



Research article

Adsorption of Cd²⁺ onto apatite surface: Equilibrium, kinetics and thermodynamic studies

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ARTICLE INFO

Keywords:

Adsorption
Isotherm
Equilibrium
Apatite
Kinetics
Cadmium

ABSTRACT

This study examined the application of chemically synthesized apatite (CHAp) powder as a potential adsorbent for the elimination of Cd²⁺ in aqueous medium. The synthesized hydroxyapatite (HAp) powder before and after adsorption was elucidated by XRD, EDX, FT-IR, SEM, and TEM analytical techniques. The role of time, initial Cd²⁺ concentration, amount of CHAp used, temperature and solution pH on the adsorption process were investigated. Data from the adsorption process were subjected to Dubinin-Radushkevich, Langmuir, Freundlich, and Temkin adsorption isotherms, while pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion kinetic models were used for the kinetics investigation. Results from XRD confirmed that chief characteristic peaks of HAp powder were detected, while functional groups such as PO₄³⁻, CO₃²⁻ and OH⁻ matching pure HAp were displayed in the FT-IR spectra. Round shape morphology of the CHAp was confirmed by SEM and TEM analyses. Langmuir isotherm best described the adsorption process with ceiling adsorption capacity of 195.711 mg/g, whereas, the adsorption mechanism obeys the pseudo-first-order model which suggests a physical adsorption process. The value of entropy change (ΔS) of the adsorption of Cd²⁺ onto CHAp surface was obtained to be 0.610 kJ/mol, while the value of enthalpy change obtained was 175.591 kJ/mol. Results from free energy change adjudged the adsorption process to be spontaneous and endothermic in character. Thus, the chemically synthesized HAp could be an excellent adsorbent for the elimination of Cd²⁺ in bioremediation applications.

1. Introduction

The presence of huge amount of environmental contamination and pollution resulting from increased population and industrialization coupled with natural resources extraction is of a great concern with the deposition of toxic substances into contaminated sites and water across the universe [1]. Due to the adverse effect of toxicity and visibility of contaminated water, wastewater from dye industries had been the focal point in the field of wastewater management [2]. The release of these pollutants into the ecosystem endangers the human and animal health and also affects the general physiology of plants, as a result of their toxicity, mutagenicity, and their inability to be broken down into small components by biological actions [3].

Cadmium (Cd) which is without known biological function is considered to be one of the very toxic heavy metal. Cd presence as

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Received 11 June 2022; Received in revised form 9 January 2023; Accepted 10 January 2023

Available online 12 January 2023

2405-8440/© 2023 Published by Elsevier Ltd.

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impurity in zinc galvanized pipes, water coolers and taps and water heaters are some of the contamination routes in drinking water [4]. The kidney has been reported as one of the organs that can accumulate Cd in the human body and this can lead to kidney malfunction [4,5]. Other chronic illnesses which could be associated with Cd exposure are neurodevelopmental disorder, and iron deficiency anaemia [5]. This has led the US Environment Protection Agency to classify Cd into the group B1 carcinogen [4]. The ceiling amount of Cd expected in drinking water as recommended by World Health Organization and US EPA are 0.005 ppm and 0.005 ppm respectively [4,6].

Thus, the thorough screening of Cd in water purification is very essential and of a great importance.

Over the years, methods such as adsorption, coagulation by chemical agents, oxidations, ion-exchange, electrochemical method, membrane separation, and many more have been discussed for possible treatment of wastewater [2,7]. Reports have it that some of these methods are inefficient, very expensive to operate and do lead to the generation of secondary contaminants [2,7]. Among the available methods mentioned above, adsorption is widely acknowledged as the most economically and friendly favourable method for water treatment and this is in addition to its simple mode of operation [8,9]. Activated carbon is the widely-utilized adsorbent; however, it's expensive when compared with other adsorbents coupled with the fact that its usage depends largely on the availability of activated carbon and the degree of the required treatment process [10]. Furthermore, complexing agents which are also known as enhancer will be required to elevate the effectiveness of the activated carbon in elimination of inorganic pollutants [6].

Several adsorbents such as commercial activated carbon and mussel shells [8], calcined oyster shells [11], waste eggshell [12], modified maize straw [13], modified cantaloupe peel [14], orange peel derived biochar [15], aragonite shells-derived biosorbent [16], waste shells of golden apple snail [17] and orange peel [18] among others have been effectively deployed in the remediation of different kinds of pollutants in wastewater. Hydroxyapatite (HAp) is one of the apatite minerals constituting 60–70% of bone matrix containing high affinity for cations and thus enables it to be highly biocompatible, bioactive and as an adsorbent [9]. Besides, many applications of HAp such as bone and food supplements, drug delivery, carriers of genes, dental treatment, sorbent material in proteins and pollutants removal [19–23] have been well documented in literature. HAp was selected as adsorbent in this present work due to its well developed porous structure, low solubility, good ion-exchange ability and ease of preparation. In this study, our aim is to develop hydroxyapatite adsorbent for cadmium ion removal from aqueous solution. The HAp structure was analyzed with FT-IR, SEM, XRD, EDAX, and TEM. The effects of Cd²⁺ concentration, contact time, pH, and HAp quantity were investigated alongside with the equilibrium, kinetics, and thermodynamics properties.

2. Experimental

2.1. Preparation of the adsorbent

The chemically synthesized HAp was done by following Gross et al. [24] method with some adjustments. 0.1 M Ca(NO₃)₂•6H₂O was made and magnetically stirred for 10 min and added to 0.06 M solution of (NH₄)₂PO₄ in dropwise and keeping the pH at 11 with ammonia solution. The mixture was constantly stirred for 12 h, filtered and washed with deionized water. The resultant product was dried at 135 °C for 8 h and labeled as CHAp.

2.2. Characterization of adsorbent

A Hitachi, Japan, S-3000H model scanning electron microscope coupled with energy dispersive X-ray (EDX) was deployed for the elemental composition analysis of CHAp, while a PANalytical, X'Pert PRO, Netherland model of X-ray diffractometer was used to determine the phase purity and crystallinity in an incremental step size of 0.02 using CuKα (γ = 1.54178 Å) within the range of 10° to 60°. A TENSOR 27 Fourier transform infrared (Bruker, Germany) (FT-IR) was utilized for the functional group investigation from 400 to 4000 cm⁻¹. A Tecnai 20 G2 FEI (Netherland) model of Transmission electron microscope (TEM) was used to further investigate the surface morphology of the adsorbent. The zero point charge (pH_{zpc}) of CHAp was performed by using a Zetasizer Nano ZS instrument (Malvern, UK) from a solution of cadmium ion prepared by dissolving 0.1 g of CHAp in 25 ml of cadmium solution.

2.3. Cd²⁺ preparation

Cd²⁺ stock solutions were made from Cd(NO₃)₂•4H₂O (99%) obtained from Aldrich, Germany. 1 g of Cd(NO₃)₂•4H₂O was weighed and dissolved in 1 L de-ionized water and other standard solutions were thereafter made from this using dilution principle. In order to investigate the effect of solution pH on the adsorption process, 1.0 mol L⁻¹ of HCl or NaOH solution was used to adjust the pH to a desired value prior to the addition of the metal ions.

2.3.1. Equilibrium study

Equilibrium study was performed in 250 ml Erlenmeyer flasks which consist of 25 mL of metal ions solution in the range of 40–240 mg/L and 0.004 g of CHAp. The contents were placed on a thermostated shaker at 150 rpm and 30 ± 1 °C for 120 min to attain equilibrium. A Varian Model SPECTRA 220 of Atomic Absorption Spectrophotometer was used to determine Cd(II) concentrations before and after adsorption process. The amount of Cd²⁺ sorbed by CHAp was obtained using equation (1) below:

$$Q_e = \frac{C_o - C_e}{m} \times V \quad (1)$$

The adsorbed amount of Cd^{2+} is denoted as Q_e in mg/g, while the concentrations of Cd^{2+} (initial and equilibrium) in mg/L are given as C_o and C_e respectively, volume (V) in L is the amount of Cd^{2+} used and the mass of the CHAp used is denoted as m in g.

2.4. Kinetics evaluation

The kinetics evaluations were performed at time intervals between 0 and 240 min. The quantity of the solutes adsorbed at certain t, Q_t (mg g^{-1}), was determined using equation (2) below:

$$Q_t = \frac{(C_o - C_t)V}{W} \quad (2)$$

Such that the liquid-phase initial concentration of Cd^{2+} is C_o , (mg L^{-1}) and C_t (mg L^{-1}) is the amount of liquid-phase left at time t, volume V in L of the solution and the mass (g) of CHAp used is given as W.

2.5. Adsorption kinetics studies

Pseudo-first order, pseudo-second-order, Elovich and Intra-particle diffusion kinetic models as described by equations (3)–(6) below were used for the evaluation of the data generated [25-27]:

$$Q_t = Q_e(1 - e^{-k_1 t}) \quad (3)$$

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \quad (4)$$

$$Q_t = 1/\beta \ln(\alpha \beta^* t) \quad (5)$$

$$Q_t = K_{id} t^{0.5} + C_i \quad (6)$$

All the parameters in these equations are defined by Adeogun et al. [25].

2.6. Statistical test

The sum square error function (SSE) was used to validate the better fits between the first- and second-order models as given in equation (7):

$$SSE = \sum_{i=1}^N (Q_{(\text{exp})} - Q_{(\text{cal})})^2 \quad (7)$$

2.7. Isotherms studies

Adsorption data generated the equilibrium investigation were analyzed with four common adsorption isotherm models namely, Langmuir, Freundlich, Dubinin–Radushkevich (D-R) and Tempkin isotherm as described in equations (8)–(11) [25,28–31].

2.8. Langmuir isotherms

$$Q_{eq} = \frac{Q_{\max} b C_e}{1 + b C_e} \quad (8)$$

2.9. Freundlich isotherm

$$Q_{eq} = K_F C_e^{1/n} \quad (9)$$

2.10. Tempkin isotherm model

$$Q_e = \frac{RT}{b_T} \ln a_T C_e \quad (10)$$

2.11. The Dubinin–Radushkevich isotherm

$$Q_e = Q_s e^{-\beta e^2} \quad (11)$$

Details about the definitions of all the parameters are well documented by Adeogun et al. [25].

The adsorption's mean free energy per mole of the adsorbate is given in equation (12) as:

$$E = (2\beta)^{-0.5} \quad (12)$$

If E is within the range of 8 and 16 kJ/mol, it is chemisorption, but when the value is below 8 kJ/mol, it's a physical process [9,12].

2.12. Thermodynamics study

The distribution of the Cd^{2+} molecules in the solution at equilibrium is given in equation (13) as:

$$K_d = \frac{Q_e}{C_e} \quad (13)$$

The equilibrium constant K_d is temperature dependent which was deployed to determine the thermodynamic parameters, ΔH° , ΔS° and ΔG° using the equations listed in (14)(14) & (15)(15) [9,12]:

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

$$\ln K_d = \Delta S^\circ/R - \Delta H^\circ/RT \quad (15)$$

2.13. Desorption studies

In order to assess the reusability of the prepared adsorbent, 0.1 L of 0.05 M HCl, 0.05 M NaOH, and distilled water were contacted with 0.2 g of the exhausted adsorbent and agitated for 100 min and thereafter analyzed using a AAS. Percentage desorption was computed using the equation below:

$$\%d = \frac{C_d}{C_a} \times 100$$

where C_a is the concentration of adsorbed pollutant (mg/g), and C_d is the concentration of the pollutant desorbed (mg/g).

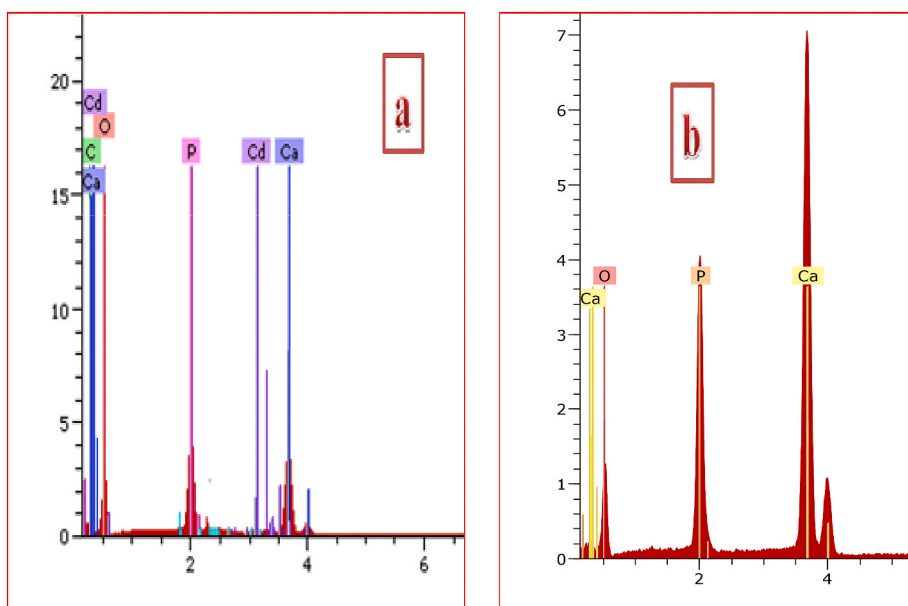


Fig. 1. EDAX analysis of CHAp (a) before and (b) after adsorption of Cd^{2+} .

3. Results and discussions

3.1. Characterizations

EDAX analyses of CHAp before and after adsorption of Cd^{2+} are as presented in Fig. 1a and b respectively indicating Ca, O and P as the main constituents of CHAp. However, Cd was detected after adsorption process thus suggesting that Cd^{2+} were sorbed onto the apatite surface. FT-IR spectra of the CHAp before and after Cd^{2+} uptake is shown in Fig. 2. Chief functional bands of CHAp were seen with slight dissimilarities observed after cadmium adsorption and this further corroborate the integration of Cd^{2+} onto the surface of the apatite. Bands in the range of 1028 and 1055 cm^{-1} were assigned to asymmetric mode of PO_4^{3-} . The peaks observed at 886 cm^{-1} corresponds to CO_3^{2-} which was adsorbed during the synthesis process from open air. Bands such as 1650, 1674, 3145 and 3154 cm^{-1} were attributed to water molecules adsorbed, while the bands notices between 3526 and 3625 cm^{-1} were assigned to the stretching of O–H group. Bands assigned to PO_4^{3-} and OH^- after cadmium adsorption became broadening which further suggest the uptake of the pollutant onto the apatite surface.

The prepared CHAp was examined for phase purity and stability by XRD technique and match up with JCPDS file no. 09–432 (see Fig. 3). Broad peaks were seen which is as a consequence of the poor crystallinity of the prepared CHAp. Most prominent diffraction peaks such as (002), (211), (310) and (213) planes correspond to pure HAp were detected. Broadening and slight changes in the peak positions after the uptake of Cd^{2+} were noticeable and this also corroborates the FT-IR result.

The SEM morphology of the synthesized CHAp is presented in Fig. 4a whereas, TEM images before and after the uptakes of Cd^{2+} are shown in Fig. 4b & c respectively. The SEM result depicts fine particles with round shapes and this was corroborated by the TEM micrograph. After the adsorption process, the particles appear bigger suggesting the incorporation of Cd(II) ions onto the apatite surface.

3.2. Equilibrium studies

Uptake of Cd^{2+} was studied for initial adsorbate concentrations of 40, 80, 120, 160, 200 and 240 mg/L and at pH of 6.0 as presented in Fig. 5. It is evident from the plots that the reaction was rapid at the initial stage and slows down as the reaction approaches equilibrium stage. Highest adsorption potential of Cd^{2+} by CHAp was obtained at 120 min of contact time and 240 mg/L of adsorbate concentration. The amount of Cd^{2+} adsorbed increased from 10.2 to 24.5 mg/g when the contact time was move up from 10 to 120 min at 40 mg/L initial metal concentration. At an elevated metal concentration of 240 mg/L, an increase from 50.2 to 193.4 mg/g was observed. According to Maingi et al. [32], the extent of sorption increased expeditiously till optimum equilibrium was reached at 80 min for cadmium ions adsorption by geopolymers. In a similar work by Akinhanmi et al. [18], utmost uptake of Cd(II) ion was obtained at a contact time of 120 min. Ofudje et al. [9] reported a rapid uptake of the cadmium ions in the first 15 min, followed by a gradual increase for the next 120 min maximum adsorption capacity 134.3 mg/g.

The relationship between CHAp dosage and the amount of Cd^{2+} adsorbed was evaluated and is presented graphically in Fig. 6. The results indicated that the percentage adsorption of Cd^{2+} increased alongside with increase in the amount of the synthesized HAp until saturation was attained at a dosage of 0.04 g of the adsorbent. When the dosage of the CHAp was adjusted from 0.01 g to 0.04 g, it was observed that the percentage adsorption of cadmium was found to have increased from 68.3 to 96.4% at 120 min, 240 mg/L of Cd^{2+} concentration, temperature of 45 °C and solution pH of 6.0 [25–28].

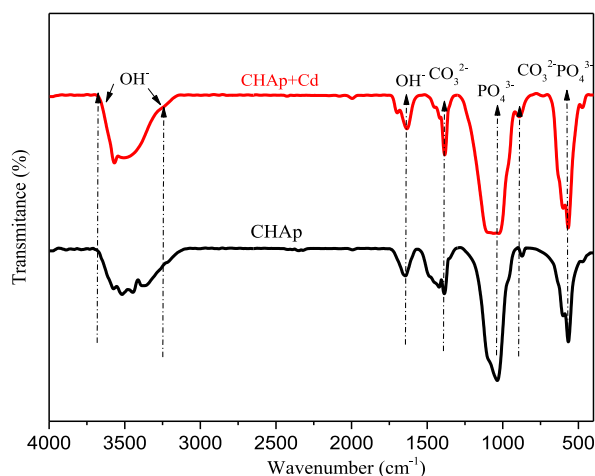


Fig. 2. FTIR spectra of CHAp before adsorption and after adsorption of Cd^{2+} .

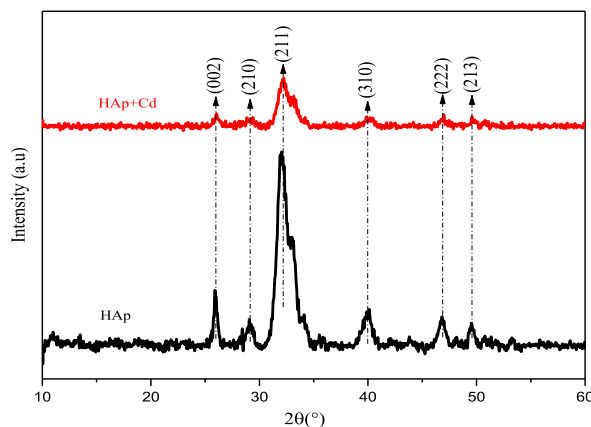


Fig. 3. XRD spectra of CHAp before adsorption and after adsorption of Cd^{2+} .

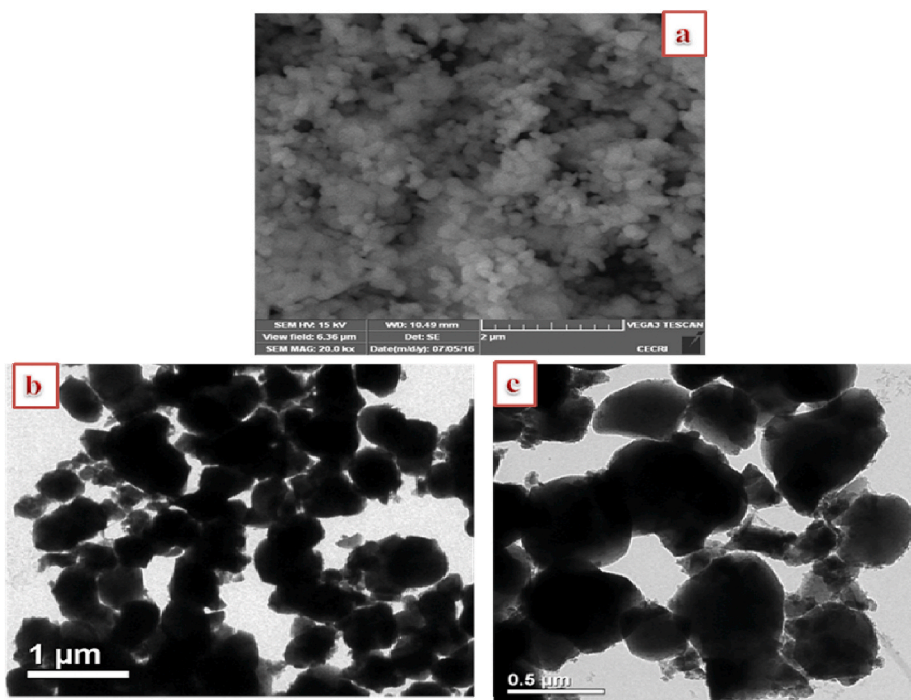


Fig. 4. (a) SEM of CHAp, (b) TEM image of CHAp before and (c) TEM after adsorption.

3.3. Study on pH

The study on the role of pH on Cd^{2+} adsorption was evaluated by varying the solution pH between 2.0 and 8.5 as represented graphically in Fig. 7. The elimination of Cd^{2+} rose significantly from 61.2 to 94.5% when the pH was adjusted from 2.0 to 6.0. Lower adsorption was noticed at a pH higher than 6.0. According to Gerçel and Gerçel [33], the competition between pollutant and H^+ at low pH for the unoccupied sites and the positive charge density of the binding sites of the metal resulted in the low adsorption observed within this region. However, deprotonation which occurred on the metal binding sites as a result of the increase in the negative charge density on the surface of the adsorbent at higher pH improved the adsorption efficiency [33,34]. The precipitation of Cd^{2+} at higher pH may also be responsible for the low adsorption at higher solution pH. According to Schubert et al. [34], reduction in surface charge of metal ions could be due to charge screening on the surface and insufficient proton (pH). Thus, the occurrence of hydroxides depends on pH, redox potential and ion concentration. This implies that at a particular pH, the metal ion could be transformed into its hydroxides forms and subsequently results in insufficient surface charges responsible to the adsorption process [35].

The zero point charge (pHpzc) of CHAp was estimated to be 5.21 and it's expected that the surface of CHAp will be positive at pH less than the value of the pHpzc and negative at a pH higher than the pHpzc value [36]. Thus, the positive charges on the surface of

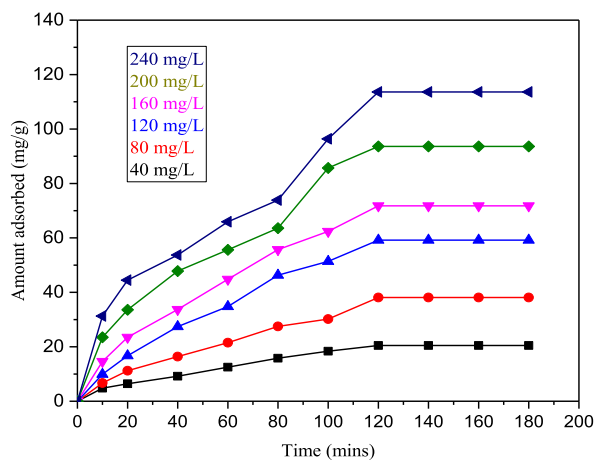


Fig. 5. Equilibrium studies showing the impacts of time and initial concentrations on the adsorption of Cd²⁺.

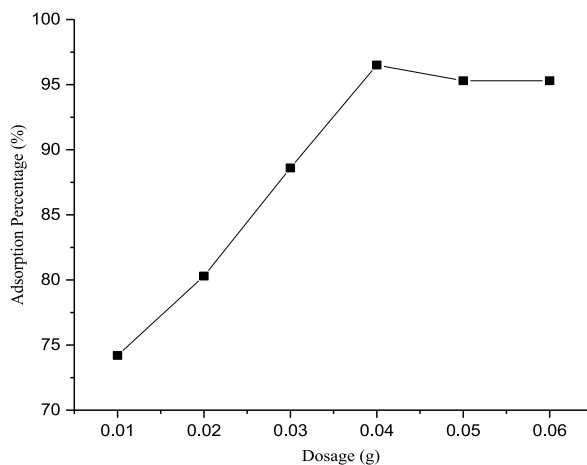


Fig. 6. Equilibrium studies showing the impacts of CHAP dosage on the adsorption of Cd²⁺.

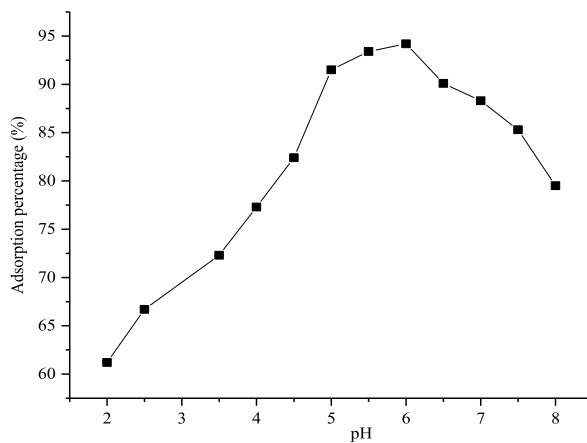


Fig. 7. Equilibrium studies showing the impacts of pH on the uptake of Cd²⁺.

CHAp at $\text{pH} < \text{pH}_{\text{pzc}}$ justifies the low adsorption of cadmium ions in high acidic medium but with the surface becoming negative at $\text{pH} > \text{pH}_{\text{pzc}}$, the uptake of cadmium was greatly enhanced due to the strong electrostatic attraction between the positively charged cadmium ions and the negatively charged surface of the CHAp adsorbent [36]. Maingi et al. [32] reported that optimum adsorption of cadmium ion by geopolymer was achieved at pH 5. Literature reports from Akinhanmi et al. [18] showed that with a rise in the pH from 2 to 5.5, the sorption capacity of orange peel adsorbent for the elimination of Cd(II) ions rose from 24.62 to 44.42% with the highest adsorption accomplished at a solution pH of 5.5. It was reported further that with elevated pH, the negative charge network on orange peel increases which is due to the deprotonation of the binding sites and this enhances the uptake of Cd(II) ions. Ofudje et al. [9] reported that the uptake of Cd^{2+} by bone meal-derived apatite increased drastically from 60.3 to 84.3% as the solution pH was raised from 3.5 to 6. It was further reported that at lower pH, contest arising from metal ions and hydrogen ions for the empty sites coupled with the positive density charge on the adsorbent sites were responsible for the lower removal efficiency as observed, but that as the solution pH increases, there is less competition by the hydrogen ions for the adsorption sites due to deprotonation and this gave rise to better uptake of the metal ions at optimum solution pH of 6.

3.4. Adsorption isotherms studies

Fig. 8 shows Langmuir, Dubinin-Radushkevich, Freundlich and Tempkin isotherms plots for the adsorption of cadmium, while the isotherm parameters are given in Table 1. Taking the coefficient of correlation (R^2) as a criterion for good fit of the system, the equilibrium adsorption data of cadmium fitted with Langmuir model, although other isotherms also showed good fitting. The utmost sorption capacity calculated from Langmuir equation is 195.711 mg/g, Freundlich isotherm is $6.703 \text{ mg/g} (\text{mg/L})^{-1/2}$ while that of D-R isotherm is 98.924 mg/g in that order. Langmuir adsorption intensity (R_L) were found to be in the range of 0–1; indicating favourable adsorption process; i.e when $0 < R_L < 1$; adsorption is favourable [25]. From the Tempkin adsorption isotherm, the values of Tempkin constant (α_T) and heat of adsorption (b_T) were obtained to be 0.292 (L/g) and 62.378 J/mol respectively. The D–R isotherm matches well with the data obtained experimentally. The value of E so calculated is 0.106 kJ/mol which indicates that the adsorption of Cd^{2+} onto CHAp adsorbent follows physical adsorption since E is less than 8 kJ/mol [37]. Table 2 showed that the adsorption capacity of CHAp for the uptake of Cd^{2+} compete favorably with other adsorbents in literature.

4. Kinetics evaluations

Data from cadmium adsorption by the chemically synthesized hydroxyapatite (CHAp) were subjected to pseudo-first- and second-orders, intra-particle diffusion and Elovich models as shown in Fig. 9a–d, while physical parameters are as given in Table 3. Values of R^2 obtained from pseudo-first and second-orders models were greater than 0.9 for all the initial metal concentrations. However, on the comparison of the values of experimental adsorption capacity ($q_{e,\text{exp}}$) of the pseudo-first-order model with computed adsorption capacity ($q_{e,\text{cal}}$), showed closeness than the pseudo-second-order model. Also, values from the sums of error squares computed in the case of pseudo-second-order were found to be higher than those of first order and it can therefore be deduced that the uptake of Cd^{2+} by CHAp followed pseudo-first-order kinetic model.

4.1. Thermodynamic studies

The role played by temperature during the uptake of Cd^{2+} was conducted at diverse temperatures (25–55 °C). When the temperature is increased, the rate of distribution of Cd^{2+} particles across the external border layers and the internal pores of CHAp increased, as a result of decline in the fluidity of the Cd^{2+} [37]. The plots of $\ln K_D$ versus the reciprocal of temperature in Fig. 10 for Cd^{2+} adsorption was used to evaluate the thermodynamic constants given in Table 4. The distribution ratio (K_D) values increased with temperature from 1.0028 to 1.0072 on adjusting the temperature from 298 to 318 K thus inferring the endothermic character of the process of adsorption. The free energy change, ΔG , was found to have increased from -5.937 to -20.035 kJ/mol with rise in

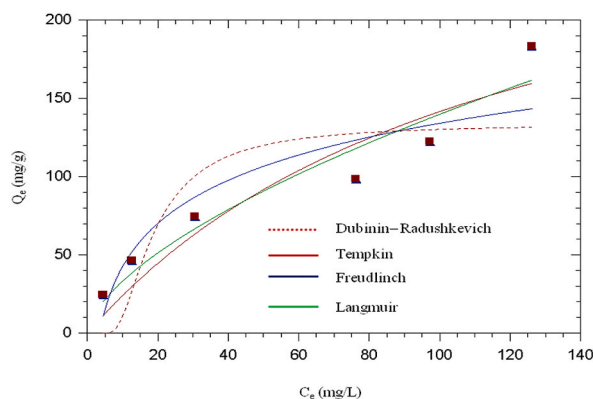


Fig. 8. Isotherm fits for Cd^{2+} adsorption onto CHAp at metal conc: 40–240 mg/L, CHAp dosage: 0.04 g/L, Temp: 45 °C and pH: 6.0.

Table 1
Isotherm constants Cd²⁺ adsorption by CHAp surface.

Langmuir	Q _{max} (mg/g)	195.711
	R _L	0.008
	b (mg/L)	0.517
	R ²	0.998
Freudlinch	K _F (mg/g) (mg/L) ^{-1/2}	6.703
	1/n	0.624
	R ²	0.981
Tempkin	α _T (L/g)	0.292
	b _T (J/mol)	62.378
	R ²	0.959
Dubinin– Radushkevich	Q (mg/g)	98.924
	E (kJmol ⁻¹)	0.106
	ε (mol/J) ²	15.550
	R ²	0.921

Table 2
Adsorption capacities of CHAp in comparism with others in literature.

Adsorbent	Adsorbent capacity (qe)	References
Commercial activated carbon	31.9	Van et al. [8]
Mussel shells	26.0	Van et al. [8]
bone meal-derived apatite	116.16	Ofudje et al. [9]
calcined oyster shells	29.5	Alidoust et al. [11]
Waste eggshell	23.4	Baláz et al. [12]
modified maize straw	196	Guo et al. [13]
Modified cantaloupe peel	30.4	Tran and Chao [14]
orange peel derived biochar	115	Tran et al. [15]
aragonite shells-derived biosorbent	189	Veneu et al. [16]
waste shells of golden apple snail	81.3	Zhao et al. [17]
Orange peel	128.23	Akinhanmi et al. [18]

temperature. The ΔH and ΔS for the sorption process were estimated as be 175.591 and 0.610 kJ/mol respectively. Increasing the temperature could generate a swelling effect in the internal structure of CHAp, thus causing huge penetration of adsorbate molecules [38–40].

4.2. Mechanism of Cd²⁺ adsorption by CHAp

Several mechanisms are involved during the adsorption process of heavy metal ions and some of them include electrostatic interaction, ion exchange, complexation, physical adsorption, chemical adsorption, and precipitation [36,41]. These mechanisms can be understood by exploiting the various information provide from structural elucidation techniques such as XRD, FT-IR, kinetics, isotherms, etc. The information from the isotherm analysis revealed that the mechanism of cadmium ion adsorption by CHAp is physical in nature due to the conformity of the equilibrium data with Langmuir isotherm. This was also corroborated by the kinetic studies which fitted perfectly with the Pseudo-first-order model. FT-IR analysis showed that the of the CHAp contained some negatively charged functional groups such as phosphate, carbonate, and hydroxyl which are attached to the positively charged Cd²⁺ thus indicating electrostatic attraction mechanism [36,41]. This was supported from the report on the zero point charge (pHpzc) of the adsorbent surface.

Maingi et al. [32] using kinetic analysis, proposed that Cd (II) ions adsorption on geopolymer adsorbents occurs through chemical processes involving the valence forces or the shared exchangeable electrons since pseudo-second-order kinetic mode is more predominant in the rate-controlling step for the cadmium system. Similarly, Akinhanmi et al. [18] through careful inspection of values of the Q_{ecal} from the first-order model which correspond well with the Q_{exp}, explained that the whole adsorption process of Cd(II) ion onto the surface of orange peel adsorbent was physisorption. Ofudje et al. [9] observed by FT-IR analysis that the mechanism of Cd(II) ions uptake by bone meal-derived apatite is as a result of the electrostatic attractions forces between the various negative charges such as CO₃²⁻, OH⁻, PO₄³⁻ on the surface of the adsorbent and the positive pollutants.

5. Conclusion

In this study, we chemically prepared hydroxyapatite via precipitation technique and characterized by TEM, XRD, FT-IR and SEM. CHAp showed round shape as indicated by TEM and SEM images. FT-IR spectra revealed the presence of phosphate, hydroxyl and carbonate groups. The sorption potential of CHAp was investigated for the removal of Cd²⁺ from aqueous system. Adsorption kinetics fitted well with the pseudo-first-order model. Equilibrium models results showed that the Cd²⁺ adsorption data using CHAp followed the Langmuir model which inferred that monolayer and homogeneous surfaces are more effective when compared with heterogeneous

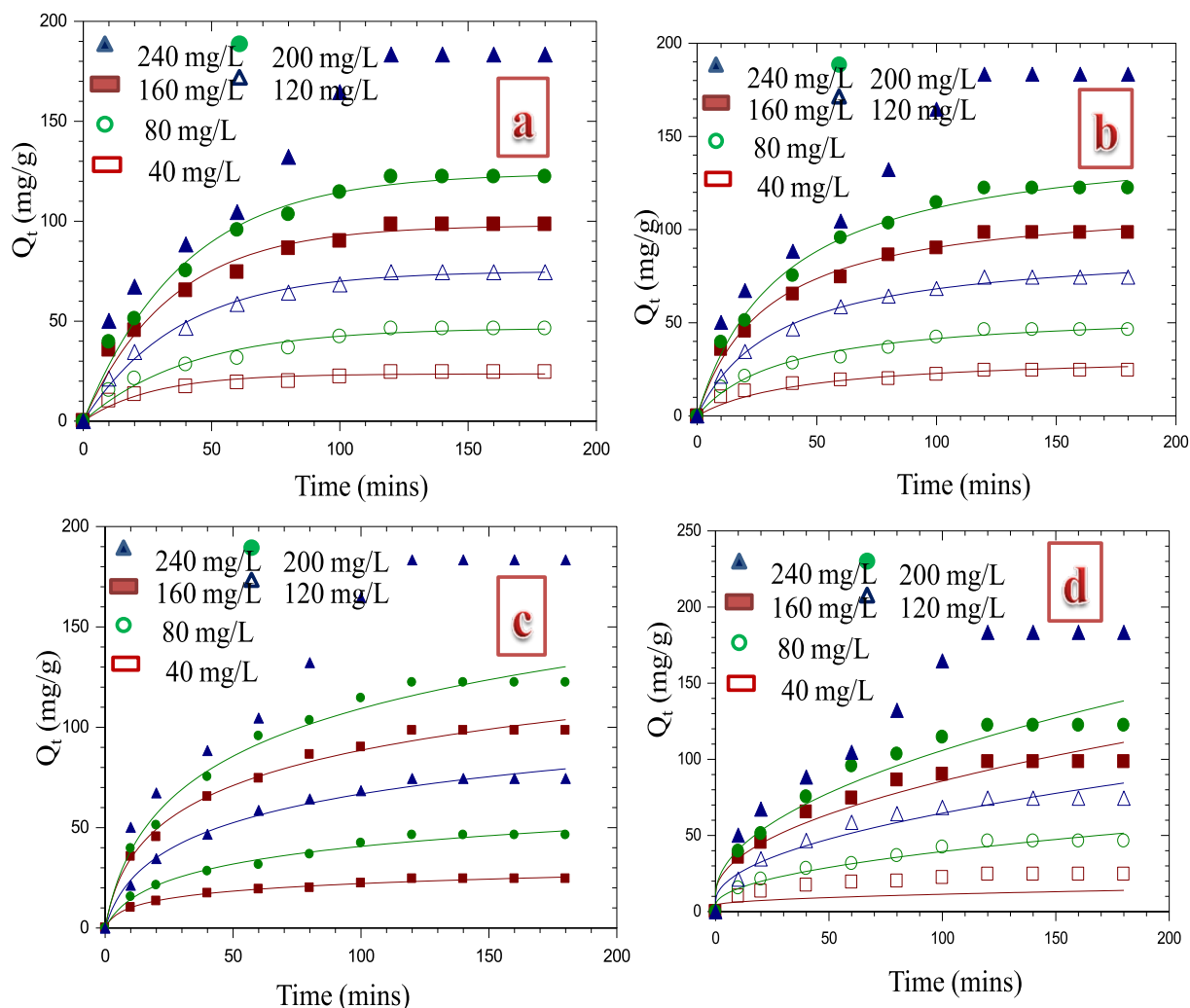


Fig. 9. Kinetics plots for Cd²⁺ adsorption by CHAp using (a) pseudo-first order (b) pseudo-second-order (c) Elovich model & (d) intra-particle diffusion.

Table 3
Kinetics constant values of Cd²⁺ adsorption by CHAp.

	C ₀ (mg/L)	40	80	120	160	200	240
First order	Q _e (exp) (mg/g)	24.500	46.300	74.500	98.400	122.300	183.400
	Q _e (cal) (mg/g)	23.621	46.669	75.086	98.002	124.046	201.942
	k ₁ (mins ⁻¹)	0.017	0.024	0.027	0.029	0.036	0.036
	R ²	0.994	0.995	0.999	0.997	0.998	0.993
	% SSE	0.011	0.002	0.002	0.001	0.004	0.030
Second order	Q _e (cal) (mg/g)	32.987	56.705	91.366	116.896	151.544	267.324
	k ₂ × 10 ⁴ (g/mg/min)	6.802	4.824	3.200	2.904	1.831	5.323
	R ²	0.991	0.997	0.999	0.999	0.999	0.994
	% SSE	0.104	0.068	0.068	0.057	0.072	0.138
Elovich	α (mg/g/mins)	2.868	2.527	4.284	7.087	6.758	4.891
	β (g/mg)	0.179	0.073	0.045	0.037	0.027	0.013
	R ²	0.999	0.998	0.998	0.999	0.998	0.994
Intra particle diffusion	K _p (mg/g/mins ^{1/2})	1.752	3.547	5.798	7.433	9.533	14.891
	C (mg/g)	3.971	3.941	6.631	11.428	10.511	0.742
	R ²	0.990	0.995	0.992	0.992	0.992	0.994

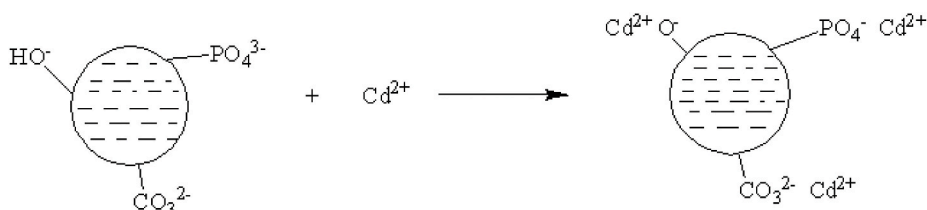


Fig. 10. Schematic mechanism of Cd^{2+} adsorption by CHAP.

Table 4

Thermodynamic constants for Cd^{2+} adsorption by CHAP.

T (K)	K_D	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol)	R^2
298	1.0028	-5.937	175.591	0.610	0.968
303	1.0035	-8.817			
308	1.0044	-11.261			
313	1.0064	-16.656			
318	1.0072	-20.035			

surfaces. Furthermore, results obtained from n and R_L values confirmed that the adsorption process is favourable. The study on the thermodynamic parameters indicated that Cd^{2+} adsorption process is spontaneous and endothermic. Conclusively, CHAP can be introduced as an effective and efficient adsorbent in removing Cd^{2+} from industrial wastewaters.

Author contribution statement

Edwin Andrew OFUDJE: Conceived and designed the experiments; Performed the experiments; Wrote the paper.
 Ezekiel F. SODIYA: Contributed reagents, materials, analysis tools or data; Performed the experiments.
 Olajire S. Olanrele: Contributed reagents, materials, analysis tools or data; Analyzed and interpreted data.
 Fatai AKINWUNMI: Performed the experiments; Wrote the paper.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Data availability statement

Data will be made available on request.

Declaration of interest's statement

The authors declare no competing interests.

Acknowledgments

Technical staff of CSIR-CECRI, Central Instrumentation Facility (CIF) of Karaikudi, India are well appreciated for their supports during characterization.

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