

## Modeling of lead (II) adsorption on sodium hydroxide treated rice husk: Fixed-bed studies

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### Abstract

Sodium hydroxide treated rice husk was explored as an adsorbent for the removal of lead (II) ions from aqueous solutions in a column studies. This paper evaluate the effect of flow rates of 3 mL/min and 9 mL/min; bed depth of 0.9 cm, 1.8 cm and 2.8 cm and influent lead concentration of 5 mg/L and 20 mg/L on the adsorption capacity of the sample in fixed-bed mode were investigated. The highest adsorption capacity of 78 % using 20 mg/L initial lead (II) ions solution was achieved at flow rate of 9 mL/min and bed depth of 2.8 cm. The experimental results obtained from the adsorption studies were correlated with the Thomas, Adams–Bohart and Yoon–Nelson models. The results of the adsorption parameters showed that, Adams–Bohart model fitted the adsorption studies well over all the other models.

**Keywords:** Adsorption, rice husk, fixed-bed modeling, breakthrough curves

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## INTRODUCTION

In developing countries, the multinational factories have adequate facilities for wastewater treatment, while many locally based and small businesses does not have that facilities due to their high cost and maintenance. Several companies which generate wastewater laden with various metal ions which become toxic when their concentrations exceeds the standards. Therefore, such smaller industries need cheap and effective ways of toxic metals removal from wastewater. Although, the concentrations of such heavy metals in wastewater from the industries is negligible, such contaminated waters has adverse effects to the environment and aquatic organisms. The main methods employed for this metal ions removal include adsorption, membrane separation, ion–exchange and electrolysis. Adsorption of such contaminants using agricultural waste was preferred over other methods, because it is cheap, effective and the procedure is easy to carry out (Naiya *et al.*, 2009; Cruz-Olivares *et al.*, 2016). Among this heavy metals, lead had been found to be one of the most toxic in its ionic state. Due to high toxicity of lead, when it accumulates in living tissues, it becomes an enzyme inhibitor in the cells and it is therefore termed as metabolic poison. The major effects of lead to the humans include, damage to kidney, liver, reproductive system, nervous system, and the brain (Shi *et al.*, 2016; Duruibe *et al.*, 2007).

The aim of this paper is to study the removal of Pb (II) ions using treatment process that requires small amount of chemicals so as to reduce environmental pollution and as well keep the cost of the adsorbent cheaper.

## EXPERIMENTAL

### Materials and methods

Merck chemicals Malaysia supplied the sodium hydroxide pellets, hydrochloric acid, Lead solution (1000 mg/L) and the rice husk was obtained from a local vendor. Fresh rice husk designated as Raw–RH was milled and passed through different sieve sizes. The fraction with size between 250 µm to 500 µm was selected, washed and soaked in 2 % NaOH solution for 4 hrs. The excess NaOH was washed off with distilled water, it was then dried at 40°C and was labelled RH- NaOH.

### Wastewater preparation

The synthetic water containing lead ions was prepared by diluting appropriate amount of lead solution (1000 mg/L) in distilled water to get 5 and 20 mg/L concentrations.

### Fixed–bed Adsorption

The column adsorption was carried out using a glass column at room temperature and pressure and constant pH 6.5. Three adsorption parameters were studied which include initial lead concentration (5 mg/L and 20 mg/L), flow rate of (3 mL/min and 9 mL/min) and bed depth of (0.9 cm, 1.8 cm and 2.8 cm respectively). The effluent lead solution were withdrawn at intervals and its concentrations were determined using PerkinElmer HGA 900 atomic absorption spectrophotometer.

### Characterization

The rice husk was characterized using Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS), X-

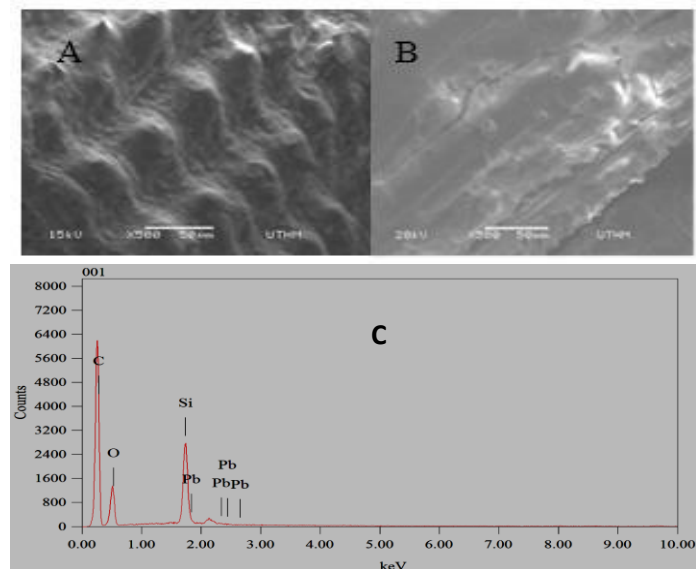
ray Diffraction (XRD) and Fourier Transform Infrared spectroscopy (FTIR).

## RESULTS AND DISCUSSION

### Characterization of the adsorbent

#### SEM-EDS Analysis

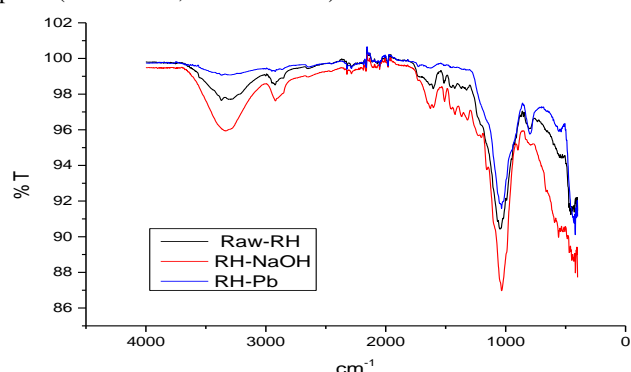
The SEM results of the raw rice husk in **Fig. 1** (A) revealed that, the surface of the husk has no developed pores due to blockage by the volatiles, as the volatiles escaped after treatment as in (B), pores start to develop which are responsible for adsorption of the lead (II) ions. The EDS result (C) confirmed the uptake of lead ions after the adsorption process (Garba et al., 2016a; Wang et al., 2010).



**Fig. 1** SEM images of raw (A), treated (B) rice husk and EDS of treated rice husk (C).

#### FTIR Analysis

The FTIR results (in **Fig. 2**) shows bands at 3374, 2920, 1635 and 1048  $\text{cm}^{-1}$ . After the sample was treatment with NaOH solution, the band at 1048 shift to 1034 and a new band at 861  $\text{cm}^{-1}$  was observed due to adsorption of Pb on the rice husk and this confirmed the lead uptake (Garba et al., 2016b & 2015).



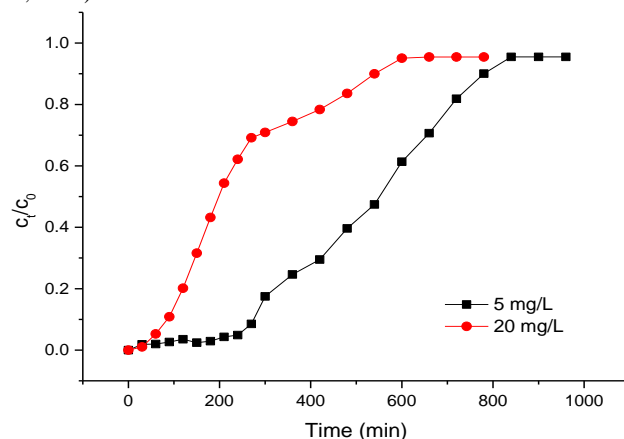
**Fig. 2** FTIR spectra of raw, treated and lead-adsorbed rice husk.

### Adsorption parameters

#### Effect of initial concentrations

Adsorption of Pb (II) ions by the sample was carried out using 5 mg/L and 20 mg/L concentrations at flow rate of 3 mL/min and height of 2.8 cm. The lead concentrations were monitored at intervals to get the breakthrough curves. From **Fig 3.**, the breakthrough times were 840 minutes and 600 minutes for 5 mg/L and 20 mg/L respectively. The variation in the exhaustion times for the concentrations could be associated with low concentration gradient due to low mass transport coefficient of the Pb (II) ions in the lower 5 mg/L concentration which

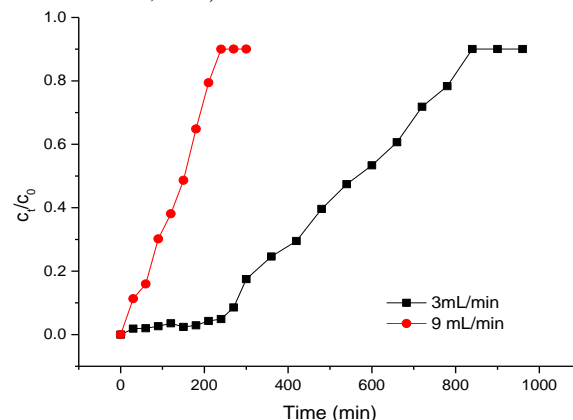
leads to extension of the breakthrough curve. On the contrary, the 20 mg/L breakthrough curve was shorter and became saturated more quickly due to larger amount of Pb (II) ions in the solution that leads to higher mass transport coefficient. However, the two phenomena leads to formation of shorter breakthrough curve and also a shorter exhaustion time was obtained. Similar study was reported by Olgun et al., (2013) for the adsorption of phosphate ions and nitrate ions using a waste from Boron and a heat treated Boron waste. The study illustrated that, high initial solution concentrations of the ions was responsible for higher mass driving force which subsequently leads to shorter exhaustion time for the 200 mg/L concentration, followed by 150 mg/L concentration. The least 100 mg/L concentration have the longest breakthrough curve due to less contaminants concentration which was responsible for lower driving force and longer exhaustion time (Olgun et al., 2013).



**Fig. 3** Effects of initial Pb concentrations at constant flow rate of 3 mL/min and bed height of 2.8 cm.

#### Effect of flow rates

The effects of lead solution flow rates were explored using different flow rates of 3 mL/min and 9 mL/min at bed height of 2.8 cm and initial lead solution concentration of 5 mg/L. From the Figure (**Fig. 4**), it could be seen that higher flow rates comes with corresponding shorter breakthrough time. On the other hand, the reverse case was observed for the much low flow rate of 3 mL/min. This is due to the fact that, when the Pb (II) ions solution passes through the fixed-bed, more of the ions were adsorbed by the available pores of the sample that makes the pores to get saturated quickly. Consequently, increase in Pb (II) ions flow rates leads to an increase in zone speed. Likewise, increasing the zone speed leads to a decrease in breakthrough time because the lead ions have a limited residence time as there is no enough time to make efficient contact with the adsorbent. On the other hand, low solution flow rates possesses less zone speed with high residence time that allow for enough contact with the adsorbent. This process leads to higher breakthrough time (Gupta et al., 2011). Similar results were reported by Khobragade and Pal (2016) on the studies they conducted about removal of selected heavy metals on a bilayer supported alumina (Khobragade and Pal, 2016).



**Fig. 4** Effect of Pb solution flow rate at constant bed height of 2.8 cm and 5 mg/L concentration.

### Effect of bed depth

Effects of bed depth on lead ions adsorption on a treated rice husk at different bed depth was illustrated in Fig. 5. The effect was determined at constant lead solution concentration of 5 mg/L and flow rate of 3 mL/min. The bed depth was obtained at various heights of 0.9 cm, 1.8 cm and 2.8 cm that corresponds to 0.5 g, 1.0 g and 1.5 g of the treated sample. The figure shows that the breakthrough time as well as the exhaustion time increases with increase in the bed depth. The breakthrough times appreciates from 480 minutes, 600 minutes and 720 minutes at 0.9 cm, 1.8 cm and 2.8 cm heights respectively. As the bed depth increases, both breakthrough time and exhaustion time would be delayed which as a result increases the column performance. However, when the bed depth is reduced, the breakthrough time and exhaustion time would also be accelerated which accordingly reduce the fixed-bed capacity. The fixed-bed performance would be increased as bed depth increases which could be due to packing of more adsorbent in the column. This provides more adsorption sites to accommodate the lead ions. Also, it provides longer residence time for the lead ions to interact with the adsorbent in the column and thus enhance better adsorption (Yahya et al., 2011). Similar results were reported by Kamarudzaman

et al. (2015) on manganese biosorption on spent mushroom compost (Kamarudzaman et al., 2015).

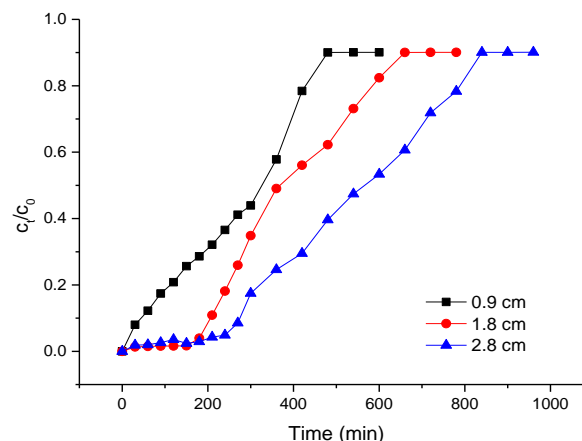


Fig. 5 Effects of bed depth at constant flow rate of 3 mL/min and lead concentration of 5 mg/L.

### Breakthrough curve modeling

Table 1 The adsorption model constants for Pb (II) ions adsorption on a treated rice husk packed column

Operating conditions				Adams – Bohart model			Thomas model			Yoon – Nelson model		
pH	Z	Q	Ci	K <sub>AB</sub>	N <sub>0</sub>	R <sup>2</sup>	K <sub>Th</sub>	q <sub>0</sub>	R <sup>2</sup>	K <sub>YN</sub>	τ	R <sup>2</sup>
6.0	3	0.9	5	0.001	-863	0.954	0.0024	4194	0.795	0.012	-0.004	0.795
6.0	9	0.9	5	0.007	-54	0.84	0.0144	2757	0.960	0.072	-0.018	0.960
6.0	3	1.8	5	0.002	-104	0.848	0.0022	3523	0.947	0.011	-0.002	0.947
6.0	3	2.8	5	0.0011	-141	0.921	0.0015	3056	0.975	0.008	-0.002	0.975
6.0	3	0.9	20	0.0017	-209	0.958	0.0007	5302	0.967	0.015	-0.013	0.967
6.0	9	0.9	20	0.0001	-539	0.972	0.0006	-3262	0.846	0.013	0.061	0.847
RMSE (%)				1.88			3.86			3.86		
SS (%)				1.88			3.86			3.86		
R <sup>2</sup>				0.9954			0.9803			0.9803		

### Adams–Bohart model

From the Adams–Bohart equation, K<sub>AB</sub> and N<sub>0</sub> could be determined by a plot of ln(C<sub>0</sub>/C<sub>t</sub>) versus time (t) as indicated by Table 1. The model's rate constant K<sub>AB</sub>, increases with an increase in the solution flow rate (from 0.001 to 0.007) when the flow rate increases from 3 mL/min to 9 mL/min at constant lead concentration of 5 mg/L. The K<sub>AB</sub> also increases with an increase in concentration from 5 mg/L to 20 mg/L (from 0.0011 to 0.0017). Also, the K<sub>AB</sub> decreases with increase in the depth from 0.9 cm, 1.8 cm and 2.8 cm (from 0.007, 0.0012 and 0.0011). However, the (N<sub>0</sub>) saturation concentration increases with an increase in flow rates from 3 mL/min to 9 mL/min (from -863 to -54), but as well decreases with an increase of initial lead concentration from 5 mg/L to 20 mg/L (from -141 to -209). However, increase in the adsorbent depth from 0.9 cm, 1.8 cm and 2.8 cm results to a decrease in N<sub>0</sub> values (from -54, -104 and -141). Adams–Bohart model fitted the experimental results well even though it only has two R<sup>2</sup> that have values above 0.9 for the experiments. The fitness is because, the model has the lowest values for RMSE and SSE (1.88 for both) and as well have the highest R<sup>2</sup> model value of 0.9954 in comparison with the other models. This result shows common characteristics to one reported by Biswas and Mishra (2015) on lead ions removal from solutions on a charcoal obtained from carbonized rubber wood sawdust (Biswas and Mishra, 2015).

### Thomas model

From Table 1, the values for Thomas rate constant (K<sub>Th</sub>) increases with increase in the solution flow rates from 3 mL/min to 9 mL/min (from 0.0024 to 0.0144). The K<sub>Th</sub> value decreases with an increase in the initial lead concentration from 5 mg/L to 20 mg/L (from 0.0015 to 0.0007). In addition, the equilibrium adsorption capacity of the column

for lead decreases when the lead solution flow rates increases from 3 mL/min to 9 mL/min (from 4194 to 2757), but it sharply increases as the adsorbent depth increases from 0.9 cm to 1.8 cm (from 2757 to 3523). In contrast, the q<sub>0</sub> value increases by increasing the lead concentrations from 5 mg/L to 20 mg/L (from 3056 to 5302). Though, the R<sup>2</sup> values for the model that were above 0.9 obtained were 3 values out of the 6, which were higher than the values obtained from Adams–Bohart model's 2 values out of 6. Thomas model cannot provide good fit for the adsorption of lead ions on the treated sample. This is due to the fact that, Thomas model has higher RMSE and SSE values of 3.86, as well as lower model coefficient of determination (0.9803) in comparison with the Adams-Bohart model values. The result agreed with the results reported by Lim and Aris (2014) on adsorption and modeling of Lead and Cadmium ions in a fixed-bed using calcareous skeleton as adsorbent (Lim and Aris, 2014).

### Yoon–Nelson model

The Yoon–Nelson rate constant (K<sub>YN</sub>) increases with increase in both solution flow rates and initial lead concentration. From 3 mL/min to 9 mL/min (from 0.012 to 0.072) for flow rates and from 5 mg/L to 20 mg/L (from 0.008 to 0.015) for initial lead concentrations. Furthermore, the 50% breakthrough time (τ) decreases with increase in lead solution flow rates from 3 mL/min to 9 mL/min (from -0.004 to -0.018). It remains almost constant with an increase in bed depth from 0.9 cm to 1.8 cm and 2.8 cm (from -0.018 to -0.002 and -0.002). The Yoon–Nelson model cannot give a good fit to the experimental results even though its R<sup>2</sup> values that were over 0.9 for the experiments under this model were found to be high (4 values out of the total 9 values). The model lacks low values for RMSE and SSE (3.86) and also it has low R<sup>2</sup> (0.9803) compared to the Adams–Bohart model (0.9954).

Therefore, a model can only fit experimental results when it has lower values for RMSE and SSE (error functions) and higher values for coefficient of determination ( $R^2$ ). The result was in total agreement with the studies reported by Afroze et al. (2016) about removal of a dye (malachite green) from solutions on a nano zero valent iron algal biocomposite (Afroze et al., 2016).

## CONCLUSION

This study investigate the ability of an adsorbent (treated rice husk) as a low cost sample for the uptake of Pb (II) ions from solution in column mode. The Pb (II) ions removal from aqueous solution was affected by fixed-bed parameters such as initial Pb (II) ions concentration, adsorbent depth and solution flow rates. The Adams–Bohart model fitted the experimental data well compared to the other models used. This study illustrates the potentials of rice husk as adsorbent which requires small amount of chemicals and cheap treatment that gives a reasonable removal capacity for the prepared adsorbent.

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