Research Article

Equilibrium isotherm and kinetic study of biosorption of cadmium from synthetic water using wastes leaves of *Averrhoa carambola*

Bhabani Devi*
Department of Environmental Science, Guwahati University,
Guwahati-781014 (Assam) India
H P Sarma
Department of Environmental Science, Guwahati University,
Guwahati-781014 (Assam), India

*Corresponding author. E-mail: baanibhandari@gmail.com

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Abstract

Globally, the discharge of heavy metals into the water bodies is a matter of serious concern. Heavy metals like cadmium are considered as toxic even at very low concentration. Several conventional methods are available to remove heavy metals from the wastewater. They bear high costs, generate high sludge, and consume high energy. Biosorbents provides many beneficial properties due to their good adsorption capacity for heavy metals. The present work focuses on the potential of waste leaves of *Averrhoa carambola* (WACLP) as an adsorbent for its ability to remove Cd (II) ions from synthetic water by batch experimental process. The adsorbent was characterized by using elemental analysis, Energy Dispersive X-ray or EDAX and Scanning Electron Micrograph (SEM). The batch experiment was carried out considering various parameters such as pH, initial metal ion concentration, contact time and dose of the adsorbent. The fitting of the experimental data was done by Langmuir, Freundlich and Temkin isothermal models. The study on isothermal models revealed that the experimental parameters were best fitted to the Langmuir isothermal model with R^2 value of 0. 976.The Kinetic studies showed pseudo second order depicting chemisorption. The results showed that *Averrhoa carambola* is a good adsorbent for cadmium and hence it can widen the scope and prospects for future studies on heavy metal removal from the aqueous solution.

Keywords: Adsorption isotherm, *Averrhoa carambola,* Cadmium, Conventional, Heavy metals, Kinetics

INTRODUCTION

Cadmium is one of the most priority heavy metals due to its high toxicity. Though it, is an essential heavy metal for living organisms, its increased levels have detrimental effects on living organisms (Purkayastha *et al*., 2014). Cadmium is found naturally by the process of rock and soil erosion. The cadmium concentration in the environment also gets elevated due to forest fires and volcanic eruptions (Rao *et al*., 2014). The various sources of cadmium are the electroplating industry, battery manufacturing units, textile operation, refineries, by-products from fertilizer industry and textile units (Patterson 1985, Poon, 1986). As per WHO (2011) guidelines for drinking water, the permissible limit of cadmium in drinking water is 0.03mg/L.

One of the important properties of cadmium is its solubility. Its compounds show variation in solubility ranging from high degree of solubility to insoluble (Zheng *et al*., 2014) According to EPA (Environment Protection Agency) it is regarded as a human carcinogen (Group B1) (Pandey *et al*., 2008). Cadmium toxicity includes bronchitis, pulmonary oedema, emphysema (Tchounwou *et al*., 2012). Cadmium also causes Itai-itai disease. Cadmium poses serious health threats even at very low concentrations (Ajay Kumar *et al*., 2009). As studied by (Friberg *et al.,*1986) in natural unpolluted water the cadmium concentration is below 0.001mg/L. The toxic nature of cadmium makes it essential to remove from various industrial effluents before it is dumped into water bodies. Nowadays, various conventional water treatment methods are available to remove heavy metals from the industrial effluents. It includes reverse osmosis, ultrafiltration and electrodialysis;(Bazrafshan *et al.,* 2015). These conventional methods possess both advantages and disadvantages.

The major drawbacks are its high operation charges, energy consumption, less effectiveness for low metal ion concentration, etc. To overcome the problem, the adsorption process has come up as an effective tool for heavy metal removal from various effluents. Adsorption has the significant advantage of being low-cost implementation, less energy usage, and effective at low metal concentrations. Available literature showed that there are a large number of naturally occurring adsorbents which are used for the removal of heavy metal cadmium from aqueous solution. Biomaterials like rice husk (Ajmal *et al.,* 2003), sugarcane baggase (Krishnan and Anirudhan, 2003), cashew nutshell (Tangjuank *et al*., 2009), waste tea (Ahluwalia and Goyal, 2005), agricultural wastes (Yingjie Dai *et al*., 2018) coffee ground (Azouaou *et al.,* 2010), areca catechu (Chakravarty *et al*., 2012), pine cone (Thakur *et al*., 2020), *Peganum harmala* seeds (Zamani *et al*., 2012) , rice bran biochars (Amen *et al*., 2020), orange peel (Gupta and Nayak, 2012) , algae (Sulaymon *et al*., 2013).The present work emphasizes removing cadmium from synthetic water using leaves of *Averrhoa carambola* as an adsorbent by the process of adsorption. The factors which affect the process of adsorption are pH, contact time, metal ion concentration and dose of adsorbent.

Averrhoa carambola belongs to the Oxalidaceae family. *A. carambola* is commonly known as star fruit. It contains a several high oxalic acids. Previous studies on chemical constituents of carambola leaves show the presence of steroids, triterpenes (Moresco *et al*., 2012) cyanidin glycosides (Dan Yang *et al*., 2017), O-glycosyl flavonoids (Yang *et al*., 2015), and C-flavones (See Wan Yan *et al*., 2013). The presence of the above chemical constituents suggests that it may act as a good adsorbent in removing the cadmium from the synthetic water; hence it was taken as bio adsorbent in the present work.

MATERIALS AND METHODS

Preparation of stock solution
A stock solution of cadmium of 1000 mg/L was prepared by dissolving Cd (No3)2 salts in 1000 ml of distilled water. Using a stock solution of 1000 mg/L, lower concentrations of 5 mg/L, 10 mg/L, 15 mg/L, 20 mg/L, 25 mg/L and 30 mg/L were prepared by serial dilutions of stock solution. The pH of the solution was adjusted using 0.1 M NaOH and 0.1 M HCl.

Preparation of adsorbent
A. carambola waste leaves were collected from a village area in Sonapur, Kamrup rural, Assam. The collected leaves were washed with tap water to remove dirt and impurities. They were then washed with distilled water and kept for sun drying for three days followed by oven drying for a week. The oven dried sample were ground to powder using a mixer grinder. The powdered leaves were again washed with distilled water to remove colour of the leaves that may hamper AAS analysis. The washed powdered leaves were oven dried till the moisture was completely removed. The completely dried powdered leaves were sieved using 75 μm and kept in a plastic container and stored inside a desiccator for future use (Rao *et al*.,2010) The leaves powder of *carambola* is named waste *A. carambola* leaves powder (WACLP)

Experiment
Batch experiments were conducted under various experimental conditions like pH dose of adsorbent, initial metal ion concentration and contact time. In a 250ml conical flask, 100 ml cadmium nitrate stock solution was taken followed by WACLP powder. The mixture was set inside the shaker for 180 mins at 120 rpm. The pH varied from 2-6. Adjustment of pH was done using 0.1M NaOH and .1 M HCl. The experiment was carried out for the initial concentration ranging from 5-30 mg/L and a dose of 0.5 -0.4 gm. After reaching equilibrium time, the mixture was filtered using Whatman filter paper 41 and the filtrate was analyzed for cadmium concentration in AAS. The raw and metal adsorbed adsorbent (WACLP) was characterized by a carbon-hydrogen nitrogen analyzer (CHNS) and SEM-EDAX studies.

Analytical methods
The removal efficiency of the WACLP by adsorption process can be evaluated using Equations 1 and 2 (Gupta *et al*., 2022)

$$\%(R) = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

where, C_0 is the initial metal ion concentration (mg/L), C_e is concentration of metal ion at equilibrium(mg/L), and % R is the percentage removal

The amount of metal adsorbed on the surface of adsorbent is calculated as

$$q_e = \frac{C_0 - C_e}{M} \times V \tag{2}$$

Where, q_e is the amount of metal adsorbed by adsorbent, C_0 is the initial metal concentration (mg/L), C_e is the metal concentration at equilibrium (mg/L), M is the mass of the adsorbent (g), V is the volume of solution (L).

RESULTS AND DISCUSSION

Elemental analysis
The elemental analysis of the adsorbent using carbon, hydrogen, nitrogen and sulphur analyzer (CHNS) showed that 40.45% of carbon content in the adsorbent imparted good adsorbent capacity. The other elements

Fig. 1. *Wastes Averrhoa Carambola leaves powder (WACLP) powder*

included hydrogen (6.53%), Nitrogen (2%) and Sulphur (.05%) which were less in amount.

Energy Dispersive Xray of raw and cadmium loaded sample

The elemental analysis was determined by Energy Dispersive Xray (EDAX). The EDAX spectra image showed that the major elements present are chlorine, potassium, silicon, phosphorus, calcium, magnesium, sulphur, oxygen (Fig 2). It is clear from Figure 2 and Fig 3 that the elements like silicon, calcium, magnesium, oxygen, etc. were replaced by cadmium through an ion exchange mechanism and the peak intensity got reduced after the uptake of cadmium ions. The reduction in the intensity of the peak could be due to the binding of the cadmium ions onto the surface of adsorbent. Similar reports were marked by Zulfi *et al.*, 2013 on *Annona muricata L. seeds for Pb (II) and Cu (II) ions.*

Scanning Electron Microscopy

The Scanning Electron Micrography (SEM) of cadmium loaded biosorbent taken at 20kv and 1000x magnification of Cd (II) before adsorption and showed uneven

and porous structures. The irregular texture and cavity-like structures were modified into smooth texture after adsorption. The cavity-like structures acted as adsorption sites for the cadmium. SEM micrographs suggested a porous, heterogeneous rough surface which made it potential to adsorb cadmium ions. After cadmium treatment adsorbent appeared to be smooth and altered in the texture. Similar reports were observed in *Lemna polyrhiza* L. for cadmium metal removal (Unadkat *et al*., 2018)

Batch equilibrium studies
Effect of pH on cadmium adsorption by WACLP

The process of adsorption is highly influenced by pH of the solution. The pH undertaken in the present study varied from (1-6). At low pH, Cd (II) ions compete with H^+ ions which are more in numbers for the adsorption sites on the surface of the adsorbent. This causes low adsorption in the lower pH range. As the pH increases, the concentration of H^+ ions decreases and the competition for the adsorption sites between H^+ and Cd (II) ions reduces. This results in the occupation of adsorption sites by Cd (II) ions. The availability of more negative charge on the surface of the adsorbent results in a strong bond of attraction between Cd (II) ions and the adsorption sites. Above pH 6 precipitation of metal hydroxide takes place. As studied by Pavasant *et al.,* (2006) formation of metal hydroxide could occur above pH of 6.5. Hence, In the present work experiment was conducted at below pH 6. As studied by various researchers, pH value of 5 is considered good for equilibrium and Kinetics studies (Ajay Kumar *et al*., 2009). According to Salim *et al*. (2008) cadmium removal by combination of leaves was maximum at pH 5. Panda *et al*. (2006) studied the husk of Lathyrus sativus and
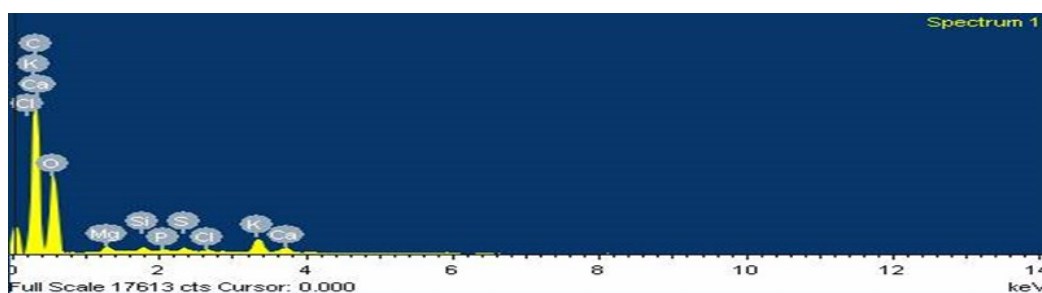

Fig. 2. *Energy dispersive X ray (EDAX) of raw wastes leaves of Averrhoa   carambola (WACLP)*
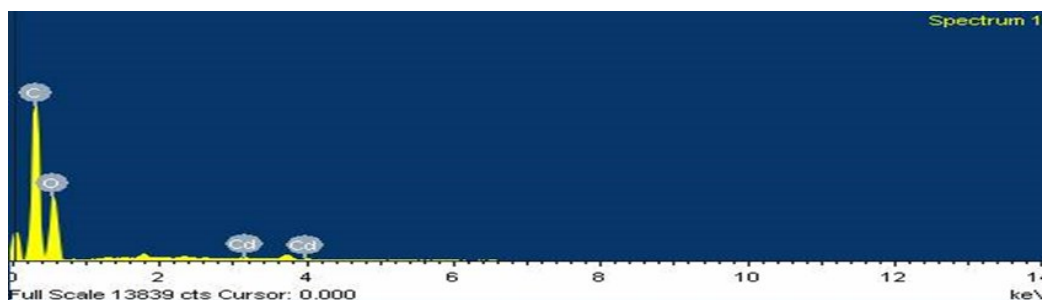

Fig. 3. *Energy Dispersive X ray (EDAX) of cadmium loaded spectra*

Table 1. Elemental analysis of WACLP

Carbon	Hydrogen	Nitrogen	Sulphur
40.45 %	6.53 %	2%	.05 %

showed maximum adsorption at pH value of 5. Bilal *et al.* (2021) showed optimum pH of 6 for the removal of cadmium by *Capparis decidua* and *Ziziphus mauritiana*. Ali *et al.* (2022) also reported the adsorption of cadmium onto guava leaves at pH value of 5.6.

Effect of initial metal on adsorption by WACLP
The effect of initial metal ion concentration on adsorption was studied in the range of 5 to 30 mg/L. Experimental values showed that the removal percentage increases as the initial metal concentration increases from 5 mg/L to 10 mg/L. Further increase in metal ion concentration does not increase the metal removal percentage. This can be because the binding sites get saturated on the adsorbent surface. From Fig. 6, it was evaluated that the removal efficiency decreased from 92.6% to 91% as the initial metal ion concentration increased from 5 to 30 mg/L. The maximum removal was at 15 mg/L and hence 15 mg/L was considered as optimum metal ion concentration for equilibrium and kinetic studies The reason for the decrease in removal percentage as metal ion concentration increases is the accumulation of adsorbent particles at higher metal ion concentration (Ajay Kumar *et al.*, 2009). The binding sites get occupied at lower metal ion concentrations.

Effect of adsorbent dose on cadmium adsorption by WACLP
The effect of adsorbent dosages on the concentration of Cd (II) ions is presented in Fig. 8. The dose of the adsorbent varied from 0.5 to 4 g/L. Fig. 7 indicated that as the dose of the adsorbent increased from 0.5 to 2 gm there is increase in the percentage removal of cadmium. Further, when the dose was increased, the removal percentage was reduced due to the overloading of the adsorbent particles and due to the intercellular dissociation binding capacity of the metal ion affected (Zhao *et al.*, 2017). The maximum removal percentage was at 2 gm dose of adsorbent. The significant increase in Cd (II) adsorption took place when the dose increased from 0.5 to 2g/L. Similar reports have been observed for cadmium ion adsorption onto mushrooms (Vimala and Das., 2009) and mango peel waste (Iqbal *et al.,* 2009).

Effect of contact time on cadmium adsorption by WACLP
The effect of contact time on the removal of cadmium was studied at contact times ranging from 30-180 mins. Fig. 8 showed the removal percentage by WACLP increased as the time increases from 30 mins to 90 mins.

During the initial period the increase in removal of cadmium was due to the availability of active binding sites on the adsorbent surface. Gradually, the sites get occupied by metal ions and hence further increase in time does not increase the cadmium adsorption. The equilibrium time for maximum cadmium removal was 90 mins. This suggests that no adsorption occurred after 90 mins as most of the vacant sites were filled up at 90 mins (Al-Homaidan *et al.,* 2015).

Adsorption isotherm
Langmuir, Freundlich and Temkin Isothermal models were studied to fit the experimental data. The Langmuir isotherm assumes monolayer adsorption without interaction between adsorbed ions (Langmuir I, 1918). The equation is expressed as:

$$\frac{Ce}{qe} = \frac{1}{q_{L \times K_L}} + \frac{C_e}{q_L} \qquad (3)$$

Where C_e represents the equilibrium concentration of the metal ions (mg/L), q_e represents the amount of metal ions adsorbed by a unit mass adsorbent (mg/g), q_L denotes the maximum amount of the metal ions adsorbed by the unit mass adsorbent (WACLP) in (mg/g), and K_L represents the Langmuir constant (L/mg). Langmuir constant is related to affinity of the binding sites and sorption energy.
A plot between $1/q_e$ and $1/C_e$ gives the value of slope and intercept. One of the important parameters of Langmuir is the separation factor R_L. It is expressed by the equation (4) given below

$$R_L = \frac{1}{(1+bC_{i)}} \qquad (4)$$

Where, Ci is the initial concentration (mg/L). Values of separation factor provides an idea about the type of adsorption. The value of R_L ranges from (0-1). If the value is 0, adsorption is irreversible, favourable adsorption when $0 < R_L < 1$, linear when R_L is 1 and unfavourable when R_L is above 1.
The Freundlich isotherm depends on the interaction between adsorbed ions. It is expressed as by equation (5).

$$Log\, q_e = Log\, K_{f +} \frac{1}{n} \times log\, C_e \qquad (5)$$

Where, K_f and n are Freundlich constants. K_f is adsorption capacity and n being dimensionless constant relating to adsorption intensity. A plot between Log q_e and Log C_e gives the value of slope and intercept (Freundlich, 1906).
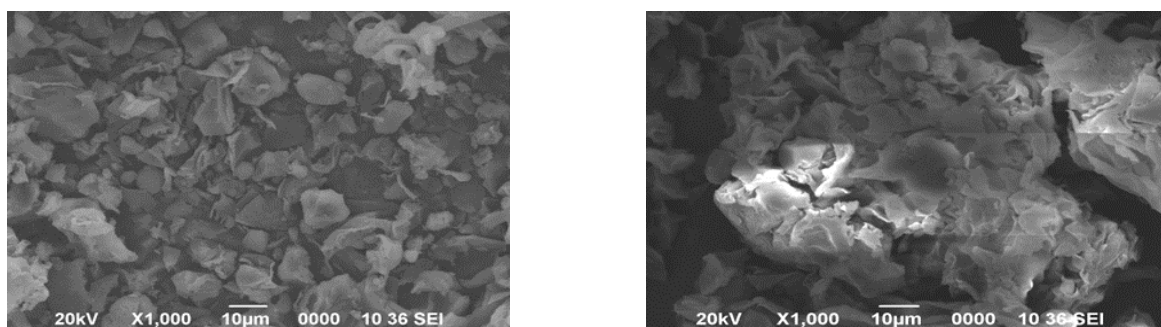
Fig. 4. *Scanning electron micrograph (SEM) before and after Cd (II) adsorption by wastes leaves of Averrhoa carambola (WACLP)*
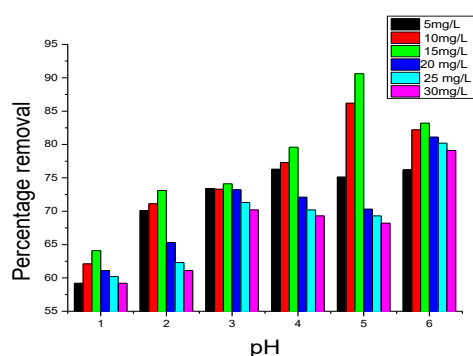

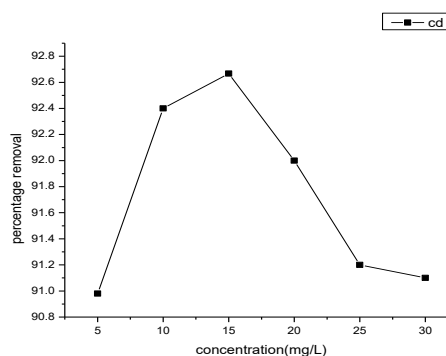**Fig. 5.** *Effect of pH on Cd (II) adsorption by WACLP*

Fig. 6. *Effect of initial metal concentration on Cd (II) adsorption by WACLP*

Temkin isotherm

It assumes that heat of adsorption of all the molecules on the adsorbent surface decreases linearly. The linear form is expressed by Equation 6

$$q_e = \left(\frac{RT}{b}\right) \times \ln A + \left(\frac{RT}{b}\right) \times \ln C_e \qquad (6)$$

Where (RT/b) = B, R is universal gas constant, T is the absolute temperature and b is Temkin constant. B (j/mol) is constantly related to the heat of adsorption. A(L/mg) is equilibrium binding constant.

Table 2 inferred that the maximum adsorption capacity

(q_{max}) on the surface of *A. carambola* was estimated to be 10 mg/g. Lower Cd (II) ion adsorption capacity have been reported for other adsorbent such as, Wheat bran (0.7 mg/g) (Singh *et al.,2006*), Rice polish (0.972 mg/g) (Singh *et al.,*2005). Based on regression coefficient (R^2) values, the adsorption isotherm was best fitted to the Langmuir isotherm model with an R^2 value of 0. 976. Previous studies on the removal of Cd (II) by the modified algae and ash as adsorbent indicated the Langmuir model as the Best fitted model for adsorption for removal of Cd (II) ions (Maria Harja *et al*., 2015).

Table 2. Langmuir, Freundlich and Temkin adsorption isotherm of Cd (II) ions by WACLP

Langmuir isotherm	$q_{m(mg/g)}$		$K_{L(L/g)}$
	10.35	0.976	0.193
Freundlich isotherm	K_f	R^2	n
	1.2	0.966	1
Temkin isotherm	B_T(J/mol)	K_T(L/mg)	R^2
	1.458	1.58	.974

Table 3. Pseudo first order kinetic parameters for biosorption of Cd (II) by WACLP

C_e(mg/L)	q_e(exp)(mg/g)	q_e(cal)(mg/g)	K_1	R^2
5	0.2274	0.021126	0.0065	0.97154
10	2.18	0.066848	1.16	0.99903
15	0.695	0.308822	1.28	0.96544
20	0.92	0.37723	1.38	0.78706
25	1.14	0.563099	0.0000085	0.86263
30	1.37	0.578625	1.3	0.912045

Table 4. Pseudo second order kinetic parameters for biosorption of Cd (II) by WACLP

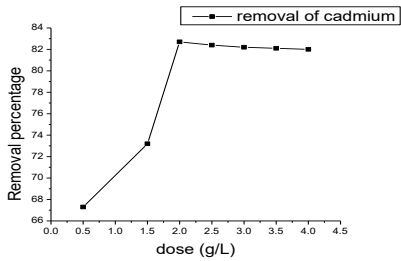| C_e(mg/L)	qe(exp)(mg/g)	qe(cal)(mg/g)	K_1	R^2
5	0.22745	0.248843	0.004798	0.99971
10	0.462	0.451875	0.00575	0.99997
15	0.695	0.620544	0.00675	0.99976
20	0.92	1	0.00743	.9991
25	1.14	1.043798	0.00834	0.99999
30	1.37	2	0.00865	0.99986

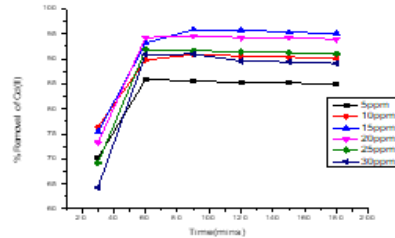**Fig. 7.** Effect of adsorbent dose on *adsorption by WACLP*

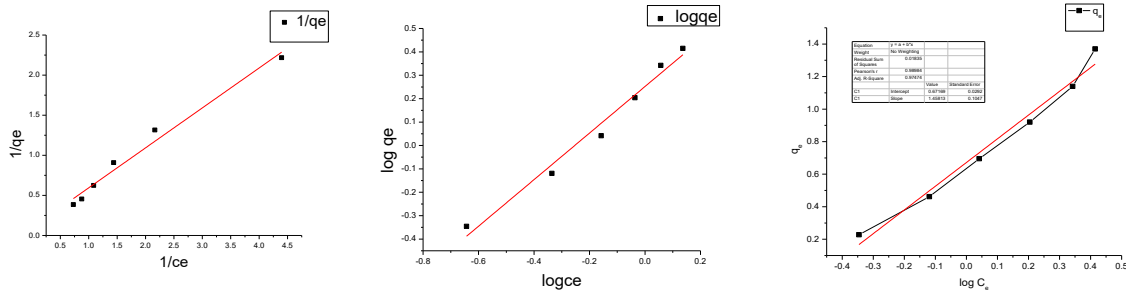**Fig. 8.** *Effect of contact time on cadmium Cd (II) adsorption by WACLP*

Fig. 9. *Langmuir, Freundlich, Temkin isotherm for Cd (II) ions adsorption by ACLP*

Adsorption kinetics

Two important kinetic models were studied to evaluate the adsorption process. The Kinetic experiment was investigated for the concentration range 5-30 mg/L and operating optimum conditions of pH 5, a dose of 2 gm and an equilibrium time of 90 mins at 120 rpm. The equation for Pseudo first order is expressed by equation

$$\text{Log (qe-qt)} = \log(qe) - \frac{K_1}{2.303t} \qquad (7)$$

where, q_e (mg/g) and q_t (mg/g) are adsorption capacity of Cd (II) ions at equilibrium and time t. K_1 is rate constant. A plot between $\ln(q_e-q_t)$ versus time gives slope and intercept, k_1, q_e.

The Pseudo second order kinetics is expressed by equation 8

$$t/qt = \frac{1}{k_2 q_{e2}} + \frac{t}{q_e} \qquad (8)$$

where, k_2 is second order rate constant. A plot between t/qt and t gives slope and intercept and k_2 value from slope and intercept. The slope was obtained as $1/q_e$ and $1/k_2 qe^2$ as the intercept

Table 3 and Table 4 present the summary of kinetic parameters. The plots are shown in Fig 10. The pseudo - second order regression coefficients were higher than the first -order. Moreover, the calculated values of adsorption capacities q_e at equilibrium of pseudo-second order were close to the experimental q_e values. Hence, the adsorption of Cd (II) on WACLP followed pseudo-second order kinetics and was based on chemisorption and there was ion exchange between adsorbent surface and metal solution (Abbas *et al*, 2019).

A similar study on cadmium adsorption by *Erythrina variegata orientalis* leaf powder (Kumar *et al*.,2009); *Psidium guvajava* L leaf powder (Rao *et al*., 2010) and bamboo stem biomass (Akinyeye *et al*., 2019) showed pseudo-second order reactions. Removal of cadmium and copper by biosorption on *Typha angustifolia* leaves also showed pseudo-second order kinetics (Guechi *et al*., 2020).

Conclusion

The present study concluded that adsorption by leaves powder of *carambola* named waste *A. carambola* leaves powder (WACLP) depended on various parameters like pH, initial metal ion concentration, contact time and dose of the adsorbent. The removal percentage was maximum at 15 mg/L concentration and an in-
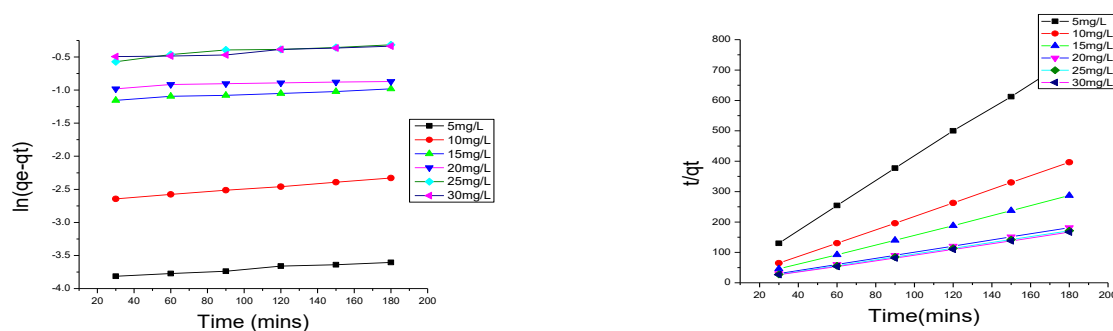
Fig. 10. *Pseudo first order and Pseudo second order kinetics for Cd (II) adsorption by WACLP*

crease in further initial concentration did not increase removal capacities. Results showed best fits to Langmuir isotherm suggesting monolayer adsorption. Further, the adsorption by WACLP also best fitted to Pseudo second order kinetics. Henceforth, WACLP bore good potential in the removal of Cd (II) from synthetic water.

ACKNOWLEDGEMENTS

Conflict of interest
The authors declare that they have no conflict of interest.

REFERENCES

1. Abbas, M., Harrache, Z. & Trari, M. (2019). Removal of gentian violet in aqueous solution by activated carbon equilibrium, kinetics, and thermodynamic study. *Adsorption Science & Technology, 37(7-8), 566-589.*

2. Ahluwalia, S. S. & Goyal, D. (2005). Removal of heavy metals by waste tea leaves from aqueous solution. *Engineering in Life Sciences*, 5(2), 158-162.

3. Ajay Kumar, A. V., Darwish, N. A. & Hilal, N. (2009). Study of various parameters in the biosorption of heavy metals on activated sludge. World *Applied Sciences Journal, 5 (5), 32-40.*

4. Ajmal, M., Rao, R. A. K., Anwar, S., Ahmad, J. & Ahmad, R. (2003). Adsorption studies on rice husk: removal and recovery of Cd (II) from wastewater. *Bioresource technology, 86(2), 147-149.*

5. Akinyeye, O. J., Ibigbami, T. B., Odeja, O. O. & Sosanolu, O. M. (2020). Evaluation of kinetics and equilibrium studies of biosorption potentials of bamboo stem biomass for removal of Lead (II) and Cadmium (II) ions from aqueous solution. *African Journal of Pure and Applied Chemistry, 14(2), 24-41.*

6. Al-Homaidan, A. A., Alabdullatif, J. A., Al-Hazzani, A. A., Al-Ghanayem, A. A. & Alabbad, A. F. (2015). Adsorptive removal of cadmium ions by Spirulina platensis dry biomass. *Saudi Journal of Biological Sciences*, 22(6), 795-

800.

7. Ali, A. E., Mustafa, A. A., Eledkawy, M. A., Ahmed, A. M., Alnaggar, G. A., Elmelegy, E. & Kolkaila, S. (2022). Removal of Cadmium (II) from Water by Adsorption on Natural Compound. *Journal of Environmental Treatment Techniques*, 10(2), 164-169

8. Amen, R., Yaseen, M., Mukhtar, A., Klemeš, J. J., Saqib, S., Ullah, S. & Bokhari, A. (2020). Lead and cadmium removal from wastewater using eco-friendly biochar adsorbent derived from rice husk, wheat straw, and corncob. *Cleaner Engineering and Technology*, 1, 100006.

9. Azouaou, N., Sadaoui, Z., & Mokaddem, H. (2008). Removal of cadmium from aqueous solution by adsorption on vegetable wastes. *Journal of Applied Sciences*, 8(24), 4638-4643.

10. Bazrafshan, E., Mohammadi, L., Ansari-Moghaddam, A. & Mahvi, A. H. (2015). Heavy metals removal from aqueous environments by electrocoagulation process–a systematic review. *Journal of environmental health science and engineering, 13, 1-16.*

11. Bi lal, M., Ihsanullah, I., Shah, M. U. H. & Younas, M. (2021). Enhanced removal of cadmium from water using bio-sorbents synthesized from branches and leaves of Capparis decidua and Ziziphus mauritiana. *Environmental Technology & Innovation*, 24, 101922.

12. Chakravarty, P., Deka, D. C., Sarma, N. S. & Sarma, H. P. (2012). Removal of copper (II) from wastewater by heartwood powder of Areca catechu: kinetic and equilibrium studies. *Desalination and Water Treatment*, 40(1-3), 194-203.

13. Dai, Y., Sun, Q., Wang, W., Lu, L., Liu, M., Li, J., ... & Zhang, Y. (2018). Utilizations of agricultural waste as adsorbent for the removal of contaminants: *A review. Chemosphere, 211, 235-253.*

14. Edition, F. (2011). Guidelines for drinking-water quality. *WHO chronicle*, 38(4), 104-8.

15. Friberg, L., Kjellstrom, T. & Nordberg, G.F. (1986). Cadmium. In: Friberg, L., Nordberg, G.F. & Vouk, V. (eds.) *Handbook on the toxicology of metals, 2nd edition,* Elsevier Science Publishers, Amsterdam, New York.

16. Freundlich, H. (1906). Over the adsorption in solution Z. *Phys. Chem*, 57, 358-471.

17. Guechi, E. & Benabdesselam, S. (2020). Removal of cadmium and copper from aqueous media by biosorption on cattail (Typha angustifolia) leaves: Kinetic and isotherm studies. *Desalin. Water Treat*, 173, 367-382.

18. Gupta, S., Garg, D. & Kumar, A. (2022). Cadmium biosorption using Aloe. barbadensis Miller leaves waste pow-

der treated with sodium bicarbonate. *Cleaner Waste Systems*, 3, 100032.

19. Gupta, V. K. & Nayak, A. (2012). Cadmium removal and recovery from aqueous solutions by novel adsorbents prepared from orange peel and Fe2O3 nanoparticles. *Chemical engineering journal*, *180*, 81-90.

20. Harja, M., Buema, G., Bulgariu, L. *et al.* Removal of cadmium (II) from aqueous solution by adsorption onto modified algae and ash. *Korean J. Chem. Eng.* 32, 1804–1811 (2015). https://doi.org/10.1007/s11814-015-0016-z

21. Iqbal, M., Saeed, A. & Zafar, S. I. (2009). FTIR spectrophotometry, kinetics and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd2+ and Pb2+ removal by mango peel waste. *Journal of hazardous materials*, *164*(1), 161-171.

22. Krishnan, K. A. & Anirudhan, T. S. (2003). Removal of cadmium (II) from aqueous solutions by steam-activated sulphurised carbon prepared from sugar-cane bagasse pith: Kinetics and equilibrium studies. *Water Sa*, *29*(2), 147-156.

23. Kumar, P. R., Rao, M. V., Babu, N. C., Kumar, P. V. & Venkateswarlu, P. (2009). Utilization of Erythrina variegata orientalis leaf powder for the removal of cadmium.

24. Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical society*, *40*(9), 1361-1403.

25. Moresco, H. H., Queiroz, G. S., Pizzolatti, M. G. & Brighente, I. (2012). Chemical constituents and evaluation of the toxic and antioxidant activities of Averrhoa carambola leaves. *Revista Brasileira de Farmacognosia*, *22*, 319 -324.

26. Panda, G. C., Das, S. K., Bandopadhyay, T. S. & Guha, A. K. (2007). Adsorption of nickel on husk of Lathyrus sativus: behavior and binding mechanism. *Colloids and Surfaces B: Biointerfaces, 57(2), 135-142.*

27. Pandey, P. K., Verma, Y., Choubey, S., Pandey, M. & Chandrasekhar, K. (2008). Biosorptive removal of cadmium from contaminated groundwater and industrial effluents. *Bioresource technology*, *99*(10), 4420-4427.

28. Patterson, J. W. (1985). Industrial wastewater treatment technology.

29. Pavasant, P., Apiratikul, R., Sungkhum, V., Suthiparinyanont, P., Wattanachira, S. & Marhaba, T. F. (2006). Biosorption of Cu2+, Cd2+, Pb2+, and Zn2+ using dried marine green macroalga Caulerpa lentillifera. *Bioresource technology*, *97*(18), 2321-2329.

30. Poon CP. Removal of cadmium from wastewaters. Cadmium in the Environment. 1986:46-55.

31. Purkayastha, D., Mishra, U. & Biswas, S. (2014). A comprehensive review on Cd (II) removal from aqueous solution. *Journal of water process engineering*, *2*, 105-128.

32. Rao, K. S., Anand, S. & Venkateswarlu, P. (2010). Adsorption of cadmium (II) ions from aqueous solution by tectona grandis Lf (teak leaves powder). *BioResources*, *5*(1).

33. Salim, R., Al-Subu, M. & Dawod, E. (2008). Efficiency of removal of cadmium from aqueous solutions by plant leaves and the effects of interaction of combinations of leaves on their removal efficiency. *Journal of environmental management*, *87*(3), 521-532.

34. See Wan Yan, Rajesh Ramasamy, Noorjahan Banu Mohamed Alitheen & Asmah Rahmat (2013) A Comparative Assessment of Nutritional Composition, Total Phenolic, Total Flavonoid, Antioxidant Capacity, and Antioxidant Vitamins of Two Types of Malaysian Underutilized Fruits (*Averrhoa Bilimbi* and *Averrhoa Carambola*), *International Journal of Food Properties,* 16:6, 1231-1244, DOI: 10.10 80/10942912.2011.582975

35. Singh, K. K., Rastogi, R. & Hasan, S. H. (2005). Removal of cadmium from wastewater using agricultural waste 'rice polish'. *Journal of hazardous materials*, *121*(1-3), 51-58.

36. Singh, K. K., Singh, A. K., & Hasan, S. H. (2006). Low-cost bio-sorbent 'wheat bran'for the removal of cadmium from wastewater: kinetic and equilibrium studies. *Bioresource technology*, *97*(8), 994-1001.

37. Sulaymon, A. H., Mohammed, A. A. & Al-Musawi, T. J. (2013). Competitive biosorption of lead, cadmium, copper, and arsenic ions using algae. *Environmental Science and Pollution Research*, *20*, 3011-3023.

38. Tangjuank, S., Insuk, N., Tontrakoon, J. & Udeye, V. (2009). Adsorption of lead (II) and cadmium (II) ions from aqueous solutions by adsorption on activated carbon prepared from cashew nut shells. *International Journal of Chemical and Molecular Engineering*, *3*(4), 221-227.

39. Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K. & Sutton, D. J. (2012). Heavy metal toxicity and the environment. *Molecular, clinical and environmental toxicology: volume 3: environmental toxicology*, 133-164.

40. Thakur, R. S., Katoch, S. S. & Modi, A. (2020). Assessment of pine cone derived activated carbon as an adsorbent in defluoridation. *SN Applied Sciences*, *2*(8), 1-12.

41. Unadkat, K., & Parikh, P. (2019). Localization of Cadmium metal ion in Lemna polyrhiza L. using SEM morphology and EDX analysis. *Environment Conservation Journal*, *20* (1&2), 81-86.

42. Vimala, R. & Das, N. (2009). Biosorption of cadmium (II) and lead (II) from aqueous solutions using mushrooms: a comparative study. *Journal of hazardous materials*, *168* (1), 376-382.

43. Yang, D., Jia, X. & Xie, H. (2019). Heptyl vicianoside and methyl caramboside from sour star fruit. *Natural product research*, *33*(8), 1233-1236.

44. Yang, D., Xie, H., Jia, X., & Wei, X. (2015). Flavonoid C-glycosides from star fruit and their antioxidant activity. *Journal of Functional Foods*, *16*, 204-210.

45. Zamani, A. A., Shokri, R., Yaftian, M. R. & Parizanganeh, A. H. (2013). Adsorption of lead, zinc and cadmium ions from contaminated water onto Peganum harmala seeds as biosorbent. *International Journal of Environmental Science and Technology*, *10*, 93-102.

46. Zheng, Y. F., Gu, X. N. & Witte, F. (2014). Biodegradable metals. *Materials Science and Engineering: R: Reports*, *77*, 1-34. Pandey, P. K., Verma, Y., Choubey, S.,

47. Zheng, Y., Capra, L., Wolfson, O., & Yang, H. (2014). Urban computing: concepts, methodologies, and applications. *ACM Transactions on Intelligent Systems and Technology (TIST)*, *5*(3), 1-55.

48. Zulfi, A., Melia, I. K., Rahmiana, Z., Hermansyah, A. & Edison, M. (2013). Prediction of Pb (II) and Cu (II) ions biosorption by Annona muricata L. seeds using Artificial Neural Network (ANN) approach. *Research Journal of Pharmaceutical, Biological and Chemical Sciences*, *4*(4), 1443-1451