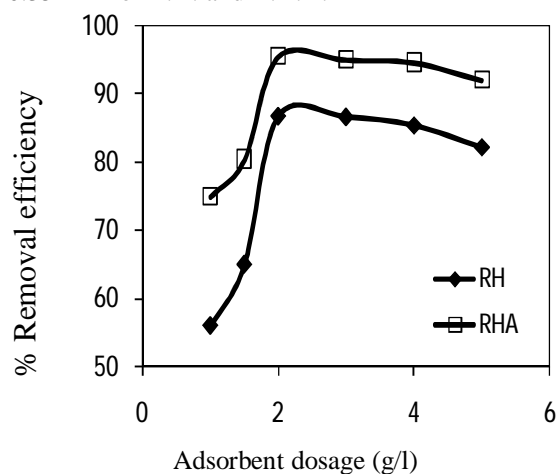


Fig. (2): Effect of adsorbent dosage on biosorption of Pb(II) by selected adsorbents $pH=4.6 \pm 0.5$, initial concentration = 30 mg/l, contact time 2h

Table (1) : Effect of adsorbent particle size in the removal of Pb(II) ion.

Mech. (n°) size (mm)	R.H.	R.H.A.
0.180	24%	23%
0.355	60%	54%
0.850	18%	14%

3.4. Effect of initial metal ion concentration

As seen from results, the sorption capacities of the sorbents increased with increasing Pb (II) concentration while the adsorption yield of Pb(II) showed the opposite trend Fig. (3). The results shown that Pb(II) ions removal is concentration dependent. Increasing the mass transfer driving force and therefore the rate at which Pb(II) ions pass from the bulk solution to the particle surface. This would result in higher adsorption [23].

3.5. Effect of contact time:

The rate at which adsorption take place is of most important when designing batch adsorption

experiments. Consequently, it is important to establish the time dependence of such systems under various process conditions. The experimental runs measuring the effect of contact time on the batch adsorption of metal solution containing 30mg/l of Pb(II) at 30°C and initial pH value 4.60 ± 0.5 is shown in Fig.(4). The adsorption of Pb(II) increased with increasing contact time and became almost constant for 60 min for R.H. and 40 min for R.H.A. These results also indicate that the sorption process can be considered very fast because of the largest amount of Pb(II) attached to the sorbent within the first 30 min of adsorption. Higher adsorption efficiency of R.H.A. could be attributed to available absorbing sites (Surface functional groups) on the adsorbent surface.

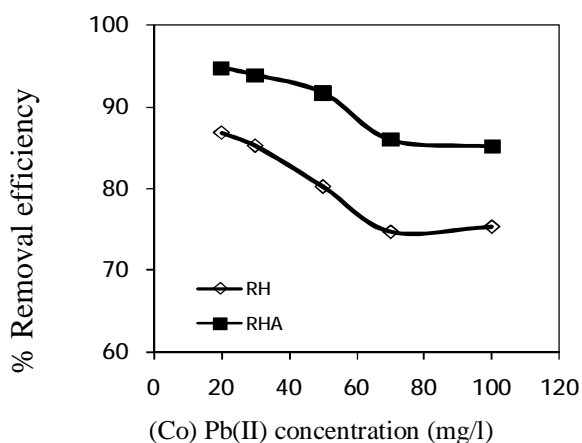


Fig. (3) : Effect of Pb(II) concentration on biosorption of Pb(II) by selected adsorbents pH=4.6 \pm 0.5, adsorbent dosage 2g/l, contact time 2h.

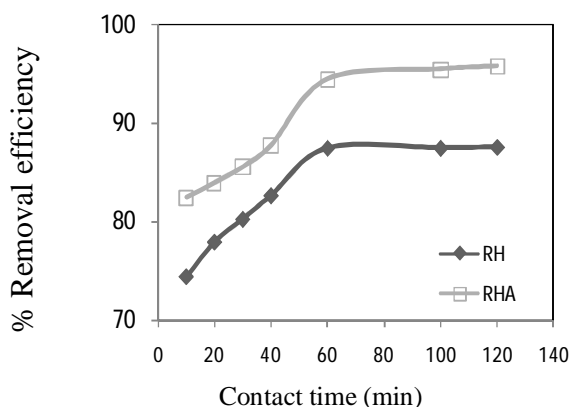


Fig. (4): Effect of the contact time on biosorption of Pb(II) by selected adsorbent pH=4.6 \pm 0.5, adsorbent dosage 2g/l, initial concentration 30mg/l

3.5. Adsorption kinetic study:

To analyze the mechanism of adsorption the data was fitted to various kinetic models such as pseudo-first order reaction and pseudo- second order reaction. Intraparticle diffusion model and Boyds kinetic expressions were employed to find out the rate controlling step in the process of adsorption of Pb(II) on to R.H. and R.H.A. Adsorption phenomenon can be described as the diffusion control process assuming a non-dissociation molecular adsorption of Pb(II) on rice husk particles as follows:

$$A + S \rightleftharpoons AS \quad (6)$$

If initially no adsorbate present the adsorbent i.e. ($C_s=0$ at $t=0$) assuming the pseudo first order rate Lagergren model is [24]:

$$\log_{10}(q_e - q_t) = \log_{10} q_e - \frac{k_1(\text{ads})t}{2.303} \quad (7)$$

Where q_e , the equilibrium sorption uptake is extrapolated from the experimental data at time $t = \infty$, q_t (mg/ g) is the amount of adsorbed metal ion on the adsorbent at time t and $k_{1,(\text{ads})}$ (min^{-1}) is the rate constant of the first-order adsorption. A straight line of $\log_{10}(q_e - q_t)$ versus t suggests the applicability of this kinetic model. Then q_e and $k_{1,(\text{ads})}$ can be determined from the intercept and slope of the plot, respectively. The results are depicted in Fig. (5) and Table (2)

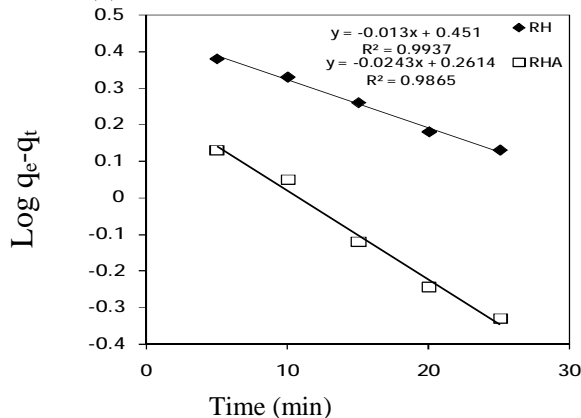


Fig. (5): Lagergen plot on biosorption of Pb(II) by selected adsorbents of Pb(II) by pH 4.6 \pm 0.5, initial concentration 30mg/l ,adsorbent dosage 2g/l.

Table (2): The kinetics constants for the biosorption of Pb(II) on R.H. and R.H.A.

Adsorbent	$C_0(\text{mgL}^{-1})$	Pseudo-first-order		Pseudo-second-order		Intra particle-diffusion K_{int}	
		$K_1(1/\text{min})$	R^2	$K_2(\text{g}/\text{mg min})$	R^2	$(\text{mg}/\text{g min}^{1/2})$	R^2
R.H.	30	0.013	0.993	0.038	0.990	0.428	0.988
R.H.A. 30		0.024	0.986	0.040	0.990	0.777	0.996

The pseudo-second order kinetic model is expressed as [25]:

$$\frac{dq}{dt} = k_{2,(\text{ads})} \cdot (q_e - q_t)^2 \quad (8)$$

Where $k_{2,(\text{ads})}$ ($\text{g}/\text{mg min}^{-1}$) is the rate constant of the second-order adsorption.

$$\frac{t}{q_t} = \frac{1}{k_{2,(\text{ads})} \cdot q_e^2} + \frac{t}{q_t} \quad (9)$$

The equation constants can be determined by plotting (t/q_t) against (t) as shown in Fig. (6) and Table (2).

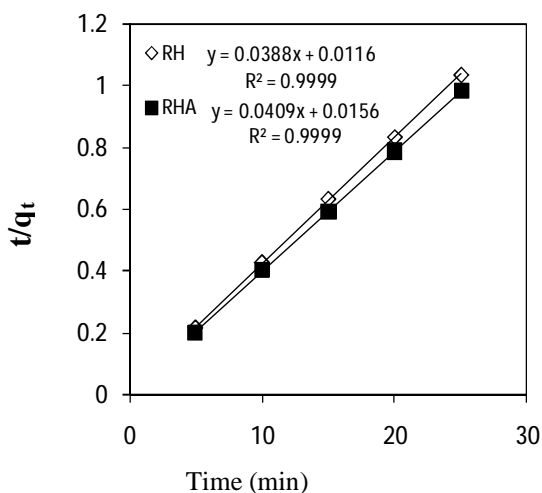


Fig. (6): Pseudo-second order plot on biosorption adsorption of Pb(II) by selected adsorbents pH 4.6 ± 0.5 , initial concentration 30 mg/l adsorbent dosage 2 g/l.

Intra particle diffusion model:

The adsorbate transport from the solution phase surface of the adsorbent particles may be controlled either by one or more steps, e.g. film or external diffusion, pore diffusion, surface diffusion and the adsorption on the pore surface, or a combination of more than one steps. In a rapidly stirred batch adsorption, the diffusive mass transfer can be related by an apparent diffusion coefficient which will fit the experimental sorption rate data. Generally, a process is diffusion controlled if its are dependent upon the role at which components diffuse towards one another. The possibility of intra particle

diffusion was explored by using the intra particle diffusion model [26].

$$q_t = k_{id} t^{0.5} \quad (10)$$

where k_{id} is the intra particle diffusion rate constant, q_t is the amount sorbed time t . the linearity as designated in Fig. (7). If the Weber, Morris plot of q_t versus $t^{0.5}$ gives a straight line, then the adsorption process is controlled by intra particle diffusion only. However, if the data exhibit multi-linear plots, two or more steps influence the absorption processes. The mathematical dependence of fractional uptake of the adsorbate on $t^{0.5}$ is obtained if the adsorption process is considered to be influenced by diffusion in the cylindrical and convective diffusion in the adsorbate solution. It is assumed that the external resistance to mass transfer surrounding the particles is significant only in the early stage of the adsorption. In Fig.(7) the data points are related by two straight lines for R.H. and R.H.A., first straight portion depicting the macropore diffusion and second representing the micropore diffusion. These show only the pore diffusion data.

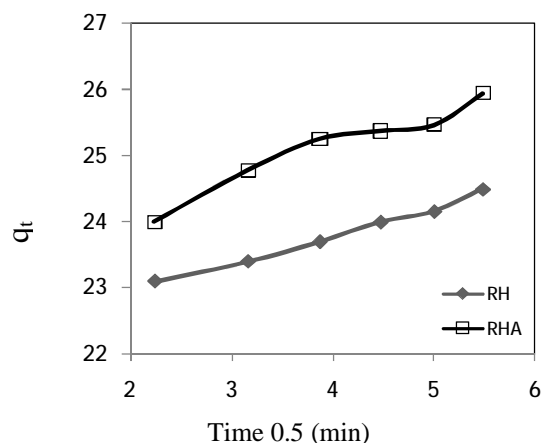


Fig. (7): Weber and Moris plot for the adsorption of Pb(II) by selected adsorbent pH 4.6 ± 0.5 , initial concentration 30 mg/l, adsorbent dosage 2 g/l.

The straight line of the plots do not pass through origin, suggesting that adsorption proceeds from boundary layer mass transfer across the interface to the intra particle diffusion within the

pores of adsorbent. The adsorption data for q_t versus $t^{0.5}$ for the initial period usually attributed to boundary layer diffusion effects or external mass transfer effects [27]. This indicates the mechanism of Pb(II) adsorption by rice husk and its ash is complex and both, the surface adsorption as well as intraparticle diffusion contribute to the rate determining step.

3.6. Adsorption isotherms:

The purpose of the adsorption isotherm is to relate the adsorbate concentration in the bulk solution and the adsorbed amount at the interface. The analysis of the isotherm data is important to develop an equation which accurately represents the results and which could be used for the design purpose.

Several isotherm equations are available which corresponding to the relationship between the mass of the solute adsorbed per unit mass of adsorbent q_e (mg/g) and the solute concentration for the solution at equilibrium C_e (mg/l). The experimental data obtained were fitted to the Langmuir adsorption [28] applied to equilibrium adsorption assuming monolayer adsorption onto a surface with a faint number of identical sites and is represented as:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \quad (11)$$

Table (3): A comparison of langmuir, Freundlich and Dubinin-Radushkevich constants resulting from equilibrium uptake studies of Pb (II) on R.H. and R.H.A.

Adsorbent	Langmuir model				Freundlich model			Dubinin-Radushkevich	
	K_L (L/g)	a_L (L/mg)	Q_o (mg/g)	R^2	K_f (mg/g) (mg/L) ^{1/n}	n	R^2	x_m	(10) ⁷ R^2
R.H.	12.59	0.33	37.88	0.996	1.40	0.39	0.958	1.53	0.22 0.988
R.H.A.	19.65	0.17	112.36	0.992	1.43	0.39	0.970	2.17	0.22 0.996

The constant K_L is the langmuir equilibrium constant and the K_L/a_L gives the theoretical monolayer saturation capacity Q_o . Therefore shows the linear plots of C_e/q_e versus C_e gives a straight line of slope a_L/K_L and intercept $1/K_L$. The data obtained were listed in Table (3) for adsorption of Pb(II) onto rice husk and its ash. The essential characteristics of the Langmuir isotherm may be expressed in terms of adimensionless constant separation factor or equilibrium parameter [29] R_L which is defined as:

$$R_L = \frac{1}{1 + K_L C_o} \quad (12)$$

The R_L value lying between 0 and 1 indicate favorable adsorption. Freundlich isotherm it is another form of Langmuir approach for adsorption on a morpous surface. It assumes the heterogeneity of surface and the exponential distribution of active sites and their energies. Freundlich equation form could be written as follows [30]:

$$\log_{10} q_e = \log K_F + \frac{1}{n} \log C_e \quad (13)$$

The constants K_F and $1/n$ were calculated from the intercept and slope of the plot of $\log_{10} q_e$ versus $\log C_e$ and tabulated the results in Table (3).

The Dubinin-Radushkevich (D.R) isotherm approach assumes that there is a surface area where the adsorption energy is homogeneous [31]. The D.R isotherm has the form:

$$\ln q_e = \ln x_m - \frac{E^2}{2RT \ln 10} \quad (14)$$

x_m represents the maximum sorption capacity of the sorbent, a constant related to sorption energy and polanyi sorption potential can be expressed as $\ln(1 + \frac{1}{C_e})$.

The polanyi adsorption theory postulates [32] fixed volume of sorption site close to sorbent surface and existence of sorption potential over these site. The sorption potential is related to an excess of sorption energy over the condensation energy and is independent of temperature. A plot of $\ln q_e$ versus $\ln(1 + \frac{1}{C_e})$ gave a straight line, from which values of x_m and for Pb(II) in R.H. and R.H.A. was evaluated in Table (3). Using the calculated value of λ , it was possible to evaluate the mean sorption energy E , from

$$E = \frac{1}{\sqrt{-2\lambda}}$$

The isotherm constants were determined from linear isotherm graphs for each of the isotherm equations tested. The values of the isotherm constants with the correlation coefficients are give in Table (3). The langmuir equation represents the better fit of experimental data than other isotherm equations. The maximum amounts of Pb(II) adsorbed are 37.88 and 112.36 mg/g for R.H. and R.H.A respectively.

4. Conclusions:

In this study, batch adsorption experiments for the removal of Pb(II) from aqueous solutions have been carried out using R.H and R.H.A as a low cost, readily available adsorbent. The adsorption characteristics have been examined at different pH values, initial metal ion concentrations, contact time and adsorbent dosage. The obtained results can be summarized as follows:

- (1) The pH experiments showed that the governing factors affecting the adsorption characteristics of all adsorbents are competition of the (H⁺) ions with metal ions at low pH values, maximum adsorption at pH 4.6 ±0.5 for R.H. and R.H.A and at higher pH precipitation of hydroxyl species onto the adsorbents.
- (2) Increase in adsorbent dosage leads to increase in Pb(II) adsorption due to increased number of adsorption sites. Maximum uptake of Pb(II) was obtained at adsorbent dosage 2g L⁻¹ and 0.35 mmesh size
- (3) The equilibrium time for adsorption of Pb(II) from aqueous solutions was achieved within 60 min of R.H. and 40 min of R.H.A.
- (4) The experimental data were better described by pseudo-second order model as evident from correlation coefficient.
- (5) The adsorption isotherm studies showed that Langmuir model were found to provide the best fit of the experimental data.
- (6) The results showed that R.H husk and its ash might have been successfully used as an adsorbent for the removal of Pb(II) from aqueous solution. Moreover, R.H.A has adsorption capacity more than R.H for Pb(II) removal.

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