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Modelling of Cadmium (II) Uptake from Aqueous Solutions using Treated Rice Husk: Fixed – Bed Studies

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Rice husk is an agricultural waste material obtained mainly from rice mills. Treated rice husk was evaluated as a sorbent for cadmium (II) ions removal from solutions by utilising fixed-bed adsorption mode. In this study, the influence of flow rate (3 and 9 mL/min), adsorbent heights of (0.9, 1.8 and 2.8 cm) and influent cadmium ions concentration of (5 and 20 mg/L) on the sorption capacity of the adsorbent in a fixed-bed column were explored. The highest uptake of 87 % was obtained using 20 mg/L initial Cd (II) solution was achieved at high flow rate of 9 mL/min and a bed height of 2.8 cm. The experimental results obtained from the column adsorption studies were correlated with the Thomas, Yoon–Nelson and Adams–Bohart models. The modelling results for the adsorption indicated that the Adams–Bohart model fitted well over the other models.

1. Introduction

Excessive discharge of industrial and municipal waste laden with heavy metals causes environmental pollution which is a serious problem that needs immediate attention (Khairy et al., 2014). Heavy metals such as cadmium were regarded as environmental pollutants that were listed as category–1 carcinogen and as Group–B1 carcinogen by International Agency for Research on Cancer and US Environmental Protection Agency (EPA) due to their irreparable effects on the environment. Cadmium being a heavy metal has attracted serious attention because of its hazardous nature. It is frequently found in wastewater effluents from chemical, metallurgical, paint, coating, mining, nuclear and other related industries. Being a transition metal, cadmium is a soft whitish silver or bluish–white coloured metal that has identical chemistry with mercury and zinc. Averagely, there is about 0.1 – 0.5 mg/L cadmium concentration in the earth crust and its total world production is 22,300 t as at 2010 based on British Geological survey (Hetherington et al., 2008). The maximum concentration limit for cadmium that can be present in wastewater and be considered as risk free to living organisms was established by different regulatory agencies around the world. The permitted limit set by EPA is 0.5 mg/L for wastewater, while WHO guide lines sets 0.003 mg/L as drinking water limit (Barragán et al., 2016).

Cadmium is extensively utilised in plasticisers, pigments, batteries and solar panels. Human exposure to large volume of cadmium lead to bone demineralisation, cardiovascular disease, renal dysfunction, arthritis, osteoporosis, osteomalacia, anaemia, learning disorder, cancer, itai–itai disease, hypertension, pneumonitis,

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lung insufficiency and weight loss (Nessa et al., 2016). A number of techniques were adopted for cadmium removal from solutions which include precipitation, evaporation, filtration, membrane separation, ion exchange, coagulation/flocculation, complexation, cementation, electrochemical operation and adsorption (Lavecchia et al., 2016). Adsorption process has been adopted for cadmium removal because it is cost–effective, environmental friendly, sustainable and the spent adsorbent can easily be regenerated (Garba et al., 2016).

The aim of this study is to explore the removal of cadmium ions using cheap, sustainable and efficient agricultural waste materials that undergoes simple treatment process which requires little amount of chemicals in order to reduce chemical pollution and at same time keep the cost of the adsorbent as cheap as possible.

2. Experimental

2.1 Materials and methods

Sodium hydroxide pellets, hydrochloric acid and cadmium stock solution (1,000 mg/L) were all supplied by Merck chemicals Malaysia. Rice husk was purchased from a local mill in Parit Raja, Johor, Malaysia. The fresh rice husk designated as (RH–Raw) was washed dried at 60 °C for 24 h, milled and sieved using sieve and shakers. The RH–Raw fractions that passed through 250 – 500 μm were retained as starting material. The retained sample was then soaked in 2 % NaOH solution for 4 h. the excess NaOH was washed off using deionised water, then oven dried at 60 °C over a period of 24 h. The treated rice husk was designated as RH–NaOH.

2.2 Wastewater preparation

The synthetic cadmium ion solution was prepared by dilution of appropriate amount of the cadmium stock solution (1,000 mg/L) using deionised water to obtain concentrations of 5 mg/L and 20 mg/L.

2.3 Fixed–bed adsorption studies

The fixed–bed adsorption studies were performed at pH 6.5 and at room temperature using a glass column (1.2 cm internal diameter x 19.5 cm height). The synthetic cadmium ions solution was introduced into the column from the top using a peristaltic pump. Figure 1 shows the experimental set-up of the cadmium adsorption. Three adsorption parameters were investigated, initial cadmium concentration (5 and 20 mg/L), cadmium solution flow rate (3 and 9 mL/min) and adsorbent height (0.9, 1.8, and 2.8 cm). Cadmium ions concentration adsorbed on the sample were determined using atomic adsorption spectrophotometer (PerkinElmer HGA 900 model) by collecting effluents from the column at intervals.

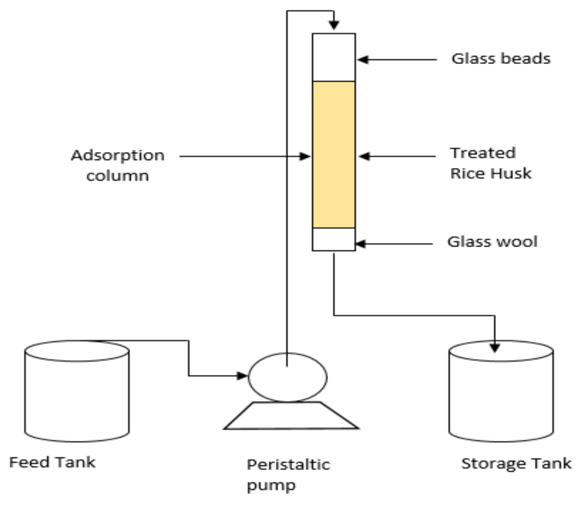


Figure 1: The cadmium adsorption set-up

2.1 Characterisation of the sample

The treated rice husk was characterised using X-ray powder diffraction (XRD), scanning electron microscopy attached with Energy dispersive spectroscopy (SEM–EDS) and Fourier transform infrared spectroscopy (FTIR)

3. Results and discussion

3.1 Fourier transform infrared spectroscopy (FTIR)

The FTIR analysis is an important tool for identification of surface functionalities which are instrumental in adsorption of the heavy metal ions. The FTIR results (Figure 2) of the raw rice husk indicated bands at 3,370, 2,920, 1,423 and 1,048 cm^{-1} which corresponds to peaks for –OH stretching vibration with range between 3,100 – 3,500 cm^{-1}, $–CH_2$ asymmetric stretching vibration, –COO vibration or the aromatic ring absorption for C=C–C arising from lignin since it contains aromatic rings and stretching vibrations related to C–C–O from carbohydrates or Si–O–Si stretching vibration (Zhang et al., 2013). After treatment with sodium hydroxide, the broad band at 1,048 shift to 1,034 and new band at 861 cm^{-1} disappear due to removal of lignin from the sample.

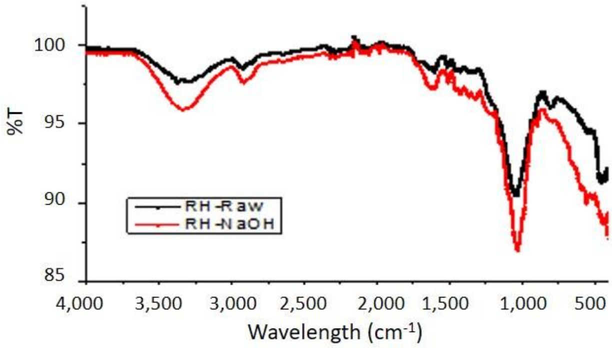
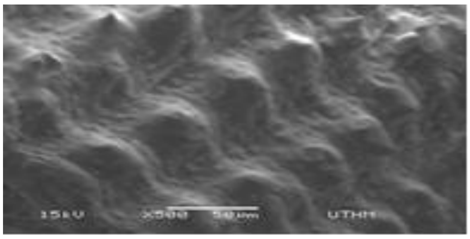


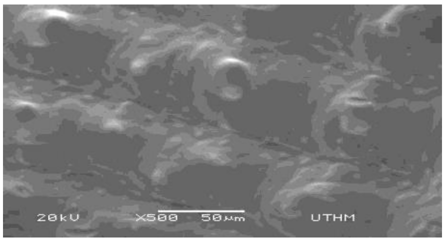
Figure 2: FTIR spectra of the raw and NaOH treated rice husk

3.2 Scanning electron microscopy – Energy dispersive X-ray spectroscopy (SEM- EDS)

The SEM image of the raw rice husk as presented in Figure 3 indicated that the raw rice husk has no developed pores and the surface was highly rough. The NaOH treated rice husk surface was converted to a more ordered surface with heterogeneous pores due to partial removal of hemicellulose and reduction in crystallinity of the cellulose in the material (Ashrafi et al., 2016). From Figure 4, the EDS spectra of the untreated rice husk surface contain only elements C, O and Si. After treatment of the rice husk with NaOH solution, Na was fixed on their surface and the peak intensity of Si increases (Wang et al., 2010).

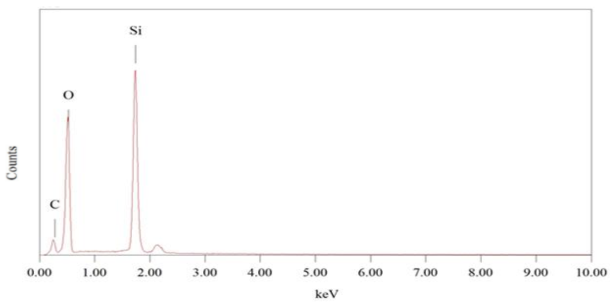


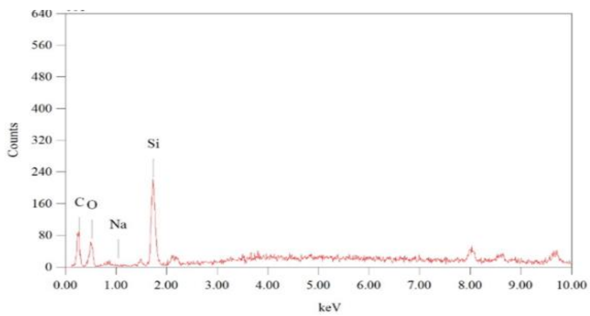
(a)



(b)

Figure 3: SEM micrograph of (a) raw, (b) treated rice husk





(a) *(b)*

Figure 4: EDS results of (a) raw and (b) treated rice husk

3.3 Effects of initial cadmium concentration

The influence of initial cadmium concentration on the breakthrough curves at constant adsorbent height of 2.8 cm and flow rate of 3 mL/min was presented in Figure 5. The results showed that the breakthrough time decreased from 780 to 660 min when the cadmium concentration was increased from 5 to 20 mg/L. The result means that, the breakthrough curve and time of saturation decreases as the concentration of the influent cadmium solution is increased. The result revealed that, high initial cadmium concentration saturates the rice husk more rapidly and the breakthrough was reached before all the pores were filled by the cadmium ions. High cadmium ions concentration initiates high driving force for the adsorption process and this explains why higher adsorption capacities were obtained at high cadmium ion concentrations (Ji et al., 2013).

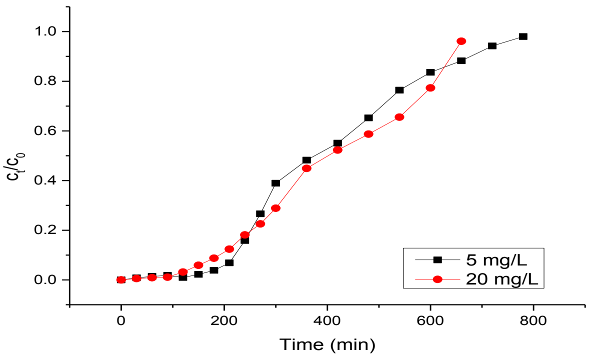


Figure 5: Effect of cadmium concentration at fixed bed height of 2.8 cm and flow rate of 3 mL/min

3.4 Effects of cadmium solution flow rate

The effect of cadmium solution flow rate was determined by running the column at two flow rates of 3 mL/min and 9 mL/min at fixed initial cadmium concentration of 5 mg/L and bed height of 2.8 cm. From Figure 6, it can be noted that the exhaustion time decreases from 780 to 180 min as flow rate increases from 3 to 9 mL/min. This could be attributed to an increase in the zone speed as the cadmium solution flow rate increases which results to reduction in the time required to achieve both breakthrough and exhaustion times. Decrease in flow rates provides appropriate residence time for the adsorbent – adsorbate interactions which results to obtaining a longer exhaustion time. These results were in agreement with other reported studies (Ahmad and Haydar, 2016).

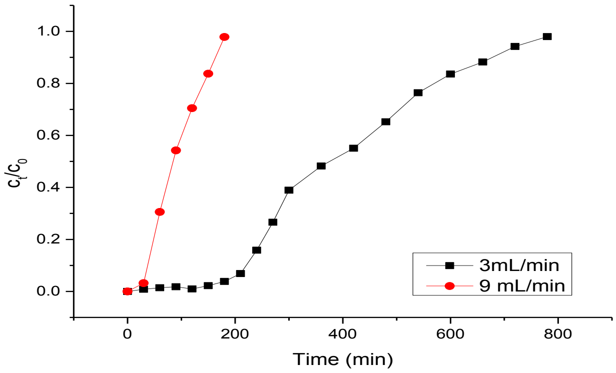


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Figure 6: Effect of cadmium solution flow rate at constant bed height of 2.8 cm and 5 mg/L concentration

3.5 Effects of bed depth

From Figure 7, that the sharp breakthrough curve and lower breakthrough times were obtained at lower bed heights. This is because, as the bed height reduce, there will be less adsorption sites for the cadmium uptake. As the bed height increases, more sites were available for cadmium adsorption. The breakthrough curve becomes steeper and the breakthrough time becomes bigger (Mondal, 2009). The results agreed well with other studies reported (Li and Champagne, 2009).

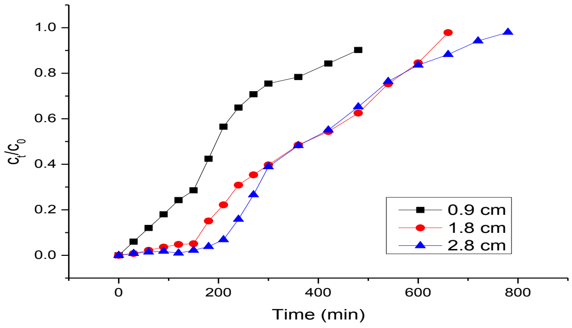

Figure 7: Effect of bed heights at 5 mg/L concentration and flow rate of 3 mL/min

3.6 Breakthrough curve modelling

Table 1: The Adams–Bohart, Thomas and Yoon–Nelson model constants for cadmium adsorption by treated rice husk packed column.

Conditions				Adams–Bohart			Thomas			Yoon – Nelson		
pH	Z	Q	Ci	K_{AB}	N_0	R^2	K_{Th}	q_o	R^2	K_{YN}	τ	R^2
6.0	3	0.9	5	0.0011	-746	0.7923	-0.0107	-757	0.9417	0.011	-0.0044	0.9417
6.0	9	0.9	5	0.0007	-66	0.7560	-0.0218	249	0.7609	0.022	0.04	0.7609
6.0	3	1.8	5	0.00134	-102	0.8	-0.011	-638	0.9364	0.011	-0.0026	0.9364
6.0	3	2.8	5	0.0014	-118	0.8132	-0.0113	-466	0.9599	0.011	-0.0023	0.9599
6.0	3	0.9	20	0.0002	-241	0.9842	-0.0112	-344	0.8904	0.011	-0.0097	0.8904
6.0	9	0.9	20	0.0001	-540	0.9823	-0.0121	219	0.8663	0.012	0.0458	0.8663
RMSE (%)				2.60			3.70			3.67		
SSE (%)				2.60			3.70			3.67		
R^2				0.9935			0.9914			0.9914		

3.7 Adams – Bohart model

From Table 1, the Adams–Bohart rate constant (K_{AB}) decreases with an increase in both flow rate (3 to 9 mL/min) and initial cadmium ions concentration (5 to 20 mg/L). The rate constant increases as bed height increases (from 0.9 to 2.8 cm). The column saturation concentration (N_0) values increases with increase in flow rate of 3 to 9 mL/min, but it decreases with both increase in cadmium ion concentrations from 5 to 20 mg/L and adsorbent bed height of 0.9 to 2.8 cm. Adams – Bohart model gives the best fit because, the model has the highest coefficient of determination of 0.9935, but lower RMSE and SSE values. The results agree with those reported by Li et al. (2016) on removal of manganese from aqueous solution using rice husk ash in a fixed column.

3.8 Thomas model

From the results presented in Table 1, the Thomas rate (K_{Th}) constant decreases with increase in flow rate (3 to 9 mL/min), but increases with increase in cadmium ions concentration from 5 to 20 mg/L. A mixed trend was observed when the adsorbent bed height increases from 0.9 to 1.8 cm in which the rate constant at first increases. The equilibrium cadmium sorption capacity constant increases with increase in both flow rate from 3 to 9 mL/min and initial cadmium ions concentration from 5 to 20 mg/L. The Thomas model has high number of experiments with coefficient of determination greater than 0.9, but it did not fit the experimental results. This is because, the model has lower R^2 value compared to the Adams–Bohart model and as well it has larger values for both RMSE and SSE. The results was in agreement with those reported by Sarma et al. (2015) on removal of Copper and Lead from aqueous solution using cheap agricultural wastes.

3.9 Yoon – Nelson model

The model rate constant (K_{YN}) appreciates with an increase in the flow rate, but decreases when the cadmium concentration increases. The constant decreases with increase in bed height and the time needed for 50 % breakthrough (τ) increases with increase in solution flow rate. The 50 % breakthrough time decreases with both increase in bed height and increase in cadmium ions concentration. The model has the highest coefficient of determination, but does not give good fit because of higher RMSE and SSE values compared to Adams–Bohart model. The results agree with those reported by Farooq et al. (2013) on biosorption of Lead and Chromium ions on a wheat straw.

4. Conclusions

The study explores the ability of a treated rice husk as low cost adsorbent for the uptake of cadmium ions from solution in fixed-bed mode. The cadmium uptake was affected by column parameters such as initial cadmium ions concentration, adsorbent bed–height and solution flow rate. The Adams–Bohart model fitted the experimental data well over the other models employed. This indicates the potentials of using rice husk as cheap adsorbent that requires small amount of treatment, but gives a reasonable removal capacity for cadmium.

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Reference

Ahmad M.F., Haydar S., 2016, Evaluation of a newly developed biosorbent using packed bed column for possible application in the treatment of industrial effluents for removal of cadmium ions, Journal of the Taiwan Institute of Chemical Engineers 62, 122-131.

Ashrafi S., Kamani H., Soheil Arezomand H., Yousefi N., Mahvi A., 2016, Optimization and modelling of process variables for adsorption of basic blue 41 on NaoH-modified rice husk using response surface methodology, Desalination and Water Treatment 57 (30), 14051-14059.

Barragán P.P., Macedo M.M.G., Olguín M.T., 2016, Cadmium sorption by sodium and Thiourea-modified zeolite-rich Tuffs, Journal of Environmental Sciences, DOI: 10.1016/j.jes.2016.03.015

Farooq U., Athar M., Khan M.A., Kozinski J.A., 2013, Biosorption of Pb (II) and Cr (III) from aqueous solutions: Breakthrough curves and modelling studies, Environmental Monitoring and Assessment 185, 845-854.

Garba A., Nasri N. S., Basri H., Ismail R., Abdul Majid Z., Hamza U., Mohammed J., 2016, Adsorptive removal of phenol from aqueous solution on a modified palm shell-based carbon: Fixed-bed adsorption studies, Desalination and Water Treatment 57 (60), 29488-29499.

Hetherington L., Brown T., Benham A., Bide T., Lusty P., Hards V., Hannis S., Idoine N., 2008, World mineral production 2002-2006, British Geological Survey, Nottingham, United Kingdom

Ji F., Li C., Xu J., Liu P., 2013, Dynamic adsorption of Cu (II) from aqueous solution by zeolite/cellulose acetate blend fiber In Fixed-bed, Colloids Surfaces A: Physicochemical and Engineering Aspects 434, 88-94.

Khairy M., El-Safty S.A., Shenashen M.A., 2014, Environmental remediation and monitoring of cadmium, TrAC Trends in Analytical Chemistry 62, 56-68.

Lavecchia R., Medici F., Patterer M.S., Zuorro A., 2016, Lead removal from water by adsorption on spent coffee grounds, Chemical Engineering Transactions 47, 295-300.

Li C., Champagne P., 2009, Fixed-bed Column study for the removal of cadmium (II) and nickel (II) ions from aqueous solutions using peat and mollusk shells, Journal of hazardous materials 171, 872-878.

Li N., Zhao J., Jiang Z., Cao B., Lu Y., Shan D., Zhang Y., 2016, Continuous manganese (II) ions removal from aqueous solutions using rice husk ash-packed column reactor, Desalination and Water Treatment 57 (46), 21916-21924

Mondal M., 2009, Removal of Pb (II) ions from aqueous solution using activated tea waste: Adsorption on a Fixed-bed column, Journal of Environmental Management 90, 3266-3271.

Nessa F., Khan S.A., Abu Shawish K.Y.I., 2016, Lead, cadmium and nickel contents of some medicinal agents, Indian Journal of Pharmaceutical Sciences 78, 111-119.

Sarma P., Kumar R., Pakshirajan K., 2015, Batch and continuous removal of copper and lead from aqueous solution using cheaply available agricultural waste materials, International Journal of Environment Research 9 (2), 635-648.

Wang X.S., Chen L.F., Li F.Y., Chen K.L., Wan W.Y., Tang Y.J., 2010, Removal of Cr (VI) with wheat-residue derived black carbon: Reaction mechanism and adsorption performance, Journal of Hazardous Materials 175, 816-822.

Zhang Y., Zheng R., Zhao J., Zhang Y., Wong P.-K., Ma F., 2013, Biosorption of zinc from aqueous solution using chemically treated rice husk, BioMed Research International 2013, DOI: 10.1155/2013/365163