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Removal of Pb(II) from aqueous solution using pretreated rice husk at low concentrations

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ABSTRACT

In this research effect of different concentrations of sodium bicarbonate were investigated on increase of rice husk capacity in lead adsorption at low concentrations. The maximum adsorption efficiency occurred at pH 6.0 and adsorption equilibrium time was obtained 25 minutes. The results of chemical experiments and also scanning of the pretreated adsorbent treatments by Scanning Electron Microscope showed that there is suitable relation between the average numbers of adsorbent pores with adsorption efficiency. Also the maximum lead adsorption efficiency by rice husk was obtained at 99.1%. That was related to the usage of 0.3 M sodium bicarbonate (0.3M $NaHCO_3$) solution. In this research the kinetic adsorption models were also studied. Although both the Lagergren model (1898) and Ho et al (1996) describes the data at 95 % level of significant, but Ho et al. model describes the data better than Lagergren model. The comparison of the obtained coefficients with model coefficients in other researches showed that lead surface adsorption by pretreated rice husk in 0.3M sodium bicarbonate solution was very fast.

KEYWORDS

Rice husk;
Lead;
Kinetic adsorption;
Sodium bicarbonate solution;
Porosity.

INTRODUCTION

Today Existence of heavy metals such as Pb, Cd, Cu, Ni, etc causes harmful effects in human life. In many countries concentrations of heavy metals in water are exceeding the limits. The permissible concentrations of Pb, Zn, Cu and Cd in drinking water have been set as 0.1, 5.0, 0.05 and 0.01mg/l in India. About 0.005, 5.0, 1.0 and 0.01mg/l in USA, 0.05, 5.0, 3.0 and 0.005mg/l in UK, and 0.01, 5.0, 1.0 and 0.005mg/l in Canada, respectively[1-3].

The studies related to heavy metals adsorption by plant residues was generally started from 1970-1980[4-7]. In this period adsorption studies were generally about using raw plant residues and their coals. In recent 1990 adsorption studies using plant residues improved a lot, therefore, chemical activation or chemical modification was used instead of physical activation. In this method with increasing adsorption capacity and decreasing equilibrium time activation costs was less than physical activation[8]. Increase of adsorption capacity of rice husk by 0.1M K_2HPO_4 solution[9], 0.5M Tartaric Acid (TARH)[10] and 0.75M NaOH[11] is such examples of these studies.

Also studies on cadmium adsorption from aqueous solution using pretreated rice husk in 0.5M sodium bi-

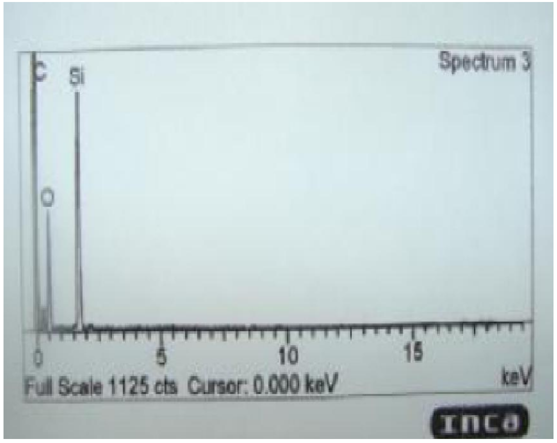

Figure 1 : Qualitative analysis of pretreated rice husk adsorbent (NCRH3)

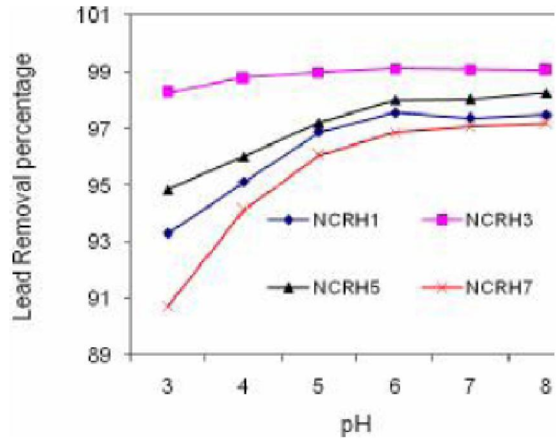

Figure 2 : Effect of pH on lead adsorption efficiency using pretreated rice husk

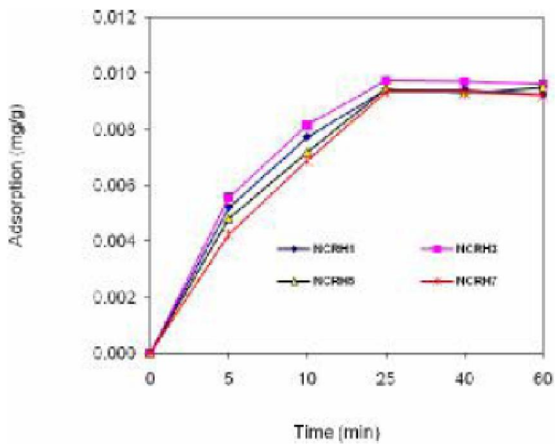

Figure 3 : Effect of equilibrium time on lead adsorption amount in different treatment of pretreated rice husk

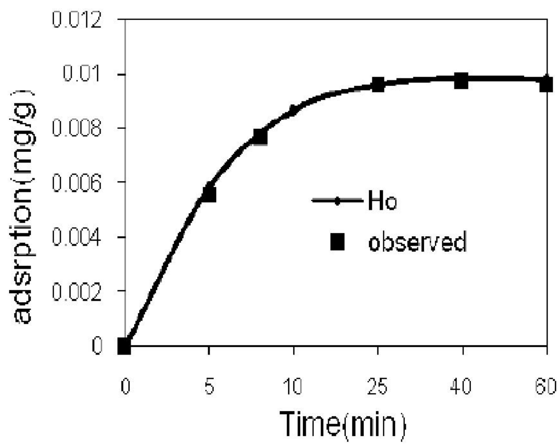

Figure 4 : Fitness of Ho et al. model on lead adsorption amounts by NCRH3 versus time

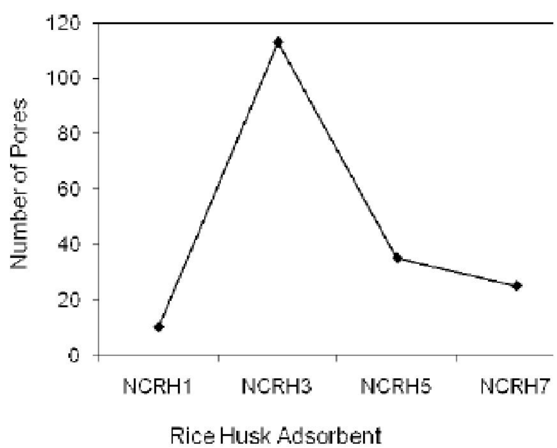

Figure 5 : Effect of sodium bicarbonates solution concentration on the number of pores of rice husk

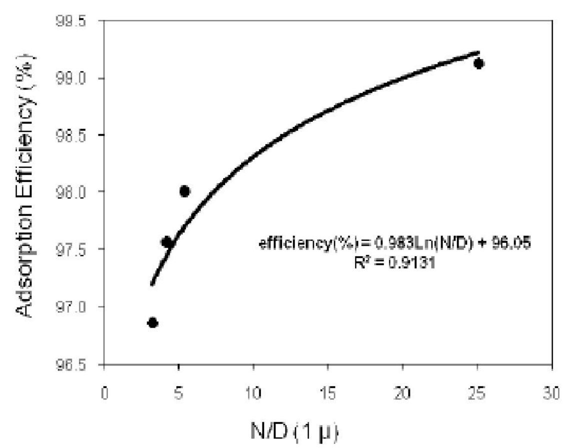

Figure 6 : Relation between the pores number and pores diameter with maximum adsorption efficiency on pretreated rice husk

carbonate solution showed that low cost modification can improve the adsorption capacity from 8.55mg/g by row rice husk to 11.12, 20.24 and 16.8 and decrease of equilibrium time from 10 hrs for row rice husk to 2, 4 and 1 hrs for pretreated rice husk by Epichlorohydrin, NaOH and sodium bicarbonate solutions respectively. In this research as preparing of sodium bicarbonate solution has lower cost than Epichlorohydrin preparation, this solution was chosen as a better solution for

TABLE 1 : Parameters of lagergren and Ho et al. models in 95 % level of significant

Model	Equation	R*
Lagergren	$q_t = 0.095\,[(1 - \exp(-0.168\,t)]$	0.996
Ho et al.	$\frac{t}{q_t} = \frac{1}{[2(1.32)(0.1019)^2]} + \frac{t}{(0.1019)}$	0.998

TABLE 2 : Comparing Lagergren and Ho et al. models coefficients in lead adsorption

Research source	Ho Model coefficient	Lagergren coefficient	Lead concentration	Adsorbent
Mathialagan and Viraraghavan. 2002	3.67	3.29	1	Perlite
Mathialagan et al.	12.56	4.7	1	A.biusporus
Mathialagan and Viraraghavan. 2002	50.54	10.01	1	L.edodes
Raji and et al 1997	-	0.0134	-	Peat
Kapoor and et al 1999	-	0.44	10	Pretreated A.niger
Current research	79.2	10.08	0.1	NCRH3

modification[12].

At this time the usage of household water purification systems extends in south of Iran. The adsorbent used in these systems is activated carbon which is very expensive. The purpose of this study is using rice husk in removal of lead at low concentrations. According to the maximum level of lead concentration which is 50mg/l in drinking water the initial concentration of lead is chosen of 100mg/l.

MATERIALS AND METHODS

At first row rice husk was prepared from local factories near Zahedan and passed through sieve sizes of 30 and 40 with particle sizes of 425 to 600μm (with 510μm average particle sizes). The rice husk particles were washed with water and they were dried at 70°C for 3 hrs.

Chemical preparation on rice husk

The prepared samples of adsorbent treatments were washed with deionized water. Then they were dried in oven at 80°C for 3 hrs and immediately the essential experiments were made on them. For preparing different adsorbent treatments, at first a specific volume of 0.1, 0.1, 0.5 and 0.7mgL^{-1} sodium bicarbonate solution were made then 100g of dried rice husk was mixed with 2 liter of 0.1M of sodium bicarbonate solution for 4 hrs and then the mixture was filtered. In order to remove the extra sodium bicarbonate from pretreated rice husk, it was washed with deionized water. The obtained adsorbent was dried at 80°C for 5 hrs and was preserved in close bottom at room temperature. This process was repeated for 0.3, 0.5 and 0.7M solutions. Finally 4 different adsorbents of 100g were prepared. The attained adsorbents were named NCRH1, NCRH3, NCRH5 and NCRH7 respectively. In the next step the samples were scanned by Scanning Electron Microscope. After the experiments for all 4 treatments NCRH1, NCRH3, NCRH5 and NCRH7, the statistical parameters of them were attained by counting the numbers of pores and measuring the effective diameter of porous. Also the qualitative analysis of all the treatments was experimented by Scanning Electron Microscope.

Batch sorption studies

In order to determine the optimum pH of lead adsorption, 6 Erlenmeyer were chosen and preserved in acid solution for 24 hrs and then they were washed with water and after that with deionized water. 100 ml of lead solution with 100 ppb from prepared solution was poured in to each Erlenmeyer. Then 1g of NCRH1 adsorbent was added and their pH was adjusted at 3, 4, 5, 6, 7 and 8. The Erlenmeyer containing the solution were put on the Shaker for 12 hrs with the speed of 180 rpm and their pH were measured after they took from shaker and the differences were noted. Using qualitative filter paper (Whatman) the solutions were filtered and poured in to plastic cans which had been washed completely. By adding a specific amount of Nitric acid their pH reduces to fewer than 2 and immediately the adsorption experiment were done in order to measure the amount of adsorbed lead. This process was repeated for 3 other adsorbents.

Sorption kinetic experiments

7 numbers of Erlenmeyer which had been washed with acid were washed with water and then with deionized water and 100 ml of lead solution with 100 ppb concentration was added to them. In each Erlenmeyer 1g of NCRH1 adsorbent were added and the pH of the solution was adjusted at 6 according to past experiments. Each Erlenmeyer containing solution was put on the shaker with the speed of 180 rpm for 5, 10, 25, 40, 60, 90 and 120 minutes. After that the samples were respectively taken from the shaker then immedi-

ately the lead amount was measured. This process was repeated for other adsorbents.

RESULTS AND DISCUSSION

Treatments chemical analysis showed that pretreated rice husk contains averagely 26.95 % Silica, 21.11 % carbon and 51.96 % oxygen. The lead element wasn't found in the combination of rice husk. Therefore the experimented rice husk didn't contain adsorbed lead and the error due to adsorption efficiency is negative. On the other hand it's expected that with forming surface Hydroxyl groups of silicon atoms, the surface adsorption capacity of rice husk should increase[9]. Figure 1 shows the qualitative analysis o NCRH3 adsorbent.

Effect of pH

The removal of a pollutant from an aqueous medium by adsorption is highly dependent on the solution pH which affects the surface charge of the adsorbent and ionization of it[13-15].The studies of the other researchers showed that the optimum pH of adsorption varies between 4 and 8[8,16]. For this reason the pH range used in this study was chosen between 3 and 8 and the experiments were done in this pH range[17]. Effect of pH on lead adsorption efficiency by pretreated rice husk is shown in figure 2. As fig. 2 shows that to dispense with the amount of sodium bicarbonate which is used to make pretreated rice husk, the minimum adsorption efficiency occurs at pH = 3, which is 93.3%, 98.3%, 98.8% and 90.7% for NCRH1, NCRH3, NCRH5 and NCRH7 adsorbents respectively. With increasing the pH, adsorption efficiency increases that in pH = 6 the adsorption efficiency reaches to 97.6%, 99.1 5%, 98.6% and 96.8% for all the treatments. In pH range from 6 to 8 the adsorbents treatment differs. The adsorption efficiency for NCRH1 adsorbent decreases about 0.5% at pH = 7 and then increases again at pH = 8, but adsorption efficiency for NCRH7 adsorbent increases gradually from pH = 6. Other 2 adsorbents also have a fixed adsorption efficiency from pH = 6.

As can be seen from figure 2 pH increase from 3 to 5 motivates a considerable increase in lead adsorption in all the treatments. This rapid increase in adsorbents also can due to two factors, first existence of H^+ ion in solution at low pH ranges which competes for surface adsorption with lead ion and second factor is the existence of a critical pH range for each hydrolysable metal ion, the range in which the adsorption efficiency reaches from a low amount to maximum which this amount is named surface adsorption limit amount[12].

Also the decrease in lead adsorption at pH levels higher than 6 in NCRH1 adsorbent could due to the formation of soluble Hydroxyl groups[18]. The little decrease in adsorption at pH levels higher than 6 obtained in this research is match with the results of Gupta et al., Krishnan et al. and Mathialagan et al. studies[19-21].

The lower removal of the studied metal ions at below optimum pH values can be attributed to effective competition between higher concentration of H^+ or $H_3O^+$and metal ions present in the forms of M^{2+} and $M(OH)^+$ according to their (Pb, Zn, Cu and Cd) speciation diagrams[22,23,3]. Comparing the curves in figure 2 shows that the adsorption efficiency in NCRH3 adsorbent is more than other adsorbents in all pH ranges. The reason of this difference is the number of pores of this adsorbent. Because counting the pores showed that number of pores on the surface of NCRH3 adsorbent is 3 times more than NCRH1 pores, 4 times more than NCRH7 and 11 times more than NCRH5 pores.

Sorption kinetics

Figure 3 shows the differences of adsorption amount with contact time at pH 6.0 for all the treatments. As figure 3 indicates in initial contact time the adsorption speed is high, as more than 50% of lead amount is adsorbed in the first 5 minutes and after 10 minutes more than 80% of lead amount is adsorbed, but with time spending the adsorption gradient decreases that after 25 minutes the adsorption reaches to it's maximum level and after that adsorption gradient reaches to zero. This is true about all the treatments. Adsorption efficiency in equilibrium time for NCRH1, NCRH3, NCRH5 and NCRH7 adsorbents is 99.2%, 95.9%, 95.0%, and 93.4% respectively. Maximum surface adsorption occurs for NCRH3 adsorbent that this is match with the results of figure 2. The obtained Equilibrium tome in this research was 25 minutes for all the treatments. There is a relation between low equilibrium time and low initial concentration in this process. The reason is the initial lead concentrations, because the equilibrium time decreases with decreasing in initial concentration of lead[24].

For describing lead kinetic adsorption on pretreated rice husk, Lagergren model (1989)[25] and Ho et al. model (1996)[26] are used. The equations 1 and 2 relates to the models respectively.

$$q_t = q_e(1 - e^{-k_2 t}) \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{2kq_e} + \frac{t}{q_e} \quad (2)$$

Obtained results from past experiments shows that pretreated rice husk with 0.3mgL^{-1} sodium bicarbonate solution NCRH3 has a better adsorption efficiency than other treatments. Therefore using SPSS (Version 9.0) and analyzing nonlinear regression the above models were fitted with the results of the adsorption kinetic experiments and the results showed in fig. 4. Although both Lagergren model and Ho et al. model describes the data at 95 % level of significant, but Ho et al. model describes them better than Lagergren model. TABLE 1 shows the models coefficients. As can be seen k_1 = 0.168 (l/min) and k = 1.32 (g/mg min) or in the case of considering by other researchers the time on hrs the coefficients will be: k_1 = 10.08 (l/hr) and k = 79.2 (g/mg hr).

Comparing these coefficients with attained coefficients by other researchers shown in TABLE 2 indicates that surface adsorption of lead on pretreated are so rapid. This matter can be related to the lead concentration and the kind of adsorbent.

Effect of chemical properties of treatments on adsorption

Different reasons have been given regarding the sorption affinity of biosorbent such as rice husk. The amount of sorbed ions depends on the equilibrium between sorption competition from all the cations, ionic size, stability of bonds between metal ions and biosorbent[29,30]. Counting the numbers of pores showed that pretreated rice husk by 0.3mg/l sodium bicarbonate solution (NCRH3) has the most pores; it means 113 pores are in the surface of this adsorbent and NCRH5 treatment has 35 pores. Also NCRH7 and NCRH1 have 25 and 10 pores on their surface respectively. The scanned images from Scanning Electron Microscope showed that all the treatments took effect of sodium bicarbonate completely and they are damaged except NCRH1, but in spite of complete surface explosion in these treatments the number of pores decreases with increasing the modifier solution concentration from 0.3 to 0.7M (Figure 5). Because adsorbent surface explosion in concentrations more than 0.3 M of sodium bicarbonate motives the increase of pores diameter, consequently, the number of pores will decrease. Also comparing the adsorption efficiency between NCRH1 and NCRH7 (Figure 5) shows that increase of pores diameter motives the decrease in adsorption efficiency. Because in NCRH1 treatment pores diameter average is 2.4μm that is less than pores diameter average in NCRH7 treatment; which is 7.7μm, but the adsorption efficiency of NCRH1 is 97.6 5 that is more than NCRH7 adsorption efficiency; which is 96.9%. This can be true in other treatments also. Therefore the coincident of the effects of pores diameter and the number of pores on the adsorbent surface should be considered on adsorption efficiency. For that is reason the relation between adsorption efficiency and pores number to average pores diameter ratio (N/D) is studied. According to this matter adsorption efficiency plotted against N/D by SPSS and by analyzing estimation regression curve, which is shown in figure 6.

CONCLUSIONS

Lead maximum adsorption efficiency occurs by rice husk pretreated with 0.3M sodium bicarbonate solution. Lagergren model describes the data well and it shows that the adsorption speed is high. Studying the relation between adsorption efficiency and pores diameter showed that there is a good correlation between adsorption amount and the pores number to pores diameter ratio (N/D) of adsorbent.

SYMBOLS

- q_e : Lead adsorbed amount in equilibrium time (mg/g)
- q_t : Lead adsorbed amount in time of t (mg/g)
- k_1 : Constant coefficient of adsorption gradient in Lagergren model (min^{-1} or hr^{-1})
- k : Constant coefficient of surface adsorption in made conditions (g/mg min or g/mg hr)
- t : The time (min or hr)

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