REMOVAL OF DIVALENT CADMIUM IONS FROM AQUEOUS SOLUTION USING LANTANA CAMARA LEAVES BIOCARBON

S. Starlin Shyla[1], R. Mohan Kumar[2], M. Singanan[3*]

[1] Department of Physical Science, Our Lady College of Education, Maduravoyal, Chennai, Tamil Nadu, India

[2] Department of Chemistry, Government Arts College for Men (Autonomous), Nandanam, Chennai, Tamil Nadu, India

[3] PG and Research Department of Chemistry, Presidency College (Autonomous), Chennai, Tamil Nadu, India

Abstract

The objective of this study is to investigate the removal of divalent cadmium ions from an aqueous solution using Lantana camara leaves biocarbon (LCBC). Batch experiments are conducted to test the effects of various parameters such as pH, initial metal ion concentration, amount of biocarbon, and contact time on the cadmium removal process at room temperature, which allows establishing as the optimum conditions a pH value of 4.0 and 2.5g/100 mL of biocarbon dose at the equilibrium time of 180 min. The maximum percentage removal of cadmium is 93.30%. Langmuir and Freundlich adsorption isotherms are used to verify the adsorption parameters, and the experimental data is well fitted to the Langmuir model. Analysis of the biosorption kinetics shows that the pseudo-second-order model is well fitted for Cd (II) ions removal. The correlation coefficient (r^2) for the second-order model is 0.9848. The results reveal LCBC as an efficient, low cost, and harmless to environment adsorbent for the removal of Cd (II) ions in the biosorption process.

Key words: Lantana camara; biocarbon; synthetic wastewater; cadmium removal; biosorption kinetics.

1. Introduction

Excessive release of heavy metals into the environment as a result of industrialization and urbanization has posed a great problem worldwide. Heavy metals account for a number of disorders in plants and animals; therefore, their removal from aqueous media is an important and challenging task [1, 2]. The major problem in heavy metal pollution is that these metals are nonbiodegradable and, accordingly, accumulate in the bodies of living organisms causing dangerous diseases and serious cell disorder. Consequently, efficient and effective methods are needed for the removal of heavy metal pollutants, especially from chemical industries. Moreover, essential elements for life support become toxic for all organisms if present in high concentration. Thus, mercury, cadmium, arsenic, and lead are responsible for poisoning and death of many living organisms on earth. Heavy metals such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium are generated in electroplating, electrolysis, conversion coating, anodizing-cleaning, milling, and etching industries.

Cadmium is a toxic metal regularly found in ores together with zinc, copper, and lead. Volcanic activity is one of the natural reasons for the temporary increase in environmental cadmium concentration. It has been reported that one cigarette contains about 1–2 µg of cadmium, and about 10 % of the cadmium content is inhaled when the cigarette is smoked [3].

Cadmium forms different compounds that are used in industry for electroplating, pigments, plastic stabilizers, Ni-Cd rechargeable batteries, semiconductors, and solar cells [4]. All of these industrial processes produce a large quantity of wastewater, residues, and sludge that can be categorized as hazardous wastes requiring extensive waste treatment [5]. According to USEPA guideline, the maximum contaminated level of cadmium in drinking water is 0.01 mg/L [6].

Due to its toxicity, metal-contaminated wastewater needs to be treated prior to its discharge to the environment. Removal of heavy metals from industrial wastewater can be accomplished through various treatment processes such as chemical precipitation, coagulation, complexation, activated carbon adsorption, ion exchange, solvent extraction, foam flotation, electrodeposition, cementation, and membrane operations. However, conventional methods for the removal of heavy metals from wastewater are often cost prohibitive. Hence, there is a need for cheap methods for effluent treatment. Biosorption is a physicochemical process that includes mechanisms such as absorption, adsorption, ion exchange, surface complexation, and precipitation. It has long been considered an ideal technology for pollutant removal from solution and/or pollutant recovery because of its efficiency and simplicity. The main advantage of biosorption is that it is a cheap and eco-friendly process with good metal recovery results.

In this context, the use of biomass directly and/or in the form of activated carbon prepared from materials of biological origin for the removal of metal ions from industrial wastewater has attracted the attention of many researchers. These biomass sources include low-cost agricultural waste byproducts such as sugarcane bagasse [7–11], rice husk [12–15], sawdust [16–18], coconut husk [19], and neem bark [20], and their applications in the removal of heavy metals from wastewater have been investigated by various research groups. Biocarbon has recently emerged as a new adsorbent material produced mainly from plant leaves. In the present research work, a low-cost biocarbon is produced from Lantana camara plant leaves, and its applicability to the removal of cadmium from synthetic wastewater is evaluated.

2. Materials and methods

2.1. Preparation of metal ion solutions

A stock solution of Cd (II) ions of 1000 mg/L concentration was prepared by dissolving 2.744 g of pure analytical grade $Cd(NO_3)_2 \cdot 4H_2O$ in 1L of deionized water. This stock solution was used to prepare a series of diluted solutions. The pH of the solutions was adjusted in the range of 3–8 by adding 0.1 N HCl and 0.1N NaOH. The pH value of the resulting solutions was measured on a Hanna pH meter (HI98107P). The concentration of Cd (II) ions in aqueous solutions was determined using a PerkinElmer PinAAcle 900AA spectrometer with an air–acetylene flame system using a calibration curve prepared with standard metal ion solutions. All the chemicals and reagents were analytical grade and were purchased from the British Drug Houses (BDH), Mumbai, India.

2.2. Preparation of biocarbon

Lantana camara leaves were collected and air-dried for 48 h. The dried leaves were grounded in a ball mill, and the screened homogeneous powder was used for the preparation of biocarbon. Biocarbon was prepared by treating the powdered leaves with analytical grade concentrated sulfuric acid (density: 1.84 g/cm³ at 20 °C, purity ≥ 98 %) in a biomaterial: acid weight ratio of 1:1.8. The resulting black product was washed with double-distilled water and kept in a hot air oven (Thermostatic RSTI-101Series, Haryana, India) maintained at $150 \pm 2°C$ for 6 h. The obtained biocarbon was pulverized in a ball mill, and the particles sized between 90 and 125 µm were used for the sorption studies. The resulting biocarbon (LCBC) was preserved and used as an adsorbent.

2.3. Biosorption process

Batch experiments were carried out at various pH (3-8), biocarbon dose (BCD) (1–3.5g), contact time (CT) (30–210 min), and initial metal ion concentrations (C_o) (10–100 mg/L). For each batch experiment, the solution volume (SV) of 50 mL Cd (II) ion of 100 mg/L concentration was used. After setting the pH, the desired amount of LCBC was added, and the resulting mixture was agitated in an orbital shaker at 250 rpm and 28 ± 2 °C until reaching the equilibrium. After decantation and filtration through Whatman 42 filter paper, the equilibrium concentration of metal ions in the solution was measured using an atomic absorption spectrometer (PerkinElmer PinAAcle 900). Blank solutions without adsorbent were treated similarly, and the recorded concentration at the end of each operation was taken as the

initial one. Experiments were conducted in duplicate, and mean values were used.

The percent removal of cadmium (II) ions from the solution was calculated from the following equation (1):

$$\% \text{ Removal } = \left(\frac{C_o - C_e}{C_o} \right) \times 100 \tag{1}$$

and the amount of cadmium (II) ion adsorbed per gram of biocarbon was obtained using the general equation (2):

$$q_e = \left(\frac{C_o - C_e}{w} \right) \times V \tag{2}$$

where C_o and C_e are the initial and equilibrium concentrations of cadmium (II) ions in the solution (mg/L), q_e is the metal ion uptake (mg/g), V is the volume of the solution (L), and w is the weight of biocarbon (g).

3. Results and discussion

3.1. Characteristics of the biocarbon

3.1.1. Scanning electron microscope (SEM) analysis

SEM analysis is an important tool used in the determination of the surface morphology of adsorbents. Therefore, the surface morphology of the biocarbon prepared in this work was studied before and after the removal of Cd (II) ions by SEM analysis using a Hitachi SU6600 instrument (Singapore). Figures1 and 2 show the SEM images of pure LCBC and a sample of LCBC after Cd (II) ion adsorption, respectively. In Figure 1,the presence of microcrystalline structures is evident, as well as an irregular distribution of microcrystalline phases and cavities that can act as active sites for the interaction of Cd ions on the biocarbon surface. As can be seen in Figure 2, the morphology changes completely after the adsorption process. The spongy white surface indicates that the Cd (II) ions are adsorbedon the biocarbon surface.

3.1.2. Fourier-transform infrared spectroscopy (FTIR) analysis

FTIR spectroscopy is considered the most useful technique for the identification of functional groups present on the biocarbon surface [21]. The FTIR spectra of the biocarbon before and after the removal of Cd (II) ions (Figures 3 and 4, respectively) were recorded on a Bruker FTIR spectrometer (Alpha II),

USA, to determine the vibrational frequency changes in the functional groups present in the adsorbent. As can be extracted from the spectra, the biocarbon contains different functional groups that may act as selective active sites for the coordination of metal ions. Thus, the adsorption bands at 3417 cm^{-1} for pure LCBC and at 3416 cm^{-1}for Cd (II)-adsorbed biocarbon are attributable to –OH groups. The strong band at 2925 cm^{-1} can be assigned to aliphatic C–H groups [22]. The adsorption bands at 1630 cm^{-1} for pure LCBC and at 1711 cm^{-1} for Cd (II)-adsorbed biocarbon can be attributed to C=O and C=C strong stretching vibrations. The peaks observed at 1114 and 1161 cm^{-1} correspond to C–O groups present in LCBC and the Cd (II)-adsorbed biocarbon matrix. No shift in wavelength was observed when comparing the two spectra, which indicates that –OH,–CH, and C=O groups participate in the adsorption of Cd (II) ions. These are ionizable functional groups, and their ionization leaves vacant sites that can be occupied by metal ions. This ion-exchange process is most likely the mechanism involved in the Cd (II) ion removal process. The IR spectra of pure biocarbon and Cd (II) adsorbed biocarbon are highly similar, which indicates that LCBC could be used as a reusable adsorbent for heavy metal removal.
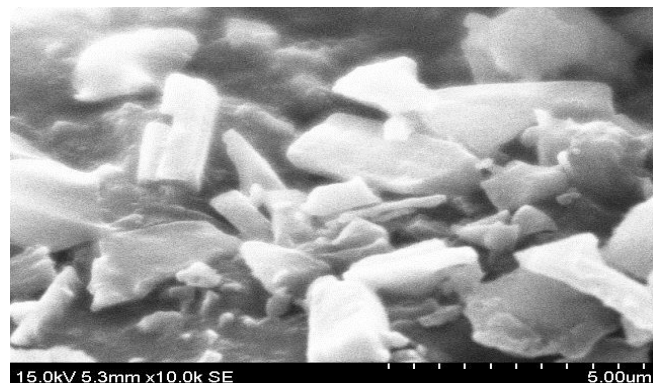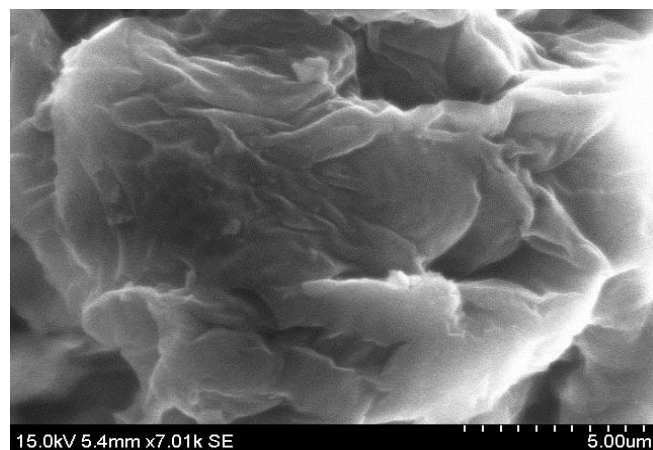

Fig. 1. SEM image of pure LCBC
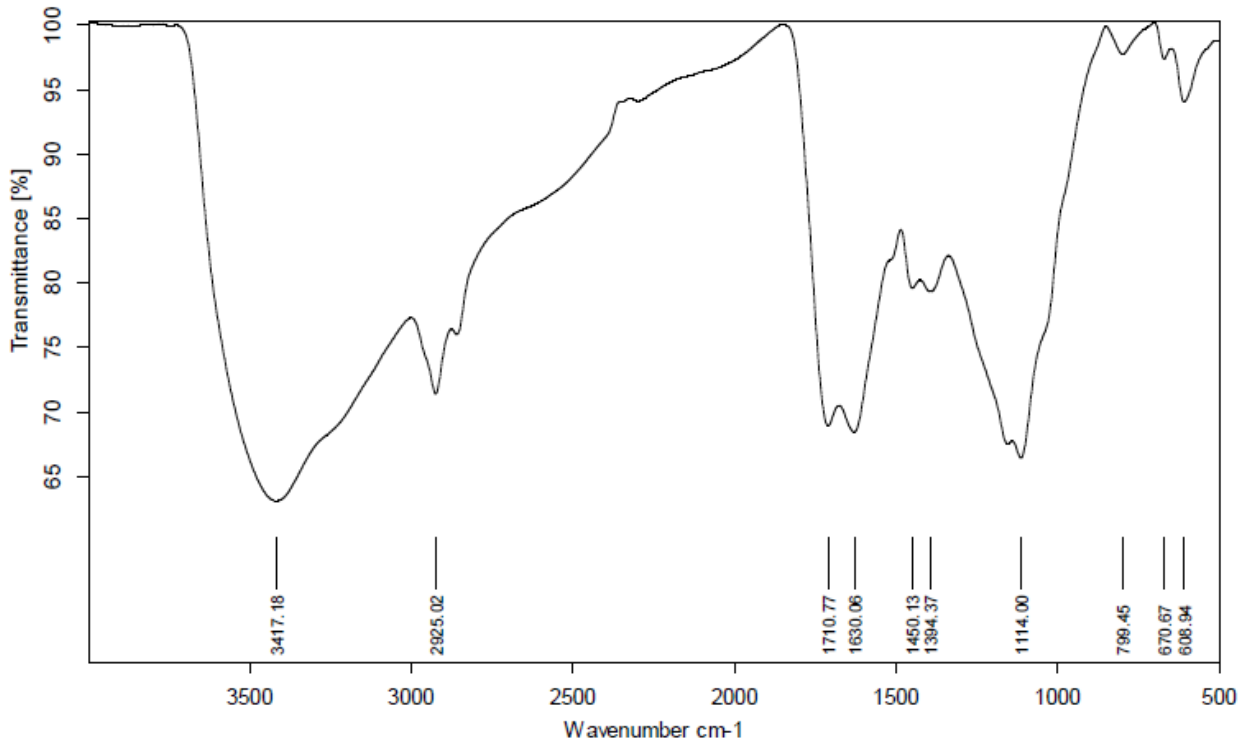

Fig. 2. SEM image of LCBC after Cd (II) ion removal

Fig. 3. FTIR spectrum for pure LCBC
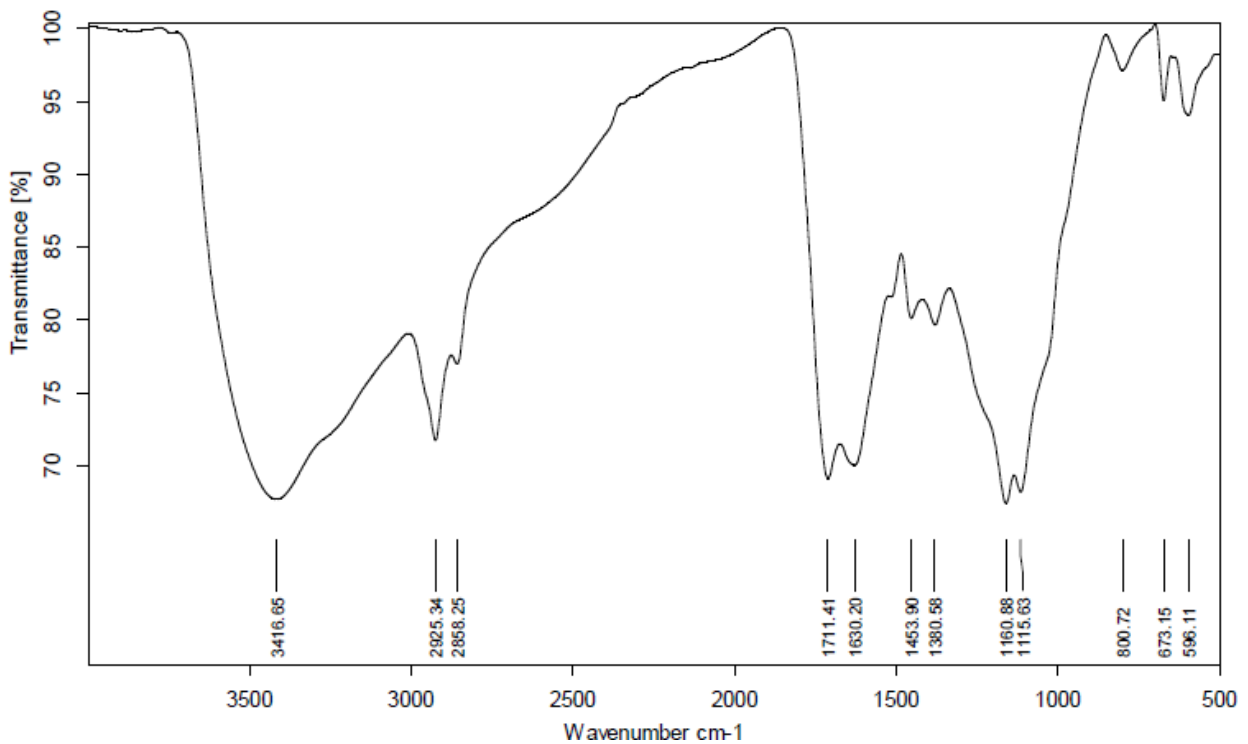

Fig. 4. FTIR spectrum of Cd (II)-adsorbed LCBC

3.2. Influence of biosorption parameters

3.2.1. Effect of pH

The pH of aqueous solutions is one of the most important factors to be considered for the adsorption process, since it eventually determines the surface properties of the adsorbents in terms of ionization of functional groups and surface charge. The effect of pH on the removal of Cd (II) ions from synthetic wastewater was investigated by varying the pH of metal ion solutions in the range of 3–8 (Figure 5). A gradual enhancement of the adsorption of Cd (II) ions with the increase of pH from 3 to 4 can be observed in the figure. The Cd (II) ion removal efficiency increases from 60 % to 92.8 %. At low solution pH, a large quantity of hydronium ions (H_3O^+)

in solution is expected to compete with the Cd (II) ions for binding on the functional groups of the adsorbent surface. Hence, there is a decrease in the adsorption of metal ions. On the other hand, the adsorption of metal ions increases with pH due to the decrease in the concentration of hydronium ions (H_3O^+). The slight decrease in the removal of metal ions at higher pH values is most likely due to the formation of hydroxides of Cd (II) ions.
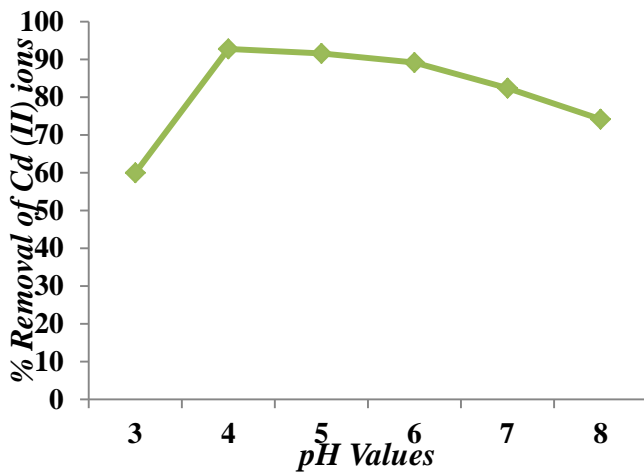

Fig. 5. Effect of pH value. C_o = 100 mg/L, SV = 100 mL, CT = 180 min, BCD = 2.5 g at 28±2 °C

3.2.2. Effect of contact time

The effect of contact time on the biosorption process is a clear indicative of the adsorption efficiency, and it also helps to determine the optimum conditions for the removal of contaminants. To estimate the adsorption capacity, it is important to allow sufficient time for the experimental system to reach equilibrium. In this work, the effect of contact time on the removal of Cd (II) ions was studied for a period of 30–210 min. As can be seen from the results depicted in Figure 6, the adsorption process steadily increases up to 180 min and then becomes slower. The progressive sorption in the initial stages of the process can be attributed to extracellular binding, and the subsequent slower sorption is likely due to intracellular binding as the biocarbon surfaces becomes mostly covered by metal ions. In fact, the metal ion uptake as a function of time is a continuous process that eventually leads to saturation, which has been attributed to the formation of a monolayer of metal ions on the surface of the adsorbent [23].

3.2.3. Effect of biocarbon dose

The effect of the biocarbon dose on the adsorption of Cd (II) ions from synthetic wastewater onto

LCBC was studied, and the results are shown in Figure 7. As can be seen, the adsorption of Cd (II) ions increases from 42.8 % to 93.5 % with increasing the adsorbent dose from 1 to 2.5 g. This increase of Cd (II) ions removal with the adsorbent dosage is due to the increase in the number of adsorption sites [24]. Further increase of the LCBC dose does not lead to any significant change in the Cd (II) ion adsorption, which can be attributed to overlapping or aggregation of adsorption sites resulting in a decrease of the total adsorbent surface area available to metal ions and an increase in the diffusion path length.
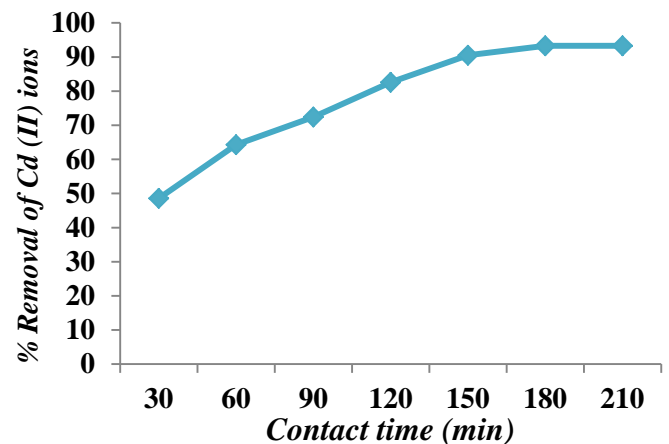

Fig. 6. Effect of contact time. C_o = 100 mg/L, SV = 100 mL, pH = 4.0, BCD = 2.5 g at 28±2 °C
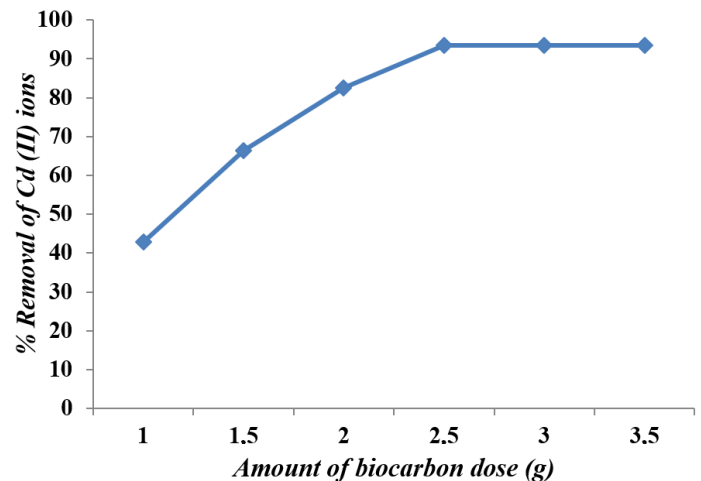

Fig. 7. Effect of biocarbon dose. C_o = 100 mg/L, SV = 100 mL, pH = 4.0, CT = 180 min at 28±2 °C.

3.2.4. Effect of initial metal ion concentration

The influence of initial metal ion concentration on the removal of Cd (II) ions was studied by varying the concentration from 10 to 100 mg/L. The results depicted in Fig. 8 show that the removal rate of Cd (II) ions increases from 40.5 % to 93.30 %. The increase in the equilibrium adsorption capacity of

the adsorbent with the metal ion concentration could be attributed to an increased rate of mass transfer due to an increased concentration of driving force. The extent of this increase is not proportional to the initial metal ion concentration, which can be explained in terms of the surface area of the substrate on which the competitive adsorption of metal ions occurs [25, 26].
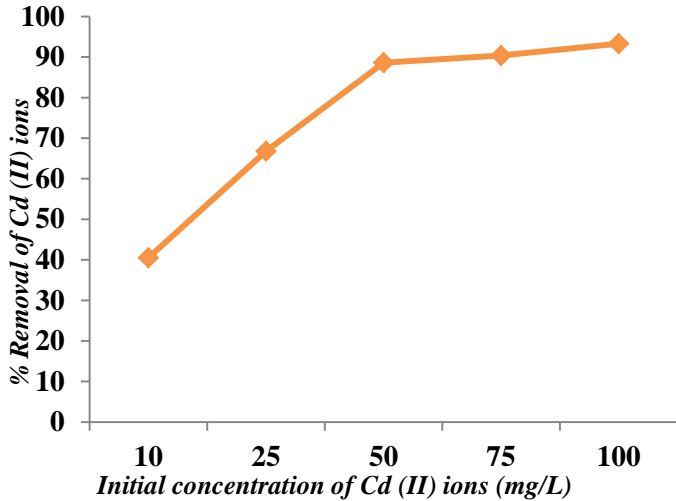

Fig. 8. Effect of initial metal ion concentration. BCD = 2.5 g, SV = 100 mL, CT = 180 min, pH = 4.0 at 28 ± 2 °C

3.3. Adsorption isotherms

The adsorption isotherms correlate the adsorbate concentration in the bulk and the adsorbed amount at the interface [27]. To obtain the adsorption isotherms, all adsorption sites are assumed to be equivalent, and the ability of a particle to bind is considered independent of the occupation or availability of adjacent sites [28]. Langmuir and Freundlich isotherms are commonly used in batch adsorption studies.

3.3.1. Langmuir model

The Langmuir adsorption isotherm describes quantitatively the buildup of a layer of molecules on an adsorbent surface as a function of the concentration of the adsorbed material in the liquid with which it is in contact. The Langmuir isotherm assumes that a monomolecular layer is formed upon biosorption, and no interaction is expected to occur between molecules (i.e., metals) adsorbed on adjacent binding sites [29]. The sorption isotherms were evaluated using the most used linearized Langmuir model, which is represented by equation (3):

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}}, \tag{3}$$

where q_e is the equilibrium metal ion concentration on the biosorbent (mg/g), q_{max} is the maximum biosorption capacity of biosorbent (mg/g), and C_e is the equilibrium concentration of the metal ion in solution (mg/L). The data obtained from the biosorption of heavy metals were analyzed using the Langmuir isotherm. The plot of C_e versus C_e/q_e gives a straight line, its slope equals to $1/q_{max}$, and the intercept can be expressed as $1/q_{max}b$, where b is the biosorption coefficient (L/mg). The q_{max} and r^2 values of Cd (II) ions were calculated from the plot depicted in Figure 9, and the results are summarized in Table 1.
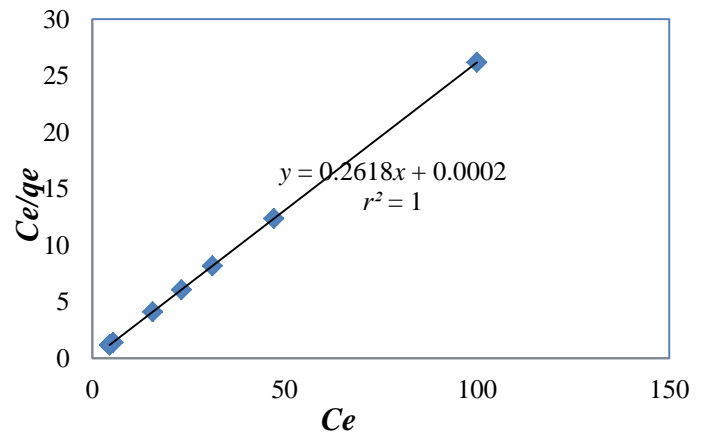

Fig. 9. Langmuir isotherm for the removal of cadmium (II) ions

3.3.2. Freundlich model

The Freundlich biosorption isotherm model is an empirical equation based on the biosorption on a heterogeneous surface. The linear form of the Freundlich biosorption isotherm can be defined by equation (4) as follows:

$$Log\ q_e = Log\ K_f + \frac{1}{n}\log C_e, \tag{4}$$

where the constant K_f is an approximate indicator of the adsorption capacity, $1/n$ is a function of the strength of adsorption in the adsorption process [30, 31], and the constant n is an empirical parameter that reflects the intensity of adsorption, which varies with the degree of heterogeneity.

The constants n and K_f were calculated by plotting log C_e against log q_e, being the slope $1/n$ and the intercept log K_f. The results are illustrated in Figure 10. The values of n lying between 1 and 10 represent a favorable adsorption. The obtained value of n is shown in Table1, and it indicates that the biosorption is a favorable process.

The Langmuir and Freundlich parameters for the removal of Cd (II) ions on biocarbon are given in

Table 1. The correlation coefficient (r^2) for the Langmuir model is high, which suggests that the adsorption of Cd (II) ions onto this adsorbent is a monolayer process, and the adsorption behavior is homogeneous rather than heterogeneous.
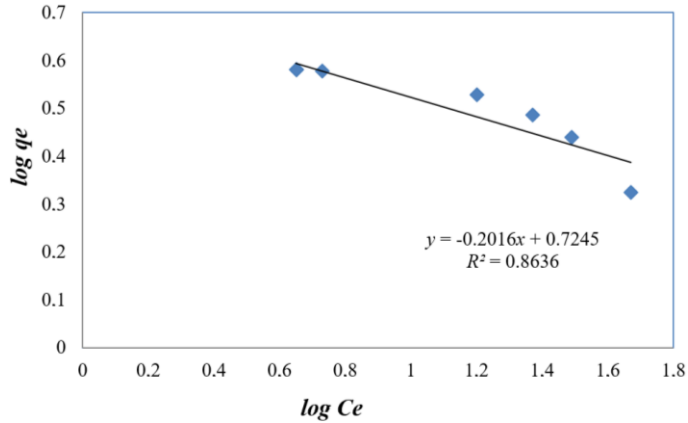

Fig.10. Freundlich isotherm for the removal of Cd (II) ions

Table 1. Langmuir and Freundlich parameters for the removal of Cd (II) ions on biocarbon.

Metals	Langmuir parameters		Freundlich parameters		
	q_{max} (mg/g)	r^2	K_f (mg/g)	n	r^2
Cd(II)	3.831	1	5.297	4.759	0.8636

3.4. Biosorption kinetics

Several kinetic models have been described to investigate the reaction order in sorption systems. However, over the past few years, the Lagergren equation has been the most widely used for the adsorption of an adsorbate from an aqueous solution [32]. This model is based on the assumption that the adsorption rate is directly proportional to the number of free sites present in the sorbent surface [33].

The kinetics of the biosorption of Cd (II) ions was studied using the pseudo-first-order and pseudo-second-order Lagergren equations. The general pseudo-first-order equation (5) can be expressed as follows:

$$\log\left(q_e - q_t\right) = \log\left(q_e\right) - \left(\frac{k_1}{2.303}\right) \qquad (5)$$

where q_e and q_t are the amounts of metal ions adsorbed onto the biocarbon (mg/g) at equilibrium and at time t (min), respectively. By plotting $\log(q_e - q_t)$ versus time t, the first-order rate constant k_1 (1/min) and the equilibrium capacity q_e can be obtained from

the slope and intercept, respectively. Meanwhile, the linear form of the pseudo-second-order chemisorption kinetics rate can be expressed by equation (6):

$$\left(\frac{t}{q_t}\right) = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{t}{q_e}\right)t. \qquad (6)$$

The constants can be determined by plotting t/q_t versus time t. The second-order rate constant k_2 (g/mg/min) and the q_e (mg/g) values can be calculated from the intercept and slope of the plot, respectively.

All the kinetic data of the respective metal ions were tested using the pseudo-first-order and pseudo-second-order rate equations. In the case of the first-order-rate equation, the data were poorly fitted, and the Lagergren correlation coefficient (r^2) value was very low. This suggests that the removal of Cd (II) ions follows only Lagergren pseudo-second-order kinetics. The results of the pseudo-second-order kinetics are shown in Figure 11.

The Lagergren parameters for the biosorption kinetics of Cd (II) ions are presented in Table 2. The pseudo-second-order model is well fitted for Cd (II) ions removal, with a correlation coefficient (r^2) for the second-order model of 0.9848.
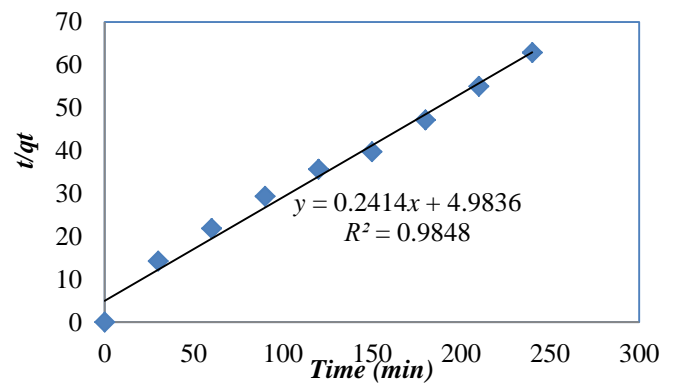

Fig. 11. Pseudo-second-order plot for the removal of Cd (II) ions

Table 2. Biosorption kinetics for the removal of Cd (II) ions on biocarbon

Metal	Second order	
	k_2 (g mg^{-1}min^{-1})	r^2
Cd(II)	1.375×10^{-2}	0.9848

A comparative evaluation of the maximum removal of cadmium (II) ions from wastewater by different biosorbents reported in the literature is given in Table 3. As can be seen, the removal of Cd (II) ions from synthetic wastewater using LCBC de-

scribed in the present research shows very good results that parallel those of other adsorbents.

Table 3. Comparative evaluation of maximum removal of Cd (II) ions from wastewater by different biosorbents

Adsorbents	Maximum removal (%)	References
African palm fruits	99.23	Sani Abdulrazak et al., 2017 [34]
Tridax procumbensbio-carbon	98.00	Singanan M. 2011 [35]
Moringastenopetala	82.70	Mataka et al., 2010 [36]
Moringaoleifera	70.70	Mataka et al., 2010 [36]
Lantana camara biocarbon	93.30	Present study

4. Conclusion

The potential use of biocarbon prepared from Lantana camara leaves as an adsorbent for the removal of Cd (II) ions from synthetic water is studied. This new biocarbon is able to remove Cd (II) ions from aqueous solution, and the sorption capacity is strongly dependent on the amount of biocarbon dosage, initial metal ion concentration, contact time, and initial pH of the solution. Langmuir model suggests that the adsorption of Cd (II) ions onto LCBC is a monolayer process and the adsorption behavior is homogeneous rather than heterogeneous. The pseudo-second-order model is well fitted for the removal of Cd (II) ions and the correlation coefficient (r^2) for the second-order model is 0.9848. The biosorption results indicate that the maximum removal of Cd (II) ions onto LCBC is 93.30 %. The biocarbon prepared from Lantana camara leaves can be successfully used as an adsorbent material for the removal of Cd (II) ions from aqueous solution even at low concentration.

References

[1] Jiwan S., Kalamdhad A.S. Effects of heavy metals on soil, plants, human health, and aquatic life. *Int. J. Res. Chem. Environ.,* 2011, vol. 1, no. 2, pp. 15–21

[2] Sprynskyya M., Buszewski B., Terzyk A.P., Namiesnik J. Study of the selection mechanism of heavy metal (Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+}) adsorption on clinoptilolite. *J. Coll. Interf. Sci.,* 2006, vol.304, no. 1, pp. 21–28. doi: 10.1016/j.jcis.2006.07.068

[3] WHO (1992) Environmental health criteria 134-cadmium international programme on chemical safety (IPCS) monograph. World Health Organization, Geneva

[4] Hooser S. B., Cadmium, Veterinary Toxicology: Edited by Ramesh C. Gupta, 2012, pp. 503–507.

[5] Babel S., Kurniawan T. A. Low-cost adsorbents for heavy metals uptake from contaminated water: A review. *J. Hazard. Mater.,* 2003, vol. 97, no. 1–3, pp. 219–243. doi: 10.1016/S0304-3894(02)00263-7

[6] Babel S., Kurniawan T. A. Cr (VI) removal from synthetic wastewater using coconut shell charcoal, and commercial activated carbon modified with oxidizing agents and/or chitosan. *Chemosphere*, 2004, vol. 54, no. 7, pp. 951–967. doi: 10.1016/j.chemosphere.2003.10.001

[7] Mohan D., Singh K. P. Single and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse–an agricultural waste. *Water Res.,* 2002, vol. 36, no.9, pp. 2304–2318. doi: 10.1016/S0043-1354(01)00447-X

[8] Khan N.A., Ali S.I., Ayub S. Effect of pH on the removal of chromium (Cr) (VI) by sugar cane bagasse. *Sci. Technol.,* 2001, vol.6, pp.13–19.

[9] Ayub S., Ali S.I., Khan N.A., Rao R.A.K. Treatment of wastewater by agricultural waste. *Environ. Prot. Control J.*, 1998, vol. 2, no. 1, pp. 5–8.

[10] Ayub S., Ali S.I., Khan N.A. Study on the removal of Cr(VI) by sugarcane bagasse from wastewater. *Pollut. Res. J.,* 2001, vol. 20, no. 2, pp. 233–237.

[11] Ayub S., Ali S. I., Khan N. A. Adsorption studies on the low cost adsorbent for the removal of Cr(VI) from electroplating wastewater. *Environ. Pollut. Control J.*, 2002, vol. 5, no. 6, pp. 10–20.

[12] Srinivasan K., Balasubramaniam N., Ramakrishna T.V. Studies on chromium removal by rice husk carbon. *Indian J. Environ. Health.*, 1988, vol. 30, no. 4, pp. 376–387.

[13] Munaf E., Zein R. The use of rice husk for removal of toxic metals from wastewater. *Environ. Technol.*, 1970, vol. 18, pp. 359–362

[14] Ajmal M., Rao R.A.K., Anwar S., Ahmad J., Ahmad R. Adsorption studies on rice husk: removal and recovery of Cd (II) from wastewater. *Bioresour. Technol.*, 2003, vol. 86, no. 2, pp. 147–149. doi: 10.1016/S0960-8524(02)00159-1

[15] Suemitsu R., Venishi R., Akashi I., Nakano M. The use of dyestuff-treated rice hulls for removal of heavy metals from waste water. *J. Appl. Polym. Sci.,* 1986, vol. 31, no. 1, pp. 75–83. doi: 10.1002/app.1986.070310108

[16] Ajmal M., Rao R.A.K., Siddiqui B.A. Studies on removal and recovery of Cr(VI) from electroplating wastes. *Water Res.*, 1996, vol. 30, no. 6, pp.1478–1482. doi: 10.1016/0043-1354(95)00301-0

[17] Kadirvelu K., Kavipriya M., Karthika C., Radhika M., Vennilamani N., Pattabhi S. Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solution. *Bioresour. Technol.,* 2003, vol. 87, no. 1, pp. 129–132. doi: 10.1016/S0960-8524(02)00201-8

[18] Selvi K., Pattabhi S., Kadirvelu K. Removal of Cr(VI) from aqueous solution by adsorption onto activated carbon. *Bioresour. Technol.*, 2001, vol. 80, no. 1, pp. 87–89. doi: 10.1016/S0960-8524(01)00068-2

[19] Tan W.T., Ooi S.T., Lee C.K. Removal of Cr(VI) from solution by coconut husk and palm pressed fibre. *Environ. Technol.,* 1993, vol. 14, pp. 277–282.

[20] Ayub S., Ali S. I., Khan N. A. Efficiency evaluation of neem (Azadirachta indica) bark in treatment of industrial wastewater. *Environ. Pollut. Control. J.,* 2001, vol. 4, no. 4, pp. 34–38.

[21] Yang T., Lua A. C. Characteristics of activated carbons prepared from pistachio-nut shells by physical activation. *J. Colloid Interface Sci.,* 2003, vol. 267, no.2, pp. 408–417 doi: 10.1016/S0021-9797(03)00689-1

[22] Shriner R.L., Hermann C.K.F., Morrill T.C., Curtin D.Y., Fuson R.C. The systematic identification of organic compounds, 7th ed. New York, Wiley, 1997, 604 p.

[23] Pimentel P.M., Melo M.A.F., Melo D.M.A., Assução A.L.C., Henrique D.M., Silva Jr C.N., González G. Kinetics and thermodynamics of Cu(II) adsorption on oil shale wastes, *Fuel Process. Technol.,* 2008, vol. 89, no. 1, pp. 62–67. doi: 10.1016/j.fuproc.2007.07.003

[24] Garg U.K., Kaur M.P., Sud D., Garg V. K. Removal of hexavalent chromium from aqueous solution by agricultural waste biomass. *J. Hazard. Mater.,* 2007, vol. 140, no. 1–2, pp. 60–68. doi: 10.1016/j.jhazmat.2006.06.056

[25] Ho Y.S., Chiang C.C., Hsu Y.C. Sorption kinetics for dye removal from aqueous solution using activated clay. *Sep. Sci. Technol.,* 2001, vol. 36, no. 11, pp. 2473–2488. doi: 10.1081/SS-100106104

[26] Mckay G., Otterburn M.S., Sweny A.G. Surface mass transfer processes during colour removal from effluent using silica. *Water Res.,* 1981, vol. 15, no. 3, pp. 327–331. doi: 10.1016/0043-1354(81)90036-1

[27] Demirbas O., Alkan M., Dogan M. The removal of victoria blue from aqueous solution by adsorption on a low-cost material. *Adsorption,* 2002, vol. 8, no. 4, pp. 341–349. doi: 10.1023/A:1021589514766

[28] Shukla S.S., Yu L.J., Dorris K.L., Shukla A. Removal of nickel from aqueous solutions by sawdust. *J. Hazard. Mater.,* 2005, vol. 121, no. 1–3, pp. 243–246. doi: 10.1016/j.jhazmat.2004.11.025

[29] Liu H.L., Chen B.Y., Lan Y.W., Cheng Y.C. Biosorption of Zn(II) and Cu(II) by the indigenous Thiobacillus thiooxidans. *Chem. Eng. J.,* 2004, vol. 97, no. 2–3, pp. 195–201. doi: 10.1016/S1385-8947(03)00210-9

[30] Voudrias E., Fytianos F., Bozani E. Sorption description isotherms of dyes from aqueous solutions and waste waters with different sorbent materials. *The Int. J. Global Nest,* 2002, vol. 4, no. 1, pp.75–83.

[31] Dada A.O., Olalekan A.P., Olatunya A.M., Dada O. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn^{2+}unto phosphoric acid modified rice husk. *IOSR J. App. Chem.,* 2012, vol. 3, no. 1, pp. 38–45. doi: 10.9790/5736-0313845

[32] Ho Y.S. Citation review of Lagergren kinetic rate equation on adsorption reactions. *Scientometrics,* 2004, vol. 59, no. 1, pp. 171–177. doi: 10.1023/B:SCIE.0000013305.99473.cf

[33] Ata S., Din M.I., Rasool A., Qasim I., Ul Mohsin I. Equilibrium, thermodynamics, and kinetic sorption studies for the removal of coomassie brilliant blue on wheat bran as a low-cost adsorbent. *J. Anal. Meth. Chem.,* 2012, vol. 1, no. 1, Article number 405980, doi: 10.1155/2012/405980

[34] Abdulrazak S., Hussaini K., Sani H.M. Evaluation of removal efficiency of heavy metals by low-cost activated carbon prepared from African palm fruit. *Appl. Water Sci.,* 2017, vol. 7, no. 6, pp. 3151–3155. doi 10.1007/s13201-016-0460-x

[35] Singanan M. Removal of lead(II) and cadmium(II) ions from wastewater using activated biocarbon. *ScienceAsia.,* 2011, vol. 37, no. 2, pp. 115–119. doi: 10.2306/scienceasia1513-1874.2011.37.115

[36] Mataka L.M., Sajidu S.M.I., Masamba W.R.L., Mwatseteza J.F. Cadmium sorption by moringa stenopetala and moringa oleifera seed powders: Batch, time, temperature, pH, and adsorption isotherm studies. *Int. J. Water. Res. Env. Eng.,* 2009, vol. 2, no. 3, pp. 50–59.