Adsorption of Cadmium (II) and Mercury (II) onto Natural Adsorbent Rice Husk Ash (RHA) from Aqueous Solutions: Study in Single and Binary System

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Abstract: The present study deals with the competitive adsorption of cadmium (Cd(II)) and mercury (Hg(II)) ions onto rice husk ash (RHA) from single component and binary systems. Equilibrium adsorption is affected by the initial pH (pH_0) of the solution. The $pH_0 \approx 6.0$ is found to be the optimum for the individual removal of Cd(II) and Hg(II) ions by RHA. The pH of the system, however, increases during the initial sorption process for about 60 min and, thereafter, it remains constant. The equilibrium adsorption data were obtained at different initial concentrations (C_0 = 10–100 mg/l), 6 h contact time, 25 °C temperature, RHA dosage of 10 g/l at pH_0 6. The single ion equilibrium adsorption data were fitted to the non-competitive Langmuir and Freundlich isotherm models. The Freundlich models represent the equilibrium data better than the Langmuir model in the studied initial metal concentration range (10–100 mg/l). The adsorption capacity of Cd(II) is higher than that for Hg(II) for the binary metal solutions and is in agreement with the single-component adsorption data. The equilibrium metal removal decreases with increasing concentrations of the other metal ion and the combined action of Hg(II) and Cd(II) ions on RHA is generally found to be antagonistic. Equilibrium isotherms for the binary adsorption of Cd(II) and Hg(II) ions onto RHA have been analyzed by using Langmuir and Freundlich models.. Desorption with various solvents showed that the nitric acid is the best solvent; the maximum elution being about 28.41 % for Cd(II) and about 31.53 for Hg(II).

[A.G. El-Said, N.A. Badawy, and S.E. Garamon. **Adsorption of Cadmium (II) and Mercury (II) onto Natural Adsorbent Rice Husk Ash (RHA) from Aqueous Solutions: Study in Single and Binary System.** Journal of American Science 2010;6(12):400-409]. (ISSN: 1545-1003). http://www.americanscience.org.

Keywords: Mercury (II); Cadmium(II); Binary adsorption; Rice husk ash (RHA); Simultaneous metal removal; Adsorption isotherms.

1. Introduction:

Most of the metals are known to be toxic and half of these, including cadmium, chromium, copper, lead, mercury, nickel, selenium, silver and zinc, are released into the environment in quantities that pose a risk to human health [1].

Heavy metal contamination exist in aqueous waste streams from diverse industries such as metal plating, manufacturing, batteries, as well as agricultural sources where fertilizers and fungicidal sprays are intensively used. Cu, Zn, Hg, and Cd are harmful wastes produced by industry that pose a risk of contamination groundwater and other water resources. Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders [2-11]. For example, Cadmium causes serious renal damage, anemia, hypertension and itai-itai [2].

The reduction of the pollutant to an acceptable level is necessary when toxic metals are present in aquatic system [12]. Adsorption and ion exchange processes are the most useful methods to remove them. These methods explore the availability of different kinds of adsorbents associated with convenient procedures for obtaining high efficiency [13-14]. A large number of different adsorbent materials containing a variety of attached chemical functional groups have been reported for this purpose. For instance, activated carbon is the most popular material; however, its high cost restricts its large-scale use [15, 16].

In recent years, special attention has been focused on the use of natural adsorbents as an alternative to replace the conventional adsorbents, based on both the environmental and the economical points of view [15, 16]. Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive sorbents. Due to their low cost, when these materials the end of their lifetime, they can be disposed of without expensive regeneration. The abundance and availability of agricultural by-products make them good sources of raw materials for natural sorbents. Rice husk is used as a fuel by a number of industries to produce steam, thus, conversing both energy and resources. During the burning of rice husk, the residue ash, called rice husk ash (RHA) is collected from the dust collection device attached upstream to the stacks of rice husk – fired boilers and furnaces. RHA has good adsorptive properties and has been used previously for the adsorptive removal of metal ions [17] and dye [18], and filtration of arsenic from water [19]. RHA, obtained from heating rice husk at 300 C, has been shown to adsorb more gold – thiourea than the conventionally used activated carbon [20].

The main techniques used to remove heavy metal ions from aqueous streams include ion-exchange chromatography, reverse – osmosis, Chemical precipitation and adsorption. Adsorption as a waste water treatment process has aroused considerable interest during recent years [21].

Much of the work on the adsorption of heavy metal ions by various kinds of adsorbents has focused on the uptake of single metal ions. Since industrial effluents can contain several metals, it is necessary to study the simultaneous sorption of two or more metal ions. Since industrial effluent can contain several or more metal ions and also to quantify the interactive affect of one metal ion on the other. Thus, the study of adsorption of heavy metal ions from binary and ternary system is important. No information is available in literature for the simultaneous removal of mercury (II) and cadmium (II) ions by rice husk ash.

In this paper the work aims to study the feasibility of using RHA as an adsorbent for the single and binary removal of Hg (II) and Cd (II) metal ions from aqueous solution, study the effect of initial pH, determine the applicability of adsorption isotherm models (e.g. Langmiur and Freundlich) for single component, and gather experimental data on adsorption equilibrium for the binary system containing Hg (II) and Cd (II) ions.

2. Materials and Methods

2.1. Adsorbent and its characterization

The rice husk used was obtained from agriculture land in kaluobia governmental, Egypt. The rice husk were crushed and sieved with 30-mesh siever. Then, the husks were thoroughly washed distilled water to remove all dirt and were dried at 100 °C till constant weight. The dried husks were stored in desiccator until used. The rice husk ash (RHA) obtained from burning of rice husk in electrical oven at 700 °C for 1 hour. The rice husk ash was sieved [with Retsch Prufsieb / sieve, Type (ASTM), practical size was found to be 40% (0.18mm), 44 %(0.355mm) and 16% (0.855mm)] and stored with a desiccators until used. The particular chemical and physical properties are shown previous show the x-ray diffraction analysis, which indicates that the RHA mainly consist of amorphous materials [22].

2.2. Adsorbates

All the chemical used in the study were of analytical reagent (AR) grade, cadmium sulphate octahydrate ($3CdSO_4.8H_2O$), mercury chloride ($HgCl_2$), NaOH and HCl. Stock solution having concentrations of 1000mg/l of Cd(II) and Hg(II) were prepared by dissolving exact amount of $CdSO_4$. $8H_2O$ and $HgCl_2$ in double-distilled water (DDW), respectively.

2.3. Batch adsorption studies

For each experimental run, 100 ml aqueous solution of known concentration of Cd (II) and Hg (II) for the single and binary mixture of these components was taken in 250 ml conical flask containing fixed amount of RHA. These flasks were agitated at a constant shaking rate of 150 rpm in a temperature controlled orbital shaker(VOR TEX MVOR-03, Spain) maintained at 30°C .The initial pH (pH_0) of the adsorbate solution was adjusted using 1 N (36.5 g/l) HCl or 1 N (40 g/l) NaOH aqueous solution without any further adjustment during the sorption process. The samples were withdrawn from the flasks at different time intervals to check whether equilibrium has been attained. The sample were centrifuged using research centrifuge (Hettich, Germany, EBA-20 Baujahr E xin) at 5000 rpm for 5 min and the supernatant liquid was analyzed for residual concentration of metal ions using inductively coupled plasma .

2.4. Effect of initial pH (pH_0)

The effect of (pH_0) on the sorption was studied by adjusting the (pH_0) in the range of 2.0-8.0. In these experiments, the RHA loading was kept at 10 g/l of solution containing 100 mg/l each of Cd (II) and Hg (II) at 30 °C. The contact time (t) was kept as 6 hr for Cd (II) and Hg (II), since equilibrium was found to have been attained in 6 hr contact time for Cd (II) and Hg (II).

2.5. Adsorption isotherm experiments

For single metal-ion-RHA systems, initial metal ion concentration was varied from 10 to 100 mg/l. In binary metal ion mixture RHA systems, for each initial concentration of Cd(II) and Hg(II) solution : viz., 10,20,30,50 and 100 mg/l, the Cd(II) or Hg(II) concentration was varied in range of 10-100 mg/l (viz., 10, 20, 30, 50 and 100 mg/l). In all cases, the (pH_0) of solution was maintained at 6.0 for Cd (II) and Hg (II).

2.6. Desorption studies

For batch desorption experiments, a series of 250 ml Erlenmeyer flask containing 100 ml of DDW or aqueous solution of HCl, H_2SO_4, HNO_3 and

CH_3COOH of know concentration were conducted with metal-loaded RHA (1 g) at 30 °C the mixtures were agitated at 150 rpm for 6 hr in the orbital shaker. Thereafter, the mixture was centrifuged and the supernatant was analyzed for metal ion released into the solvent.

2.7. Analysis of cadmium (II)and mercury (II)

The concentration of Cd (II) and Hg (II) and in the sample was determined by Inductively Coupled Plasma, (ICAP), 6500 DUO, Thermo Scientific England. 1000 mg/l multi-element certified standard solution, Merck, Germany was used as stock solution for instrument standardization.

Percentage metal ion Removal,

$$(\%) = 100\ (Ci - Ce)/Ci \qquad (1)$$

where Ci and Ce are the initial and equilibrium metal ion concentrations, respectively.

Amount of adsorbed metal ions per g of solid,

$$qe(mg/g) = V(Ci - Ce)/m \qquad (2)$$

where, Ci is the initial metal concentration in solution (mg/l) V is the volume (l) and m is the mass of adsorbent (mg)[23].

3. Results and Discussion:

3.1 Effect of initial pH (pH_o)

The pH of the solution affects on the surface charge of the adsorbents as well as the degree of ionization and speciation of different pollutants [24]. It is known that metal species [M(II)= Cd(II), Hg(II)] are present in deionized water in the form of M^{+2}, $M(OH)_2$, M(OH) (S), etc.[25].

It is obvious that the adsorption of M (II) must be higher in alkaline solution. But at higher pH, the precipitation as $M(OH)_2$ (S) plays the main role in removing the M (II) ions. Therefore, all the experiments were conducted at $pH \leq 8.0$.

The influence of the pH of metal ion solution on the extent of adsorption of Cd (II), and Hg (II) ions onto RHA is shown in Fig. 1. The adsorption of metal ions increases with an increase in pH. Up to pH 4, the increase in adsorption is gradual, which however, increase drastically at pH > 4. At higher pH ≥ 6.0, Cd (II) and Hg (II) ions adsorption become nearly constant. During the initial stage of the sorption process up to 30 min., the pH of the solution was found to rise sharply. Thereafter, the pH of the solution remained invariant with time.

. Fig. 1. Shows the final pH values (pH_f) as a function of pH,the pH_f values are higher than the pH_o values for pH < 7.5 for Co =100 mg/l. Although the metal removal increases sharply with an increase in pH_o, the pH_f values were almost constant for $6 \leq pH_o \leq 7.5$. The pH_f values, are therefore, considered to indicate the equilibrium pH values [26]. Surface charge developed at low pH_o is not favorable to adsorption of the RHA. Besides, a higher concentration of H^+ in the solution competes with Cd (II) and Hg (II). However, it was found that with pH_o 6.0, the pH_o of the solution rises sharply and stabilizes at pH 7.2 and 7.6 for Hg (II) and Cd (II) respectively. Therefore, it may be concluded that the H^+ in the solution competes with Hg (II) and Cd (II) for the adsorption sites of RHA at pH_o 6.0. Also, the rise in pH for Cd-RHA system is lower than that of Hg-RHA system. It means that the amount of H^+ adsorption is more than that of Cd (II) and Hg (II) ions. The lower adsorption value observed for Hg (II) it can also be presumably due to the stronger interaction of Hg (II) with Cl^- species such as $HgCl^+$ and $HgCl_2$ in solution phase while for Cd (II) this interaction is negligible. The effectiveness of the process can be expressed by the quantity adsorbed (q_e (mg/g)) versus pH_o plot for the cations involved, as represented in Fig. 2.

The metallic ion (Cd) could be suffering hydrolysis, starting at pH higher than 6, forming $Cd(OH)^+$ species, which promotes a reduction of the adsorption capacity, due to the diminution of the formal charge of the metallic ion. In case of Hg (II) in solution, these ions are extensively hydrolyzed and the specie formed is HgO, and require acidification to prevent the formation of poly nuclear hydroxyl-bridged species or the precipitation of basic salts [27]. This specie does not present electrostatic interaction with active site of the RHA.

3.2 Effect of adsorbent dosage (m)

The effect of adsorbent dosage on the uptake of cadmium (II) and mercury (II) ions onto rice husk ash (RHA) was studied and is shown in Fig. 3. This figure reveals that the removal of metal ions increases with an increase in the adsorbent dosage from 1 to 10 g/l. The removal remains unchanged above 10 g/l of rice husk ash; dosage can be attributed to the larger availability of greater surface area and more adsorption sites. At m < 7 g/l, the adsorbent surface becomes saturated with metal ions and the residual metal ion concentration in the solution is large. At m > 7 g/l, the incremental metal ions removal becomes very low, and at m = 10 g/l, the removal efficiency becomes almost constant [23]. Maximum removal of metal ions at C_o = 100 mg/l was found to be (53.68 %) for Cd (II) and (35.06 %) for Hg (II).

3.3 Effect of initial metal ion concentration (C_o)

There are various possible interaction effects between different species in solution and, in particular, potential interactions on the surface depending on the adsorption mechanism. Factors that affect the binding sites (e.g. functional groups, structures, surface properties, etc.), the properties of the adsorbates (e.g. concentration, ionic nature or standard redox potential, etc.) and the solution chemistry (e.g. pH, ionic strength, etc.). In the context of adsorption, a number of properties have been suggested for use in the ordering of affinity rank, including ionic radius and solubility product constant as hydroxides [28], puling electro negativity and standard reduction potential [29], first hydrolysis constant [30] . The properties may play an important role in metal ion adsorbent interaction, but can only partly explain high- or low-adsorption capacities.

The atomic weight of Hg(II) is highest as compared to Cd (II), and the ionic radius of Hg(II) is highest (1.02 A^o) as compared to Cd(II) (0.96 A^o). Both the tested adsorbent showed higher adsorption capacity for Cd (II) ions as compared to Hg (II).

However, the adsorption order is found to be in the order of increasing molecular weight and ionic radius, e.g. Cd(II) > Hg(II)..

The increase in C_o also enhances the interaction between the metal ions in the aqueous phase and the adsorbents. Therefore, an increase in the C_o of the metal ions enhances the adsorption uptake of Cd (II) and Hg (II) and ions onto RHA as shown in Fig 4.

3.4 Effect of contact time (t)

At pH 6, aqueous metal ion solution with C_o = 100 mg/l were kept in contact with the RHA for 24 hr. The residual concentrations at 6 hr. Contact time were found to be higher by a maximum of ≈ 1 % than those obtained after 24 hr. Contact time, a steady state approximation was assumed and equilibrium situation was accepted. Accordingly all the batch experiments were conducted with a contact time of 6 hr. under vigorous shaking conditions. Fig. 5. Show the effect of (t) on the uptake of Cd (II), and Hg (II) ions from aqueous metal ion solutions. The rate of metal ion removal is found to be very rapid during the initial 15 min and there fore, the rate of metal ion removal decreases. No significant change in metal ion removal is observed after about 120 min. During the initial stage of sorption, a large number of vacant surface sites are available for adsorption. After laps of some time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules adsorbed on the solid surface and the bulk phase. Besides, the metal ions are adsorbed into the meso-pores that get almost saturated with metal ions during the initial stage of adsorption. Thereafter, the metal ions have to traverse farther and deeper into the pores encountering much larger resistance. This results in the slowing down of the adsorption during the later period of adsorption. Da Fonseca et al; [31] have reported 12 hr. Equilibrium contact time for removal of Cd (II) by vermiculiteat.

3.5. Single and binary adsorption of cadmium (II), and mercury (II) ions

Binary adsorption studies are particularly important for assessing the degree of interference posed by common metal ions in adsorptive treatment of wastewaters.

The equilibrium uptakes and the adsorption yield obtained for single component (Cd (II) and Hg (II)) solution at pH_o are shown in Fig (6,7). As seen from the figures, an increase in the initial metal concentration up to 100 mg/l increases the equilibrium uptake and decreases the adsorption yield of both the components. When the initial ion concentration increase from 10 to 100 mg/l, the loading capacity of RHA increases from 0.875 to 5.316 mg/g for Cd (II)and from 0.807 to 3.401 for Hg (II). The initial concentration provides the necessary driving forces to over come the resistance to the mass transfer of Cd (II) and Hg (II) ions between the aqueous and the RHA. The increase in initial concentration also enhances the interaction between the metal ions in the aqueous phase and the RHA [32]. Therefore, an increase in initial concentration of metal ions enhances the adsorption uptake of the Cd (II) and Hg (II) ions. Also, it is observed that the adsorption capacity of RHA for Cd (II) is greater than that for Hg (II). Binary component adsorption systems were prepared by solubilizing a combination of either Cd (II)-Hg (II), with presence of each metal [Cd (II)/ Hg (II)]. Binary adsorption of metal ions was conducted with the same operating conditions as for mono-component adsorption in terms of volume (100 ml.), RHA weight (1 g.), agitation time (2 hr.) and agitation rate (150 rpm). Initial individual concentration of three metal ions in binary system ranged from 10 to 100 mg/l.

The simultaneous adsorption of Cd (II) and Hg (II) ions from binary mixtures also investigated at pH_o 6.0 . In the first stage of adsorption studies, while initial Hg (II) concentration was changed from 0 to 100 mg/l, at each initial Cd (II) ion concentration of 0, 10, 20, 30, 50, and 100 mg/l. The non –linear adsorption isotherms of Hg (II) ions in the absence and presence of increasing concentration of Cd (II) ions are shown in Fig 7. It is seen that the equilibrium Hg(II) uptake increase with an increase in the initial Hg(II) concentration up to 100 mg/l at all Cd(II) ion concentration. The equilibrium uptake of Hg (II) decrease continuously with increasing Cd (II) ion concentration. The individual and total adsorption equilibrium uptakes and yields of Hg (II) and Cd (II) ions on RHA as obtained at different Hg (II) concentration in the absence of Cd (II) or the presence of Cd (II) ions with increasing concentration are also listed in Table 1.

In general, an increasing in Cd (II) ion concentration decreases the individual adsorption yield of Hg (II) and total adsorption yield for each experiment run. The results also show that the equilibrium uptake of Hg (II) ion decreases with increasing initial Cd (II) ion concentration. At 100 mg/l initial Hg (II) concentration, without Cd (II) ions and in the presence of 100 mg/l Cd (II) ion concentration, adsorbed Hg (II) quantities at equilibrium are found to be 3.401 and 1.806 mg/g, respectively. Fig. (6) depicts the variations in the uptake of Cd (II) at equilibrium with increasing initial Cd (II) concentration (from 0 to 100 mg/l) at a constant initial Hg (II) concentration (10-100 mg/l) at pH_o 6.0. Similar adsorption pattern are observed both in the individual –Cd(II) ion and binary Cd(II)-Hg(II) ion systems; Cd(II) ion equilibrium uptake increase with an increase in the initial Cd(II) concentration up to 100 mg/l. Increase in Hg(II) concentration decrease the equilibrium uptake of Cd(II) ions. With no Hg (II) present in the solution, equilibrium uptake of Cd (II) ion is found to be 5.316 mg/g at 100 mg/l initial Cd (II) ion concentration. When the Hg (II) concentration is kept at 100 mg/l at the same initial Cd (II) ion concentration, the equilibrium Cd (II) uptake decreases to 2.248 mg/g.

In general, multi-component adsorbates – adsorbents generally exhibit three possible types of behavior:

- Synergism (the effect of the mixture is greater than that the single components in the mixture).
- Antagonism (the effect of the mixture is less than that of each of the components in the mixture).
- Non-interaction (the mixture has no effect on the adsorption of each of the adsorbates in the mixture), [33].

The combined effect of the binary mixture of Cd (II) and Hg (II) seems to be antagonistic. To analyze the antagonistic sorption behavior of the two components, the adsorption yield of single and binary component systems were also compared. The experimental equilibrium sorption data obtained for the single component and the binary systems indicate that the adsorption capacity of RHA for Hg (II) is, in general, less than that of Cd (II). Kandah et al, Singh and Yenkie, Flogeac et al, and Sharma et al, has reported similar results using waste ship manure waste, granular activated carbon columns, franc soil and shelled moringa oleifera seeds, respectively, as adsorbents [34-37].

3.6. Single-component adsorption isotherm models

The individual Langmiur and Freundlish adsorption isotherm parameters [23] for Cd(II) and Hg(II) at pH_o 6.0 obtained from the fitting of experimental data are listed in Table (2) along with the regression coefficients, R^2 . The R^2 values are closer to unity for the Freundlish models in comparison to that for Langmiur model. Therefore, the equilibrium adsorption data of Cd(II) and Hg (II) –RHA can be represented more appropriately by the Freundlish models in the studied concentration range.

Langmiur: $q_e = q_m K_L C_e / 1+ K_L C_e$ (3)

Freundlich: $qe = K_F C_e^{1/n}$ (4)

The data in Table (2) also indicate that the amount of Cd(II) ions per unit weight of RHA for the complete monolayer surface coverage was higher than that of Hg(II). A large value of K_L also implies the strong affinity of Cd(II) ions to RHA. K_F and n, the single-component Freundlish constants, indicate the adsorption capacity and adsorption intensity, respectively.. It is found from Table (2) that the RHA shows greater heterogeneity for Cd(II) than that for Hg(II) ions. Since $1/n < 1$; both the Cd (II) and Hg (II) ions are favorably adsorbed by RHA. The magnitude of K_F also showed the higher uptake of Cd(II) that than of Hg(II) ions by RHA at pH_o 6.0. The comparison of the single component experimental equilibrium adsorption. Uptake and the predicted uptake (q_e) from the Langmuir and Freundlich models for Cd(II) and Hg(II) onto RHA at pH_o 6.0 are presented in Table (3) .

3.7. Binary- component adsorption isotherm models

Adsorption behaviors of metal ions in binary system have been modeled using Langmuir and Freundlich equation as presented in Table (3). As depicted in the Figures (6,7) for each metal ion, co-adsorption induces a decrease in equilibrium adsorption capacity but the percentage depends on co-metal ion present in the system . Adsorption behavior of metal ions in binary system was modeled using Langmuir and Freundlich isotherm equation as predicted in mono-component system. Values of Langmiur and Freundlich parameter for each metal ion of binary system, that is, Cd(II) + Hg(II), and their respective determination coefficient R^2 value are presented in Table (4).

3.8. Desorption study and disposal of spent RHA

The regeneration of the adsorbent and/or disposal of the adsorbate-loaded adsorbent (or spent adsorbent) is very important. For the desorption experiments, several solvents (acids and bases) have been used. Batch desorption experiments were carried out and the desorption efficiencies are compared in Fig 8 .Acetic acid showed the maximum desorption efficiency of 17.53 % for cadmium (II) and 24.58 % for mercury (II). On the other hand, mineral acids, HCl, H_2SO_4, and HNO_3 showed almost equal but higher recovery efficiency (≈ 31.5 %) for Hg (II). However, for Cd (II), H_2SO_4 proved to be the best. Hydrogen ions released from the acids replace metal cations on the RHA. Overall, any of the mineral acids can be selected as the optimal eluting agent for the system studied, however, the desorption efficiency is not very significant. Several authors have demonstrated that the sorption process of trace metals is not completely reversible. Several explanations have been proposed for such observations, including diffusion of trace metals within oxide particles or into micro-pores [38-40], precipitation [41], incorporation of metals into oxides [42], and re-adsorption [43]. For the present study, it seems that the chemisorptive adsorption of metal ions onto RHA hinders the desorption of metal ions from the spent RHA.

Table 1. Comparison of individual and total adsorption equilibrium uptake and yields found at different mercury (II) concentrations at varying concentration of cadmium(II) ions onto rice hush ash.

C_o,*Hg*	C_o,*Cd*	C_e,*Hg*	C_e,*Cd*	q_e,*Hg*	q_e,*Cd*	*AdHg%*	*AdCd%*	*AdTot%*
0	10	0	1.25	0	0.875	0	87.50	87.50
0	20	0	3.97	0	1.603	0	80.15	80.15
0	30	0	8.04	0	2.196	0	73.20	73.20
0	50	0	17.10	0	3.290	0	65.80	65.80
0	100	0	46.84	0	5.316	0	53.16	53.16
10	0	1.93	0	0.807	0	80.7	0	80.70
10	10	3.45	2.26	0.655	0.774	65.5	77.40	71.47
10	20	4.58	6.93	0.542	1.307	54.2	65.34	59.77
10	30	5.26	12.65	0.474	1.735	47.4	57.83	52.62
10	50	5.79	27.12	0.421	2.288	42.1	45.76	43.93
10	100	6.42	55.34	0.358	4.466	35.8	44.66	40.24
20	0	7.13	0	1.287	0	64.2	0	64.20
20	10	8.52	3.57	1.148	0.643	57.4	64.30	60.85
20	20	11.34	7.87	0.866	1.213	43.3	60.65	51.98
20	30	11.66	15.01	0.804	1.499	40.2	49.97	45.08
20	50	13.52	28.23	0.648	2.177	32.4	43.54	37.97
20	100	14.66	69.41	0.547	3.059	27.35	30.59	28.97
30	0	12.55	0	1.745	0	58.1	0	58.10
30	10	15.56	4.62	1.414	0.539	47.13	53.80	50.46
30	20	16.54	9.89	1.346	1.011	44.867	50.55	47.71
30	30	19.23	16.73	1.077	1.327	35.5	44.23	40.06
30	50	19.95	30.05	1.005	1.995	33.5	39.90	36.70
30	100	21.26	72.42	0.874	2.758	29.13	27.58	28.35
50	0	29.59	0	2.410	0	48.04	0	48.04
50	10	36.23	4.92	2.045	0.508	40.9	50.80	45.85
50	20	38.59	10.83	1.940	0.917	38.8	45.85	42.33
50	30	40.06	18.02	1.770	1.198	35.4	39.93	37.35
50	50	41.58	31.24	1.530	1.876	30.6	37.52	34.06
50	100	43.22	74.26	1.178	2.574	23.56	25.74	24.65
100	0	65.99	0	3.401	0	34.01	0	34.01
100	10	69.23	5.37	3.077	0.463	30.77	46.30	38.54
100	20	70.56	12.03	2.944	0.797	29.67	39.85	34.65
100	30	76.33	19.78	2.367	1.022	23.67	34.07	28.87
100	50	79.54	34.10	2.046	1.590	20.46	31.80	26.13
100	100	81.94	77.50	1.806	2.248	18.06	22.48	20.27

Table 2. Isotherm parameters values for the removal of cadmium (II) and mercury (II) in mono-component system by rice husk ash.

Adsorbate	*K_L (l/mg)*	*q_m (mg/g)*	*R^2*
Langmuir constants			
Cadmium(II)	0.077	6.57	0.965
Mercury(II)	0.073	4.00	0.977
Adsorbate	*K_F ((mg/g) / (mg/l)$^{1/n}$)*	*1/n*	*R^2*
Freundlich constants			
Cadmium(II)	0.789	0.49	0.999
Mercury(II)	0.599	0.42	0.996

Table 3. Comparison of the experimental and calculated qe values evaluated from the mono-component Langmuir and Freundlich models for the individual adsorption of cadmium (II) and mercury (II) to rice husk ash.

C_o (mg/l)	*C_e (mg/l)*	*$q_{e,exp}$ (mg/g)*	*$q_{e,calc}$ (mg/g)*	
Cadmium (II)			***Langmuir***	***Freundlich***
10	01.25	0.875	0.577	0.880
20	03.97	1.603	1.538	1.570
30	08.04	2.196	2.510	2.228
50	17.10	3.290	3.730	3.240
100	46.84	5.320	5.140	5.340
Mercury (II)				
10	01.93	0.807	0.493	0.787
20	07.20	1.284	1.370	1.360
30	12.55	1.745	1.912	1.720
50	25.98	2.402	2.620	2.323
100	65.99	3.401	3.313	3.420

Table 4. Modeling the result of adsorption isotherm of binary system.

			Langmuir			***Freundlich***		
			Q_m	***K_L***	***R^2***	***K_F***	***1/n***	***R^2***
C_o (mg/l)	**Binary metal system**	**Metal ion**						
10	Cd +Hg	Cd	4.96	0.049	0.904	0.49	0.51	0.999
		Hg	4.02	0.043	0.966	0.36	0.51	0.995
20	Cd +Hg	Cd	3.88	0.049	0.989	0.37	0.52	0.979
		Hg	4.58	0.025	0.975	0.20	0.64	0.989
30	Cd +Hg	Cd	3.87	0.034	0.996	0.42	0.56	0.985
		Hg	3.26	0.026	0.974	0.17	0.63	0.979
50	Cd +Hg	Cd	3.73	0.029	0.989	0.21	0.60	0.969
		Hg	3.26	0.022	0.946	0.14	0.64	0.969
100	Cd +Hg	Cd	3.32	0.026	0.981	0.18	0.65	0.999
		Hg	2.88	0.019	0.954	0.11	0.60	0.989

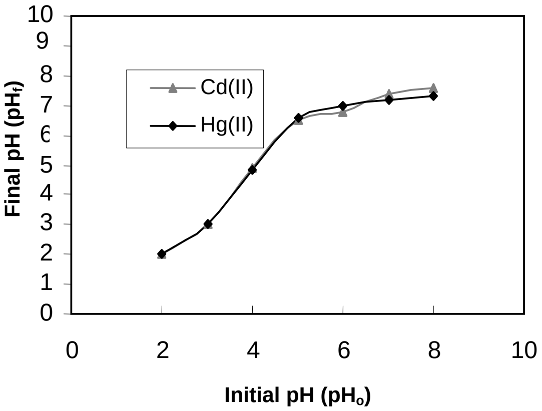

Fig. 1. The variation in equilibrium system pH_f with pH_o during the sorption of Cd(II) and Hg(II) onto rice husk ash

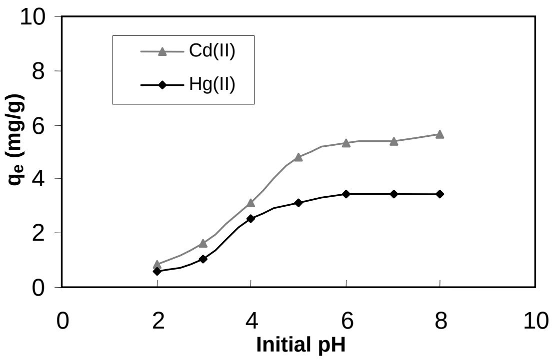

Fig. 2. Effect of pH_o on the removal of cadmium (II) and mercury (II) ions for mono-component adsorbate aqueous solution by rice husk ash. T= 25 $_o$C, t = 6 hr, C_o = 100 mg/l, and m = 10g/l.

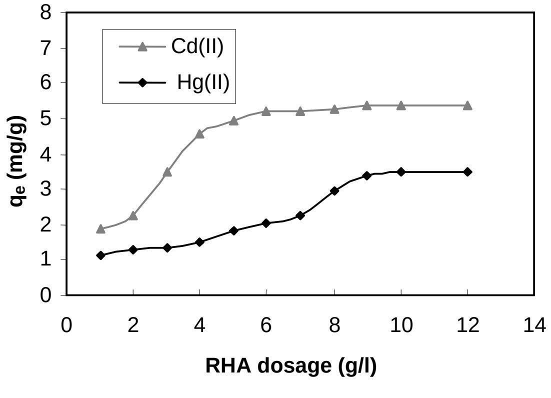

Fig. 3. Effect of rice husk ash (RHA) dosage on the removal of cadmium (II) and mercury (II). T= 25 $_o$C, t = 6 hr and C_o = 100 mg/l.

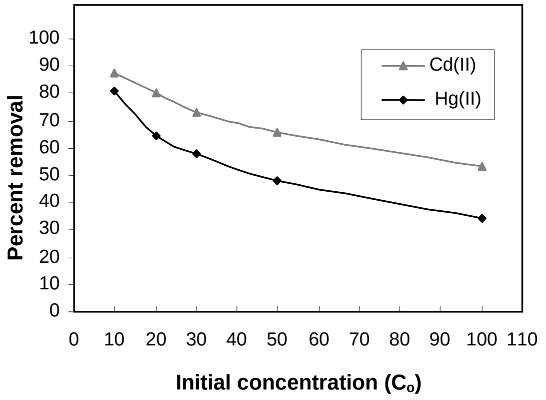

Fig. 4. Effect of the initial metal ion concentration on the removal of cadmium (II) and mercury (II) by rice husk ash. T= 25 °C, t = 6 hr, pH = 6, and m = 10 g/l.

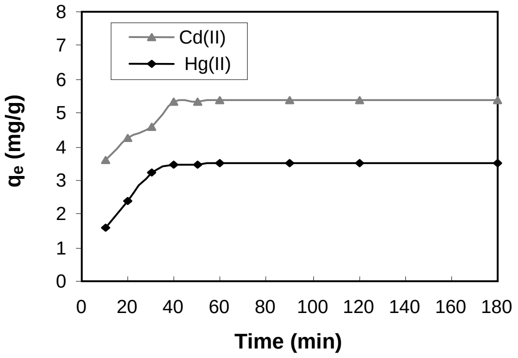

Fig. 5. Effect of contact time on the adsorption of cadmium (II) and mercury (II) by rice husk ash. T= 25 °C, t = 6 hr, C_o = 100 mg/l, and m = 10 g/l

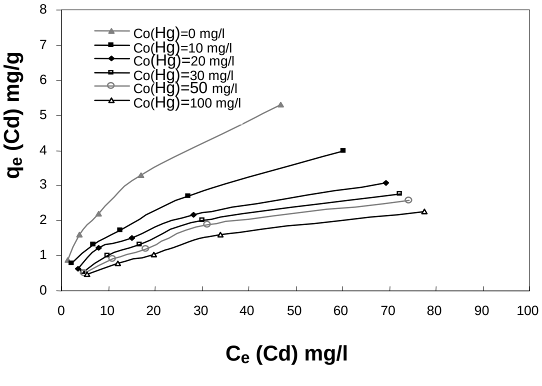

Fig. 6.Comparison of the equilibrium adsorption of cadmium (II) ion at varying concentrations of mercury (II) ion. pH_o = 6, t = 6 hr, T = 25 °C, C_o[Cd(II)] = 10-100 mg/l, and rice husk ash dosage = 10 g/l.

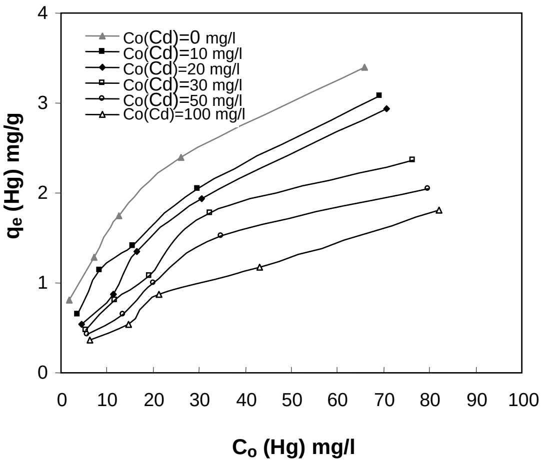

Fig. 7. Comparison of the equilibrium adsorption of mercury (II) ion at varying concentrations of cadmium (II) ion. $pH_o = 6$, t = 6 hr, T = 25 °C, C_o[Hg(II)] = 10-100 mg/l, and rice husk ash dosage = 10 g/l.

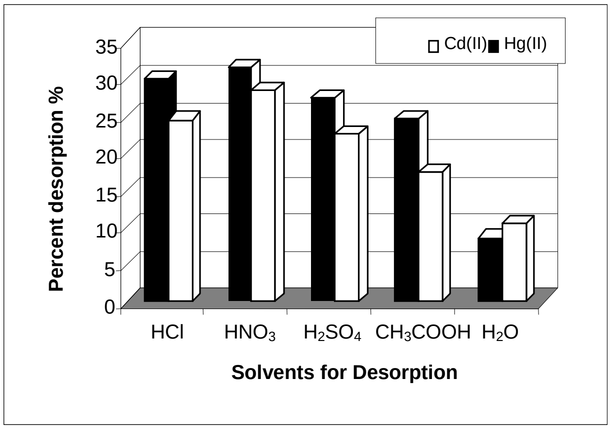

Fig. 8. Desorption of metal ions from metal loaded rice husk ash by solvents. T = 25 °C, t = 6 hr, C_o (solvent concentration) = 0.1N, and m = 10 g/l.

4. Conclusion

The present study shows that the rice husk ash is an effective adsorbent for the removal of Cd(II) and Hg(II) metal ions from aqueous solution. Maximum sorption for both mercury (II) and cadmium (II) metal ions was found to occur at pH_o 6.0. Higher percentage of metal ion removal was possible provided that the initial adsorbate concentration in the solution was low. Frendlich isotherm show very good fits with experimental single component adsorption equilibrium data. The. affinity of rice husk ash for cadmium (II) ions was greater than that for mercury (II), for both single component and the binary solutions under similar experimental conditions**.**

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