Adsorption of Cadmium from Aqueous solution using Leonardite-Bentonite Ceramic as Adsorbent

Sairoong Ouypornkonchakorn, Jintana Klamtet*

Department of chemistry, Faculty of Science, Naresuan University, Muang, Phitsanulok 65000, Thailand

*Corresponding author. E-mail: jintanakl@nu.ac.th

ABSTRACT

The leonardite-bentonite ceramic (LBC) was prepared and used in batch adsorption experiments in order to remove cadmium from aqueous solution. The prepared LBC was characterized by FTIR and BET surface area. The effect of various parameters on adsorption process such as pH, contact time and amount of LBC was carried out at room temperature to optimize the conditions for maximum adsorption. The optimum pH of cadmium adsorption onto 0.30 g of LBC was found to be 7 with a contact time 120 min. The kinetic results of adsorption indicated that the adsorption of cadmium onto LBC fitted with pseudo-second order model. The equilibrium adsorption data for cadmium was better fitted to Freundlich isotherm model which the Freundlich empirical constants, K, was 2.224 mg L^{-1} cadmium. Finally, the application studies carried out using industrial wastewater sample. The results found that LBC was applied successfully for cadmium removal from wastewater sample at cadmium concentration below 10 mg L^{-1}.

Keywords : leonardite, adsorption, cadmium, isotherm

INTRODUCTION

Nowadays the contamination of heavy metals into the environment is a significant concern because of their toxicity impacts human health and ecosystems. Cadmium (Cd) is one of the most hazardous metal even at low concentration because it effects on human health including nausea, vomiting, diarrhea, muscle cramp, salivation, reduction of red blood cells, loss of calcium from bones, yellow coloration of teeth, hypertension, damage to kidneys, liver and lungs (Silva, Roldan et al., 2009, 1133; Javadian, Ghorbani et al., 2015, 838; Naiya, Bhattacharya et al., 2009, 14). Cadmium can be introduced into natural water resources by wastewater from industries such as metallurgical alloying, ceramics, metal plating, tanneries, batteries, paper, pesticide, and sewage sludge (Javadian, Ghorbani et al., 2015, 838; Naiya, Bhattacharya et al., 2009, 14). According to these information, the World Health Organization (WHO) has established the maximum allowable limit of cadmium in drinking water smaller than 5 µg L^{-1} (WHO, 1996) and the Indian standard code IS 10500 has set the tolerance limits for cadmium concentration discharged to inland surface and public sewers as 2.00 and 1.00 mg L^{-1} (Naiya et al., 2009, 14; Ahali Abadeh and Irannajad, 2017, 318), respectively.

For this reason, the removal of cadmium from aqueous solution was investigated by many researchers. The method for this metals removal such as

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precipitation (Ennaassia et al., 2002, 101; Abu-El-Halawa and Zabin, 2017, 58), ion exchange (Bai and Bartkiewicz, 2009,1191; Dąbrowski et al., 2004, 91), adsorption (Javadian et al., 2015, 837; Naiya et al., 2009, 14; Lao et al., 2005, 79) and ultrafiltration (Jellouli Ennigrou et al., 2009, 363). Among various method described, the adsorption method is generally preferred for the removal of heavy metal ions due to its easy handling, high efficiency, availability of different adsorbents and cost effectiveness (Javadian et al., 2015, 838; Lao et al., 2005, 79; Zheng et al., 2007, 534). Recently, using low cost natural and inexpensive adsorbents which used to be considered as waste have been interested in removal of cadmium from aqueous solution. Leonardite is low cost material and naturally occurred in conjunction with deposits of lignite (Srisomang et al., 2014, 1622). This material was widely applied for remediation of wastewater (Lao et al., 2005, 79; Solé et al., 2003, 57). In addition, bentonite is a natural clay and low cost adsorbent which found abundant in nature (Manohar et al., 2006, 195). Bentonite has a 2:1 layer structure and it consists of two tetrahedrally coordinated sheets of silicon surrounding and an octahedrally coordinated sheet of aluminium ions (Manohar et al., 2006, 195; Mockovčiaková and Orolínová, 2009, 47). It was used as a binder for ceramic slurry at room temperature and the sintering additive at elevated temperature (Acton, 2012, 35). The increase in amount of bentonite addition gives higher strength of ceramic performs (Acton, 2012, 35). So, many researchers have studied on leonardite and leonardite char as low cost adsorbents for removal cations in water and gas (Manohar et al., 2006, 195; Mockovčiaková and Orolínová, 2009, 47; Acton, 2012, 35). However, there is a few reports on improve leonardite effectiveness as a ceramic material. Therefore, this work was focusing on leonardite-bentonite ceramic (LBC) as adsorbent for cadmium removal in aqueous solution. This adsorption of cadmium carried out in a series of the batch experiments. The adsorption parameters such as pH, contact time and cadmium concentration were investigated. The adsorption capacities are also studied by adsorption isotherms.

EXPERIMENTAL

Materials

All Chemicals used were analytical reagent grade. An appropriated dilutions of cadmium solution were freshly prepared from 1000 mg L^{-1} cadmium (Loba chemie, India) stock standard solution and adjusted volume with deionized water. HNO_3 2.0 mol L^{-1} (70% RCI Labscan) or NaOH 2.0 mol L^{-1} (RCI Labscan) was used to adjust pH value of solution.

Preparation of adsorbent

Leonardite sample used in this study was collected from Mae Moh lignite mine in Lampang province, Thailand. Sample was cleaned, ground and sieved through a grain size 75-149 μm. Commercial bentonite was used as receive from purchased. The 90% of leonardite sample was mixed with 10% bentonite into small amount of water and molded in a small piece (~2 mm length) by squeeze cake. Then, the leonardite-bentonite ceramic (LBC) was heated at 60, 80 and 200 °C for an hour each before carbonization at 600 °C (2 °C/min) for 1 hour.

Materials characterization

FTIR (Perkin Elmer Frontier with ATR) data of LBC were collected in the transmission mode over the range of 4000-400 cm^{-1} at room temperature. The surface area and pore volume (BET) of LBC were determined by Micromeritics model TriStar II 3020 (Germany) using decomposition temperature 300°C.

Batch adsorption experiments

The adsorption of cadmium by LBC was carried out in batch experiment. The optimum parameters of cadmium adsorption were studied by adding 0.30 g LBC to flask containing 50 mL of 10 mg L^{-1} cadmium solution at pH 7 and stirred at rate 625 rpm for 30 min. Then, the aqueous solution was filtered through Whatman paper no.5 and the remaining concentration of cadmium was determined by atomic absorption spectrometer (Varian Spectra AA220) with an air–acetylene flame. The instrument was calibrated using cadmium standard solution in the range of 0.05-1.00 mg L^{-1}. The adsorbed amount of cadmium was calculated from difference between initial concentration of cadmium and its concentration in the filtrate.

The effects of various parameters for cadmium removal by LBC such as pH, contact time and amount of LBC were investigated. The adsorption capacity of LBC for cadmium was studied under optimum parameters in solutions from 3 to 50 mg L^{-1} Cd concentration in 0.30 g LBC.

RESULTS AND DISCUSSION

Characteristics of adsorbent

The FTIR spectra of parent leonardite, bentonite and LBC are presented in Fig. 1. As can be seen from the results, the absorption band of leonardite at ~3698 and 3621 cm^{-1} assigns to hydroxyl group (Si-OH, Al-OH). The absorption band at 2923 and 2852 cm^{-1} corresponds to symmetric and asymmetric stretching of aromatic and aliphatic C-H bonding. In addition, the band at 1619 and 1428 cm^{-1} were related to C=C stretching in aromatic ring (Ausavasukhi et al., 2016, 508). This confirms the organic substance and aromatic molecule in the structure of leonardite (Olivella et al., 2011, 795). The FTIR band of bentonite at 3617 cm^{-1} are vibration of Si-OH groups of silica and OH groups of adsorbed water. The band at 1634 cm^{-1} belongs to O-H stretching of H_2O molecule. The broad intense band at about 1000 cm^{-1} assigns to Si-O-Si of SiO_4 tetrahedra in the silicon–oxygen framework and the band at 794 cm^{-1} corresponds to vibrations of silanol groups (Alekseeva et al., 2017). The FTIR spectrum of LBC shows the band at ~1435 cm^{-1} which could be represented to C=C stretching of aromatic substance. The broad intense band near 1000 and 470 cm^{-1} of Si-O-Si of clay mineral and of Si-O-Si bending (Sathya et al., 2012, 778) were observed. This could be the LBC properties as ceramic material. The BET data of leonardite and LBC in Table 1 show that the surface area and pore volume of LBC higher than leonardite because the minerals in leonardite were transformed to char to give the micro-sized (Chammui et al., 2014, 2379). Therefore, this is confirmed that

LBC could be used as adsorbent for adsorption of cadmium in aqueous solution due to its high surface area and pore volume for adsorption of cadmium in the aqueous solution.

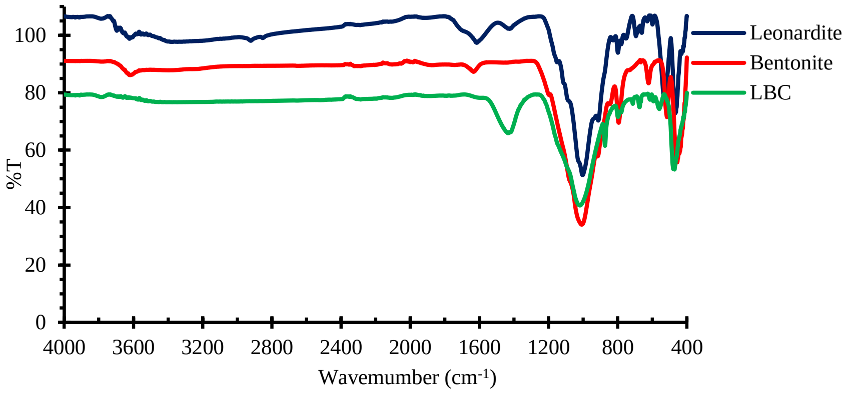

Fig. 1. FTIR spectra of leonardite, bentonite and leonardite-bentonite ceramic (LBC)

Table 1 BET surface area, pore volume and pore size of leonardite and leonardite-bentonite ceramic (LBC)

	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
Leonardite	19.3	0.065	3.47
LBC	29.3	0.081	11.08

Adsorption experiments

1) Effect of pH

The pH of the aqueous solution is one of important parameters in the adsorption process. The adsorption of cadmium onto LBC was investigated by carrying out the experiment at pH from 2 to 9 for 30 min of contact time. The adsorption data show in Fig. 2. The removal efficiency of cadmium actually increased when the pH increased with a maximum at pH 7. This could be due to the competition between protons and cadmium ions for exchange site on the surface of LBC (Zengin, 2013, 3036; Lao-Luque, et al., 2014, 129). Thus the adsorption efficiency of cadmium was low below pH 7. As the pH higher than 7, the percentage of adsorption slightly decreased because partial of cadmium was eliminated by precipitation as $Cd(OH)_2$. Therefore, the pH 7 was used for further experiments.

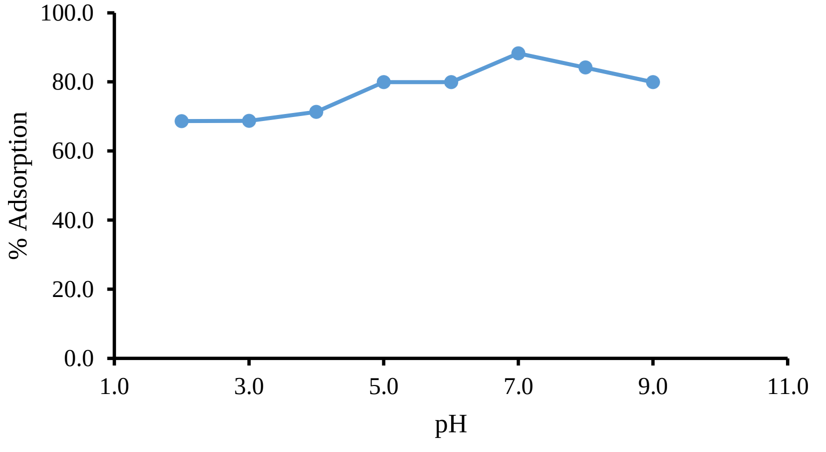

Fig. 2. Effect of pH of aqueous solution for cadmium adsorption onto LBC

Condition: [Cd] = 10 mg L^{-1}, LBC = 0.10 g, Time 30 min, Volume of Cd = 50.00 mL

2) Effect of contact time

The effect of stirring time on adsorption of cadmium was studied using initial cadmium concentration of 10 mg L^{-1} and the results are presented in Fig. 3. As can be seen from the results, LBC removed about 80% of cadmium concentration in the solution in the first 10 min and the adsorption reached the equilibrium in 60 min. This could be attributed to instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface (Lao et al., 2005, 81). Therefore, this study used stirring time at 120 min to be sure that full equilibrium was obtained.

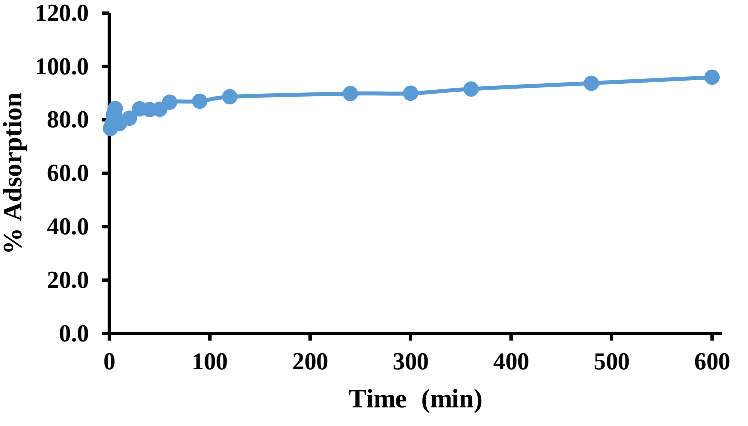

Fig. 3. Effect of contact time on the adsorption of cadmium onto LBC

Condition: [Cd] = 10 mg L^{-1}, LBC = 0.10 g, pH =7, Volume of Cd = 50.00 mL

3) Effect of amount of LBC

The effect of LBC amount on the adsorption of cadmium was studied while keeping the concentration and volume of cadmium solution (10 mg L^{-1} Cd and 50 mL) constant as shown in Table 2. It can be observed that the adsorption efficiency slightly increased with increasing amount of LBC. This possibly caused by the surface of LBC was increased. In order to achieve high adsorption efficiency when cadmium concentration was higher than 10 mg L^{-1}, the 0.30 g of LBC was chosen as a study parameter.

Table 2 The effect of LBC amount on the adsorption of cadmium

Amount of LBC (g)	%Adsorption
0.10	87.85 ± 0.13
0.20	89.61 ± 0.01
0.30	92.04 ± 0.04
0.50	92.20 ± 0.03

4) Adsorption kinetics

The kinetic of adsorption of cadmium in aqueous solution onto LBC was analyzed using pseudo-first order and pseudo-second order models. The pseudo-first-order kinetic was proposed by Lagergren (Gusmão et al., 2013, 141; Zengin, 2013, 3039) based on solid capacity. This equation applies for sorption of liquid/solid system which the rate of change that occurred in sorbate uptake with the passage of time is directly proportional to the difference in the saturation concentration and the rate of solid uptake with time (Javadian et al., 2015, 842). The Lagergren equation is the most commonly used rate equation in liquid phase sorption (Javadian et al., 2015, 842). The pseudo-first order equation of Lagergren in linear form (Gusmão et al., 2013, 141; Zengin, 2013, 3039) is given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (1)$$

Where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amount of cadmium adsorbed on the adsorbent at equilibrium and time t, respectively; k_1 (min^{-1}) is the pseudo first-order rate constant which can be obtained from linear regression analysis of equation (1). The pseudo-second order kinetic model involves chemisorption, where the removal from a solution is due to physicochemical interactions between the two phases (Wang et al., 2007, 278) is presented by Ho and McKay (Gusmão et al., 2013, 141; Zengin, 2013, 3039) as:

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

Where k_2 (g mg^{-1} min^{-1}) is the pseudo second-order rate constant. It can be noted that k_2 and q_e can be obtained from the linear regression analysis of equation (2).

The experiment data were calculated and collected in Table 3. As can be seen from Table 3, the R^2 value derived from the pseudo-second order model was 0.9991, as well as the good agreement of $q_{e(cal)}$ (1.571 mg g^{-1}) and $q_{e(exp)}$ (1.563 mg g^{-1}) confirming that the adsorption data are well fitted with pseudo-second order kinetics. This indicated that the rate-limiting step may be chemical sorption involving valence forces to sharing or exchange of electron between sorbent and sorbate (Lao-Luque et al., 2014, 130). The linear plot of pseudo second-order model of cadmium shows in Fig. 4.

Table 3 Parameters of pseudo-first and pseudo-second order for the adsorption of cadmium onto LBC

Model	Parameters	Value
pseudo-first order	k_1 (min^{-1})	-5.76×10^{-2}
	$q_{e,cal}$ (mg g^{-1})	5.28×10^{-3}
	R^2	0.9047
Pseudo second-order	k_2 (g/ mg min)	1.816×10^{-1}
	$q_{e,cal}$ (mg g^{-1})	1.571
	R^2	0.9991
	$q_{e,exp}$ (mg g^{-1})	1.563

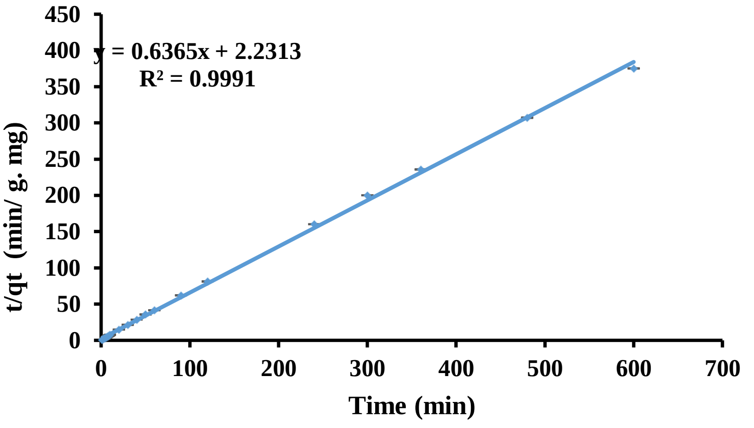

Fig. 4. Pseudo second-order plot for the adsorption of cadmium onto LBC (N=3)

5) Adsorption isotherm

The experiment data of cadmium adsorption on LBC were fitted with the Langmuir and Freundlich models. The Langmuir equation is based on assuming monolayer coverage of adsorbate on a homogeneous surface of adsorbent with a finite number of identical sites (Gusmão et al., 2013, 140; Langmuir, 1918, 1361-1403). This equation is often represented in the form as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_{max} b} + \frac{C_e}{Q_{max}} \qquad (3)$$

Where C_e is the cadmium concentration at equilibrium (mg L^{-1}), q_e is the amount of metal ion adsorbed per specific amount of LBC (mg g^{-1}), Q_{max} is the maximum amount of adsorption metal ions (mg g^{-1}), b is adsorption Langmuir constant (L mg^{-1}). The linear plot of C_e/q_e versus C_e (Fig. 5) was employed to determine the value of Q_{max} and b from the intercept and the slope of the plot (Naiya et al., 2009, 22; Gusmão et al., 2013, 140).

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems in which it is characterized by the heterogeneity factor, n (Naiya et al., 2009, 22). The Freundlich equation can be linearized in logarithmic form as Eq. (4)

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (4)$$

Where K_F is represented the adsorption capacity and n indicated the intensity of adsorption according to Freundlich equation. The constants K_F and n were calculated from Eq. (4) and Freundlich plots (Fig. 6) (Javadian et al., 2015, 845). The values of n between 1 and 10 (i.e. 1/n less than 1) represent a favorable adsorption (Naiya et al., 2009). The value of Langmuir and Freundlich constants and correlation coefficients (r^2) are shown in Table 4.

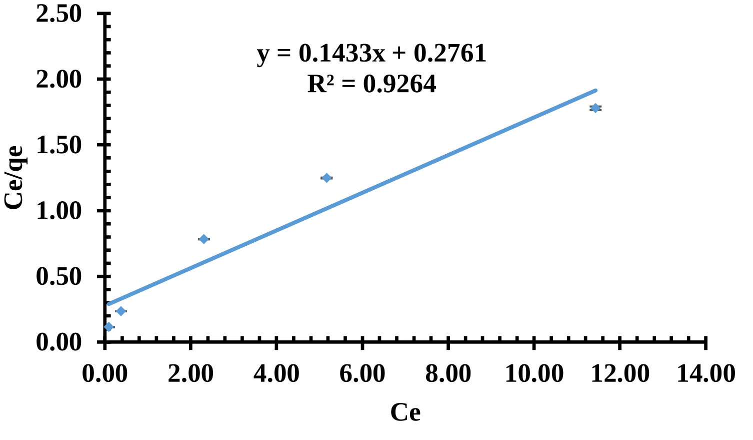

Fig. 5. Langmuir adsorption isotherm of cadmium onto LBC (N=3)

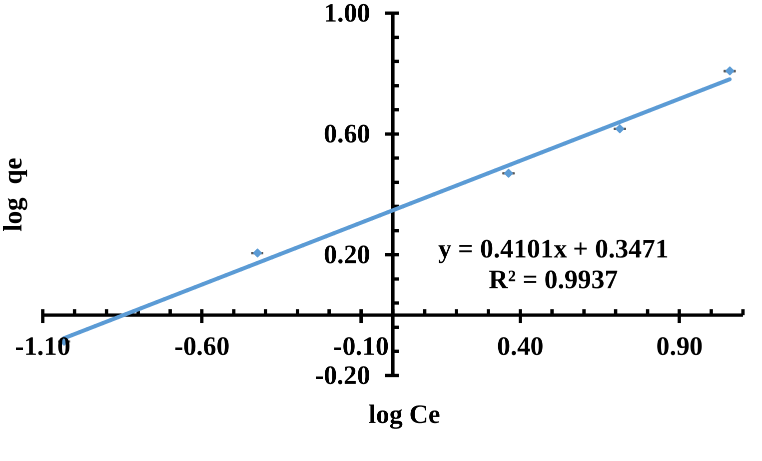

Fig. 6. Freundlich adsorption isotherm of cadmium onto LBC (N=3)

Table 4 Langmuir and Freundlich adsorption isotherm constants and correlation coefficients for cadmium adsorption onto LBC

Langmuir			Freundlich		
Q_{max} (mg g^{-1})	b (L^{-1} mg)	r^2	K_F (L^{-1} mg)	n	r^2
6.98	0.519	0.9264	2.224	2.438	0.9937

From Table 4, it is seen that the adsorption of cadmium onto LBC are better fitted Freundlich than Langmuir adsorption isotherm. This indicated that the adsorption involves heterogeneous surface energy system with interaction between the molecules adsorbed and adsorbent (Al-Ghouti et al., 2009, 592; Azlina et al., 2013, 39). The value of n = 2.438 and 1/n = 0.4101 indicate that the physical process is favorable (Azlina et al., 2013, 42).

Application studied of cadmium adsorption from industrial wastewater

The industrial wastewater was collected from paint manufacturing. Batch adsorption experiment carried out using optimum parameters. The 10.00, 50.00 and 100.00 mg L^{-1} of cadmium standard solution was added into a wastewater sample before adsorption. The results of sample adsorption were shown in Table 5. It was found that the percentage of cadmium adsorption was between 92 and 54%. This indicated that cadmium was successfully removed from wastewater using LBC at cadmium concentration below 10 mg L^{-1}.

Table 5 Application studies of cadmium in wastewater sample using LBC as adsorbent

Concentration of Cd (mg L^{-1})		% Adsorption
Initial	Final	
10.03	9.294	92.62
50.03	13.25	73.52
100.03	45.15	54.86

CONCLUSION

In this work, the LBC prepared from leonardite shows more surface area and pore volume than parent leonardite. The batch adsorption experiment for cadmium removal from aqueous solution was performed using LBC as adsorbent with respect to different experimental parameters including pH, contact time and adsorbent amount. The optimum parameters of cadmium adsorption were as follows: 0.30 g of LBC in 50 mL of cadmium solution at pH 7 and contact time 120 min. The kinetic studied showed that adsorption of cadmium was found to follow pseudo second-order model. Moreover, the adsorption isotherm investigations found that Freundlich isotherm model was proved to be the best in fitting the adsorption process. The study on batch adsorption using industrial wastewater indicated that LBC has a good potential to remove cadmium from wastewater sample at cadmium concentration below 10 mg L^{-1}.

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