

# Fixed Column Removal of Lead (II) Ions from Industrial Effluent using Pig Bone Char, Rice-Husks Ash and Water Hyacinth Composite Adsorbent

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**Abstract:** *The adsorption potential of pig bone char (PBC), rice husk ash (RHA) and water hyacinth biomass (WHB) composite mixture to remove lead (II) ions from industrial waste water was investigated using a fixed bed column. The effects of bed height (2-10 cm), flow rate (5-10 mL/min) mL and feed concentration on the breakthrough characteristics of the column were determined. The highest bed capacity of 476.2 mg/g was obtained using 10-cm bed height, 1:2 feed concentration and 5 mL/min flow rate. The result indicated that adsorption capacity increased with increase in the inlet ion concentration and bed height and decreased with increase in flow rate. Increasing the flow rate resulted in a shorter time of bed saturation. Adsorption data was fitted to Adam-Bohart, Thomas and Yoon-Nelson models. The data was well fitted by the Thomas and Yoon-Nelson models with correlation coefficient  $R^2 \geq 0.96$  and for Adam-Bohart model,  $R^2 \leq 0.94$ . It was noted that the rate constant for the Yoon-Nelson model increased with increase in flow rate, initial ion concentration and bed height. The breakthrough and exhaust times between the cycles did not differ significantly at 95 % confidence level. The adsorption of PBC/RHA/WHB had approximately 20 % more adsorption capacity than the commercially available materials.*

**Keywords:** Adsorption; Pig Bone char; Fixed bed column; lead (II) ions, Rice husks ash, water hyacinth biomass, wastewater

## List of Abbreviations

AAS	Atomic absorption spectroscopy
AC	Animal charcoal
BOD	Biological oxygen demand
COD	Chemical oxygen demand
$C_t$	Outlet of metal concentrations
$C_0$	Influent concentration
ICRAF	International center for agroforestry research
$k_{AB}$	Adams bohart adsorption rate constant
$k_{YN}$	Yoon-Nelson rate constant
$k_{Th}$	Thomas rate constant
m	Mass of the adsorbent
NEMA	National environment management authority
$N_0$	Saturation concentration
Q	Total flow time
$Q_0$	Equilibrium adsorbate uptake capacity
RHA	Rice husk ash
$R^2$	Regression values
$t_b$	Break through time
$t_e$	Bed exhaustion time
$t_{\frac{1}{2}}$	Time required for 50 % adsorbate break-through
XRD	x-ray diffraction
z	Bed depth

alarming levels [1]. High levels of heavy metal have now been reported in fish and animal products according to current data from a study undertaken along the Kenyan coastline [2]. Heavy metal pollution has serious health consequences, which include mental retardation, kidney, liver and skin diseases. Recently in Mombasa at Changamwe Owino-Uhuru estate of the coastal region of Kenya, people were reported to have suffered serious consequences of lead pollution. As a consequence and in view of the dangers posed by environmental heavy poisoning, the Kenya National Environment Management Authority (NEMA) has set the maximum allowable limits of heavy metals concentration industrial effluents [3]. The industries are now required devise more efficient technology of removing excess heavy metal from their effluents to meet these stringent standards.

Traditionally heavy metal residues are removed from wastewater by such techniques as: chemical precipitation [4], biological uptake [5] and reverse osmosis [6]. Whereas these techniques have previously been applied to varying degrees of successes, most of them are now found ineffectual, inadequate or too expensive in face of the new developments. The development of new, efficient and more affordable clean-up technologies for the treatment of large volumes of water contaminated with these metals is now of major interest [7, 8]. Materials such as, water hyacinth [9], charcoal dust [10], bone charcoal [11,12], spent bleaching earth ash [13] and rice husks [14] have all been investigated and found to have the capacity to adsorb high amounts of heavy metals in batch experiments.

## 1. Introduction

Pollution caused by industrial wastewater has become a major environmental concern in many countries of the world and toxic heavy metal pollution in particular has reached

Batch experiments provide an easier way of categorizing the adsorbent materials than column flow experiments [15]. In terms of the practical applicability, however, the former are

not as useful. Thus, more investigations need to be conducted on the use of these materials, in column experiments with a view of optimizing on their uptake capacity of wastewater contaminants. The potential of composite adsorbents in a column tests presents a viable opportunity to exploit mechanistic synergy of plausible adsorbents to enhance their performance. It presents an opportunity to formulate adsorbents and their mixes to exploit their individual qualities and improve on their hydraulic conductivity and address the problem of column clogging, which is prevalent with pulverized adsorbents. Some industrial water treatment plants have already exploited this approach based on the use of activated charcoal-sand mixture in their treatment columns to great advantage and performance of the columns [16].

The current work was initiated to investigate lead (II) removal from industrial effluent based on pig bone char (PBC), rice husk ash (RHA) and water hyacinth biomass (WHB). In this case real industrial waste rather than the usual simulated water was used in column experiments. This provided opportunity for fore-insight into the practical adsorption potential of the adsorbent. It is anticipated that the results of this study will be useful for future scale up using these materials as a cost-effective adsorbents. And for construction of efficient effluent clean up stream(s) that could offer a desired solution to industrial effluent disposal.

## 2. Materials and Methods

### 2.1 Preparation of the adsorbents

#### 2.1.1 Animal charcoal (AC)

The bones, as obtained from various sampling sites from various meat processing firms in Nairobi, Kenya, were boiled for 10 h to remove the flesh and fats. About 1 kg of the bones was impregnated with 100 mL of 10 M KOH and carbonized in furnace from Shadong company limited (Model, SX2-5-12T) at 550°C for 5 h. They were then cooled in a dessicator and pulverized to 150 µm. The activated carbons obtained were washed with excess distilled water until a leachate pH of 6.5 to 7. The resultant product was dried at 110 °C for 5 hours and finally stored in plastic bottles.

#### 2.1.2 Rice husks ash (RHA)

Rice husks were obtained from Mwea rice milling station (Kenya). They were washed in excess tap water and thereafter in 0.01 M Nitric acid. They were then rinsed with distilled water until a leachate pH of between 6.5 and 7 was obtained. The husks were dried at room temperature and calcined in a furnace at 500 – 600 °C for 24 h. The resulting ash was then ground to fine powder and screened through a 250-400 µm mesh. It was then stored in an air-tight glass bottles until further treatment [17].

#### 2.1.3 Preparation of PBC, RHA and WHB composite

To obtain the composite adsorbent based the PBC, RHA, and WHB adsorbents were blended by mass at a ratio of 2:1:1, respectively. After accurate measurements of the fractions they were placed in 250 cm<sup>3</sup> conical flask containing de-ionized water and stirred using a magnetic stirrer for 1 minute. Then it was allowed to dry.

### 2.2 The industrial effluent

The effluent used was obtained from a local manufacturing firm in Nairobi Kenya. The pH of the effluent was determined on the spot using a portable pH meter. The physicochemical characteristics, which included biological oxygen demand (BOD), chemical oxygen demand (COD), turbidity and pH of the effluent, were determined using standard analytical methods [18]. The concentration of lead (II) ions was analyzed using atomic absorption spectroscopy (AAS)

### 2.3 Adsorption studies

The test adsorbent PBC/RHA/WHB in the ratio 2:1:1 was packed in three identical cylindrical glass columns of heights 8.3 cm and internal diameters of 1.2 cm were packed to desired quantities. The pH of the wastewater was adjusted to 6.5–7.0 and fed into the column. The raw effluent was pumped through the column in the upward-flow fashion using a Charles Auston variable peristaltic pump model A. 85.S/E (By fleet, UK). Aliquots of the effluent were collected at the outlet of the column at predetermined regular time intervals for 700 minutes. The concentration of lead (II) ions in the waste streams was analyzed using an atomic absorption spectrophotometer (AAS) (Buck, model 210 VGP). The tests were repeated for 1:1 and for 1:2 diluted industrial effluent, respectively. The results were subjected to Thomas model, Yoon-Nelson and Adams–Bohart models [19].

### 2.4 Desorption tests

Desorption experiments were then conducted using 0.01 M HNO<sub>3</sub> as an eluting agent at flow rate of 5 mL/min for 12 h. Each time the columns were rinsed with deionized water to leachate pH 6.0–7.0 and reused to clean the wastewater at optimized bed height and adsorbate flow rates.

### 2.5 Treatment of industrial effluent using commercial and PBC/RHA/WHB adsorbents

The breakthrough curves for commercial adsorbent and PBC/RHA/WHB adsorbents were obtained and used to predict the performance of each adsorbent. The statistical comparison of the adsorption ability of the two adsorbents was done using ANOVA.

## 3. Results and Discussion

### 3.1 Effluent Characterization

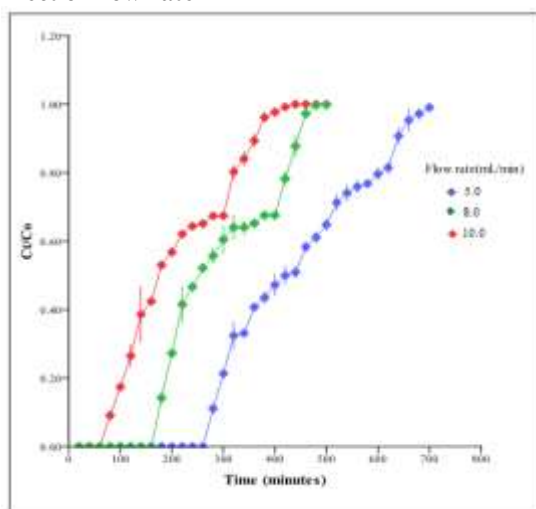
**Table 1:** Effluent characterization

PARAMETERS	EFFLUENT PARAMETERS			
	Before treatment	Treatment using commercial adsorbent	Current study using PBC/RHA/WHB mixture	Nema standards

pH	4.0	5.0	6.5	6.5-8.5
Temperature (°C)	28.4	26.5	24.0	
Turbidity (NTU)	99.90	42.50	8.80	30
BOD (mg/L)	787.0	234.0	25.0	30
COD (mg/L)	1575.0	321.0	44.0	50
Pb (II) ions (mg/L)	5.71	0.64	0.002	0.01
Zn(II) ions (mg/L)	9.47	0.53	0.043	0.05
Cr (II) ions (mg/L)	Not detected	Not detected	Not detected	0.05
Cd(II) ions (mg/L)	0.10	0.01	0.00	0.01

Table 1 shows the results for effluent characterization. The results show that the industrial treatment scheme was unable to effectively remove lead (II) ions. The use of PBC/RHA/WHB composite mixture was able to remove lead (II) ions to acceptable standards. Moreover other parameters such as BOD, COD, pH, and turbidity were reduced tremendously.

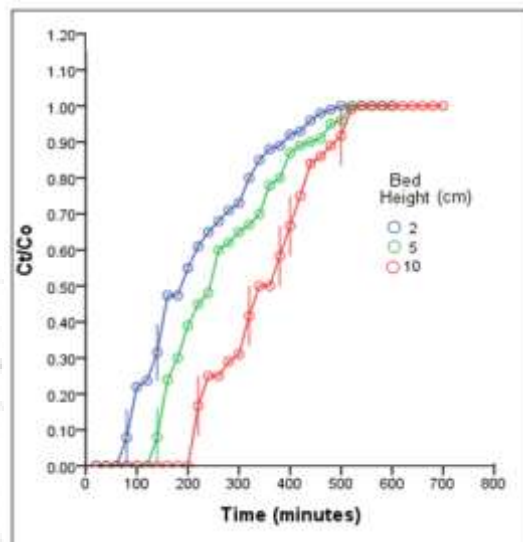
### 3.2 Effect of flow rate



**Figure 1:** Effect of flow rate on the adsorption of lead (II) ions

The effect of flow rate on the adsorption of lead (II) ions onto PBC/RHA/WHB is illustrated in figure 1. During the Lead (II) ions adsorption, the break-through times for flow rates, 5, 8 and 10 mL were 260, 180 and 80 min respectively. The results showed that breakthrough time for lead (II) uptake decreased with increasing flow rate. Ahmad and Alrozi [20] suggested that the residence time distribution of influent concentration in the adsorbent was greater in lower flow rates. The front of the adsorption zone in an upward flow system quickly reaches the top of the column and the column is saturated faster when the flow rates are high due to the reduced contact time between the adsorbent and the mobile phase. This causes a poor distribution of the liquid inside the column leading to a lower diffusivity of the solute through the adsorbent particles [21].

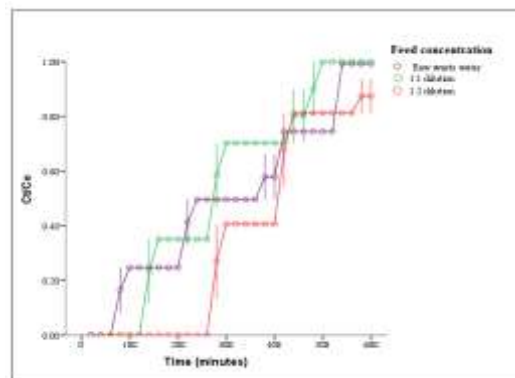
### 3.3 Effect of bed height



**Figure 2:** Effect of flow rate on the adsorption of lead (II) ions

Figure 2 shows that the breakthrough time, decreased with decreasing bed height of the adsorption column. It shows that higher lead (II) uptake was achieved at higher bed height due to the increase in the amount of the PBC/RHA/WHB mixture which provided more binding sites for the cations. Altenor *et al.* [22] observed that the increase in bed height also increase the mass transfer zone, which is the distance between the entry and exit points of bed. For same influent concentration and fixed bed system, an increase in bed height creates a longer distance for the mass transfer zone to reach the column exit resulting in an extended breakthrough time. Similarly, for higher bed depths, the increase in adsorbent mass provides a larger surface area leading to an increase in the volume of the treated solution.

### 3.4 Effect of feed concentration



**Figure 3:** Effect of feed concentration on the adsorption of lead (II) ions

The effect of feed concentration on the adsorption of lead (II) ions is reported in figure 3. The breakthrough point for raw industrial wastewater and for the wastewater diluted in the ratio 1:1 and 1:2 with distilled water for lead (II) ions adsorption were 80 min, 120 min and 240 min respectively. The break-through curve for raw waste water was achieved earlier due higher concentration of lead (II) ions. This was as a result of higher driving force of lead (II) ions at higher concentrations to overcome the mass transfer resistance in the liquid phase. Consequently, faster saturation of the available binding sites for lead (II) ions led to the decreased

breakthrough time with the increasing concentration. Dilution of the feed wastewater led to slower transport of lead (II) ions through the column due to the lower concentration gradient, which must have led to decrease in diffusion coefficient or mass transfer coefficient leading to a late breakthrough curve [23, 24]. It may be deduced, therefore, that at a lower inlet concentration more breakthrough time is required and the highest efficiency of the column to remove lead from effluent is obtained.

### 3.5 Modeling and analysis of column data

**Table 2: Thomas model parameters for lead (II) ions adsorption**

Parameters	[Pb <sup>2+</sup> ] (mg/L)			Flow rate using 1:2 diluted effluent(mL/min)			Bed height (cm)		
	Raw	1:1	1:2	5	8	10	2	5	10
$k_{Th}$ (mL/min/mg) x 10 <sup>-4</sup>	7	10.8	13	10	12	14	80	11	10
$q_0$ (mg/g)	687.3	458.7	386.2	476	356.1	332.3	419.1	439.1	591.1
$R^2$	0.99	0.99	0.99	0.89	0.94	0.95	0.96	0.86	0.91

The prediction of breakthrough curve is required for the successful design of a column-sorption process. The maximum adsorption capacity of an adsorbent is also needed for design purposes. Various mathematical models can be used to describe the fixed-bed adsorption. The Thomas model, Yoon-Nelson and Adams-Bohart models, for example, have been widely used by investigators starting at concentration ratios of  $\frac{C_t}{C_0} > 0.1$  to  $\frac{C_t}{C_0} > 0.9$  considering the safe water quality standards and operating limit of mass transfer zone of a column.

Table 2 gives a summary of the Thomas model parameters Obtained at different bed heights, flow rates and initial metal concentrations for the lead (II) ions uptake.

The Thomas model mathematical was applied in its linearized form as:

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_{Th}q_0m}{Q} - k_{Th}C_0t \quad (1)$$

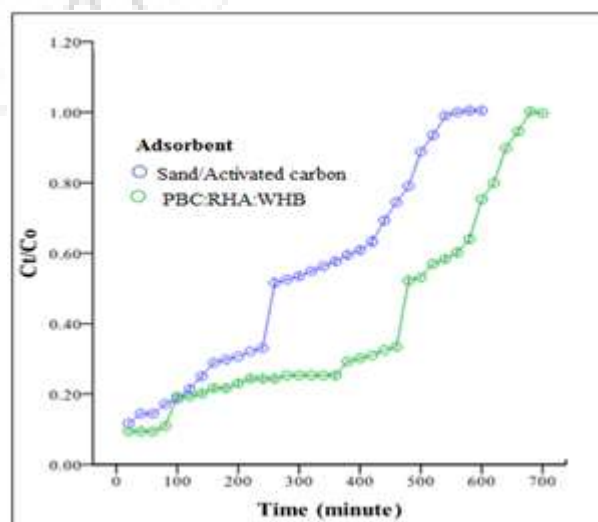
where,  $k_{Th}$  is the Thomas rate constant,  $m$  is mass of the adsorbent in the column,  $q_0$  is equilibrium adsorbate uptake capacity,  $C_t$  is the effluent concentration,  $C_0$  influent concentration and  $Q$  is the total flow time (min). A plot of

$\ln\left(\frac{C_0}{C_t} - 1\right)$  against  $t$  gives  $k_{Th}$  as the slope while  $q_0$  is

obtained from the intercept. The experimental data for lead (II) adsorption fitted well with the Thomas model with the regression coefficient of  $R^2 \geq 0.957$ . The values of Thomas rate constant  $k_{Th}$  increased with the increasing flow rate whereas the maximum adsorption  $q_0$  decreased due to insufficient residence time for the adsorbate to interact with reactive sites in the adsorbent. As the bed height was increased, the values of  $q_0$  and  $k_{Th}$  increased. [25] reported that increase in bed height leads to more adsorbent sites which increases adsorption. As the concentration

decreased the values of  $q_0$  and  $k_{Th}$  also decreased. [26] suggested that decrease of  $q_0$  value with dilution may be due to decrease in the number of metal ion available per unit volume The decrease in  $k_{Th}$  with dilution may be due to high number of adsorption sites available against a small number of lead (II) ions [27]. The high fit of the experimental data to the Thomas model indicated that the external and internal diffusion were not the rate limiting steps [28]. The breakthrough curve analysis from continuous adsorption studies revealed that the higher breakthrough time reached for lower initial concentration, slower flow rate, and higher bed height. The fit of the experimental data to the Thomas Model indicates that lead adsorption onto PBC/RHA/WHB mixture follows the second order reversible reaction kinetics based on the Langmuir kind of adsorption [29]

### 3.6 Comparing the effect of AC/sand and PBC/RHA/WHB adsorbents



**Figure 4:** Comparison of AC/Sand and PBC/RHA/WHB adsorbents.

Comparison of commercial adsorbent and PBC/RHA/WHB mixtures was conducted to confirm the viability of the proposed composite adsorbent. The breakthrough curves for lead (II) adsorption using the two composite adsorbents were constructed from respective column tests and the results presented in Figure 4. The breakthrough time for commercial adsorbent was shorter and the column was exhausted after 500 min. On the other hand, the breakthrough and exhaustion times for PBC/RHA/WHB were 100 and 640 min, respectively. The maximum adsorption capacity for commercial adsorbent column was found to be 378.93 mg/g whereas that of PBC/RHA/WHB was 476.62 mg/g. From these results it is clear that PBC/RHA/WHB was a better adsorbent for scavenging lead (II) ions from industrial effluent than the commercial adsorbent.

### 3.7 Regeneration of the column

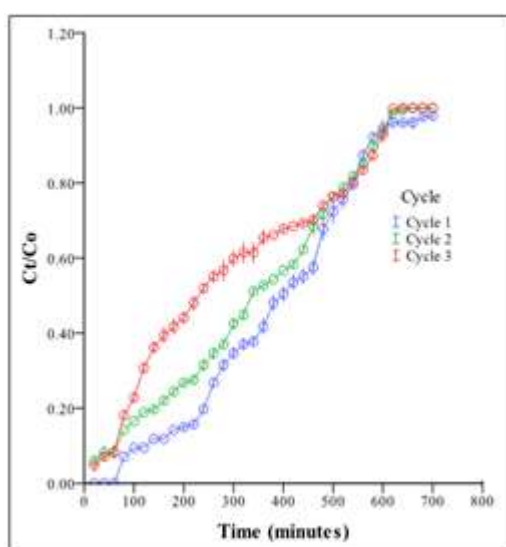


Figure 5: Regeneration of the column by considering desorption of lead (II) ions

It is essential to reuse the cation loaded sorbent for metal removal in industrial applications for economical feasibility of the process. Reusability of any sorbent can be determined by its adsorption performance in consecutive sorption/desorption cycles. PBC/RHA/WHB was tested for 3 cycles after the initial application, using 0.01 M  $\text{HNO}_3$  as an eluting regenerating agent at flow rate of 5 mL/min for 12 h. Thereafter the column was rinsed with distilled water until the leachate pH was between 6.0 and 7.0. The results for these tests are presented in Figure 5. There was little difference in the breakthrough uptake of lead (II) ions by the adsorbent between the three cycles the adsorbent reuse. This indicated that the adsorbent could be applied in several cycles without significant loss in adsorptive capacity. Table 3 shows that percentage regeneration efficiency reduced marginally from 99.25 to 96.0 when lead (II) ions were considered. This was expected because of the loss of adsorbent during the process of regeneration. The marginal reduction in the breakthrough and exhaustion time indicates that the adsorbent could be applied in a wide range of solution conditions without significant degradation as desired for a plausible feasible adsorbent [33].

## 4. Concluding Remarks

The current study has indicated that PBC/RHA/WHB composite adsorbent could be used use for inexpensive heavy metal ion removal. The PBC/RHA/WHB composite was found to be a better adsorbent than commercial adsorbent mixture used in the industry. The efficiency of the fixed-bed system was controlled by feed concentration, flow rates and bed height. The adsorption system could perform better with lower lead (II) ions inlet concentration, lower feed flow rate and higher PBC/RHA/WHB bed height. The high regression values of Thomas model fitting reveal monolayer adsorption of lead (II) ions onto PBC/RHA/WHB.

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