



Adsorption of Zn(II) and Cd(II) ions from aqueous solutions by Bamboo biochar cooperation with Hydroxyapatite and Calcium Sulphate

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Abstract: Sorption characteristics of Zn(II) and Cd(II) through lower cost adsorbent materials, like Bamboo biochar adsorbents was prepared by pyrolysis process, was used with added Calcium Sulphate and Hydroxyapatite for adsorption of Zn^{+2} and Cd^{+2} from aqueous solution. For this objective was used batch adsorption process, and comparing between two mixtures of adsorbents, HAP&CS (Hydroxyapatite & Calcium Sulphate), and BB&CS (Bamboo biochar & Calcium Sulphate), for show the efficiency of those adsorbents. The properties of the biochar were characterized by scanning electron microscopy (SEM), energy dispersive analysis system by FTIR and DTA analysis. The experiments were carried out and measure response of many parameter like contact time, initial concentration of heavy metal and comparative adsorption behaviour of Zn(II) and Cd(II). The kinetics data were fit by a pseudo second –order model, and that data were analysed by Langmuir isotherm model got high correlations coefficient. From that model the maximum adsorption capacities of HAP& CS adsorbent for Zn^{+2} and Cd^{+2} ions were 24.47 mg/g, and 18.05 mg/g respectively, capacity of BB & CS adsorbent of Zn^{+2} and Cd^{+2} ions were 14.423 mg/g and 8.0423 mg/g respectively. The results were shown advantage of using new material like BB can work as adsorbent such as HAP and replace it because of cheap, natural and many good environmental properties.

Keywords: Heavy metal, Adsorption, Bamboo biochar, Hydroxyapatite, Calcium Sulphate.

Introduction

The main goal for treatment of wastewater pollution in all field industrial, exploration, agricultural and waste application is to reduce the hazardous of toxicity like organic and heavy metal. Many industrial processes in the plating industry involve heavy metals for metal finishing and their effluent must be treated prior to discharge¹. High reservation of wastewater material emerging from this kind of industries because it contains large quantity of hazardous substances. The US Environmental Protection Agency (USEPA) prepared a list of 129 organic and inorganic pollutants found in wastewater that constitute serious health hazards. This Priority Pollutants List includes thirteen elements: Sb, As, Be, Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag, Tl and Zn². Treatment processes for metal removal from wastewaters include precipitation, membrane filtration, ion exchange, adsorption and co-precipitation/adsorption. Therefore, a novel treatment method, which requires lower construction and operating costs and can be adopted irrespectively of the size of the industry, should be developed³. Cost effective alternative technologies or adsorbents for the treatment of metal-containing wastewaters are needed⁴. However, most of these techniques have some disadvantages such as complicated treatment process and high cost⁵. The good method, have more effective and economical is adsorption process for wastewater. However, for long time search for good adsorbent and without cost to reduce the cost of treatment of heavy metal like Zn and Cd. Many years ago using biochar as adsorbent heavy metal. Biochar, which is a by-product of bio refineries, has attracted much attention recently due to its proven role in environmental management issues⁶.

When cheap biomass, particularly agricultural by-production is mainly associated with the machinery and heating, which is only about 4\$ per gigajoule⁷. Bamboo biochar is one of good natural adsorbent. Bamboo charcoal may be an ideal amendment for nutrient conservation and heavy metal stabilization due to its excellent adsorption capability⁸. Because of it has high porosity more than many biomass wood materials.

Other material recently used in this field of disposes heavy metal from wastewater and have other environmental uses, Hydroxyapatite. It was a good member in apatite group and has excellent behaviour to reduce contaminated heavy metal. The apatite mineral group has been shown to be effective both in sequestering dissolved metals and in transforming soil-bound metals to less soluble phases⁹. In this study we propose to use low cost adsorbent like Bamboo biochar cooperation with Calcium Sulphate and Hydroxyapatite, and comparative test the possibility of using this material as adsorbents for the removal of Cd²⁺ and Zn²⁺ from aqueous solution, effect of morphology on their adsorption efficiency. This material used with added Calcium Sulphate can be improved the efficiency; however in previous used to treatment by precipitate but here try to find good mixture between them. This study investigate the sorption of Cd²⁺ and Zn²⁺ ions from aqueous solutions by adsorbents materials HAP&CS, and BB&CS, by equilibrium contact time, adsorbent dose and adsorbent concentration. Also objective of this study is to investigate the sorption mechanism of Cd²⁺ and Zn²⁺ on the surface of these two adsorbents through pseudo-second order.

Material and Method

Materials

Hydroxyapatite and Zn(NO₃)₂ and Cd(NO₃)₂ standard samples used in this work were purchased from Boss official limited partnership in Thailand. All metal solutions were prepared from their nitrate salts (AR) and distilled water. For the Bamboo biochar used here was prepared in lab. The concentration of residual Zn(NO₃)₂ and Cd(NO₃)₂ ions in the supernatant was determined by using an atomic absorption spectrophotometer. The suspensions in all studies were filtered through 0.45µm syringe membrane filters. All the experiments were done in triplicate and the average value was taken for analysis.

Adsorbent characterization

The shape and pore morphology of the BB was characterized by electron microanalysis- elemental mapping analysis used device scanning electron microscope, JSM-5800 LV, JEOL Japan, attached with energy dispersive X-ray spectrometer, ISIS 300, Oxford, England. By method WI-RES-SEM-001 and WI-RES-EDX-001 and showed the content of BB sample. Analysis of functional groups in BB sample by Fourier Transform Infrared Spectrometer, EQUINOX 55, Bruker, Germany, was used method refer to WI-RES-FTIR-001 and technique pellet (KBr). It was fast and convenient method to follow the progress of pyrolysis and show the change in functional groups on the surface. For check the thermal stability of bamboo biochar used Differential Thermal Analyser, DTA7, Perkin Elmer, USA, by technique differential thermal analysis.

Production biochar from Bamboo

Bamboo wood materials collected from home gardening. The experimental design used in the laboratory pyrolysis production. Instruments used stainless steel reactor 45 cm long, and diameter of 11 with two holes, internal tray with sieve to hold, and furnace used for burning the Bamboo. The procedure used 100 grams of sample put on the sieve tray. The reactor flushed with N₂ gas for about 10 minutes at a pressure of 5 KPa to remove the air. The reactor was put inside furnace at room temp rising at an average rate of 20°C/ min until 500°C for 4 hour. The system was cooled overnight. After producing biochar, its yield was calculated.

Preparation of metal solutions

The synthetic solutions were all prepared by diluting Zn(II) and Cd(II) standard stock solutions (concentration 1000± 2mgL⁻¹) obtained by dissolving appropriate amounts of metal salt in double distilled water. Fresh dilutions were used in each experiment.

Methods

Adsorption experiments method

Metal salt of Zn(NO₃)₂ and Cd(NO₃)₂ was used to prepare metal ion (Zn(II) and Cd(II)) solution. The stock solutions concentrations (1000±2 mgL⁻¹) were prepared by dissolving appropriate amounts of metal salt in double distilled water. Fresh dilutions were used in each experiment. Use three type of adsorbent (Hydroxyapatite, Calcium Sulphate and Bamboo biochar) were used for each experiment, as (0.05:0.05:0.08) g

for HAP, CS and BB respectively, adsorbent was measured and put into a 250-mL conical flask containing 50 mL of the Zn(II) ions at the desired concentration that ranged between 50 to 150 ppm, it means 4 concentration (50, 75, 100, 150) and later on agitated, filtered and analysed by using a Perkin Elmer thermos scientific S-series model (AAAnalyst100) flame atomic absorption spectrometer, and did same step for Cd(II). Kinetic study was conducted with the known dosage of HAP 0.05g, 0.05g CS and 0.08g BB for the 50 mL of metal ion solution. Samples were shaken at an agitation rate of 250 rpm. The samples were taken out at different time intervals. The sorbent solution mixtures were centrifuged for 5 min and the supernatant was analysed for the Zn(II) concentration and Cd(II). The batch sorption studies were carried out by shaking a series of bottles containing different amounts of adsorbent in 50 mL of metal ions solution prepared in the laboratory. The samples stirred at room temperature at 250 rpm for 40 minutes (equilibrium time), and their contents were centrifuged for 5 min and the supernatant liquid was analysed for Zn(II) and Cd(II) concentration. Adsorption data obtained from equilibrium studies, contact time and initiation concentration effects, were employed in the kinetic studies and the applicability of different adsorption isotherms to Zn(II) and Cd(II) ions. The percentage removal efficiency of the adsorbents (%R), which is the sorption capacity at time t min and the sorption capacity at equilibrium were calculated as follows equation (1) and (2):

$$\% (R) \text{ adsorption} = \left(\frac{C_0 - C_t}{C_0} \right) 100 \quad (1)$$

$$q_e = (C_0 - C_t) \frac{V}{M} \quad (2)$$

Where C_0 (mg/L) and C_t (mg/L) are the liquid-phase concentrations of solute (adsorbate) at the origin and at given time t (min), respectively. C_e (mg/L) is the equilibrium concentration of Zn(II) and Cd(II) ions; V (L) is the volume of the solution while m (g) is the mass of the adsorbent.

Adsorption kinetics

From the literature, many models like pseudo- first order, pseudo- second order reaction model, for the investigated of mechanism of sorption of Zn(II) and Cd(II) in HAP+CS and BB+CS, and calculate the constant of sorption used a pseudo-second order equations model. The pseudo- second order equation model¹⁰ can explained as:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \quad (3)$$

Where q_t is the amount of metal ions adsorbed (mg g^{-1}) at any given time t (min), q_e is the amount of metal ion adsorbed (mg g^{-1}) at equilibrium and K_2 is the second order reaction rate constant for adsorption ($\text{g} (\text{mg min})^{-1}$).

Adsorption isotherms

The mechanism responsible for the adsorption of heavy metals is a physicochemical process and may be one or a combination of many ion exchanges or surface complexation, coordination, adsorption, absorption, electrostatic interaction, chelation and micro precipitation¹¹.

Various isotherms model can predict and explained the relation between sorption equilibrium and remaining metal concentration. For this study applied two isotherms model, Langmuir and Freundlich. Langmuir isotherm can explain as equation (4):

$$\frac{C_e}{q_e} = \frac{1}{b q_{\max}} + \frac{C_e}{q_{\max}} \quad (4)$$

Where q_e and q_{\max} are the observed and maximum uptake capacities (mg g^{-1}), C_e is the equilibrium concentration (mg L^{-1}), and b is the equilibrium constant (Lmg^{-1}). Langmuir is the most important model of monolayer adsorption, based on the assumption that there are a fixed number of adsorption sites, and each site can hold only one adsorbate molecule (the adsorbed layer is one molecule in thickness).

Freundlich isotherm can explain as equation (5):

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

Where K_f ($L g^{-1}$) and n are Freundlich isotherm constants, q_e is the observed uptake capacities ($mg g^{-1}$) and C_e is the equilibrium concentration ($mg L^{-1}$).

Results and Discussion

Characteristics of Bamboo biochar

FTIR analysis

FTIR was a fast and convenient method to follow the progress of pyrolysis of biochar. The FTIR spectra of the biochar sample. Figure1 was shown changes of functional groups on the surfaces of the biochar produced at 500 and FRT at 5.

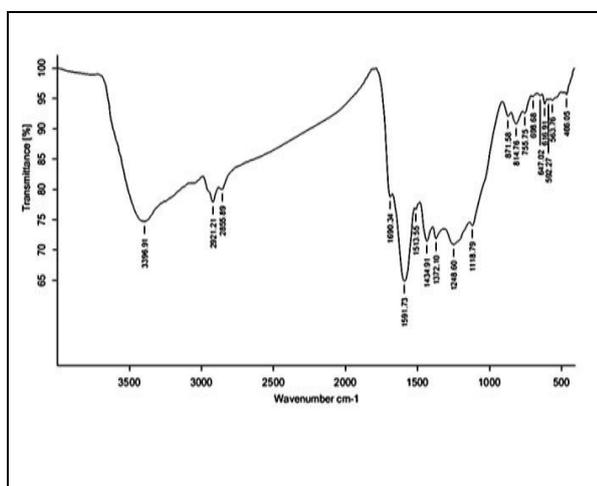


Figure 1: FTIR Analysis for progress of pyrolysis Process of characteristics the BB.

With increasing pyrolysis temperature, the bands assigned to O–H stretching vibration (near 3400 cm^{-1}) and aliphatic C–H stretching vibration ($2921.21\text{--}2855\text{ cm}^{-1}$) decreased markedly, indicating a decrease of label aliphatic compounds in the biochar with increased pyrolysis temperature and an possible occurrence of demethoxylation, DE methylation, and dehydration of lignin. The loss of OH and aliphatic groups enhanced pore formation due to a concurrent development of fused–ring structures, especially at a high pyrolysis temperature, and this hypothesis was consistent with the results of increased surface area. The a symmetric 2921.21 cm^{-1} and symmetric 2855 cm^{-1} C–H stretching bands were associated with aliphatic functional groups. The intense bands for aliphatic CH_2 decreased with increasing temperature, indicating a decrease in the contents of nonpolar groups. The intensity of the band at $1690\text{--}1591.73\text{ cm}^{-1}$ (aromatic C=C stretching and C=O stretching of conjugated ketones and Quinone’s) also diminished with increasing temperature. The peak at 1513.55 cm^{-1} represented the C=C ring stretching vibration of lignin, and the bands at 1434.91 cm^{-1} (aromatic C=C stretching) and 885 cm^{-1} (out-of-plane deformation by aromatic C–H groups) might be caused by carbonates. The sharp peaks at $1248.6\text{--}1000\text{ cm}^{-1}$ were assigned to C–O and C–C stretching, and these peaks markedly decreased probably due to the loss of polysaccharides during pyrolysis.

DTA Analysis

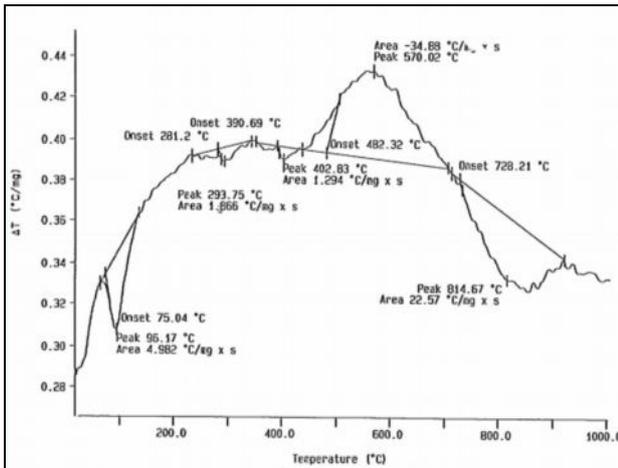
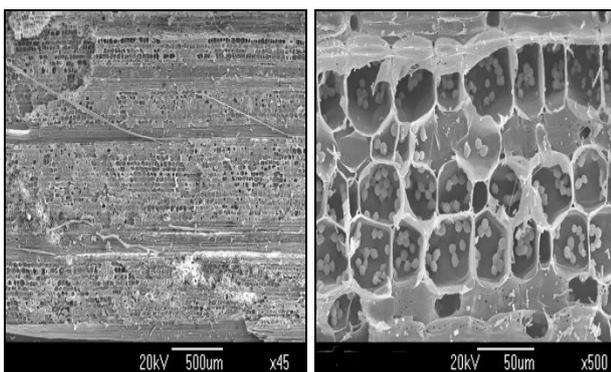


Figure 2: DTA Analysis of thermal stability for BB.

The thermal stability of Bamboo biochar described in figure 2 was checked by DTA curve can be shown clearly in that figure. These material generally showed three main peaks for loss of weight in the range 25-800 °C (see in figure). Among three peaks, the first strong peak at 75-96.17°C should be assigned to an evaporation procedure of adsorbed water molecules, the second weak peak in the range 280-294°C is likely attributed to a decomposition procedure of the surfaces, and the third broad peak appearing in the range 402-570°C may originate from the further carbonization process of this material. They have introduced new peak near 814°C. Infrared spectra 4000-400cm⁻¹ was recorded using a Nicolet IR100 FTIR spectrometer that was equipped with a TGS/PE detector and a silicon beam splitter with 1 cm⁻¹ resolution. The sample discs were prepared by mixing oven-dried (at 105°C) samples with spectroscopy-grade KBr in an agate mortar.

Scanning electron microscope images (SEM)

Results of characteristic Bamboo biochar by SEM had shown the morphology and elemental composition. In figure 3(a), shown the large internal surface and the porous structure, figure 3(b), clearly shown the approximate porous space of 38.67µm. Elemental composition of Bamboo biochar, C, S, K, and Cl were 58.61, 1.55, 30.46, and 9.38 respectively.



(a)

(b)

Figure 3: SEM for BB by different revolution (a) and (b) for porous surface

Physicochemical properties of Bamboo biochar, such as pH, surface potential, and surface area, are important factors controlling their environmental applications¹². In this work, the surface potential measurements indicated that Bamboo biochar has more negative surface charge which may be related to its higher surface area and pore volume. These data seems to suggest a greater potential to adsorb abundant positively charged heavy metals¹³. The values of charge can be shown in (Table 1). The biochar structures were not homogeneous and irregular pores with different shapes and sizes were observed¹⁴.

Table 1: Zeta potential charge for different adsorbents.

Adsorbents	Zeta Potential (mv)
BB	-56
HAP + BB + CS	-2
HAP + BB	-19

The pH of the Bamboo biochar samples was measured by combining it with DI water in a mass ratio of 1:20. The solution was then hand stirred and allowed to stand for 5 min before measurement with a pH meter ¹³. The pH was 8.00 for Bamboo biochar.

Sorption study:

Effect of initial metal concentration in adsorption equilibrium

For kinetics and isotherms equilibrium in all adsorbents used different initial concentrations from 50 to 150 ppm. It means 4 concentrations (50, 75, 100 and 150) used 50 ml in every experiment for 40 mentis after that measured the remaining metal from initial concentration. Sorption capacities of adsorbents HAP&CS and BB&CS for adsorption of Zn(II) and Cd(II) metal ions function in initial concentration of solution metal ions used Zn(II) and Cd(II) solution concentration in rang 50–150 mg/L, showed that clearly in figure 4(a), and figure 4(b), blow for HAP&CS and BB&CS respectively.

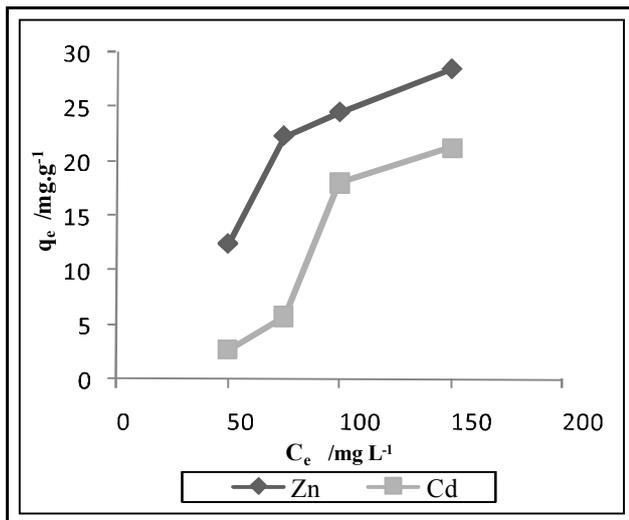


Figure 4(a): Effect of initial metal ion concentration in HAP&CS.

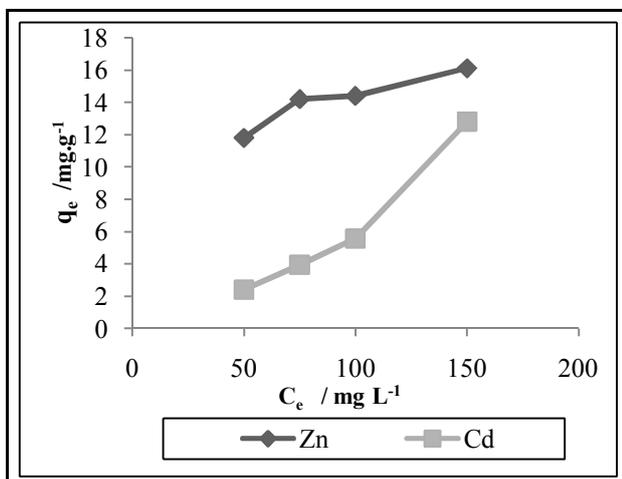


Figure 4(b): Effect of initial metal ion concentration of Zn and Cd in BB&CS.

In all the initial concentrations of Zn(II) and Cd(II), sorption capacities raises immediately in initial state, before rich in saturation and looked in space and empty site in adsorbents. The results are presented in

figure 4(b), for Zn^{+2} and Cd^{+2} adsorption capacity of the adsorbents HAP& CS and BB& CS in the beginning increased with increasing the initial concentration of metal ion and then reached a saturation values at about greater than 150 mg L^{-1} for both in HAP& CS and BB&CS, the maximum equilibrium uptake for Zn^{+2} and Cd^{+2} were $25\text{ mg Zn}^{+2}/\text{g}$ of HAP&CS, $18.05\text{ mg Cd}^{+2}/\text{g}$ of HAP&CS, and $14.42\text{ mg Zn}^{+2}/\text{g}$ of BB&CS, $8.04\text{ mg Cd}^{+2}/\text{g}$ of BB&CS.

Effect of contact time in removal of metal

Effect of contact time between adsorbent and heavy metal solutions by different time period started from 0 to 40 min, with different initial concentrations.

The plot of Cd and Zn removed by HAP&CS and BB&CS adsorbents against time min, Result can be seen in figure 5(a), and figure 5(b), when it chose the concentration 100 mg/L of metal to do the adsorption by HAP& CS and BB& CS.

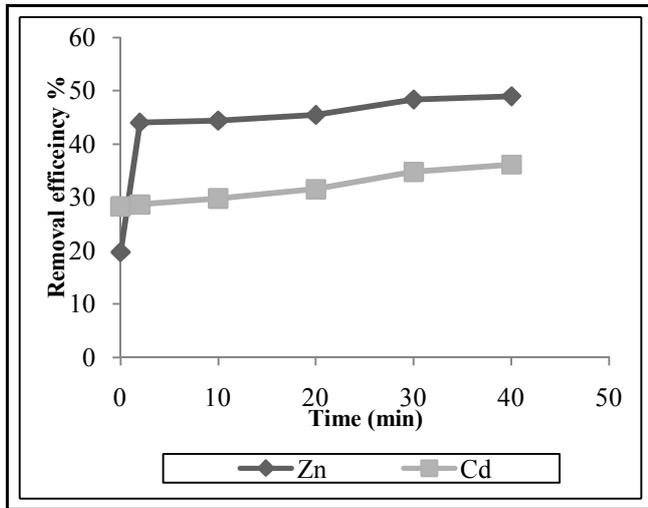


Figure 5(a): Effect of contact time in removal metal ion concentration in HAP& CS.

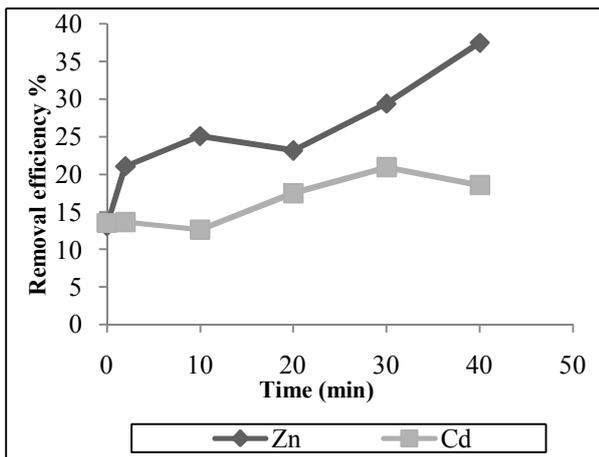


Figure 5(b): Effect of contact time in removal metal ion concentration in BB& CS.

The results elucidate that near to 50 % of Zn and 40% of Cd of metal ions by HAP&CS, were removed in the first 30 min, and 30% of Zn and more than 20% of Cd by BB&CS. It means that under same conditions of experiments no expressing adsorption was seen after 40 min.

Sorption kinetics

Sorption of Zn(II) and Cd(II) by HAP&CS and BB&CS adsorbents as function of contact time was explicated in figure 6(a) and figure 6(b) respectively. Kinetics sorption studies were applied by pseudo-

second order equation in this study. The results kinetics removal of Zn⁺² and Cd⁺² by this two adsorbents can be divided into two periods, fast 20 min, forward by a slow rise until equilibrium was about 40 minutes.

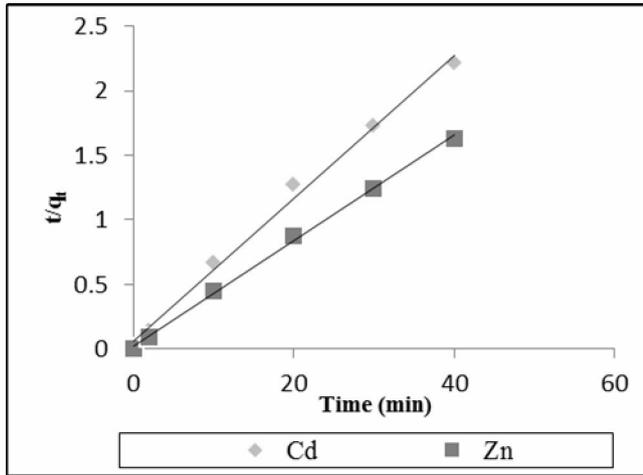


Figure 6(a): Kinetic model for removal of Zn and Cd ions in adsorbent (HAP&CS) in a pseudo-second model.

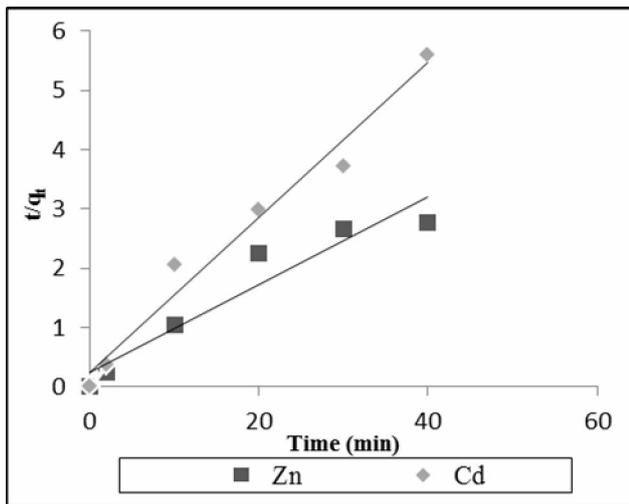


Figure 6(b): Kinetic model for removal of Zn and Cd for adsorbents (BB&CS) in pseudo-second order.

The rate constants K_2 and $q_{e(Cal)}$ of pseudo-second order kinetic model were determined from figure 6(a) and figure 6(b), by the slope and intercept of the linear plot of time versus t/q_t for both adsorbents. It can be seen in (Table 2) that the linear correlation coefficients for second-order model are good and based on the comparison between experimental and theoretically calculated q_e values; it was found that the pseudo second-order model fitted for the removal of Zn(II) and Cd(II) by HAP&CS and BB&CS adsorbents.

Table 2: Adsorption kinetic model rate constants for Zn (II) and Cd (II) removal

Adsorbent		q_{eExp} mg/g _{ad}	Pseudo second order		
			$q_{e(Cal)}$ mg/g	K_2	R^2
HAP&CS	Zn	24.47	24.51	0.073	0.99
	Cd	18.05	18.018	0.0502	0.994
BB&CS	Zn	14.423	13.51	0.023	0.923
	Cd	8.0423	7.6452	0.0729	0.975

The calculated (Cal) value of q_e from the pseudo second-order kinetics model provides a near-perfect match between the theoretical and experimental q_e values. And the pseudo second order model provide high correlation coefficients ($R^2 > 0.99$) for Zink and cadmium. By taking K_2 as the adsorption velocity, the constant K_2 0.073, 0.050 for HAP&CS is higher than those of BB&CS, 0.02, 0.07 for both metals.

Adsorption isotherms

For determining the capacity of adsorbents HAP&CS and BB&CS, we used high concentration of Zn⁺² and Cd⁺². The maximum adsorbent capacity for this heavy metals used adsorption isotherms. Langmuir and Freundlich isotherm models were applied. The constants b and q_m can be determined from the slope and intercept of the linear plot 1/q_e versus 1/C_e. Can show that in figure 7(a), and figure 7(b), for adsorbent HAP&CS and BB&CS respectively.

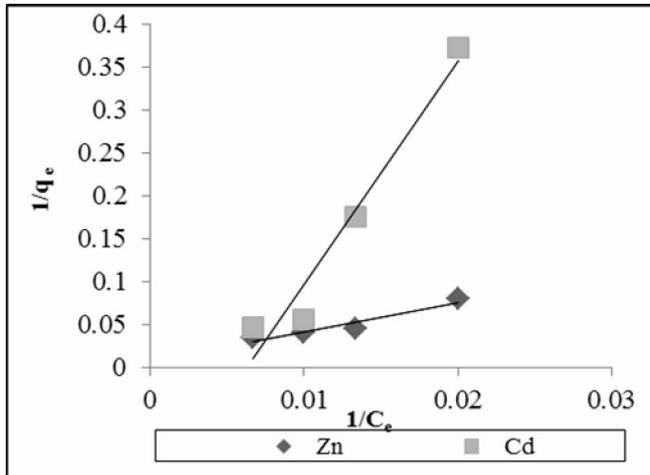


Figure 7(a): Langmuir isotherm for the adsorption of Zn and Cd in adsorbent HAP&CS.

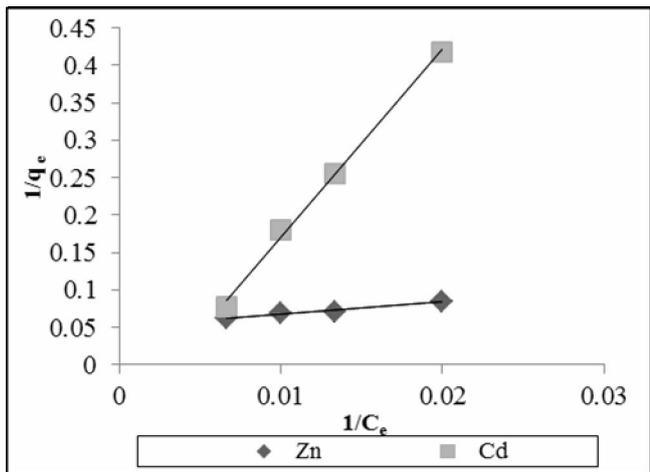


Figure 7(b): Langmuir isotherm for the adsorption of Zn and Cd in adsorbent BB&CS

The results were shown that values of correlation coefficient for the adsorption of Zn²⁺ and Cd²⁺ on HAP&CS and BB&CS adsorbents were 0.909, 0.951 and 0.959, 0.997 respectively, which demonstrated the good fitting of experimental data by this model. The Langmuir constant for Zn²⁺ and Cd²⁺ was 0.01, 0.04 and 0.002, 0.003 respectively, which illustrated that they had better adsorption affinity for Cd²⁺ than for Zn²⁺ since the Langmuir constant was proportional to the binding energy. The q_m values for the adsorption of Cd²⁺ and Zn²⁺ by the HAP&CS were 21.28 and 28.57mg/g, respectively and for BB&CS, 16.13mg/g for Zn²⁺ and 12.82 mg/g for Cd²⁺.

The empirical Freundlich isotherms model, constants n and K_f can be determined from the slope and intercept of the linear plot log q_e versus log C_e. The plots can be shown in figure 8(a), and figure 8(b), for HAP&CS and BB&CS, adsorbents respectively. Results showed that the values of correlation coefficient for the adsorption of Zn²⁺ and Cd²⁺ on HAP&CS and BB&CS adsorbents were 0.8616, 0.9096 and 0.931, 0.9782 respectively, which clearly for comparing between two models, Langmuir is good fitting more than Freundlich model. All the results can be shown in (Table 3). Maximum sorption capacity represents the monolayer coverage of sorbent with sorbate¹⁵. Comparing to other kinds of adsorbents, the adsorption capacity of Zn and Cd on BB&CS is highest than many adsorbents, as shown in (Table 4).

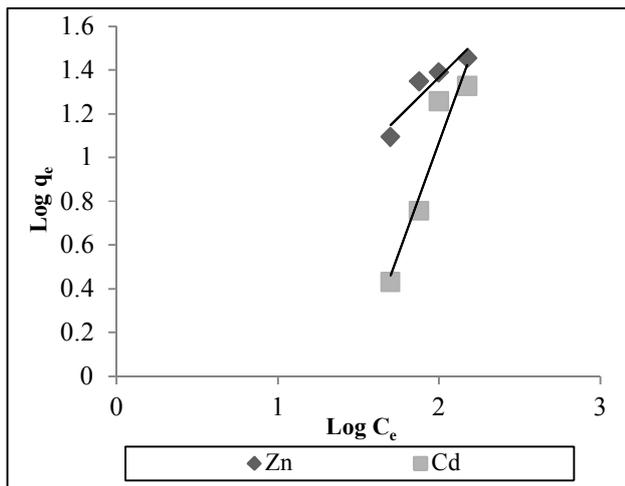


Figure 8(a): Freundlich isotherm for the adsorption of Zn and Cd ions in all adsorbent HAP&CS.

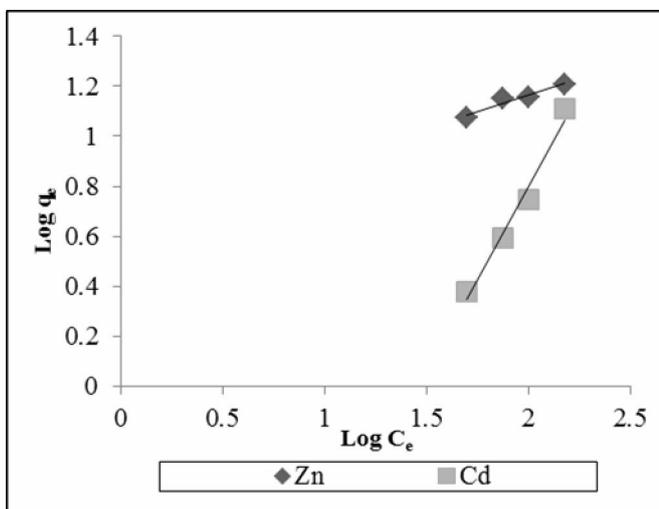


Figure 8(b): Freundlich isotherm for the Adsorption of Zn and Cd ions in adsorbent BB&CS.

Table 3: Isotherms parameters for sorption of Zn(II) and Cd(II) by different adsorbents.

Adsorbent		Langmuir			Freundlich		
		b	K	R ²	K _f	n	R ²
HAP&CS	Zn	28.57	0.01	0.9096	0.82	1.4	0.8616
	Cd	21.28	0.002	0.951	0.001	0.496	0.9096
BB&CS	Zn	16.13	0.04	0.9595	4.23	3.7	0.931
	Cd	12.82	0.003	0.9972	0.006	0.65	0.9782

Table 4: Comparison of Zn(II) and Cd(II) adsorption capacities of different adsorbents

Metal	adsorbents	q _e	Reference
Zn	Dairy manure biochar	32.8	16
Cd	Dairy manure biochar	51.4	16
Cd	Cocoa shell	4.94	17
Zn	Cocoa shell	2.92	17
Zn	Banana peel	5.8	18
Cd	Rice husk	2	19
Cd	Cassava Waste	18.05	20
Zn	Cassava waste	11.06	20
Cd	Jackfruit	52.08	21
Zn	Orange peel	5.25	18

Zn	HW450	4.54	14
Cd	BC500	13.24	22
Cd	Coffee residue- clay	39.5	23
Zn	Coffee residue- clay	13.4	23
Cd	Bagasse	2	24
Zn	Coal	1.2	25
Zn	GAC type C	20	26
Cd	CHAP	111.1	27
Cd	Chitosan-MAA nanoparticles	1.84	11
Zn	HAP&CS	24.47	This study
Cd	HAP&CS	18.05	This study
Zn	BB&CS	14.42	This study
Cd	BB&CS	8.042	This study

Conclusion

HAP&CS and BB&CS were able to substantially remove Zn and Cd from aqueous solutions. The adsorbent capacity of HAP&CS were 24.47 mg Zn(II)/g of HAP&CS, 18.05 mg Cd(II)/g of HAP&CaSO₄, 14.423mg Zn(II)/g of BB&CS, and 8.0423 mg Cd(II)/g of BB&CS. It means that the removal efficiency for HAP&CS was defiantly higher than other adsorbent but if used other adsorbent like BB still can affect to remove Zn and Cd ions. In this work discovered BB and CS can played same function of adsorption of Zn and Cadmium from water and wastewater, however the efficiency not like HAP&CS but acceptable to replaced it as low cost adsorbent.

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