



## Kinetic and thermodynamic analysis on the abolition of toxic metals from wastewater using activated carbon produced from compost waste

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### ABSTRACT

The effect of various bulking agents for the compost of municipal organic waste was examined for a total of 45 d in the compost plant. To minimize the initial moisture content (70%–75%) of vegetable waste in the composting pile, the selective bulking agents namely air-dried chana husk, wood shaving, Jamun dry leaves and bagasse were added. After the stipulated period, the mature compost was aimed to produce active carbons based on the carbon/nitrogen ratio observed every week. Owing to conversion, the dual treatment of acidic bath ( $H_2SO_4$ ) and ultrasonication were executed. It has resulted in the upliftment of carbon yield from 41.57% to 72.24%. Such amorphous carbon was found thermally stable with a weight loss of around 51.87% at 560°C. The surface characteristics of produced carbon seem conceivable for the removal of cadmium ions from the aqueous solution. Thus, the Langmuir adsorption capacity of 72.99 mg g<sup>-1</sup> is favorable; thermodynamic properties of the current system are exothermic and spontaneous.

*Keywords:* Organic waste; Composting; Activated carbon; Cd(II) ions; Thermodynamics; Kinetics

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### 1. Introduction

India is the second-largest nation in the world with a population of 1.33 billion; being the largest producer of municipal solid waste (MSW) [1]. The MSW crisis is customarily due to the improper addressing of MSW and their crucial management, the sustainability of landfills, increased volumes of MSW consuming finite landfill space, incineration of MSW residues and their reuse without adequate treatment [2]. In concern with developing economy, an environmental standard related to MSW must be regulated by providing a classification of MSW, characterization and portion of which underlying one of the three ways: landfilling; recycling and

incineration [3]. These practices can keep our environment away from toxic and heavy metal elements. On the other hand, an illegal or prohibited practice of open dumping seems existing; and more susceptible to the public who resides in filthy, marshy areas with a high risk of health hazards. Combined, all hygienic and ecological risks connected with open dumping are life-threatening [4] as well lead to produce secondary toxic waste such as elements, vectors and scavengers [5]. Therefore, it is recommended to make public awareness and participation in a critical waste management program based on stringent legislation. Technical support might be offered to the public for conceiving a proper understanding of waste management issues [6]. A

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successful waste management program begins at the collection and transportation of waste underlying institutional policies, environmental and legal aspects of converting them to a secondary valuable product by utilizing operational facilities [7].

Among various methods, traditional composting is one of the finest options whereas the organic matter of final compost ensures chemical, physical and biological characteristics [8]. For instance, the C content of compost (carbon) plays a crucial role in the greenhouse gas mitigation strategy [9] in order to prevent erosion and to improve soil quality [9]. Such quality improved compost as a fertilizer either in pellet form [10] or powder contributes nutrient to the advantageous microbes; helps the soil to hold moisture [11]; reduces water run-off; adsorbs toxic pollutants by preventing them from migrating to water resources [12]. Significantly, it also avoids the formation of leachate [13] and the production of methane in a landfill [14].

A promising approach of composting is an aerobic process [15] that involves the decomposition of organic matter under controlled temperature, moisture [16] oxygen and nutrient conditions, pathogens [17]. With the pH balance, compost can maintain the temperature of soil according to the pathogen's surveillance [18]. Yet, putrefaction is a negative sign of the compost pile [19] that can be avoided by adding extra amendments [20] which are often called bulking agents (BA) [21]. They are sufficient in size, providing structural support and airspace [22] within the composting matrix. As they are rich in carbon content, the increase of void between the interparticle of the composting system [23] is possible. But the end product is reliable on the selection of BA considerably based on age and size [24].

The present work focused on the characterization of MSW collected from the compost plant. The effect of various BAs (air-dried chana husk, wood shaving, Jamun dry leaves, bagasse) on the final compost had studied with possible process influencing parameters. The stability of compost was determined using a carbon/nitrogen (C/N) ratio for further surface modification in order to produce active carbons. The application of surface-modified compost for the removal of Cd(II) ions in the aqueous solution was examined. From experimental data, it is observed that the surface-modified compost can be a potential adsorbent.

## 2. Materials and methods

### 2.1. Collection and segregation of organic waste

The local study area in Nagpur, India merely consists of 250 families with a population of 1,000 people. The MSW was collected from the study area which accounts for 250–300 g/cap/d. Further, the MSW collected within 3 d of disposal in the colony has transferred to the composting plant, where, it is divided into organic and inorganic waste as per requirement. The non-degradable waste is rerouted to Nagpur Municipal Corporation for a safe combustion facility or landfill. In order to obtain a quality compost, the following BA such as air-dried chana husk (CH), wood shaving (WS), Jamun dry leaves (DL) and bagasse (BG) were used after collecting from the locally available market. The shredding of BA is recommended with the mass ratio (OW:BA) calculated below.

$$R = \frac{G_B}{G_F} \quad (1)$$

$$G_B = \frac{(M_F \times G_F - M_M \times G_F)}{M_M - M_B} \quad (2)$$

where  $R$  is the cycling ratio;  $G_B$  is the wet mass of bulking agent (g);  $G_F$  is the wet mass of initial feedstock (g);  $M_B$  is the moisture content of the bulking agent (%);  $M_F$  is the moisture content of feedstock (%) and  $M_M$  is the set point of moisture content of bulking agent and feedstock (%).

From the aforementioned formula, the proportionate of 7:2 (OW:BA), that is, 2 kg of each bulking agent was added to 7 kg of feedstock containing in an unbreakable plastic tub with a dimension of 424 mm × 424 mm × 225 mm (approximate). Five different sets of composting piles were made in the following order, that is, organic waste with each bulking agent namely wood shaving (set 1), bagasse (set 2), chana husk (set 3) and Jamun dry leaves (set 4), respectively. Organic waste without a bulking agent was labeled as control or set 5 for comparing the subsequent experimental variables.

### 2.2. Compost influencing parameters

The temperature of a different set of composting pile was monitored for a total period of 45 d using a digital temperature analyzer at 10.30 a.m. The bins used were circular and open pile for aerobic decomposition. The arrangement of these circular piles on the surface was easy to record temperature from four different points marked in the container based on radius. The temperature inside the compost includes four corners and a center of the pile. An average temperature of five marked places was considered to analyze the effect of composting variables. Likely, the pH and electrical conductivity (EC) of the compost pile was examined. For which, 1:10 w/v (dry weight basis) of a suspension containing 5 g of well-ground compost in 50 mL of distilled water was prepared. Then, this suspension was kept aside for half an hour with occasional stirring. Using the pH meter and electrical conductivity analyzer (EUTECH Instrument PC 510 m, Singapore), the transport of an electric charge in the composting pile was observed on a weekly basis. To determine the dry matter (DM) and moisture content of the composting pile, the samples were kept for oven drying at 105°C for 24 h. The following formulae were used.

$$\text{Dry matter \%} = \left( \frac{\text{Oven dry sample weight}}{\text{Wet sample weight}} \right) \times 100 \quad (3)$$

$$\text{Moisture content \%} = 100 - \% \text{ of dry matter} \quad (4)$$

The simplest natural aeration was given to the composting pile as no extra installation is required. The bulk density (BD) of the composting pile defines the weight of composting material per volume, which is usually expressed in kilograms per cubic meter. This had been calculated for every once in 4 d. For which, a 10 cm × 10 cm of the cubic box was prepared

instantly (Fig. S1). The manual occupancy of compost in a cubic box was determined by handy tap and handy compression with minimal pressure.

Wet particle density was analyzed using a graduate cylinder containing 5 g of compost which is later allowed to submerge in kerosene. An initial density of kerosene was marked to know the mass of how much kerosene is additionally added [25]. Similarly, the abundance of carbon, hydrogen, nitrogen, and sulfur in compost was noted using the carbon hydrogen nitrogen sulphur (CHNS) analyzer. Indeed, the C/N ratio of compost after amendment may indicate their suitability to soil [15,18].

### 2.3. Preparation of activated carbon from compost

The solid organic waste (OW) compost as a carbonaceous supplement was aimed to convert as active carbons. In order to improve the carbon yield and surface characteristics, the strategy of dual surface modification was attempted as previously reported [26]. A simple series of activation was carried out for 42 mesh particle sized compost using  $H_2SO_4$  ( $H_2SO_4$  97% P.A. Sigma-Aldrich, United States) in 2:1 mass proportion as chemical activation followed by ultrasonication for oxidation. The required amount of  $H_2SO_4$  treated material and  $dH_2O$  (mL) in 1:10 (w/v) was subject to 24 kHz ultrasonic waves at 500 rpm for 30 min. By generating high local temperature and pressure around 5,000 K and 500 atm with heating and cooling rates greater than 109 K/s, the water molecules are broken down, converted to hydrogen and hydroxyl radicals. This is how activated carbon as pores suspended solids in the aqueous solution is promoted for the interparticle collision at high velocity. The sample withdrawn from sonication was filtered; dried at 40°C for 12 h in a hot air oven and further used for batch adsorption experiments. The resultant is called as activated carbon (AC) to play the role of the inexpensive adsorbent.

### 2.4. Characterization of an adsorbent

The surface morphology was examined by scanning electron microscope (JEOL-JSM-5610LV INCA EDS, Japan). The total carbon yield was confirmed by energy-dispersive X-ray spectrometers (EDX) analysis. The surface functional compounds of AC were examined by Fourier-transform infrared spectroscopy (FTIR), (Perkin Elmer FTIR C 100566, Chennai, India). X-ray diffraction (XRD) and thermogravimetric analysis (TGA) were carried out in order to determine the crystalline nature and thermal decomposition using Siemens D5000 X-ray powder diffractometer (India) and NETZSCH STA 409 C/CD (United States), respectively.

### 2.5. Preparation of adsorbate

Cadmium nitrate of analytical grade was procured from Himedia, India. An accurately weighed amount of cadmium nitrate was dissolved in water to prepare a Cd(II) solution. The concentration is required for the batch adsorption studies have been prepared by diluting the base Cd(II) ions solution using water. The Cd(II) ions concentration in the solution was analyzed using atomic absorption spectrophotometer (AAS, ELICO SL176 Model, India).

### 2.6. Batch adsorption

Adsorption studies were conducted by adding a known quantity of adsorbent to the 100 mL of desired Cd(II) ion concentration at pH 7.0 in conical flasks, agitated at speed of 80 rpm in a temperature-controlled Hasthas Orbital Shaking Incubator for 60 min at temperature 303–333 K. The initial concentration of Cd(II) about 100 mg L<sup>-1</sup> was used as a stock solution for the adsorption studies. The adsorption influencing parameters such as initial ion concentration, dosage, contact time, pH and temperature had been studied for the different sets of batch adsorption experiments. When equilibrium attains, the concentrations of the Cd(II) in the aqueous solution was determined using AAS.

The following formula was used to determine the percentage removal of Cd(II):

$$\% \text{ Removal of Cd(II)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (5)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium concentrations (mg L<sup>-1</sup>) of Cd(II) ions, respectively.

### 2.7. Adsorption isotherm studies

Langmuir, Freundlich, Redlich–Peterson and Khan isotherm [27–30] models are the non-linear isotherm models studied for the equilibrium isotherm data. The fitness of these models was evaluated by the determination of non-linear coefficient ( $R^2$ ) and error values. Computing was done using a MATLAB R2009a software package to inspect  $R^2$  and error values. It happens at the specific homogenous site for the successful application of monolayer adsorption.

Langmuir isotherm is expressed as follows

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (6)$$

where  $q_e$  is the amount of Cd(II) ions adsorbed at equilibrium,  $q_m$  is the maximum monolayer adsorption capacity (mg g<sup>-1</sup>),  $K_L$  is the Langmuir adsorption constant related to the affinity of the Cd(II) ions to the adsorbent (L/mg) and  $C_e$  is the equilibrium concentration of Cd(II) ions in solution.

The Freundlich model is expressed as follows

$$q_e = K_F C_e^{1/n} \quad (7)$$

where  $K_F$  is the Freundlich constant ((mg g<sup>-1</sup>) (L mg<sup>-1</sup>)<sup>1/n</sup>) used to measure the adsorption capacity and  $n$  is the Freundlich exponent which is used to measure the intensity of adsorption.

Redlich–Peterson and Khan isotherms are the three-parameter equations used in the isotherm studies.

The Redlich–Peterson model is expressed as follows:

$$q_e = \frac{K_{RP} C_e}{1 + \alpha_{RP} C_e^{\beta_{RP}}} \quad (8)$$

where  $\alpha_{RP}$  is the Redlich–Peterson isotherm constant ( $L\ mg^{-1}$ ),  $1/\beta_{RP}$  and  $K_{RP}$  is Redlich–Peterson isotherm constant ( $L\ g^{-1}$ ),  $\beta_{RP}$  is the exponent which lies between 0 and 1.

Khan model equation is expressed as follows

$$q_e = \frac{q_m \times \beta_K \times C_e}{\left(1 + (\beta_K \times C_e)\right)^{\alpha_K}} \quad (9)$$

where  $q_m$  is the adsorption capacity,  $\beta_K$  is the Khan model constant,  $\alpha_K$  is the Khan model exponent, the adsorbed amount of equilibrium ( $mg\ g^{-1}$ ),  $C_e$  is the adsorbate equilibrium concentration ( $mg\ L^{-1}$ ).

### 2.8. Kinetics and diffusion mechanism

Adsorption kinetic study was conducted by adding  $3\ g\ L^{-1}$  of AC in  $100\ mL$  Cd(II) ion solution at temperature  $303\ K$ , in  $100\ mL$  conical flask at room temperature. Examining the rate of adsorption and mechanism for the removal of Cd(II) ion onto the AC with varying contact time ( $10\text{--}60\ min$ ) is essential.

Kinetic models of pseudo-first-order, pseudo-second-order and intraparticle diffusion models were fit with the experimental data to determine the adsorption rate.

The pseudo-first-order kinetic model equation is expressed as follows:

$$q_t = q_e \left(1 - \exp(-k_1 t)\right) \quad (10)$$

where  $k_1$  is the pseudo-first-order kinetic rate constant ( $min^{-1}$ ) and  $t$  is the time ( $min$ ).

The pseudo-second-order kinetic model equation is expressed as follows:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (11)$$

where  $t$  is the time ( $min$ ),  $k_2$  is the pseudo-second-order kinetic rate constant ( $g\ mg^{-1}\ min^{-1}$ ).

The intraparticle diffusion model is expressed as follows:

$$q_t = k_p t^{1/2} + C \quad (12)$$

where  $q_t$  is the adsorption capacity at time  $t$  ( $mg\ g^{-1}$ ),  $k_p$  is the intraparticle diffusion rate constant ( $mg\ g^{-1}\ min^{-1/2}$ ),  $t$  is the time ( $min$ ), and  $C$  is the intercept.

### 2.9. Thermodynamic study

Thermodynamic parameters such as the change in enthalpy ( $\Delta H^\circ$ ,  $kJ\ mol^{-1}$ ), entropy ( $\Delta S^\circ$ ,  $kJ\ mol^{-1}$ ) and Gibbs free energy ( $\Delta G^\circ$ ,  $kJ\ mol^{-1}$ ) were investigated for understanding adsorption characteristics and to identify the nature of adsorption process. These parameters can be intended from the following expressions:

$$K_c = \frac{C_{Ae}}{C_e} \quad (13)$$

$$\Delta G^\circ = -RT \ln K_c \quad (14)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (15)$$

$$\log K_c = \frac{\Delta S^\circ}{2.303 R} - \frac{\Delta H^\circ}{2.303 RT} \quad (16)$$

where  $C_{Ae}$  is the amount of Cd(II) ion adsorbed onto the adsorbent per liter of solution at equilibrium ( $mg\ L^{-1}$ ),  $R$  is the gas constant ( $8.314\ J\ mol^{-1}\ K^{-1}$ ),  $T$  is the temperature ( $K$ ) and  $K_c$  is the equilibrium constant. The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were calculated from the slope and the intercept of the plot of  $\log K_c$  vs.  $1/T$ .

## 3. Results and discussion

### 3.1. Process at compost plant

The characterization and quantification of MSW were conducted in the compost plant and reported in Table 1. Daily  $25\text{--}30\ kg$  of vegetable waste from the residential colony had transferred to the plant holding for  $70\%\text{--}75\%$  of initial moisture. To minimize moisture content, bulking agents were added, aerated at the rate of  $0.2\ m^3\ h^{-1}$ . Temperatures around  $35^\circ\text{C}\text{--}45^\circ\text{C}$  in the first  $12\ d$  of the composting period indicate mesophilic; the next  $13\ d$ , the temperature was raised to  $63^\circ\text{C}$  in which most of the pathogenic bacteria were killed. After almost a month, the total waste was gradually degraded; shifted to the maturation yard. A month later, the mature compost was crushed; sieved and stored in a plastic container. A package of  $3\ kg$  per bag was distributed for the gardening purpose at Colony, Nagpur.

### 3.2. Compost influencing parameters

#### 3.2.1. Effect of temperature

An earlier temperature of  $25^\circ\text{C}$  (initial temperature recorded after collection) in all the sets of composting piles can be seen in Fig. 1. But the sudden rise in temperature to  $45.6^\circ\text{C}$  within  $3\ d$  due to higher indigenous microbial population is evident in the presence of maximum organic matter. Temperature between  $37^\circ\text{C}$  to  $39^\circ\text{C}$  and  $42^\circ\text{C}$  to  $45^\circ\text{C}$  within  $3\ d$  for OW:WS and OW:BG and OW:CH and OW:DL shows

Table 1  
Characterization of waste

Sr. No.	Waste type	Percentage of waste
1	Vegetable waste	40%
2	Vegetable waste	30%–35%
3	Paper waste	7%
4	Glass	6%
5	Plastic	5%
6	Wood	4%
7	Metal	Below 1%
8	Coconut	1.2%
9	Rubber and leather	0.6%

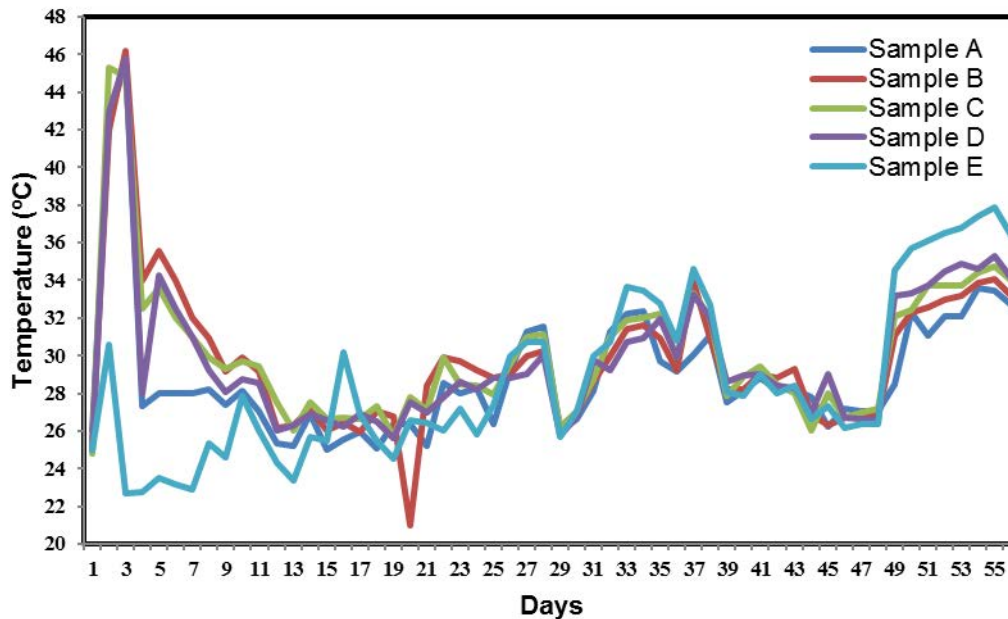


Fig. 1. Effect of the average temperature on the composting system.

prolonged thermophilic stage for the degradation of more organic matter and removal of pathogens at such elevated temperature. Control (without BA) still remained 30°C on the 3rd day, subsequently reduced to 22°C and maintained for the next 15 d. Considering an average temperature around 22°C–26°C in all the composting piles in next 15 d indicates that temperature is dependent on the degradation of organic matter by active microbes on the feed materials. This phase is particularly called a cooling phase [31]. Further, maturation or curing phase was observed in the next 10 d by maintaining a temperature between 24°C to 30°C. Fluctuation in temperature was observed in control according to the ambient temperature.

### 3.2.2. Effect of pH

The presence of organic acid in the composting pile was observed by the change in pH from 5.70 to 6.74. On day 7, the pH of these mixtures was 8.0 and 9.0 revealing organic acid degradation by microbial action in the pile [32]. Extra amendments as N (nitrogen) supplements in the pile were gradually denitrified and also added OH. During the process of composting, the pH of all mixtures was not significantly different ( $P < 0.05$ ), starting from 6.0 to rising slowly till 8.0 is due to the acidic nature of the BAs. After 7 d of composting, pH 9.7 ( $P < 0.05$ ) was achieved with 12% DM of OW. The state of final maturation of all the composting piles except control was attained at pH 7.5 while control withheld pH 8.29 for 65% DM.

### 3.2.3. Effect of electrical conductivity

The initial EC data of 7.07, 4.63, 8.1, 4.9 and 8.2 ( $\text{dS m}^{-1}$ ) were reduced to 1.6, 2.8, 3.8, 4.7 and 8.5 ( $\text{dS m}^{-1}$ ) respectively at the end of 30 d. Experimental data showed that

the EC values of composting piles increased earlier as the degradation of organic matter proceeds [33]. The common phenomenon in composting is an inability of mineral cation concentration gets attenuated by binding to stable organic complex.

### 3.2.4. Effect of dry matter and moisture content

The dry matter of the composting piles was verified every as an indication of reducing the moisture content [34]. Set A, B, C, D and E showed the rise in DM from 30% to 88%, 31% to 98%, 24% to 76%, 25% to 75%, and 12% to 74%, respectively at the end of the composting period. In the same way, the declining trend in moisture content was observed in 10 d. In 30 d, 71% to 11%; 68% to 2%; 72% to 12%; 61% to 17% and 81% to 31% of moisture reduction in the piles were seen.

### 3.2.5. Effect of BD and PD

The initial bulk density of composting matrices was  $410 \text{ kg m}^{-3}$  reported in Fig. 2. Throughout the composting period, that is, 0 to the 36th day, dry bulk density was estimated. In the first 8 d, set A and B showed a rise in BD, maintained for 20 d and later declined in the next 16 d from 170 to  $100 \text{ kg m}^{-3}$ . Similarly set C and D were declined from 240 to  $100 \text{ kg m}^{-3}$  and 280 to  $210 \text{ kg m}^{-3}$ . Control was seen reducing from 420 to  $380 \text{ kg m}^{-3}$  in 12 d, later in the next 20 d, it was  $400 \text{ kg m}^{-3}$ . Particle density was fixed constant throughout the composting period, that is,  $0.52 \text{ kg m}^{-3}$ .

### 3.2.6. Effect of free air space

Free air space (FAS) in the composting piles was exceeded 30% and which is efficient for aeration. Control exhibited 22% FAS in the first week. Later as BAs were

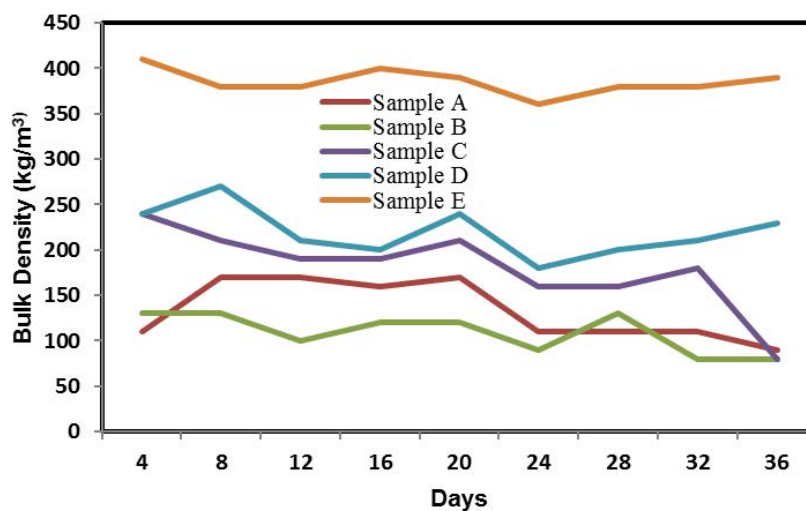


Fig. 2. Effect of bulk density on the composting system.

added 65%–80% FAS was achieved by availing carbon content [35,36]. Particularly, chana husk and dry leaves provided 40%–50% FAS whereas wood shaving offered 64%. Successful implementation of increasing void [37] between the composting molecules as evidenced by the increased FAS from 80% to 88%.

### 3.3. Maturation analysis of compost

#### 3.3.1. Elemental analysis of CHNS

The decomposition of organic matter and stability of the compost was estimated by analyzing C/N ratio reported in Table 2. In present work, C/N ratio from 14–17, 17–13, 24–11, 13–15 and 24–9 in 20 d was calculated. Thus, the C/N ratio between 10 and 15 indicates a good degree of maturity [38]. Out of all, DL offered higher C/N reduction about 11 which is practically acceptable for the application in wastewater treatment.

#### 3.3.2. Extent of decomposition and mass reduction

After 30 d of maturation, the samples demonstrated a dark brown color with no recognizable substrate holding 30% and 12% DM. However, non-decomposed BAs can be repeatedly used. After 30 d of maturation of 9 kg of OW was due to loss of water through evaporation and leaching [39]. Hence, the total dry mass of 9 kg was reduced to 0.460 kg with the aid of BAs.

### 3.4. Characteristics of compost

Physical, chemical and thermal characteristics of compost after undergone for the surface modification were studied. Notably, the impact of carbonization and oxidation of compost was examined by scanning electron microscopy (SEM-EDX) analysis. A uniformity of particles on the surface of adsorbent is shown in Fig. 3 with 5  $\mu\text{m}$  diameter. Such particle size distribution [40] is logical for solid-liquid phase adsorption. EDX analysis reports the maximum

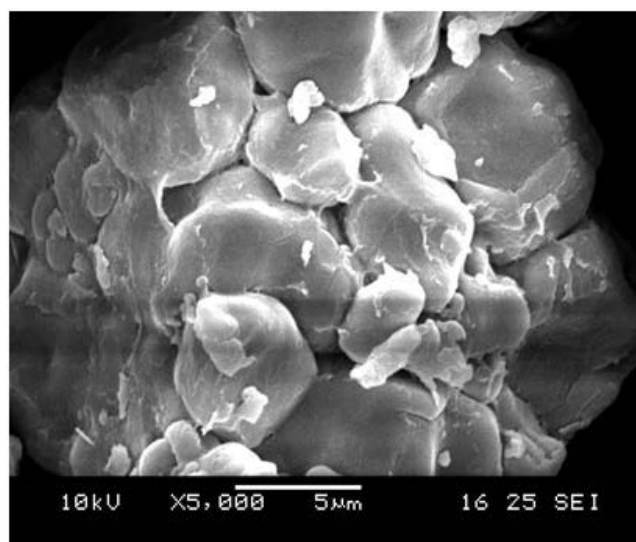


Fig. 3. Report on scanning electron microscopy analysis.

carbon yield enhanced by  $\text{H}_2\text{SO}_4$  from 40% to 72.24% stating that 30% extra carbon was yielded.

FTIR analysis ensures significant elements responsible for the binding of Cd(II) ions on the surface of activated carbon. It was observed between 400 to 4,000  $\text{cm}^{-1}$  regions on X-axis and % Transmittance on Y-axis (Fig. 4). The essential functional groups of N–H, C–H and O–H single bonds were found in the first region. Triple bonds and the double bonds (C=O, C=N, C=C) were found in the second and third regions respectively. In the fourth region, a variety of single bonds were found. All of them are responsible for the adsorption of water molecules, carbonyl, hydroxyl, and amine and amide chemical functional groups [41].

XRD analysis of an adsorbent, that is, AC declares that the sample is amorphous; crystalline [42]. The intensity of the peak is shown in Fig. 5a. Importantly, the thermal degradation of adsorbent was examined by TGA analysis (Fig. 5b),

Table 2  
Elemental analysis of the composting system

Samples	Week	N	C	S	H	C/N ratio
A	1	2.762	40.72	1.045	6.114	14.74
	2	2.34	41.57	0.214	5.941	17.76
	3	2.001	34.08	0.205	5.134	17.03
	4	2.2	37.81	0.2	5.371	17.18
B	1	1.916	32.52	0.27	5.144	16.97
	2	2.58	34.87	0.248	5.313	13.51
	3	2.036	34.57	0.195	5.141	16.97
	4	2.022	35.97	0.222	5.226	17.78
C	1	1.934	32.06	0.204	5.281	16.57
	2	2.564	29.21	0.248	4.594	11.39
	3	1.981	29.74	0.222	4.816	15.01
	4	1.958	30.26	0.233	4.747	15.45
D	1	1.493	35.94	0.186	5.261	24.05
	2	2.236	33.9	0.216	5.001	15.16
	3	1.838	38.77	0.24	5.45	21.09
	4	3.252	30.96	0.476	4.848	9.52
E	1	2.224	30.89	0.158	4.874	13.88
	2	1.63	25.27	0.169	3.918	15.55
	3	3.687	34.78	0.492	5.429	9.43
	4	3.356	35.2	0.46	5.664	10.45

showing a weight loss of about 51.87% at 560°C. These results are essential for the practical application of matured compost as an adsorbent in harsh environmental conditions [43].

### 3.5. Adsorption influencing parameters

#### 3.5.1. Effect of pH

The removal of Cd(II) ions in the aqueous solution is influenced by sorption parameters [43]. Likely, pH is the most

important factor which was varied from 2.0 to 7.0 adjusted by using 0.1 N of NaOH and HCl for experimenting batch adsorption at 303 K. How the change in pH affects the sorption capacity is shown in Fig. 6. Notably, the increase in pH also induces the removal efficiency of AC that is noted from 15.54% to 99.46%. The maximum removal at pH 7.0 was 99.46% further kept for subsequent cycles. Additionally, experiments had stopped as no change in the removal efficiency was found. Results bring an understanding of electrostatic interaction between the surface of compost and Cd(II) ions [44].

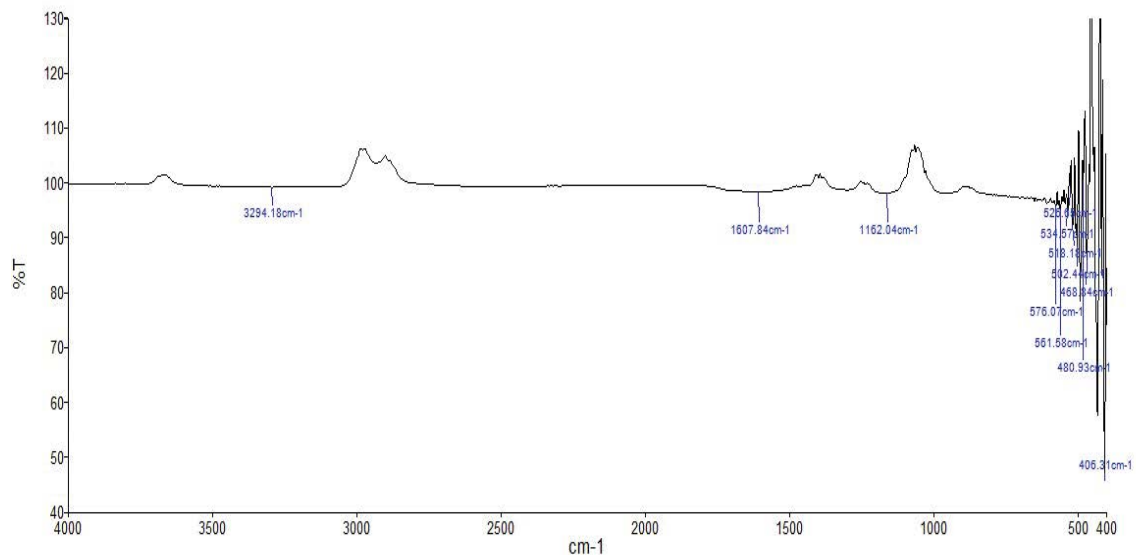


Fig. 4. Report of FTIR analysis.

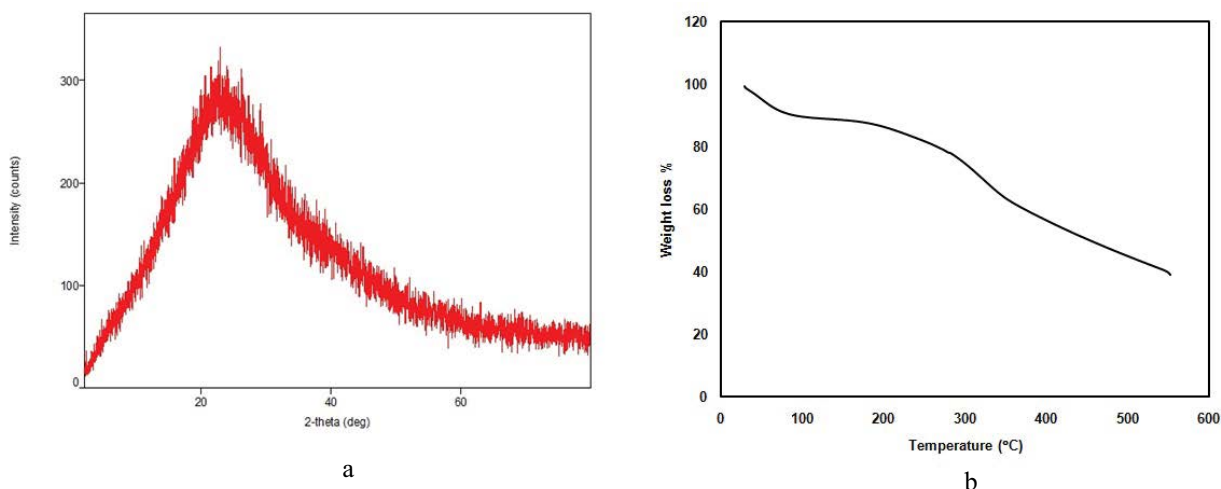


Fig. 5. Report of (a) XRD and (b) TGA analysis.

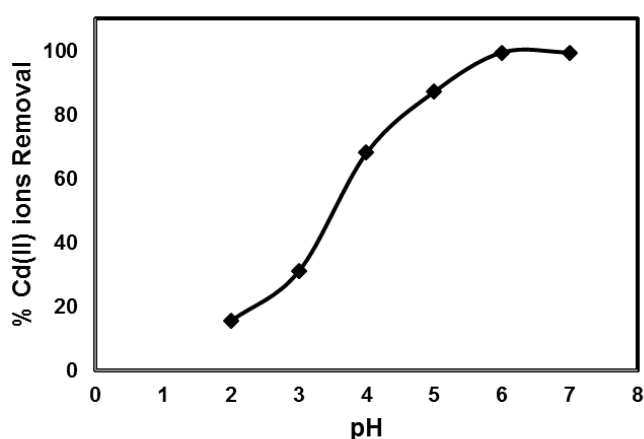


Fig. 6. Effect of pH on Cd(II) ions adsorption.

### 3.5.2. Effect of dosage

Adsorbent dosage for the removal of Cd(II) ions was set from 1.0 to 9.0 g L<sup>-1</sup>. Fig. 7 illustrates that an increase in the removal percentage from 39.427% to 99.468% is meant for the occurrence of superficial sorption on the surface of the active carbon [45]. When at equilibrium condition, the ratio of adsorbent mass to adsorbate concentration became favorable for the adsorption process [46]. Such an equilibrium condition was brought by 3 g L<sup>-1</sup> of adsorbent dosage. It is sufficient in creating a split or concentration gradient between Cd(II) ions concentration in the solution as well on the surface of the adsorbent. However, the sorption capacity of  $q_e$  is increased with an increase in the adsorbent dosage.

### 3.5.3. Effect of initial Cd(II) ion concentration

The initial Cd(II) ion concentrations were set from 50 to 250 mg L<sup>-1</sup> using 3 g L<sup>-1</sup> constant adsorbent dosage. The amount of Cd(II) ions adsorbed on the surface of activated

carbon is shown in Fig. 8 that is an indication for the clear decline in removal efficiency from 99.454% to 81.428% for the concentrations from 50 to 250 mg L<sup>-1</sup>. Lower concentration seems favorable for the adsorption phenomena yet at a higher concentration; the active sites on the surface of AC become saturated [47], resulting in less removal percentage. To this extent, Cd(II) ions cannot be accompanied by surface carbons for complete occupancy. Importantly, agglomeration plays a major role in the adsorption process. Therefore, the concentration of Cd(II) ions gets decreased once the agglomeration of Cd(II) ions to each other became large. Similarly, adsorbent also acts as a coagulant to mobilize or destabilize the Cd(II) ions on its surface which can be later separated by filtration [48]. In conclusion, the aggregation property of adsorbent is proportionate to the sorption capacity. Indeed, lower concentrations of Cd(II) ions get surrounded on the competing active sites to enhance the adsorption process.

### 3.5.4. Effect of contact time

The effect of contact time for conducted batch adsorption study by varying time from 10 to 60 min is shown in Fig. 9. The transfer of Cd(II) ions from the liquid phase to the solid surface of adsorbent at equilibrium condition was studied. As a function of contact time, more metal ions get adsorbed onto activated carbon initially but as time passes, the rate of adsorption was found to be declined. Free active sites of AC at 10 min was slowly occupied by metal ions till 30 min, further maintained the same until 60 min. But analyzing steady-state concentration of Cd(II) ions, 30 min as contact time serves better equilibrium data. Because the driving force used for mass transfer of Cd(II) ions from the liquid phase to solid is high at higher concentration [49]. The removal % of Cd(II) ions with different increasing concentration gradually decreases from 99.45% to 81.42%. The vacant adsorption sites get occupied in adsorbent over time and eventually reached equilibrium [50]. The contact time of 30 min is economically favorable and logical for subsequent batch experiments. The kinetic



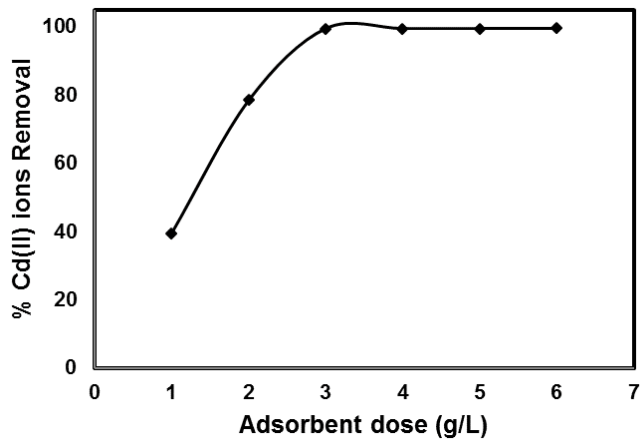


Fig. 7. Effect of adsorbent dose on Cd(II) ions adsorption.

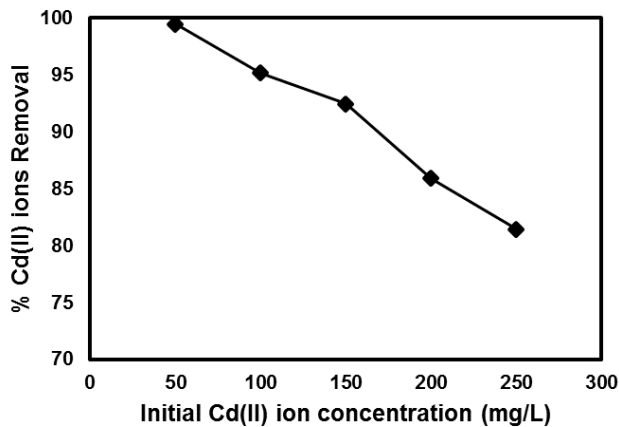


Fig. 8. Effect of initial Cd(II) ion concentration on Cd(II) ions adsorption.

models of pseudo-first and pseudo-second-order had used to fit experimental data for a better understanding of the adsorption process.

### 3.5.5. Effect of temperature

The impact of temperature on the adsorption process is explained in this section. Le Chatelier's principle defines the evolution of heat in the adsorption process as the rise in temperature decreases the magnitude of adsorption. The change in temperature from 303, 313, 323 and 333 K for the various concentrations of Cd(II) ions are shown in Fig. 10. The extent of the adsorption process relies on temperature and constant pressure [51] defined by the phenomena of chemisorption. Thus, an increase in temperature leads to a decrease in the removal percentage. Because, the exothermic condition does not offer potential surface activity of an adsorbent, indeed it hinders the adsorption balance via energy released for adsorbent to stay longer in a liquid medium [52]. When temperature increases, the requirement of energy also increases. However, compost as activated carbon can be used in wastewater abatement.

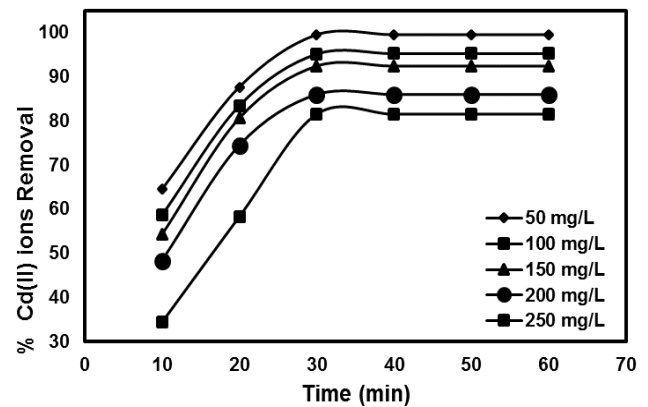


Fig. 9. Effect of contact time on Cd(II) ions adsorption.

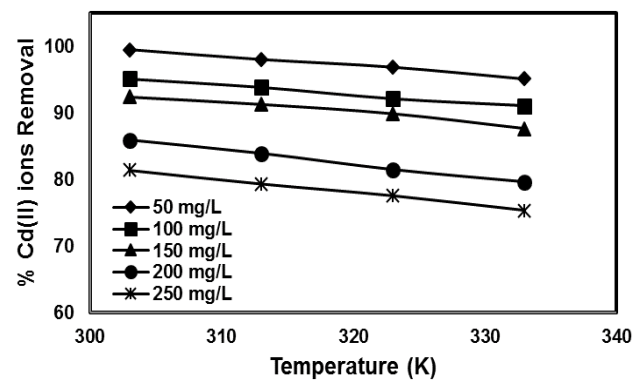


Fig. 10. Effect of temperature on Cd(II) ions adsorption.

### 3.6. Thermodynamic studies

The determination of thermodynamic parameters of Gibbs free energy ( $\Delta G^\circ$ ), the enthalpy ( $\Delta H^\circ$ ) and the entropy ( $\Delta S^\circ$ ) for the adsorption of Cd(II) ions was done for various temperatures from 303, 313, 323 and 333 K. The values presented in Table 3 were derived from the graph  $1/T$  vs.  $\log K_c$  (Fig. 11). Gibbs free energy as a function of driving force used to study the relationship between free solute compound at the initial state and the adsorbed compound at equilibrium state. Likely, the change in enthalpy, entropy, and Gibbs free energy was studied using equilibrium constants ( $K_L$ ,  $K_d$ ) (also called as distribution coefficients) whereas  $\Delta G^\circ$  is dependent on the change in ( $\Delta H^\circ$ ) and ( $\Delta S^\circ$ ). Physical or chemical adsorption or in combination can occur during the process of adsorption [53]. In the table,  $\Delta H^\circ$  values are negative, indicating that energy required or released for the attraction of molecules of Cd(II) ions onto the activated carbon. Hence, the heat of adsorption is negative, that is, exothermic [54]. In this work, the removal of Cd(II) ions is caused by both physical and chemical adsorption due to the interaction between hydrogen bond and ligand exchange. As well,  $\Delta S^\circ$  values are negative, indicating that Cd(II) ions were retained onto the activated carbon, tends to decrease the entropy. Adsorption is further confirmed by the negative values of  $\Delta G^\circ$  ( $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ ).

Table 3  
Thermodynamic analysis results for the removal of Cd(II) ions by AC

$C_0$ (mg L <sup>-1</sup> )	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol/K)	$\Delta G^\circ$ (kJ/mol)			
			303 K	313 K	323 K	333 K
50	-60.390	-157.926	-13.114	-10.145	-9.226	-8.240
100	-18.660	-36.934	-7.495	-7.104	-6.612	-6.436
150	-15.06	-28.720	-6.306	-6.126	-5.870	-5.422
200	-12.57	-26.499	-4.551	-4.296	-3.977	-3.775
250	-99.44	-20.544	-3.724	-3.505	-3.333	-3.095

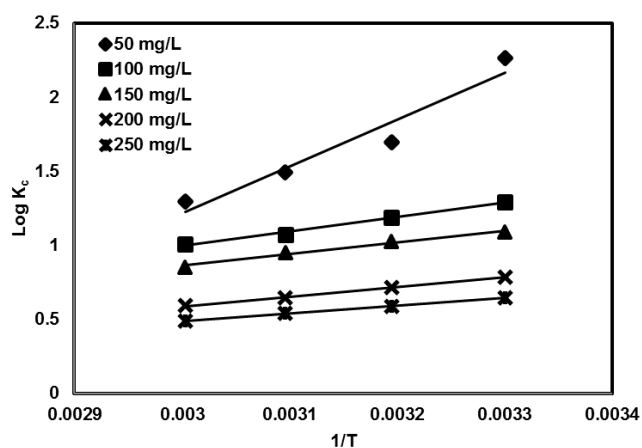


Fig. 11. Thermodynamic analysis on Cd(II) ions adsorption.

### 3.7. Adsorption isotherms

The availability of the number of active sites on the surface of the adsorbent for undergoing adsorption is determined by the Langmuir and Freundlich isotherm models. As a function of adsorption capacity, the correlation coefficients of ( $R^2$ ) for Langmuir and Freundlich isotherm

models were estimated from (Fig. 12a) slope and intercepts of the linear plot, that is,  $R^2 > 0.878$  and  $0.9905$ , respectively. The monolayer formed at low pressure can be observed from the Langmuir model during the breakdown and the attraction of molecules towards each other [55]. Equal size of adsorbent brings equal affinity for Cd(II) ions. Thus, the surface of the adsorbent is homogenous [56]. Besides, the decrease in randomness is zero when the adsorbed molecules tend to be localized as a weak force of attraction exists between the particles. Notably, similar results by using different types of compost for the reclamation of heavy metals were reported by researchers [57]. The affinity between heavy metals and the functional groups of adsorbents has elaborated in these studies.

Another dimension of the Langmuir isotherm model is the Freundlich isotherm model, that is, multilayer adsorption caused by the heterogeneous surface. Unequal size and shape of adsorbent (heterogeneous accessible sites) are responsible for the adsorption process [58]. However, the Freundlich adsorption isotherm model yielded the best fit by obtaining the highest correlation coefficient value with the lowest error value compared to the Langmuir isotherm model. The adsorption capacity ( $q_m$ ) of the carbon-enhanced adsorbent for 3 g L<sup>-1</sup> dose is 72.99 mg g<sup>-1</sup>. The sorption capacity of 3.341 mg g<sup>-1</sup> of mushroom compost for the removal of Mn(II) ions has reported [41,44]. His

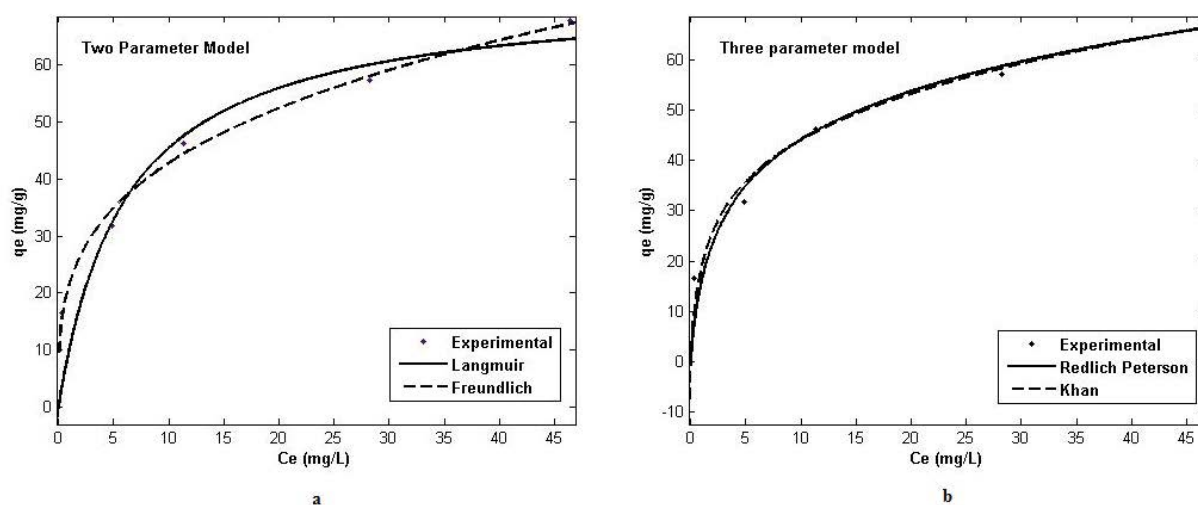


Fig. 12. Adsorption isotherm analysis on Cd(II) ions adsorption (a) two-parameter and (b) three-parameter model.

Table 4  
Adsorption isotherm analysis results for the removal of Cd(II) ions by AC

Isotherm models	Parameter	$R^2$	Sum of squared errors	Root mean squared errors
Langmuir	$q_m = 72.99$ mg/g $k_1 = 0.1647$ L/mg	0.878	201.6	8.197
Freundlich	$n = 3.394$ $K_F = 21.71$ (mg/g)/(L/mg) <sup>(1/n)</sup>	0.9905	15.67	2.285
Redlich–Peterson	$\alpha_{RP} = 1.086$ L/mg $\beta_{RP} = 0.8015$ $K_{RP} = 32.37$	0.9311	113.9	6.161
Khan	$\beta_K = 0.999$ $q_m = 4.658$ mg/g $\alpha_K = 0.7514$	0.9502	82.39	5.241

work demonstrated that exhaustion time is increased with decreases in flow rate and initial Mn(II) ions concentration.

Three parameter models of Redlich–Peterson (Fig. 12b) contains  $\alpha_{RP}$ ,  $\beta_{RP}$  and  $K_{RP}$  that represent adsorption equilibrium over a wide concentration range of adsorbate. Estimated values reported in Table 4 is ideal for the removal of Cd(II) ions by matured compost derived activated carbon. And, Khan model having  $\alpha_K$ ,  $\beta_K$  and  $q_m$  to define the surface heterogeneity [59]. From the results, the Khan model ( $R^2 > 0.9502$  is shown a better fit over Redlich–Peterson isotherm model ( $R^2 > 0.9311$ ). The obtained results show that the Redlich–Peterson model better reflects the adsorption of Cd(II) ions onto activated carbon than Khan isotherm model.

### 3.8. Kinetics and diffusion mechanism

Adsorption rate and controlling parameters were determined using kinetics. The experimental data was tested against the pseudo-first-order kinetics and pseudo-second-order kinetics. From experimental variables, it can be said that the pseudo-second-order kinetic model ( $R^2 > 0.89$ ) is not appropriate for modeling Cd(II) ions onto the adsorbent material. However, the pseudo-first-order kinetic model ( $R^2 > 0.98$ ) has been offered a correlation of experimental data. The mechanism of chemisorption is obeyed by the tested material for the experimented metal ion, shown in Fig. 13. Similar results were reported in previous studies.

In the present work, kinetic data were analyzed using the intraparticle diffusion model developed by Weber and Morris, McKay and Poots to determine the diffusion mechanism. The initial rate of intraparticle diffusion can be calculated from the rate-limiting steps of external film diffusion, intraparticle diffusion or interaction. The graph plotted between uptake  $q_t$  and the square root of time ( $t^{1/2}$ ) (Fig. 14) seems linear but not passing through the origin. Such a rate-determining step follows three stages. One is instantaneous adsorption; second is the gradual adsorption stage; the third is the final equilibrium stage [60]. In the second stage, intraparticle diffusion is being rate controlled followed by a slowdown in the diffusion mechanism in the third stage due to the lack of available adsorbate concentration in the solution. Since the linear lines do not

pass through the origin, it is concluded that some degree of boundary layer controls the adsorption process (Saravanan et al. [61]). During this, Cd(II) ions were transferred and retained in the micropores of adsorbent through intraparticle diffusion. Similarly, for various temperatures, the intraparticle diffusion,  $k_p$  values were estimated from the slope of the straight-line portions of the plot of  $q_t$  vs.  $t^{1/2}$ . External surface adsorption (stage 1) cannot be seen in Fig. 14 due to its fast completion. All plots have the same general features, an initial linear portion (stage 2) followed by a second linear portion (stage 3).

The table presents the regression correlation coefficients ( $R^2$ ) and the intra-particle rate constant values ( $k_p$ ) increased while raising solution temperature. Hence pore diffusion of adsorbent is promoted by temperature leading for a large number of ions get diffused into micropores before being gets adsorbed. Therefore, intraparticle diffusion cannot be a rate-limited or rate-controlling step. Additionally, the values of regression correlation coefficients ( $R^2$ ) are considerably smaller than those for the pseudo-second-order kinetic model represented in Table 5. In context, the intraparticle diffusion model cannot be a rate-limiting step.

## 4. Conclusion

The present study focused on the understanding of the effect of bulking agents in organic waste composting. Jamun dry leaves have created early thermophilic temperature profile; acidic to alkaline condition with low electrical conductivity in the composting matrix stating for less phytotoxic effect on soil. Dry matter and moisture content are inversely proportional holding  $0.52 \text{ kg m}^{-3}$  particle density. Elevated FAS capacity tends to C/N ratio 11 which is able to reuse as activated carbon for the removal of Cd(II) ions in the aqueous solution. The adsorption capacity of Cd(II) ions reveals the substantial contribution of compost as activated carbon for the removal of heavy metals in the aqueous solution.

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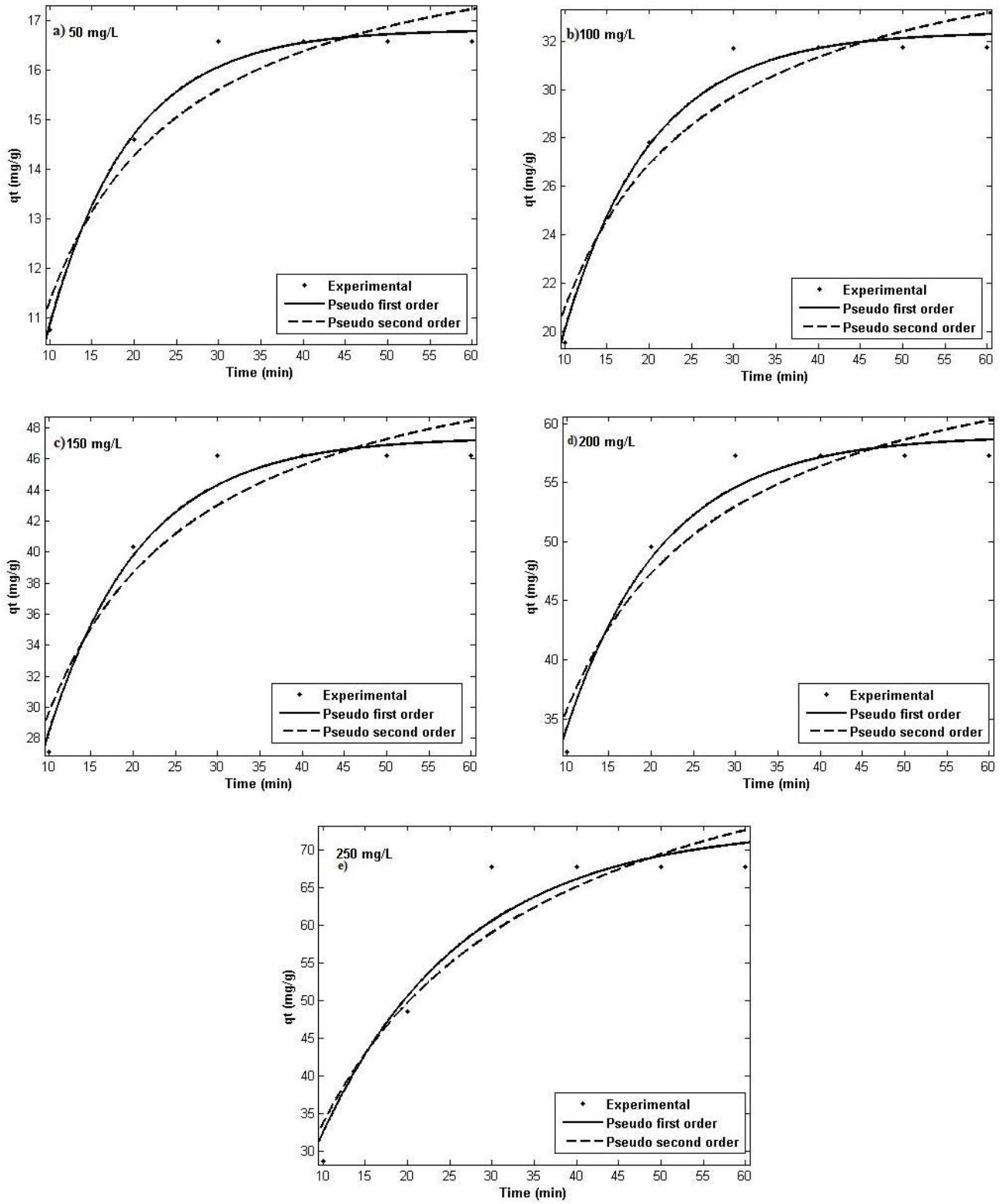


Fig. 13. Kinetic analysis on Cd(II) ions adsorption (a) 50 mg/L, (b) 100 mg/L, (c) 150 mg/L, (d) 200 mg/L, and (e) 250 mg/L.

Table 5  
Adsorption kinetic analysis results for the removal of Cd(II) ions by AC

$C_o$ (mg/L <sup>-1</sup> )	$q_{e,exp}$	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion		
		$k_1$ (min <sup>-1</sup> )	$q_e$ (mg/g)	$R^2$	$k_2$ (min <sup>-1</sup> )	$q_e$ (mg/g)	$R^2$	$k_p$ (mg/(g min <sup>(1/2)</sup> ))	$R^2$	$C$
50	16.575	0.1037	16.82	0.9877	0.0074	19.23	0.9297	1.195	0.746	8.455
100	31.714	0.0966	32.38	0.984	0.0033	37.51	0.9221	2.490	0.741	14.83
150	46.217	0.0913	47.37	0.977	0.0020	55.5	0.9123	3.872	0.733	19.95
200	57.261	0.0868	58.96	0.9708	0.0015	69.82	0.9064	5.082	0.732	22.79
250	67.856	0.0588	73.13	0.9357	0.0005	94.56	0.8972	8.566	0.781	9.202

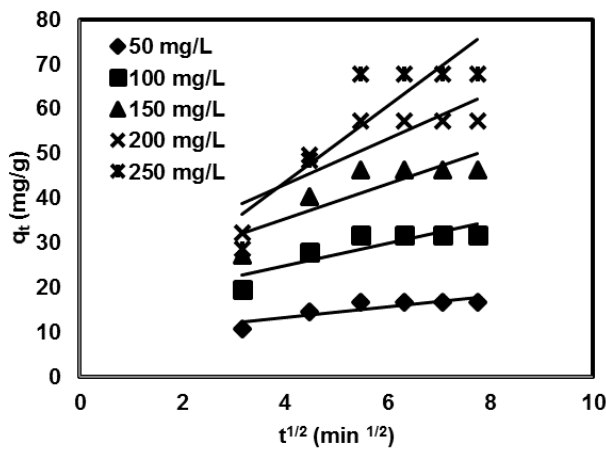


Fig. 14. Intraparticle diffusion model analysis on Cd(II) ions adsorption.

Engineering, Chennai, India for providing the facilities to complete the rest of the work in time.

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**Supplementary information**

Fig. S1. Experimental set up of different composting pile.