RICE HUSK PACKED BED COLUMN REACTOR TO REMOVE CADMIUM FROM LANDFILL LEACHATE

Reaktor Packed Bed Column Berisi Sekam Padi Untuk Mereduksi Kadmium Dalam Lindi TPA

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ABSTRACT

The landfill leachate can be a major problem due to large variability of high organic, inorganic, heavy metal content and toxicity characteristics from landfill leachate such as cadmium. Thus, this study was aimed to observe the application of rice husk packed bed column to reduce cadmium from landfill leachate. Experiment was conducted in gravity down flow system by pumping landfill leachate into packed bed column. The effect of influent flow rate to adsorption capacity was studied by varying flow rate (5 mL/min and 10 mL/min). The effluent-influent concentration ratio C_e/C_0 (%) as a function of throughput volume (L) was used to represent the breakthrough curve in column systems. Result shows that the flow rate of 5 mL/min was favorable to achieve higher removal rates with the percentage of cadmium was 57 %. At breakthrough time, the cadmium effluent concentration reached on 0.01 mg/l for both of flow rate.

Kata Kunci : Landfill leachate, packed bed column, adsorption, rice husk, cadmium.

ABSTRAK

Lindi yang dihasilkan dari TPA (Tempat Pembuangan Akhir) menimbulkan permasalahan lingkungan karena kandungan pencemarnya meliputi material organik, material anorganik, logam dan material beracun. Salah satu logam berat yang terdapat dalam lindi tersebut adalah kadmium. Penelitian ini bertujuan untuk mereduksi kadmium dalam lindi dengan menggunakan sekam padi yang diinstal dalam packed bed column. Lindi dipompakan dari tangki penampung lindi ke dalam packed bed column dan dialirkan dari atas ke bawah kolom secara gravitasi. Fokus pada penelitian ini adalah pengaruh laju alir influen terhadap kapasitas adsorpsi. Dimana lindi dialirkan dengan laju alir 5 mL/menit dan 10 mL/menit. Kurva breakthrough (titik jenuh) kolom dipresentasikan oleh hubungan antara rasio konsentrasi efluen-influen C_e/C_0 (%) dan jumlah aliran lindi yang diolah dalam kolom. Hasil eksperimen menunjukkan bahwa persentase reduksi tertinggi dicapai pada laju alir 5 mL/menit yaitu 57%. Waktu jenuh kedua laju alir (5 mL/menit dan 10 mL/menit) tercapai saat konsentrasi efluen kadmium 0.01 mg/L.

Keywords: Lindi TPA, packed bed column, adsorpsi, sekam padi, kadmium.

INTRODUCTION

The utilization of landfill for final waste disposal tends to drive some hazard pollutants when landfill leachate is percolating into ground or entering into surface water. It can lead to serious environmental problems, since the leachate contains a large amount of organic matter (both biodegradable and non-biodegradable carbon), ammonia-nitrogen, heavy metals, chlorine organic and inorganic salts. Cadmium is often found in landfill leachate. It is derived from a variety of households and industries waste which some of them are from well-known toxic and carcinogenic agents. They have been recognized as dangerous pollutant contributing to the decrease of environmental quality.

Actually, by applying good controlled management, the amount and strength of leachate produced can be reduced, but still it cannot be vanished totally. Thus, combined treatment of physical, chemical, and biological have been usually used to improve the treatment efficiency of landfill leachates [8]. For some years, searching for effective and efficient technologies for treatment of landfill leachate has been intensified, mainly physic-chemical treatment. Physico-chemical treatment has been found to be suitable not only for the removal of heavy metals from landfill leachate, but also for refining of biologically treated leachate. Before discharging, an additional effluent refining using physico-chemical treatments, such as chemical precipitation, activated carbon adsorption and ion exchange, can be carried out on-site.

Adsorption is one of common methods among physico-chemical treatments for heavy metal removal (Augustine et.al, 2007; Bhattacharya et.al, 2008; Bishnoi et.al, 2004; Feng et.al, 2004; Kiran et.al, 2006; Kumar and Bandyopadhyay, 2006; Mahvi, et.al, 2005; Mohan and Sreelakshmi, 2008; Sahu et.al, 2009; Sreejalekshmi et.al, 2009; Srivastava et.al, 2008; Teixeira and Zezzi 2004; Zulkali et.al, 2006). Today, several researchers perform byproduct from industrial, agricultural and biomass waste as adsorbent to remove heavy metals such as iron and cadmium as well as COD from either aqueous solution or real wastewater. Rice husk, for instance, a by-product of the rice milling industry, was selected as an adsorbent in several wastewater treatments by reason of its local availability, low production cost, insolubility in water, granular structure, high mechanical strength, and chemical stability (Sreejalekshmi et.al, 2009). Previous reports show that rice husk with or without chemical/physical activation can lead to decrease in concentration of Cr (Bishnoi et.al, 2004), Cd (Kumar and Bandyopadhyay, 2006; Mahvi et.al, 2005; Mohan and Sreelakshmi, 2008; Srivastava et.al, 2008; Teixeira and Zezzi, 2004), Pb (Feng et.al, 2004; Mohan and Sreelakshmi, 2008), hydroquinone (Qi et.al, 2004), Cu (Mohan and Sreelakshmi, 2008), Zn (Mohan and Sreelakshmi, 2008), Mn (Mohan and Sreelakshmi, 2008), Hg (Zhou et.al, 2004), Fe (Daifullah et.al, 2004).) and reactive dye (Ponnusami et.al, 2007). In this study reported here on the treatment of landfill leachate using rice husk packed bed column was investigated. The effects of varying flow rate as determinant factors influencing the adsorption process were studied.

RESEARCH METHODOLOGY

Raw rice husk was collected from local rice mill in Kuala Selangor, Malaysia. Adsorbent was prepared by firstly washing the collected rice husk for 2 – 4 times with tap water continued with distilled water to remove all dirt particles and impurities. Then, it was dried at $100^{\circ}C$ in oven for 4 hours to get rid of moisture and impurities until the weight of rice husk become constant. Finally, it was ground with food processor with steel blades (National MK 110) and sieved to homogenous particle size lower than 600 µm. Afterwards, the sieved rice husk was stored in air tight container at room temperature to be used.
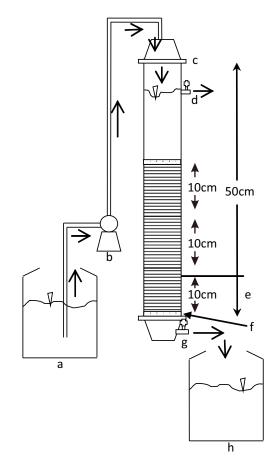
Sample of leachate was obtained from Landfill of Core Competition Company, "Sungai Kembong", Semenyih, Kuala Selangor for several times sampling. The characteristic of fresh leachate sample was analyzed immediately as shown in Table 1. Preservation of leachate samples was performed by keeping it in refrigerator at $2^{\circ}C$ temperature until used in packed bed column reactor. In this report, the analysis of

parameter was focused on pH, temperature, COD, iron and cadmium.

The value of pH was measured by Hanna pH meter while the temperature was checked by thermometer. COD was analyzed using closed reflux method and then measured by spectrophotometer. For iron and cadmium, sample of leachate was homogenized by shaking on plate stirred then filtered using Laboratory Scheleicher & Schuell model filter paper from Germany with 0.45 µm pore size and 47 mm diameter. Afterwards, the sample concentration was read by inductively couple plasma atomic electronic spectrophotometer (ICP-OES) (Perkin Elmer, Model: Optima 3000).

Table 1: Composition of Landfill Leachate in S. Kembong*

Parameter	Unit	Value	Average
pH		7.15 - 7.98	7.74
COD	mg/L	9000 - 15600	11300
Temperature	°C	27 – 28	27.6
Cd	mg/L	0.228 - 105.73	29.4
Fe	mg/L	0.1925 - 14.428	5.622

*random sampling obtained between May 2009 and August 2010

Packed bed column reactor is presented in Figure 1. The packed bed column was constructed of a vertical cylindrical Perspex column with a diameter of 5 cm and a depth of 50 cm. The conical bottom has a divergence angel 15° and a height of 5 cm. Certain amount of rice husk was filled into column as a known bed height of column. It determined the dosage of rice husk. The packed rice husk was supported by two perforated polymer.

Legend

a. Influent wastewater tank
b. Influent feed pump
c. Perforated plate
d. Overflow valve
e. Adsorbent
f. Perforated polymer
g. Effluent wastewater valve
h. Effluent wastewater tank

Figure 1. Schematic diagram of experimental setup for column studies

The perforated plastic plate was put on the top of the column to distribute landfill leachate onto the surface of adsorbent and to maintain a constant flow rate. It was also put on the bottom of column to prevent the adsorbent from leaching and clogging into the drainage area. Liquid influent was operated gravity down-flow by BT300-2J peristaltic pumps (Baoding Longer Precision Pump CO., Ltd). Reactor was also equipped with 1 overflow valve to avoid the over limit of sample in case the clogging and saturation occurs in reactor and 1 outlet valve to collect sample.

Some procedures was done to characterize the used rice husk. Composition of mineral and morphological features were identified by X-ray diffraction (XRD), a Siemens D-5000 system with Cu Kα radiation over 2θ from 5° to 80° at a rate of 0.05°/second with range of wavelength 1.5406 Å and a step time of 2 seconds. Morphological characteristics were examined by Scanning electron microscopy (SEM) (A Philip XL30 scanning electron microscope in secondary electron mode, equipped with energy dispersive X-ray, JEOL6335F-SEM, Japan). The presence of functional groups in adsorbent was identified by Fourier Transform Infrared spectrometer (Thermo nicolet, Model Magna 760). It was conducted at room temperature, using Pellet (pressed-disk) technique and chosen spectral range of 4000 to 400 cm^{-1}. BET surface area, average pore diameter and total pore volume of the supports as well as the catalysts were determined by nitrogen adsorption–desorption isotherm at 77.35K using the BET method in a Micromeritics Accusorb 2000 apparatus. Before measurement, each sample was degassed at 473K for 4 h.

Experiment was conducted in gravity down flow system. Landfill leachate was introduced into column packed with rice husk. Refilling of influent tank was done manually to be pumped into packed bed column by peristaltic pump. All the experiments were carried out at room temperature (range of 25°C – 27°C). The effluent samples were collected in regular time then filtered with membrane filter (Laboratory Scheleicher & Schuell model filter paper from Germany with 0.45 and μm and 47 mm diameter) and stored in dark cool refrigerator for analysis of cadmium. The effect of liquid flow rate to adsorption capacity was studied by adjusting it to varying of flow rate in 5 mL/min and 10 mL/min.

In the first 24 hours, samples were collected more often than in the following days to evaluate changes of cadmium concentration trend. Influent and effluent of cadmium concentrations were analyzed using ICP-OES. The effluent-influent concentration ratio C_e/C_0 (%) as a function of throughput volume (L) was used to represent the breakthrough curve in column systems. The volumetric throughput to reach breakthrough and shape of the breakthrough curve are essential in determining the operation and the dynamic response of an adsorption column as well as evaluating the adsorption capacity of the column.

The terms of breakthrough was defined as a curve ilustrating adsorbed metal concentration which was calculated from the result of differences value between the influent concentration of column. In other words, it is normalized as the ratio of effluent metal concentration to inlet metal concentration (C_e/C_o) and computed as a function of time or volume of effluent for a given bed depth. Effluent volume (V_e) can be calculated from Eq. (1):

$$Ve = Qt_{tot} \qquad \text{Eq. (1)}$$

Here t_{tot} and Q are the total flow time (min) and volumetric flow rate (mL/min), respectively. The area under the breakthrough curve (A) obtained by integrating the adsorbed concentration (C_{ad}; mg/L) versus t (min) plot can be used to find the total adsorbed metal quantity (maximum column capacity). Total adsorbed metal quantity (q_{tot}; mg) in the column for a given feed concentration and flow rate (Q) is calculated from Eq. (2):

$$Q_{tot} = \frac{QA}{1000} = \frac{Q}{1000} \int_{to}^{t8} C_{ad}\, dt \qquad \text{Eq. (2)}$$

Total amount of metal ion sent to column (m_{tot}) is calculated from Eq. (3):

$$M_{tot} = \frac{C_o Q t_{tot}}{1000} \qquad \text{Eq. (3)}$$

Total removal is calculated from Eq. (4):

$$Total\ Removal\ (\%) = \frac{Q_{tot}}{M_{tot}} * 100 \qquad Eq.\ (4)$$

Equilibrium metal uptake (q_{eq}) in the column (or maximum capacity of the column) in the column is defined by Eq. (5) as the total amount of metal adsorbed (q_{tot}) per gram of adsorbent (m) at the end of total flow time (Gulensoy, 1984):

$$q_{eq} = \frac{q_{tot}}{m} \qquad Eq.\ (5)$$

RESULTS AND DISCUSSIONS
Characterization of rice husk

General physical characteristics of rice husk are revealed in Table 2. The value of pH was neutral (6.670) and bulk density was 0.477 kg/m³. Cadmium was better reduced in pH lower than 10 (acid to neutral). The value of micropoer area and total volume pore of rice husk was high enough to have high dispersive force acting on adsorbate molecule to provide space for storing more adsorbate molecules of cadmium. It illustrates that rice husk could adsorb cadmium from liquid well (Duong, 1998).

The rice husk contains high silica noted by by a diffuse maxima at X-ray diffraction graph appearance which is approximately at $2\theta = 15°$ and $2\theta = 23°$. Silica existing in rice husk have significant function to keep adsorption process run well as reported by Lin and Chang, 2000 and Mohan and Sreelakshmi, 2008.

Table 2: Physical characteristics of rice husk

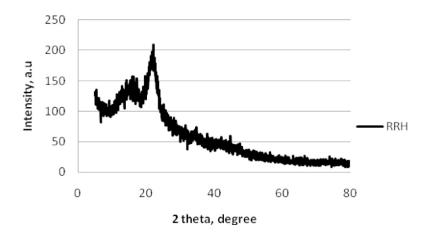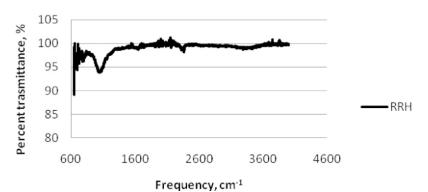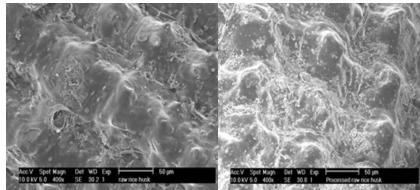| Parameter	Unit	Rice husk
Bulk density	kg/m³	0.447
Particle size	μm	≤ 600
moisture content	%	8.955
BET surface area	m²/g	4.093
Langmuir surface area	m²/g	139
Micropore area	m²/g	2.175
Average pore diameter	μm	71.8
Total pore volume	cm³/g	0.007
Micropore volume	cm³/g	0.001
Average pH	-	6.67

Fig.2. XRD – analysis for rice husk
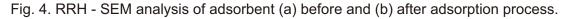
Fig.3. FTIR – analysis for virgin rice husk

According to the obtained results of FTIR, curve rice husk (Figure 3) shows identical trends. The peaks observed at about 651 – 740 cm^{-1} could be assigned to the phenyl groups C-H. The peak around 1630 cm^{-1} corresponds to C=O stretch. The alkene was observed at the peaks of 1920 and 2030 cm^{-1}. Other broad peaks between 3020 and 3290 cm^{-1} in rice husk were also observed that were attributed to – OH bond. The presence of Si–O, Si–H, Si–C, –CH and –OH bond groups on the rice husk surface is responsible for adsorption (Srivastava et.al ,2008).

Moreover, morphology of the rice husk before and after adsorption process has been verified with SEM in certain magnificent as shown in Figure 4. The figure 4 (a) configures aligned bumps composed mainly of silica onto the cellulose. The surface of adsorbent after adsorption process was fulfilled with the uptake iron and cadmium reflected with the particle agglomeration onto adsorbent surface. It is confirmed by the results obtained in Table 2, Figure 2 and Figure 3 which proven that rice husk has higher competence in adsorption capacity.

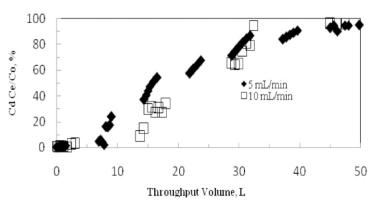Fig. 4. RRH - SEM analysis of adsorbent (a) before and (b) after adsorption process.

Fig.5. The experimental breakthrough curves for adsorption of cadmium from landfill leachate onto rice husk packed bed column at as a function of throughput volume in different flow rate.

14

Table 4: The total adsorbed quantity (q_{tot}), equilibrium uptake (q_{eq}), total amount of metal ion through column (M_{tot}) and total removal percentage for iron and cadmium adsorption from landfill leachate at RRH packed bed column

Q (mL/min)	t_{tot} (min)	Co (mg/L)	SOI	q_{total} (mg)	q_{eq} (mg/g)	m_{tot} (mg)	Removal (%)
5	7560	0.8	4300.7	172.5	0.08	303.2	57
10	5760	1.6	3001.4	47.3	0.21	907.8	52

Packed bed column study

Figure 5 illustrates cadmium breakthrough curves in different flow rate, respectively. It indicates cadmium removal reached on 0.01 mg/L at flow rate 5 mL/min. This concentration of cadmium was higher than that of flow rate 10 mL/min. The raw landfill leachate was composed of cadmium concentrations of 0.802 and 1.576 mg/L. Heavy metal removal efficiencies of columns as shown in Table 4 were computed based on cadmium concentrations entering the column. The results show the flow rate effected on concentration reduction. Higher reduction was achieved on lower flow rate (5 mg/L). Using equation 4, the respective calculated cadmium removal efficiency obtaining were about 57% and 52%.

Besides, the higher flow rate also increases medium exhaustion. The column within flow rate of 10 mL/min, for cadmium was exhausted or saturated (Ce/Co > 95%) after 32.4 L throughput volume, earlier than those of column in flow rate of 5 mL/min. The clogging of column was detected in column system using flow rate of 10 mL/min after 58.8 L throughput volume pumped through the column or after three days of column operation. For flow rate of 5 mL/min, the clogging was not still reached after six days operation of column. Li, (2008) also reported that the clogging in his column operation reaching after 7 days operation with low flow rate. The existence of biofilm which illustrate biological activity arround adsorbent surface in column assumed did not impact on adsorption capacity (Li, 2008).

Acknowledgement

REFERENCES

Augustine, A.A., Orike, B.D., and Edidiong, A.D. 2007. Adsorption kinetics and modeling of cu(II) ion sorption from aqueous solution by mercaptoacetic acid modified cassava (*Manihot Sculenta* Cranz). *Wastes, EJEAFChe* 6 (4), 2221-2234.

Bhattacharya, A.K., Naiya, T.K., Mandal, S.N., and Das, S.K. 2008. Adsorption, kinetics and equilibrium studies on removal of Cr(VI) from aqueous solutions using different low-cost adsorbents. *Chem. Eng. J.* 137, 529–541.

Bishnoi, N. R., Bajaj, M., Sharma, N., & Gupta, S. 2004. Adsorption of Cr(VI) on activated rice husk carbon and activated alumina. *Bioresource Technology, 91*(3), 305-307.

Daifullah, A. A. M., Awwad, N. S., & El-Reefy, S. A. 2004. Purification of wet phosphoric acid from ferric ions using modified rice husk. *Chemical Engineering and Processing, 43*, 193-201.

Duong, D. 1998. *Adsorption analysis: equilibria and kinetics*. London: Imperial College Press.

Feng, Q., Lin, Q., Gong, F., Shuici, S., & Shoya, M. 2004. Adsorption of lead and mercury by rice husk ash. *Journal of Colloid and Interface Science, 278*, 1-8.

Kargı, F., & Pamukoglu, M. Y. 2004. Adsorbent supplemented biological treatment of pre-treated landfill leachate by fed-batch operation. *Bioresource Technology 94*, 285-291.

Kiran, B., Kaushik, A., and Kaushik, C.P. 2006. Response surface methodological approach for optimizing removal of Cr (VI) from aqueous solution using immobilized cyanobacterium. *Chem. Eng. J.* 126, 147–153.

Kumar, U and Bandyopadhyay, M. 2006. Fixed bed column study for Cd (II) removal from wastewater using treated rice husk. *J. Haz. Waste Mat*. B129, 253 – 259.

Li, C. 2008. Aqueous solutions and synthetic landfill leachate using low-cost natural adsorbents. Thesis of Master of Science (Engineering). Canada: Queen's University Kingston.

Lin, S.H and Chang, C.C. 2000. Treatment of landfill leachate by combined electro-fenton oxidation and sequencing batch reactor method. *J. Water Res*. 34 4243–4249.

Mahvi, A.H., Alavi, N., and Maleki, A. 2005. Application of rice husk and its ash in Cadmium removal from aqueous solution. *Pak. J. Bio. Sci*. 8 (5), 721–725.

Ministry of Natural Resources and Environment. 1974. Akta kualiti alam sekitar (*Environmental Quality Act*). Kualu Lumpur, Malaysia.

Mohan, S and Sreelakshmi, G. 2008. Fixed bed column study for heavy metals removal using Phosphate treated rice husk. *J. Haz. Waste Mat.* 153, 75–82.

Ponnusami, V., Krithika, V., Madhuram, R., & Srivastava, S. N. 2007. Biosorption of reactive dye using acidtreated rice husk: Factorial design analysis. *Journal Hazardous Materials, 142*, 397–403.

Qi, J., Li, Z., Guo Y and Xu, H. (2004). Adsorption of Phenolic compounds on micro and mesoporous rice husk-based active carbons. *Mat. Che. Phys. J.* 87, 96–101.

Robinson, A.H. (2004). Landfill leachate treatment: An article based on a paper with the same title, which was presented at the 5th international Conference on Membrane Bioreactors (MBR5); 9 pp.

Sahu, J.N., Agarwal, S., Meikap, B.C., Biswas, M.N. 2009. Performance of a modified multi stage bubble column reactor for lead (II) and biological oxygen demand removal from wastewater using activated rice husk. *Haz. Waste Mat*.161, 317 – 324.

Sreejalekshmi, G., Krishnan, K.A., and Anirudhan, T.S. (2009). Adsorption of Pb(II) and Pb(II)-citric acid on sawdust activated carbon: Kinetic and equilibrium isotherm studies. *J. Haz. Mat.* 161, 1506–1513.

Srivastava, V. C., Mall, I. D., & Mishra, I. M. 2008. Optimization of parameters for adsorption of metal ions onto rice husk ash using Taguchi's experimental design methodology. *Chemical Engineering Journal 140*, 136-144.

Teixeira Tarlye, C. R., & Zezzi Arruda, M. A. 2004. Biosorption of heavy metals using rice milling by products. Characterization and application for removal of metals from aqueous effluents. *Chemosphere, 54*, 987 - 995.

Tinamaz, E., and Ongen, A. 2006. Risks posed by unsanitary landfill leachate to groundwater quality. In: Tellam, J.H. et al. (Eds.), *Nato Science Series Vol. 74: Urban Groundwater Management and Sustainability*. Netherland: Springer Publisher (pp. 259–268).

Zhou, D., Zhang, L., Zhou, J., & Guo, S. 2004. Development of a fixed-bed column with cellulose/chitin beads to remove heavy-metal ions. *Journal of Applied Polymer Science, 94*, 684 - 691.

Zulkali, M. M. D., Ahmad, A. L., & Norulakmal, N. H. 2006. Oryza sativa L. husk as heavy metal adsorbent: Optimization with lead as model solution. *Bioresource Technology 97*, 21-25.