

## Influence of the System on Adsorption of Pb(II) and Cu(II) by Rice Husks Ash: Kinetic Study

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Pb(II) and Cu(II) removal from aqueous solutions by rice husk ash was investigated using batch and fixed bed techniques, static and dynamic systems, respectively. The rice husks calcined at 500 °C showed higher potential for removing metals such as lead and copper. Batch experiments were performed at a constant temperature, adjusting the pH of the solution in contact with rice husk ash. Adsorption essays at fixed bed were also carried out according to a study of outflow determined with basis on results from mass transfer zone (MTZ). The single-component essays showed that both heavy metals have affinity to ash adsorptive sites. The maximum adsorption capacity didn't show significant changes in the dynamic system of fixed bed system compared to static batch. In the binary mixture (copper + lead) there is a greater affinity between the lead and RHA in batch, while in fixed bed copper presented higher removal.

### 1. Introduction

Contamination of water by heavy metals in industrial effluents is a serious environmental problem; the development of this research has the aim of reducing or eliminated and recovery of waste.

Rice is one of the most commonly grown and consumed grain in the world. It is considered the most economically important product in many developing countries, becoming a staple for billions of people.

During the processing of rice, the most voluminous by-product is husks, which represent about 20% of rice weight. Rice husk (RH) is a fibrous material, whose main constituents are cellulose, lignin and inorganic and organic waste. The rice husk ash (RHA) is a light material, bulky, porous and amounts to about 20% of the burnt husk.

Several alternative technologies have been associated in literature with the use of rice husks and ashes: production of silica, silicon carbide production, using the ash as filler in polymers, in concrete production and synthesis of silicates and zeolites; moreover it has used as adsorbent of heavy metals in synthetic wastewater (Srivastava et al., 2006; Naiya et al., 2009, Krishnan et al., 2008; Tarley and Arruda, 2004; Ye et al. 2010; Bhatgnar and Sillanpaa, 2010; Ahmaruzzaman, 2010), due to its low cost, abundance, ease of obtaining and reusability.

Although the literature involving the removal of metals by rice husk ashes is both important and promising, a better understanding of these results considering the type of system used for the optimization of process conditions is still necessary. Studies of metal removal in other adsorbents such as clays (Vieira et al., 2010 a, b) showed the necessity for research on the removal of heavy metals in static and dynamic systems. Thus, this study has the aim of evaluating the different systems (in batch and fixed bed) to remove lead and copper by rice husk ash.

## 2. Material and Method

In this work, *Oryza sativa L.* rice husks from Boa Vista – RR/Brazil (Amazon region) were used as bioadsorbent. They were initially crushed, sieved and prepared by size classification and then calcined at 500 °C for 1 hour.

### 2.1 Batch sorption procedure

Adsorption experiments were performed in batch at 25 °C under constant stirring (225 rpm). 1 gram of rice husk ash was added to 100 mL of Pb (II) and Cu (II) of every solution (100 mg/L). The pH of the solutions was measured at the beginning and the end of each experiment and was adjusted when it needed to avoid causing chemical precipitation of metal species. At specific time intervals, solution aliquots were removed and centrifuged. The supernatant liquid was diluted and its concentration was determined by atomic absorption spectrometry. The concentrations of metal ion in the solid phase ( $q$ ) at each instant of time were obtained by Equation 1:

$$q(t) = \frac{V}{m}(C_0 - C(t)) \quad (1)$$

where,  $C_0$  is the initial concentration of metal ions,  $C(t)$  is the concentration of metal ions at time  $t$ ,  $V$  is the volume of solution in mass of dry ash.

The removal percentage (%RT) was calculated using the following expression:

$$\%RT = \left( \frac{C_0 - C_e}{C_0} \right) \cdot 100 \quad (2)$$

where,  $C_e$  is the concentration of metal ions in the solution of the equilibrium time.

### 2.2 Column sorption procedure

Essays in dynamic system were performed in a glass column with internal diameter of 1.4 cm and 14.0 cm in height. The height of the bed used in the experiments was 14.0 cm. The rice husk ashes were deposited inside the column and put in contact with deionized water for 2 hours.

The solutions containing the metal species were fed at the base of the column through a peristaltic pump (Masterflex) at a constant flow defined by studies of mass transfer zone (MTZ) for lead. Column effluent samples were collected at time intervals preset by FC203 fraction collector (Gilson).

The amounts of metal retained in the bed to the point of rupture ( $q_u$ ) until saturation ( $q$ ) were obtained by mass balance using the data in column saturation of it, provided of the breakthrough curves, noting that the area under curve ( $1-C/C_0$ ) to the point of rupture is

proportional to  $q_u$  and to exhaustion of the bed proportional to  $q$ . The amounts retained were calculated by Equations 3 and 4 respectively.

$$q_u = \frac{C_0 V}{1000m} \int_0^{t_b} \left(1 - \frac{C|_{z=L}}{C_0}\right) dt \quad (3)$$

$$q = \frac{C_0 V}{1000m} \int_0^{\infty} \left(1 - \frac{C|_{z=L}}{C_0}\right) dt \quad (4)$$

MTZ could be calculated then basing on the  $q_u/q$  ratio according to Equation 5 (Geankoplis, 1993):

$$MTZ = \left(1 - \frac{q_u}{q}\right) \cdot Ht \quad (5)$$

MTZ has a maximum value which corresponds to the bed height ( $Ht$ ) and, like the efficacy of mass transference increases, this value decreases until reaching the ideal condition where MTZ is zero and the breakthrough curve is a step function.

The percentage of total removal (% RT) during adsorption was obtained considering the metal fraction in solution retained in the adsorbent solid, from total effluent used in the adsorption process until bed saturation. The amount of adsorbed metal was calculated considering the curve area  $(1-C/C_0)$  versus  $t$ . The integral of metal adsorption curves was determined through the Origin version 6.0 software.

### 3. Results

#### 3.1 Batch adsorption

Kinetic adsorption of Pb and Cu by rice husk ash essays were performed in batch using the concentration of 100 mg/L (0.48 mM for Pb and 1.57 mM for Cu). Figure 1 presents the kinetics removal of lead and copper from single aqueous solutions.

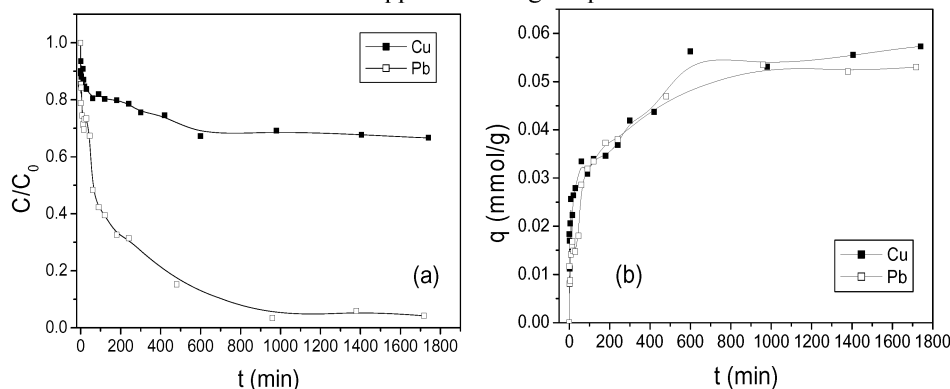


Figure 1: Kinetic curves for Pb and Cu on RHA: (a) dimensionless solution concentration as a function of adsorption time; (b) adsorbed amount at equilibrium.

From Figure 1, the equilibrium time in the removal of lead and copper was of 1000 and 600 min., respectively. The removal of copper is considerably lower than the removal of lead. The maximum amount of lead adsorbed was of 0.0530 mmol of metal/g of RHA. The maximum amount adsorbed of copper was of 0.0573 mmol of metal/g of RHA. The

percentage of total removal of lead and copper in this system was approximately of 94 and 33% respectively.

### 3.2 Lead dynamic removal

A preliminary study was conducted with different outflows of 2, 3, 4 and 5 mL/min in order to analyze lead removal in RHA. The most adequate outflow for this metal removal on RHA was determined with basis on results from the analysis on the minimum mass transfer zone (MTZ). Fig. 2 shows breakthrough curves in the different outflows studied.

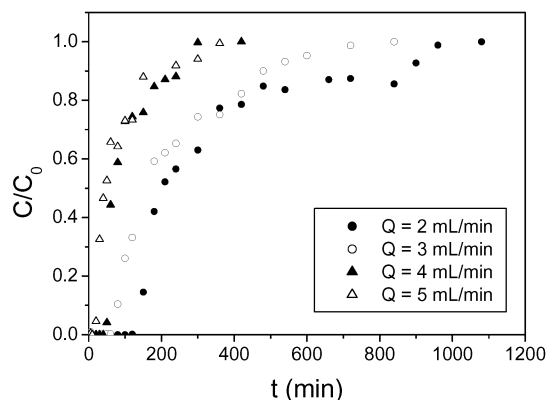


Figure 2: Breakthrough curves of systems  $Pb^{2+}/RHA$ ,  $C_0 = 0.483$  mmol/L with different flows and  $dp = 0.855$  mm.

It can notice that these curves present distinct behaviors indicating the outflow influence on diffusional resistances. The adsorption process presents strong resistance to bed saturation. Table 1 presents the calculated values of MTZ,  $q_u$ ,  $q$  and %RT.

Table 1: MTZ,  $q_u$ ,  $q$  and %RT for lead removal on the RHA

System	Flow (mL/min)	MTZ (cm)	$q_u$ (mmol/g)	$q$ (mmol/g)	%Rem
Pb/RHA/Fixed bed	2	9.077	0.0227	0.0575	33.33
	3	10.635	0.019	0.0636	31.33
	4	8.224	0.0239	0.0529	33.05
	5	12.353	0.001	0.0561	23.25
Pb/RHA/Batch	--	--	--	0.053	94.09

In the 4 mL/min outflow, the shorter length of the MTZ (8.224 cm) and a low resistance to saturation of the bed for removal of lead by RHA was obtained. Thus, considering the most adequate outflow, within the range of values studied for the removal of lead in fixed bed. Comparing the two removal systems, it was verified almost the same value for  $q$  ( $\sim 0.05$  mmol/g of RHA), what means that the saturation of the ashes of lead does not depends of the system.

### 3.3 Copper dynamic removal

Figure 3 shows breakthrough curves of copper in two different outflows studied (3 and 4 mL/min). Table 2 shows the parameters obtained in batch and in fixed bed for copper adsorption.

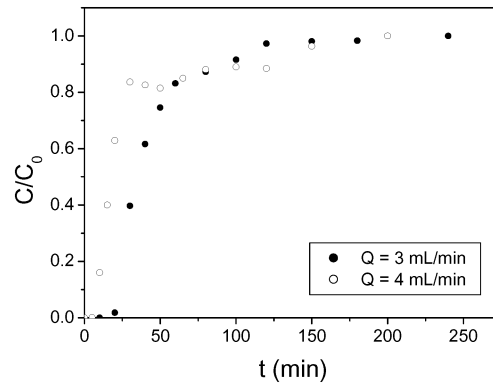


Figure 3: Breakthrough curves of system  $\text{Cu}^{2+}/\text{RHA}$ ,  $C_0=1.57 \text{ mM/L}$  and  $ps=0.855 \text{ mm}$ .

According to the results in Figure 3 and Table, the highest saturation of the solid is obtained in the system of fixed bed at flow rate of 4 mL/min, whereas the largest percentage of removal was gotten in batch.

Table 2: MTZ,  $q_u$ ,  $q$  and %RT for copper removal on the RHA

System	Flow (mL/min)	MTZ (cm)	$q_u$ (mmol/g)	$q$ (mmol/g)	%Rem
Cu/RHA/Fixed bed	3	9.124	0.0166	0.0423	17.08
	4	11.183	0.0137	0.0682	22.22
Cu/RHA/Batch	--	--	--	0.0573	33.00

### 3.4 Binary mixture removal

The kinetic and breakthrough curves obtained for Pb and Cu binary adsorptions on RHA performed in batch and in fixed bed at initial metal concentration of 0.78 mmol/L for both metals are presented in Figure 4.

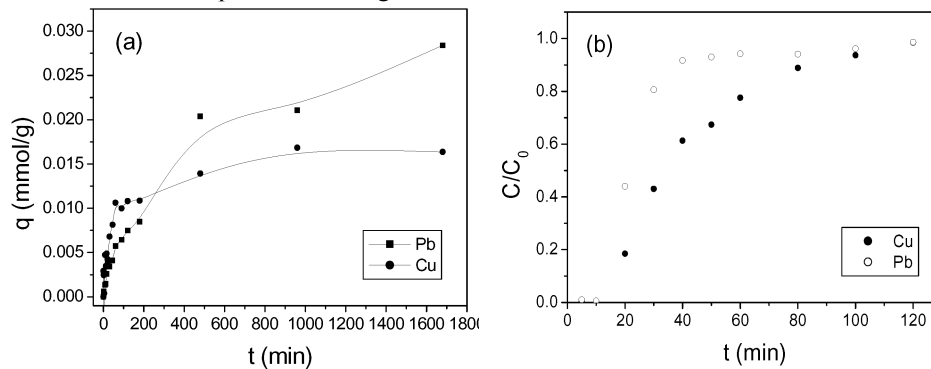


Figure 4: Kinetic curve for Pb and Cu on RHA: (a) batch stirred at 225 rpm and (b) column at flow rate 4 mL/min.

Figure 4 (a) shows that the equilibrium time for both metals in batch is almost the same, around 1000 min. Besides, the removal of lead was reduced when it was compared with adsorption experiments performed for single component solutions of this metal. Figure 4 (b) presents breakthrough curves of lead and copper removed by RHA in fixed bed. For lead, the highest percentage of removal was approximately 37% and the maximum quantity adsorbed was of 0.0284 mmol/g in batch. For copper, the highest amount adsorbed was obtained in bed (0.0355 mmol/g), although the highest percentage of removal, 18%, was obtained in batch. These results are due to the possible interaction between lead and copper ions in solution.

#### 4. Conclusions

Adsorption experiments carried out in the static and the dynamic systems were developed for removal of lead and copper ions on RHA, in the results were found that the removal of lead from single component solution does not depend on system, whereas copper ions from single component solution were more adsorbed in fixed bed. This behavior was also observed for both metal ions in a binary equimolar mixture (0.78 mmol/L).

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