



Adsorption of Cd²⁺ from mono-metal solution by pine biochar: Equilibrium and kinetic studies

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Manuscript received online 20 December 2019, revised and accepted 28 December 2019

The present study examines the removal of Cd²⁺ from mono-metal aqueous solution using pine-fruit residue (PFR) biochar adsorbent. The influence of varying pH, Cd²⁺ concentration and contact time at 303 K was examined for adsorptive removal of Cd²⁺ in batch mode. The equilibrium data were analyzed by modeling of Freundlich and Langmuir isotherm using both linear and non-linear regression methods. Langmuir model represented the best fit to the Cd²⁺ adsorption on biochar and the isotherm parameters were better predicted by non-linear regression. The kinetic data for Cd²⁺ adsorption followed pseudo-second order model.

Keywords: Pine-fruit residue, adsorption, cadmium, isotherm, kinetics.

Introduction

Industrial wastewaters are often contaminated with heavy metals and are discharged into the aquatic streams without adequate treatment. This causes hazard to the environment and public health because heavy metals are non-biodegradable and accumulate in the food chain¹. Heavy metal cadmium is mostly released into the wastewater through industrial operations such as metallurgy, batteries, pigments and alloy industries². Cadmium poisoning in human causes reproductive damage, hypertension, and decalcification of bones³. Therefore, stringent regulatory methods are required for removal of cadmium from wastewater. Various techniques such as filtration, chemical precipitation, coagulation/flocculation, ion exchange and membrane separation are conventionally available for wastewater treatment⁴. Most of these techniques are expensive, non-selective and inefficient to meet the quality standards and therefore, not feasible especially in developing countries.

A comprehensive study on treatment of effluents bearing heavy metals exhibited adsorption process to be economically viable and highly competitive to the conventional methods⁵. The adsorption efficiency can be optimized by devel-

oping the inexpensive carbon adsorbent selective to the contaminant heavy metal. A list of carbon adsorbents were derived from low-cost biomass such as coconut coirpith⁶, cashew nut shell⁷, sunflower waste⁸, rape straw⁹, torrefied loblolly pine¹⁰, grape stalks¹¹, peanut shell¹², pine tree residue¹³ and used successfully for cadmium removal from wastewater. In this work, an attempt was made to transform the inexpensive fruit processing by-product PFR into the adsorbent biochar and was tested for Cd²⁺ adsorption efficiency. Several process variables such as pH of aqueous phase, contact time and initial Cd²⁺ concentration were studied in batch operation.

Experimental

Preparation and characterization of biochar:

Industrial PFR sample containing 10.05% (w/w) moisture was received from Pineapple India, Dimapur. Dried PFR was physically activated at controlled parameters in a muffle furnace. A sealed reactor (L, 120 mm×Ø, 80 mm) was filled with a known mass of PFR and thermally decomposed at optimum activation temperature of 500°C for the hold time of 2 h under N₂ purge. Upon activation, the charred mass ob-

tained was washed with 0.1 M HCl to remove any residual ash followed by distilled water to neutral pH. Recovered char was dried, crushed to size less than 0.425 mm and named "PFR biochar".

Standard ASTM methods were used for proximate analysis of biochar. The method involving pH adjustment of KNO₃ solutions was used to estimate the Point of zero charge (pHpzc) on biochar surface¹⁴. Biochar was characterized by physical N₂ adsorption-desorption at -196°C using a surface area analyzer NOVA-1000 (Quantachrome, USA). Specific surface area (S_{BET}) was derived using BET equation, while micropore volume (V_{mic}) was obtained by applying *t*-plot at *p/p*₀ = 0.99. Surface morphology was observed by FE-SEM Hitachi S4800.

Batch adsorption studies:

A known amount of biochar (10.0 g L⁻¹) was added to 25 ml of 20 mg L⁻¹ Cd²⁺ solution in a 100 ml of conical flask. Solutions of 0.1 M HCl and 0.1 M NaOH were added to adjust the pH (2.0–10.0) of Cd²⁺ mono-metal aqueous solution. Flask content was shaken in orbital motion for 240 min to attain equilibrium. The solution was filtered with 0.2 μm syringe filter and residual Cd²⁺ concentration in the filtrate was estimated by atomic absorption spectrometer (S-series Thermo Fisher Scientific Inc., India).

Adsorption tests were conducted for initial Cd²⁺ concentrations (5–300 mg L⁻¹) with 10.0 g L⁻¹ biochar doses at optimized pH and 303 K to give equilibrium isotherm. Experiments were performed in duplicate under identical conditions. In kinetic study, 10.0 g L⁻¹ biochar was contacted with 200 ml of Cd²⁺ solutions of different concentrations from 25 to 200 mg L⁻¹. At specified contact time (5–240 min), the samples (10 ml) were drawn for Cd²⁺ analysis. Cd²⁺ sorption capacity (q_t, mg g⁻¹) of biochar was calculated as follows:

$$q_t = \left(\frac{C_0 - C_t}{M} \right) \times V \quad (1)$$

where C₀ and C_t are the Cd²⁺ concentrations (mg L⁻¹) at time *t* = 0 and *t* = *t*, respectively (min); *V* is the volume of mono-metal solution (L); *M* is the mass of biochar (g).

Results and discussion

Adsorbent biochar prepared by thermal decomposition of PFR at activation temperature of 500°C has yield of 23.3%. The activation method usually comprises of dehydration, volatilization and decomposition of hemicelluloses, celluloses and lignin components present in PFR. The physico-chemical properties of PFR biochar are given in Table 1. In case of surface textural analysis, biochar exhibited N₂ adsorption isotherm as type-II isotherm characteristic of adsorbent carbon with mixed micro and mesoporosity¹⁵. PFR biochar was mostly microporous material, in which contribution of micropores to the total porosity was 21.4%.

Table 1. Physio-chemical properties of PFR biochar

Properties	Value
Moisture content (%)	6.42
Ash content (%)	4.82
Bulk density (g cm ⁻³)	0.538
Point of zero charge (pH _{PZC})	7.2
Specific surface area (S _{BET} , m ² g ⁻¹)	282.85
Micropore volume (V _{mic} , cm ³ g ⁻¹)	0.037
Total pore volume (V _t , cm ³ g ⁻¹)	0.243

Effect of pH:

The pH of the aqueous phase is one of the controlling parameters in removal of heavy metal cation. It not only governs the ionic states of Cd²⁺ in aqueous solution¹⁶, but influences the surface charge on the adsorbent biochar when added to solution phase¹⁷. Fig. 1(A) shows the highly dependent nature of Cd²⁺ adsorption on biochar with varying solution pH.

Cd²⁺ adsorption capacity of biochar increased from 0.08 mg g⁻¹ at pH 2.0 to 1.89 mg g⁻¹ at pH 8.0. At higher pH, adsorption of Cd²⁺ remained quantitative and attained maximum 98.78% removal efficiency. At acidic pH conditions, the surface charge of biochar became protonated resulted into significant electrostatic repulsion. Moreover, H₃O⁺ ions were competitively occupying the binding sites of the biochar at low pH, restricting Cd²⁺ adsorption¹⁸. Experimental pHpzc of PFR biochar was 7.2. As the pH increased above pHpzc, the deprotonation of biochar surface functionalities occurs and the surface start gaining negative potential that favored

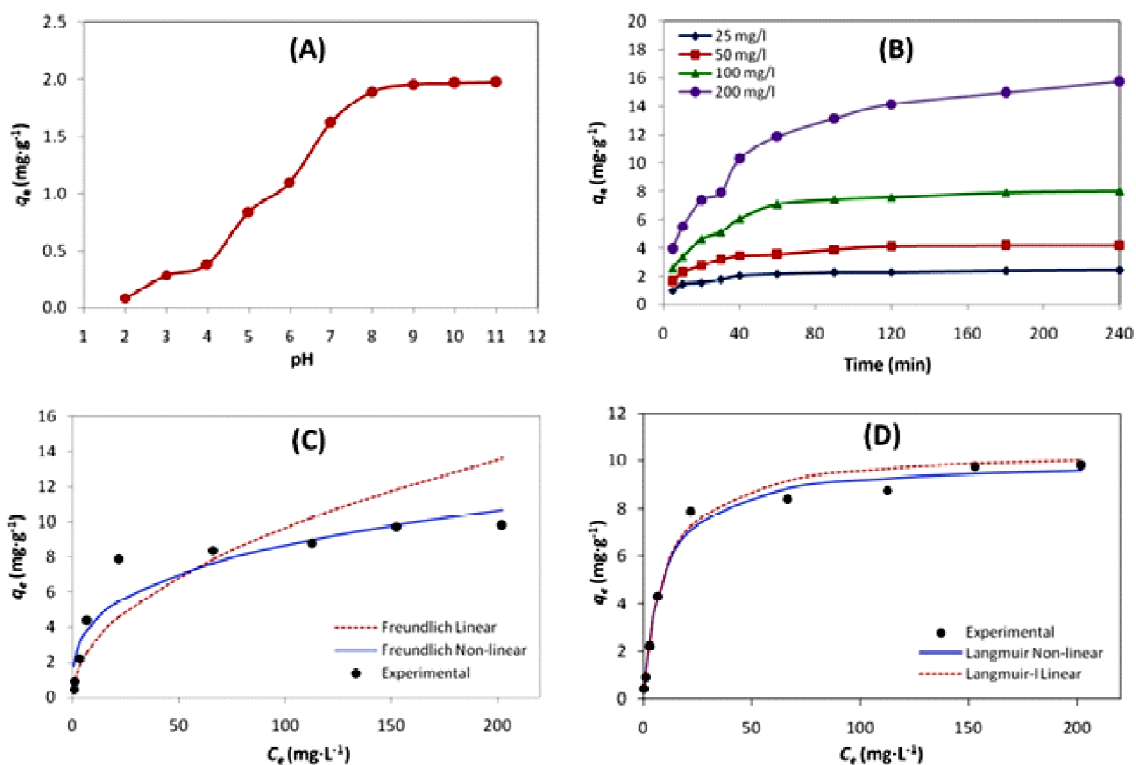


Fig. 1. (A) Effect of pH on Cd²⁺ adsorption using PFR biochar ($M = 10 \text{ g L}^{-1}$, $C_0 = 20 \text{ mg L}^{-1}$, $t = 240 \text{ min}$ and $T = 303 \text{ K}$); (B) Effect of contact time on adsorption of Cd²⁺ on PFR biochar ($\text{pH} = 7.0$, $M = 10 \text{ g L}^{-1}$ and $T = 303 \text{ K}$); (C) Freundlich and (D) Langmuir isotherms for adsorption of Cd²⁺ on PFR biochar.

the electrostatic attraction for higher uptake of Cd²⁺. However at pH > 8.0, the degree of hydration of Cd²⁺ reduces caused by formation of insoluble hydroxyl complexes and precipitation of Cd²⁺ could start at pH 8.3¹⁹. Therefore, it should be emphasized that maximum Cd²⁺ adsorption at pH around 7.0 allows the biochar to be used as effective adsorbent for treatment of Cd²⁺ contaminated wastewater without requiring pH adjustment.

Isotherm of Cd²⁺ adsorption:

The interaction of Cd²⁺ with the adsorbent biochar that describe the phenomenon of adsorbate partitioning between aqueous and solid phases at equilibrium is usually expressed by isotherm modeling. The experimental data of Cd²⁺ adsorption on biochar was modelled using Langmuir and Freundlich isotherm models.

Langmuir model is based on mono-layer coverage on solid surface and assumes that the adsorbent surface is homogeneous with energetically equal affinity for adsorbate.

Langmuir equation in its non-linear and linear form is described by eqs. (2) and (3), respectively.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m} \quad (3)$$

where q_m (mg g^{-1}) is saturated monolayer adsorption capacity of the sorbent and K_L (L mg^{-1}) is the Langmuir affinity constant related to the energy of adsorption.

Freundlich model is applicable to multi-layer sorption systems involving adsorbate adsorption on heterogeneous surfaces. The non-linear and linear form of Freundlich isotherm is described by eqs. (4) and (5), respectively.

$$q_e = K_F C_e^{1/n} \quad (4)$$

$$\ln(q_e) = \ln(K_F) + \frac{1}{n} \ln(C_e) \quad (5)$$

Table 2. Comparison of isotherm models for adsorption of Cd²⁺ on PFR biochar

	Freundlich				Langmuir			
	K_F	$1/n$	r^2	χ^2	q_m	K_L	r^2	χ^2
	Linearized model							
Test 1	1.0191	0.4880	0.9017	5.4758	10.5042	0.1038	0.9942	0.3051
Test 2	1.0283	0.4667	0.9182	4.9282	10.8226	0.1128	0.9961	0.2865
Mean	1.0237	0.47735	0.9099	5.202	10.6634	0.1083	0.9952	0.2958
	Non-linearized model							
Test 1	2.1701	0.3004	0.9111	3.2799	10.0009	0.1129	0.9884	0.2617
Test 2	2.3812	0.2883	0.9244	3.0152	10.2845	0.1682	0.9914	0.2467
Mean	2.2756	0.2943	0.9177	3.1475	10.1427	0.1405	0.9899	0.2542

where (K_F , n) are empirical constants of Freundlich isotherm related to sorption capacity and intensity.

The equilibrium data were modelled to estimate the isotherm parameters using both linearized and non-linearized regression analysis. However, linearization of non-linear isotherm equations introduces a diverse form of parameter estimation errors and fits distortion. Therefore, the validity of isotherm in describing the experimental data was examined by error function chi-square test (χ^2). The comparative of isotherm parameters and error function values are given in Table 2. The r^2 values of the Freundlich isotherm were greater than 0.9 for both regressions; however, result demonstrates that the values of Freundlich constants (K_F , n) obtained by linearized regression are not consistent with non-linear values. Hence, Freundlich model is not appropriate to fit the experimental data. The $1/n$ values of Freundlich isotherm are less than unity. Such isotherms are classified as L-type isotherms indicating the highly favorable Cd²⁺ adsorption on biochar and are indicative of chemisorption²⁰. In case of Langmuir isotherm, r^2 values are close to unity ($r^2 > 0.98$) with least chi-square (χ^2) values suggesting that Langmuir isotherm provides the best fit to Cd²⁺ adsorption system. Linearized Langmuir constants (q_m , K_L) are significantly similar to the non-linear transform values. The optimized fitting of Freundlich and Langmuir model for Cd²⁺ adsorption on biochar are shown in Fig. 1(C,D).

Kinetics of Cd²⁺ adsorption:

The contact time variation plot of Cd²⁺ adsorption from aqueous solution with initial Cd²⁺ concentrations in the range

of 25–200 mg L⁻¹ is depicted in Fig. 1(B). A faster Cd²⁺ adsorption was observed in the initial 40 min of contact, probably due to ease of active sites accessibility on biochar surface at the beginning²¹. This was followed by the sluggish sorption phase up to 240 min till equilibrium achieved, where slower rate of Cd²⁺ diffusion onto the bulk of biochar was apparent²². Time to reach the equilibrium was independent of different Cd²⁺ concentrations and therefore, to ensure the equilibrium at the solid/liquid interface a contact time of 240 min was used in this study. The increase in Cd²⁺ uptake from 2.4 to 15.8 mg g⁻¹ when Cd²⁺ concentration increased from 25 to 200 mg L⁻¹ indicated metal concentration dependent adsorption system.

Kinetics of Cd²⁺ adsorption was evaluated using pseudo-first order and pseudo-second order reaction models, the linear rate equations of which are given by eqs. (6) and (7) respectively.

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

where k_1 and k_2 are rate constant of respective kinetic model, q_e and q_t are equilibrium Cd²⁺ uptake (at $t = \infty$) and adsorption uptake at time t , respectively.

The experimental data was fitted to the kinetic models using linear regression. The rate parameters (k_1 , k_2), adsorption capacity ($q_{e,cal}$) and corresponding regression coefficient

Table 3. Kinetic parameters for adsorption of Cd²⁺ on PFR biochar

C _o (mg L ⁻¹)	q _{e,exp} (mg g ⁻¹)	Pseudo-first order model			Pseudo-second order model		
		q _{e,cal} (mg g ⁻¹)	k ₁ ×10 ⁻³ (min ⁻¹)	R ²	q _{e,cal} (mg g ⁻¹)	k ₂ ×10 ⁻³ (g mg ⁻¹ min ⁻¹)	R ²
25	2.44	1.15	0.0198	0.9643	2.53	0.0407	0.9995
50	4.20	2.36	0.0249	0.9726	4.40	0.0217	0.9995
100	8.01	5.34	0.0235	0.9863	8.55	0.0078	0.9991
200	15.79	11.42	0.0154	0.9870	17.27	0.0022	0.9961

(R²) were calculated using slopes and intercepts of the plots of log (q_e - q_t) versus t for first-order and t/q_t versus t for second-order (Table 3). A poor agreement between q_{e,cal} values derived using pseudo-first order equation and experimental q_{e,exp} values suggest that pseudo-first order model is unable to explain kinetics of Cd²⁺ adsorption on biochar. On the contrary, q_{e,cal} values from pseudo-second order are similar to q_{e,exp} values. In addition, the very large values of R² at all tested concentrations confirm that Cd²⁺ adsorption followed pseudo-second order kinetics. The values of rate constant k₂ decreased with increasing Cd²⁺ concentrations. At higher concentration, the competition among the Cd²⁺ ions to occupy the limited active sites on the surface of biochar leads to lower sorption rates.

FE-SEM analysis:

FE-SEM image of PFR biochar (Fig. 2a) shows formation of non-uniform but continuous network of vertical tubes and column like channels, caused by pyrolytic decomposition of PFR at the activation temperature. Adsorption of Cd²⁺ resulted into distinct changes in surface morphology of biochar. The tubular structure was observed as filled with cloudy mass (Fig. 2b), attributed to the possible interaction of Cd²⁺ on binding sites present on biochar surface.

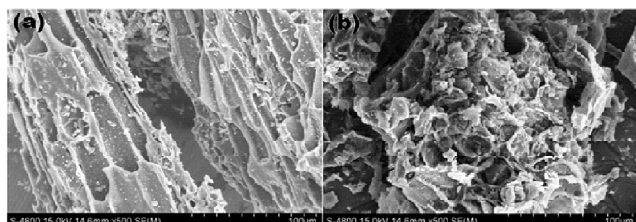


Fig. 2. FE-SEM images of PFR biochar (a) before and (b) after adsorption of Cd²⁺.

Conclusions

This study highlighted the potential of biochar derived from low-cost industrial by-product PFR for the adsorptive removal of Cd²⁺ from aqueous solution. Cd²⁺ adsorption capacities were radically influenced by solution pH values and were found to be increasing with increasing pH and initial Cd²⁺ concentration. In equilibrium isotherm study, the experimental data well fitted to Langmuir isotherm and the maximum Cd²⁺ adsorption (q_m) of 10.82 mg g⁻¹ was obtained. Kinetics of Cd²⁺ adsorption followed the pseudo-second order model, which indicates that active sites on biochar adsorbent surface are the rate-limiting step in Cd²⁺ adsorption.

References

1. M. A. Salam, G. Al-Zhrani and S. A. Kosa, *C. R. Chimie*, 2012, **15**, 398.
2. M. Chiban, A. Soudani, F. Sinan and M. Persin, *Colloid Surface B*, 2011, **82**, 267.
3. G. Mockaitis, J. A. D. Rodrigues, E. Foresti and M. Zaiat, *J. Environ. Manage.*, 2012, **106**, 75.
4. T. Kurniawan, G. Chan, W. Lo and S. Babel, *Chem. Eng. J.*, 2006, **118**, 83.
5. R. A. Rao and A. K. Moonis, *Colloid Surface A*, 2009, **332**, 121.
6. K. Kadirvelu and C. Namasivayam, *Adv. Environ. Res.*, 2003, **7**, 471.
7. S. Tangjuank, N. Insuk, J. Tontrakoon and V. Udeye, *World Acad. Sci. Eng. Technol.*, 2009, **3**, 221.
8. M. Jain, V. K. Garg, U. K. Garg, K. Kadirvelu and M. Sillanpaa, *Int. J. Environ. Res.*, 2015, **9**, 1079.
9. B. Li, L. Yang, C. Q. Wang, Q. P. Zhang, Q. C. Liu, Y. D. Li and R. Xiao, *Chemosphere*, 2017, **175**, 332.
10. C. M. Park, J. Han, K. H. Chu, Y. A. Al-Hamadani, N. Her, J. Heo and Y. Yoon, *J. Ind. Eng. Chem.*, 2017, **48**, 186.
11. H. Shariffard, Z. Hashemishahraki, E. Rezvanpanah and S. H. Rad, *Bioresour. Technol.*, 2018, **270**, 562.

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12. B. M. V. da Gama, G. E. do Nascimento, D. C. S. Sales, J. M. Rodríguez-Díaz, C. M. B. de Menezes Barbosa and M. M. B. Duarte, *J. Clean Prod.*, 2018, **201**, 219.
13. J. H. Park, J. J. Wang, S. H. Kim, S. W. Kang, C. Y. Jeong, J. R. Jeon, K. H. Park, J. S. Cho, R. D. Delaune and D. C. Seo, *J. Colloid Interface Sci.*, 2019, **553**, 298.
14. L. S. Cerovic, S. K. Milonjic, M. B. Todorovic, M. I. Trtanj, Y. S. Pogozev, Y. Blagoveschenskii and E. A. Levashov, *Colloid Surface A*, 2007, **297**, 1.
15. Y. Onal, C. Akmil-Basar, C. Sarici-Ozdemir and S. Erdogan, *J. Hazard. Mater.*, 2007, **142**, 138.
16. M. Iqbal, A. Saeed and S. I. Zafar, *J. Hazard. Mater.*, 2009, **164**, 161.
17. R. Qu, C. Sun, M. Wang, C. Ji, Q. Xu, Y. Zhang, C. Wang, H. Chen and P. Yin, *Hydrometallurgy*, 2009, **100**, 65.
18. Y. Ding, D. Jing, H. Gong, L. Zhou and X. Yang, *Bioresour. Technol.*, 2012, **114**, 20.
19. M. Ajmal, R. A. K. Rao, S. Anwar, J. Ahmad and R. Ahmad, *Bioresour. Technol.*, 2003, **86**, 147.
20. M. R. Taha, K. Ahmad, A. A. Aziz and Z. Chik, in: "Tropical Residual Soils Engineering", eds. B. B. K. Huat, G. S. Sew and F. H. Ali, CRC Press, London, 2004, pp. 391-420.
21. M. M. S. Saif, N. S. Kumara and M. N. V. Prasad, *Colloid Surface B*, 2012, **94**, 73.
22. L. Semerjian, *J. Hazard. Mater.*, 2010, **173**, 236.