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Removal of cadmium(II) from aqueous solution by agricultural waste cashew nut shell

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Abstract−Cashew nut shell (CNS) is a low cost adsorbent that has been used for the removal of cadmium(II) from an aqueous solution. The effects of various parameters such as solution pH, CNS concentration, contact time, initial cadmium(II) concentration and temperature were examined. The CNS was effective for the quantitative removal of cadmium(II) ions in acidic conditions and equilibrium was achieved in 30 min. The experimental data were analyzed by two-parameter (Langmuir, Freundlich, Temkin and Dubinin-Radushkevich) and three-parameter models (Redlich-Peterson, Koble-Corrigan, Toth and Sips) by nonlinear regression analysis. The characteristic parameters for each isotherms and related correlation coefficients have been determined by using MATLAB 7.1. Thermodynamic parameters such as ΔG^o, ΔH^o and ΔS^o have also been evaluated, and it was found that the sorption process was feasible, spontaneous and exothermic. Pseudo-first-order, pseudo-second-order, Elovich kinetic and intraparticle diffusion models were selected to follow the adsorption process. The results of the kinetic study show that the adsorption of cadmium(II) could be described by the pseudo-second order equation, suggesting that the adsorption process is presumably chemisorption. A single-stage batch adsorber was designed for different adsorbent dose-to-effluent volume ratios using the Freundlich equation. The results indicate that the cashew nut shell could be used to effectively adsorb cadmium(II) from an aqueous solution.

Key words: Cadmium(II), CNS, Isotherms, Kinetics, Thermodynamics

INTRODUCTION

Heavy metals are toxic pollutants released into the environment as a result of industrial, mining and agricultural activities [1,2]. Cadmium is a heavy metal that is regarded as an element of high toxicity. Cadmium ions are not biodegradable and can be accumulated easily in living tissue, thus can be readily adsorbed into the human body throughout the food chain [3,4]. An excessive level of cadmium ions in the water can affect the bio-systems and be a threat to human beings. Cadmium toxicity causes adverse health effects such as bone lesions, cancer, lung insufficiency and hypertension [5-8]. The drinking water guideline value recommended for this element by the World Health Organization (WHO) and American Water Works Association (AWWA) is 0.005 mg/L [9,10]. Hence the removal of cadmium ions from the water and wastewater is highly important.

The traditional methods to remove the heavy metals from aqueous environment include precipitation, filtration, ion exchange, evaporation, reverse osmosis, solvent extraction, electrochemical treatment and membrane technologies. However, these traditional methods are either inefficient or expensive when heavy metals exist in lower concentrations [11,12]. Consequently, it is essential to find new methods for effective removal of heavy metals from water and wastewater. Compared with other traditional methods, adsorption is quite popular due to its simplicity and high efficiency, as well as the availability of a wide range of adsorbents [13-18]. Activated carbon is the most widely used adsorbent for the removal of heavy metals from the aqueous media. But its high cost and loss during the regeneration restrict its applications [3,19]. When compared to activated carbon, the usage of agricultural wastes or industrial by-product as a low-cost alternative adsorbent has received considerable attention. Many materials such as RCS [3], AGCS [3], bael tree leaf powder [20], rice husk [21], sugarcane bagasse [22], grape stalk [23], corncob [24], saw dust [25], tea-industry waste [26], olive cake [27], hazelnut shell [28], bagasse fly ash [29], low-grade phosphate [30], hematite [31], wheat bran [32], pretreated *Aspergillus niger* [33], pretreated *Mucor rouxii* [34], live *Mucor rouxii* [34], Chinese herb *Pang Da Hai* [35], *Gracilaria salicornia* (red) [36], *Ceiba pentandre* hulls carbon [37], olive stone carbon [38], oak wood char [39], pine bark char [39], oak bark char [39], carbon F-400 [39], calgon F-400 [40], pure smectite [41], lewatite S100 [41], *Hypnea valentiae* biomass [42], and banana peels [43] have been tested for cadmium(II) removal from water and wastewater systems. Because of the low cost and high availability of these materials, it is not essential to undertake a complicated regeneration process.

The present research is to develop inexpensive and effective adsorbent from the agricultural wastes, such as cashew nut shell (CNS), to replace the existing commercial materials. In the present study, cashew nut shell from which the cashew nut shell liquid (CNSL) was extracted [44] was used as an adsorbent and it was examined for sorption properties towards cadmium(II) ions. The effect of various experimental parameters such as solution pH, CNS concentration, contact time, initial cadmium(II) concentration and temperature have been investigated. Adsorption isotherms and kinetics were in-

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Table 1. Properties of the cashew nut shells

Proximate analysis (wt%)		Ultimate analysis (wt%)		Ash chemical composition (wt%)	
Volatile matter	65.21	Carbon	45.21	Silica	64.53
Moisture	9.83	Hydrogen	4.25	Iron oxide	3.27
Ash	2.75	Oxygen	37.75	Aluminium oxide	2.19
Fixed carbon	22.21	Nitrogen	0.21	Calcium oxide	26.89
		Sulphur	Nil	Magnesium oxide	2.49
		Moisture	9.83	Sodium oxide	0.63
		Ash	2.75		

vestigated and different adsorbent models were used to evaluate the experimental data and to elucidate the possible adsorption mechanism. Thermodynamic studies were also conducted to estimate the standard free energy (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o).

EXPERIMENTAL

1. Adsorbent

The raw CNS was collected from Karaikudi, Sivagangai District, Tamilnadu, India and the treated CNS was collected from the CNSL recovery unit and it was used as an adsorbent. This agricultural waste was thoroughly rinsed with water to remove dust and soluble material; then it was allowed to dry at room temperature. The above dried waste was ground to a fine powder in a still mill. The resulting material was sieved in the size range of 200-30 mesh particle size. The proximate and ultimate analysis of cashew nut shells are shown in Table 1.

2. Adsorbate

All the chemicals used were of analytical reagent (AR) grade. Stock solution of 100 mg/L of cadmium(II) was prepared from $3Cd(SO_4)\cdot 8H_2O$ (Merck, India) using double distilled water. Desired test solutions of cadmium(II) ions were prepared using appropriate subsequent dilutions of the stock solution. Different concentrations of cadmium(II) ions were prepared from standard solution varied between 10 to 50 mg/L. Before mixing the adsorbent, the pH of each test solution was adjusted to the required value with 0.1 M NaOH or 0.1 M HCl.

3. Analysis

The concentrations of cadmium in the various solutions before and after equilibrium were determined by AA6300 Atomic absorption spectrometer (Shimadzu, Japan). The pH of solution was measured with a Hanna pH meter using a combined glass electrode. FTIR analysis was used to identify the different functional groups present in the CNS adsorbent. An FTIR spectrometer (PE IR SPECTRUM ASCII PEDS 1.60) was used for the IR spectral studies of CNS adsorbent (4,000 to 450 cm^{-1}). For FTIR studies, 1 mg of sample was mixed and ground with 100 mg of KBr and made into a pellet. The background absorbance was measured by using pure KBr pellet. The surface morphology of the CNS adsorbent was analyzed with a Leo Gemini 1530 scanning electron microscope at an accelerating voltage of 10 kV, and with the working distance of 100 μm for the CNS adsorbent.

4. Adsorption Studies

A series of batch adsorption experiments were conducted to study the adsorption mechanism, adsorption isotherms and adsorption kinetics by shaking the flasks at 120 rpm using a rotary shaker. The systematic process for the removal of cadmium(II) ions from aqueous solutions by the use of CNS in a batch system was studied in the present work. The data obtained in batch studies were used to calculate the percentage removal of cadmium(II) ions by using the following mass balance relationship:

$$\%\ \text{Cadmium(II) removal} = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \qquad (1)$$

Where, C_o and C_e are the initial and equilibrium concentration (mg/L) of the cadmium(II) ion solutions, respectively.

4-1. Effect of Solution pH on Cadmium(II) Adsorption

The effect of solution pH on the adsorption capacity of CNS was investigated using a 100 mL solution of 20 mg/L of cadmium(II) ion for a pH range of 2.0 to 8.0 at 30 °C. The experiments could not be performed at higher pH value due to hydrolysis and precipitation of cadmium(II) ions. The flasks were agitated on a rotary shaker for 30 min to ensure that the equilibrium was reached. The mixtures were then filtered through Whatman 42 filter paper and the concentration of cadmium(II) in the filtrates was analyzed using an AA6300 Atomic absorption spectrometer. Each determination was repeated thrice and the results obtained were their average value.

4-2. Effect of CNS Concentration

The batch adsorption experiments were conducted at a different CNS concentration from 0.1 g to 0.6 g at a 100 mL solution of 20 mg/L of cadmium(II) ion at pH 5.0, for a contact time of 30 min at 30 °C. The samples were then agitated and filtered and the filtrates were analyzed as mentioned before.

4-3. Effect of Contact Time

The batch adsorption experiments were conducted at different contact times (5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60 min) for an initial concentration of cadmium(II) ion in the range of 10-50 mg/L at pH 5.0, with the CNS concentration is 0.3 g in 100 mL solution in 250 mL conical flask at 30 °C. The samples were then agitated and filtered and the filtrates were analyzed as before.

4-4. Effect of Initial Cadmium(II) Ion Concentration

The batch experiments were carried out by contacting 0.3 g of CNS with 100 mL of cadmium(II) ion solution of different initial concentrations (10, 20, 30, 40, 50 mg/L) at pH value of 5.0 at 30 °C. A series of such conical flasks were shaken for 30 min at a speed of 120 rpm. The samples were filtered and the filtrates were analyzed as before.

4-5. Effect of Temperature

The batch experiments were performed at different temperatures of 30, 40, 50 and 60 °C for the initial cadmium(II) ion concentrations in the range of 10-50 mg/L at constant CNS dose of 3 g/L and pH of 5. A series of such conical flasks were shaken for 30 min at a speed of 120 rpm. The samples were filtered and the filtrates were analyzed as before.

5. Adsorption Isotherms

A series of solutions containing different initial cadmium(II) ions concentrations were prepared and the batch adsorption studies were undertaken at 30 °C to check the applicability of the two-parameter (Langmuir, Freundlich, Temkin and Dubinin-Radushkevich) and three-parameter adsorption isotherm models (Redlich-Peterson, Koble-Corrigan, Toth and Sips) under the specified conditions: initial solution pH of 5, contact time of 30 min, adsorbent dose of 3 g/L and an initial cadmium(II) ion concentration range of 10-50 mg/L. The cadmium(II) ion concentration of the various solutions was analyzed by atomic absorption spectrometer method. The data obtained in batch equilibrium studies were used to calculate the equilibrium cadmium(II) adsorptive quantity by using the following mass balance relationship:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{2}$$

Where q_e is the amount of cadmium(II) ion adsorbed (mg/g), V is the volume of solution treated (L), C_o is the initial concentration of cadmium(II) ion (mg/L), C_e is the equilibrium cadmium(II) ion concentration (mg/L) and m is the mass of the adsorbent (g).

6. Adsorption Kinetics

Kinetic studies were conducted in a 250 mL conical flask at room temperature (30 °C). Thus, the adsorbent dose of 0.3 g of CNS was contacted with 100 mL of a cadmium(II) ion solution of different known concentrations (10-50 mg/L). The solution mixture was shaken continuously and the samples were taken at predetermined time intervals from the mixture and were immediately filtered. The analysis of cadmium(II) ion concentration of the various solutions was determined by atomic absorption spectrometer method. The amount of cadmium(II) adsorbed at time t, q_t (mg/g), was calculated by the following expression:

$$q_t = \frac{(C_o - C_t)V}{m} \tag{3}$$

Where C_t is the concentration of cadmium(II) ion solution at any time t (mg/L).

7. Desorption Studies

Desorption studies were conducted to check the reversibility of the adsorption process. Desorption of cadmium(II) ions from the spent CNS was studied with the varying concentrations of hydrochloric acid (HCl) solution. The spent CNS was transferred to stoppered conical flasks which consist of 100 mL of HCl solution. The bottles were shaken at 30 °C using a rotary shaker, and the CNS was then removed by filtration. The concentrations of cadmium(II) in the aqueous solutions were determined by using AA6300 Atomic absorption spectrometer.

RESULTS AND DISCUSSION

1. Characterization of CNS

1-1. FTIR Studies

FTIR spectroscopy is a useful tool to identify the different functional groups present in an adsorbent. The adsorption capacity of CNS depends upon the porosity as well as the chemical reactivity of functional groups at the surface. This reactivity creates an imbalance between the forces at the surface when compared to those within the body, thus leading to a molecular adsorption by the van der Waals force. Knowledge of surface functional groups gives an insight into the adsorption capability of the CNS. The FTIR spectrum of the CNS sample is shown in Fig. 1. The intense broad band at 3,399 cm^{-1} is assigned to the O-H stretching vibration of water and the alcoholic groups. The presence of water is confirmed by its bending vibration at 1,630 cm^{-1}. The presence of the alkyl groups is evident by the intense peaks at 2,925 and 2,854 cm^{-1} due to the -CH$_2$- vibrations. Their presence is also evident by their -CH$_2$- bending vibrations at 1,374 and 1,454 cm^{-1}. A shoulder close to 1,740 cm^{-1} is assigned to the C=O vibration of the esters/keto groups. The presence of the ester groups is partly evident by their -COO- vibration at 1,233 cm^{-1}. The intense broad peak at 1,034 cm^{-1} is assigned to the C-O stretching vibration of the alcoholic groups. The -CH$_2$- rocking more is seen at 708 cm^{-1}. So from this IR spectrum the CNS is verified to have a large proportion of alkyl groups, alcoholic groups and smaller amount of ester/keto groups. The presence of a large amount of water indirectly establishes many of the alcoholic groups. Thus, the FTIR spectrum of CNS reveals that there are several functional groups in CNS that can bind cadmium(II) ions. These results agree with the surface chemistry of other agricultural by-products, such as rubber wood saw dust [45] and heartwood of Areca catechu powder [46]. The specific surface area and pore structure of the CNS were determined by using surface area and pore size analyzer (Quantachrome, Autosorb-I) on nitrogen adsorption at 77 K. The specific surface area was calculated by BET equation [47]. It was found that the BET surface area, pore volume, average pore diameter and bulk density of the CNS were 395 m^2/g, 0.4732 cm^3/g, 5.89 nm and 0.415 g/cm^3, respectively.

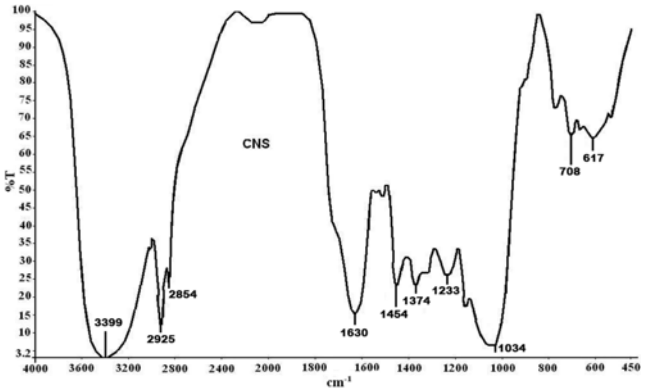
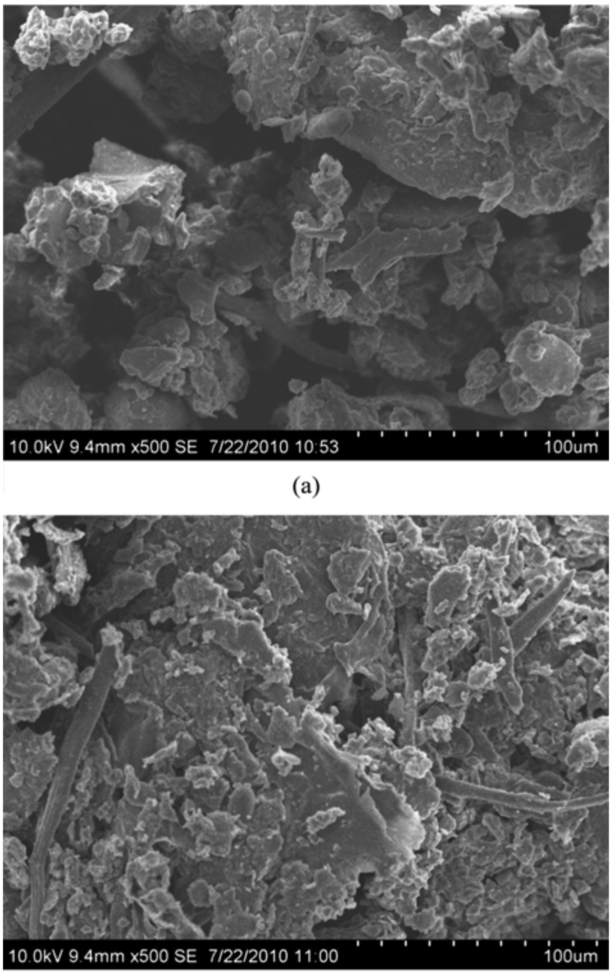


Fig. 1. FT-IR spectrum of cashew nut shell.

1-2. Scanning Electron Microscopy

The SEM images of the CNS and cadmium loaded CNS are shown in Fig. 2(a) and (b). The surface of the adsorbent appears to be irregular and porous (Fig. 2). On the basis of this fact, it can be concluded that the adsorbent has an adequate morphology for metal ion adsorption. After metal adsorption the porous surface on the CNS gets filled up by the cadmium(II) ion. This observation indicates that the metal ion was adsorbed to the functional groups present inside the wall of the CNS surface. Fig. 2(b) shows that the metal ions were



(a)

(b)

Fig. 2. (a) SEM image of cashew nut shell, (b) SEM image of cadmium loaded CNS.

heavily loaded in CNS and adsorption of metal ion occurs inside the wall of the CNS surface. So, the morphological study of metal loaded CNS confirms that the adsorption takes place inside the wall of the CNS surface.

2. Effect of Solution pH on Sorption Efficiency

The hydrogen ion concentration in the adsorption process is considered as one of the most important critical parameters that influences the adsorption behavior of metal ions in aqueous solutions. It affects the solubility of metal ions in the solution, replaces some of the positive ions found in the active sites and affects the degree of ionization of the adsorbate during the reaction [48,49]. The effect of solution pH on the adsorption of cadmium(II) ions onto CNS was evaluated within the pH range of 2.0-8.0. The studies beyond pH 8.0 were not tested because of the precipitation of the cadmium ions forming hydroxides [48]. From Fig. 3, it could be seen that the cadmium adsorption increases with the increase in the solution pH. The pH dependency of adsorption efficiency could be explained by the functional groups involved in metal uptake and metal chemistry. The FT-IR spectroscopic analysis shows that the CNS has a variety of functional groups, such as carboxyl and hydroxyl groups, which are involved in almost all the potential binding mechanisms.

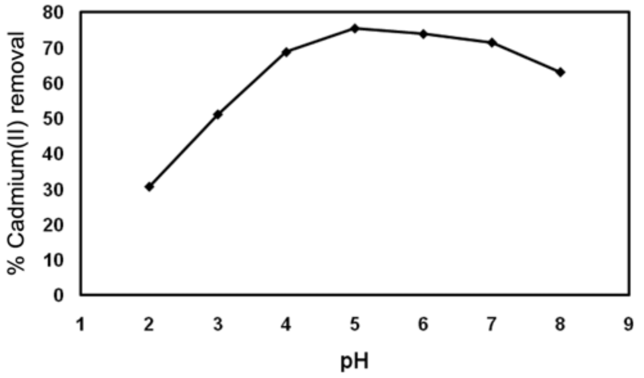


Fig. 3. Effect of pH for the adsorption of cadmium(II) onto CNS (the initial cadmium(II) ions concentration=20 mg/L, CNS concentration=3 g/L and contact time=30 min).

Moreover, depending on the solution pH, the functional groups participate in metal ion bindings. At low pH values, H^+ ions occupy most of the adsorption sites on the CNS surface and less cadmium ions could be sorbed because of electric repulsion with H^+ ions on CNS surface. When the value of pH increased, CNS surfaces were more negatively charged and the adsorption of cadmium(II) ions (positive charge) increased and reached equilibrium at pH 5.0. The decrease in adsorption efficiency at higher pH (>5.0) is due to the formation of soluble hydroxylated complexes of the cadmium ions and their competition with the active sites; as consequence, the retention would decrease again. The effect of pH on cadmium(II) removal can also be explained in terms of point of zero charge (PZC) of the CNS. The adsorbent surface is positive when solution pH is below PZC of the CNS. Moreover, at solution pH<PZC, the predominant metal species will be positively charged [M^{n+} and $M(OH)^{(n-1)+}$]; thus, the uptake of metal ions in the pH range below PZC is a H^+-M^{n+} or $M(OH)^{(n-1)+}$ exchange process. The increase in solution pH above PZC will show a slight increase in adsorption as long as the metal species are still positively charged or neutral even though the CNS surface is negatively charged. When both CNS surface charge and metals species charge become negative, then the adsorption process will decrease significantly.

3. Effect of CNS Concentration on Sorption Efficiency

The number of available sites and exchanging ions for the adsorption depends upon the amount of adsorbent in the adsorption process. The CNS concentration is an important parameter because this determines the capacity of the CNS for a given initial cadmium(II) ion concentration. The effect of CNS concentration on the cadmium(II) removal efficiency is presented in Fig. 4. The cadmium removal was found to increase rapidly with increasing concentration of CNS up to an adsorbent dose of 3 g/L. However, beyond this CNS concentration the increase in removal efficiency was marginal and this may be due to reduction in concentration gradient. The maximum adsorption efficiency of cadmium(II) ion onto CNS was found to be 75.35% at CNS concentration of 3 g/L. The increase in the removal efficiency can be attributed to the increased number of sites and exchangeable sites were available for adsorption [48].

4. Effect of Contact Time on Sorption Efficiency

The effect of contact time on efficiency of cadmium(II) adsorp-

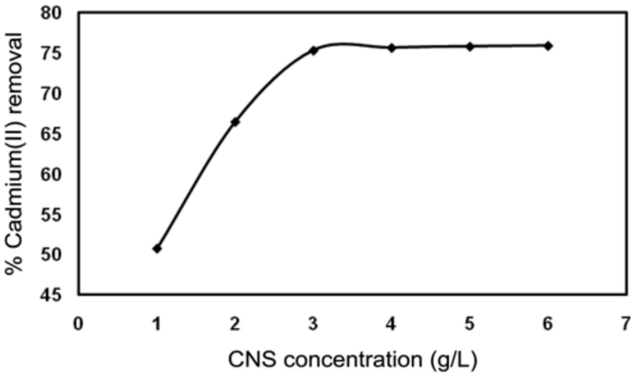


Fig. 4. Effect of CNS concentration on cadmium(II) removal (the initial cadmium(II) ions concentration=20 mg/L, pH=5.0, and contact time=30 min).

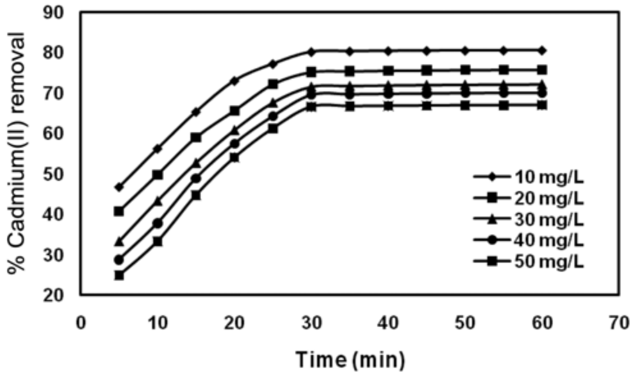


Fig. 5. Effect of contact time for the adsorption of cadmium(II) onto CNS (the initial cadmium(II) ions concentration=10 to 50 mg/L, pH=5.0 and CNS concentration=3 g/L).

tion on CNS was investigated to study the rate of cadmium(II) removal and the results are shown in Fig. 5. The data obtained from the adsorption of cadmium(II) ions onto the CNS showed that the adsorption increases with increase in contact time. The adsorption of cadmium(II) ions onto CNS was rapid for the first 25 min and equilibrium was nearly reached after 30 min for five different initial cadmium(II) ion concentrations. A further increase in the contact time has a negligible effect on the efficiency of cadmium(II) adsorption. The adsorption efficiency of cadmium(II) removal is higher in the beginning due to a larger surface area of the CNS being available for cadmium(II) adsorption. Later, as the adsorbed cadmium(II) forms a monolayer, the capacity of the CNS gets exhausted and then the uptake rate is controlled by the rate at which the cadmium(II) ions are transported from the exterior to the interior sites of the CNS particles [50]. It is also relevant that, since active sorption sites in a system have a fixed number and each active sites can adsorb only one ion in a monolayer, the metal uptake by the sorbent surface will be rapid initially and slow down as the competition for the decreasing availability of active sites intensifies by the metal ions remaining in the solution [51].

5. Effect of Initial Cadmium(II) Ion Concentration on Sorption Efficiency

The effect of initial cadmium(II) concentration (10-50 mg/L) was investigated at pH of 5.0 in the presence of 3 g/L CNS and the results are illustrated in Fig. 6. The plots reveal that an increase in the cadmium(II) concentration from 10-50 mg/L results in a decrease in percentage cadmium(II) removal from 80.13% to 66.57%, and an increase in adsorption capacity from 2.671 to 11.095 mg/g. The decrease in the percentage of cadmium(II) removal can be attributed to the saturation of available active sites on the CNS above a certain concentration of cadmium(II). The increase in adsorption capacity may be due to the higher adsorption rate and the utilization of all available active sites for adsorption at higher cadmium(II) concentration.

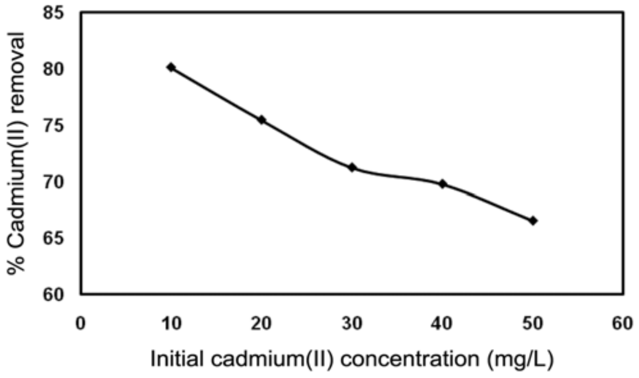


Fig. 6. Effect of initial cadmium(II) ions concentration for the adsorption of cadmium(II) onto CNS (the initial cadmium(II) ions concentration=10 to 50 mg/L, pH=5.0, CNS concentration=3 g/L and contact time=30 min).

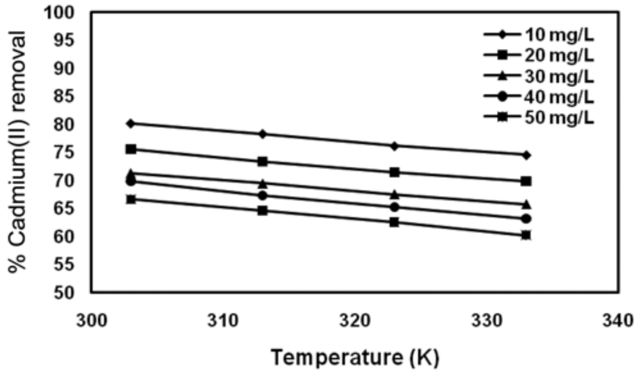


Fig. 7. Effect of temperature on cadmium(II) removal by CNS (the initial cadmium(II) ions concentration=10 to 50 mg/L, pH=5.0, CNS concentration=3 g/L and contact time=30 min).

6. Effect of Temperature on Sorption Efficiency and Thermodynamic Parameters

The adsorption of cadmium(II) ion on CNS was investigated as a function of temperature and the maximum removal of cadmium(II) ion was obtained at 30 °C. The batch adsorption experiments were performed at different temperatures of 30, 40, 50 and 60 °C for the initial cadmium(II) ion concentrations in the range of 10-50 mg/L at constant CNS concentration of 3 g/L and an optimum pH value of 5. The adsorption decreased from 80.13 to 74.32%, 75.47 to 69.21%, 71.23 to 65.82% and 66.57 to 60.24% for the initial cadmium(II) ion concentration in the range of 10-50 mg/L, respectively, with the rise in temperature from 30 to 60 °C (Fig. 7). This is mainly due to the decrease in surface activity, suggesting that adsorption between

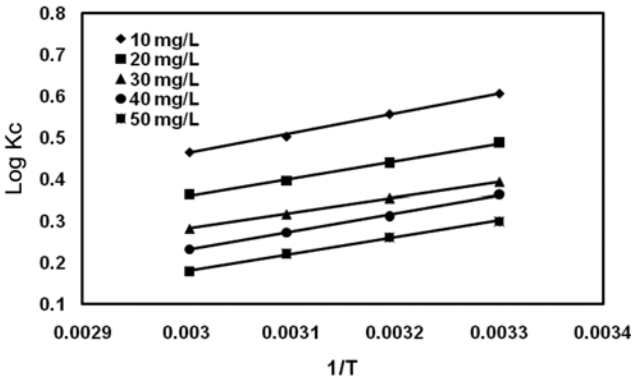


Fig. 8. Thermodynamic study.

cadmium(II) and CNS is exothermic.

Thermodynamic parameters such as free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) change of adsorption can be evaluated from the following equations:

$$K_e = \frac{C_{Ae}}{C_e} \tag{4}$$

$$\Delta G^o = -RT\ln K_c \tag{5}$$

$$\Delta G^o = \Delta H^o - TDS^o \tag{6}$$

$$\log K_c = \frac{\Delta S^o}{2.303R} - \frac{\Delta H^o}{2.303RT} \tag{7}$$

Where K_c is the equilibrium constant, C_e is the equilibrium concentration in solution (mg/L) and C_{Ae} is the amount of cadmium(II) adsorbed on the adsorbent per liter of solution at equilibrium (mg/L). ΔG^o, ΔH^o and ΔS^o are changes in Gibbs free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/mol/K), respectively. R is the gas constant (8.314 J/mol/K), T is the temperature (K). The values of ΔH^o and ΔS^o are determined from the slope and the intercept from the plot of log K_c versus 1/T (Fig. 8). The ΔG^o values were calculated using Eq. (5). Adsorption of cadmium(II) ion on CNS decreased, when the temperature was increased from 303 to 333 K is shown in Fig. 8. The process is thus exothermic. The plots were used to compute the values of thermodynamic parameters (Table 2). The value of enthalpy change (ΔH^o) and the entropy change (ΔS^o) recorded from this work are presented in the Table 2. The Gibbs free energy ΔG^o is small and negative but increases with increase in temperature, indicating that the adsorption process lead to a decrease in Gibbs energy. The negative ΔG^o value indicates that the process is feasible and spontaneous in the nature of adsorption. Negative ΔH^o value suggests the exothermic nature of adsorption and the ΔS^o can be used to describe the randomness at the CNS-solution interface during the sorption. The thermodynamic parameters indicate the adsorption process can be used for the removal of cadmium(II) ions by CNS.

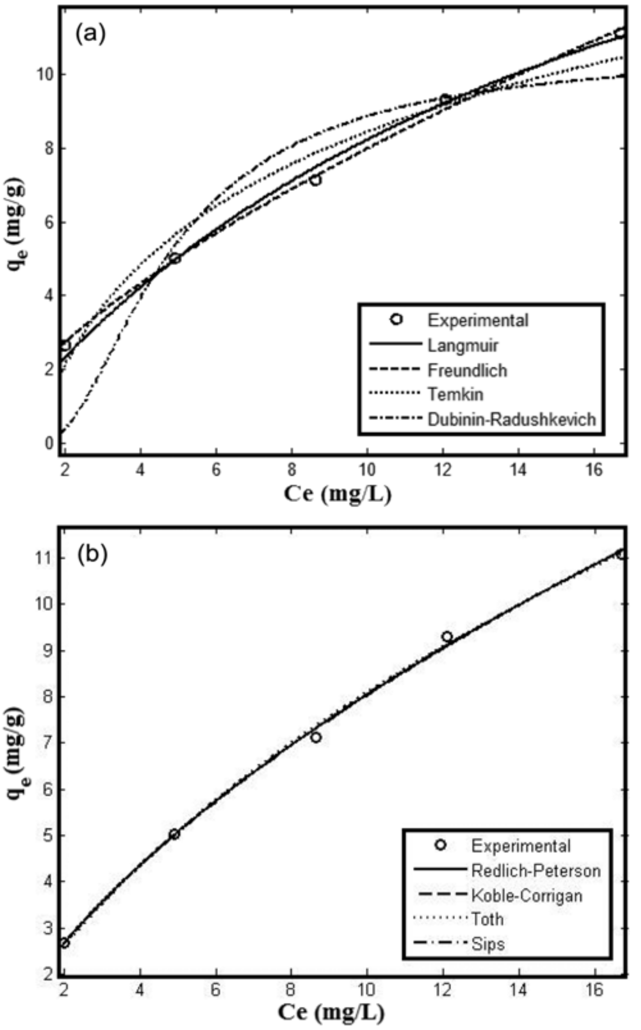


Fig. 9. (a) The two-parameter nonlinear adsorption isotherms for cadmium(II) with CNS at 30 °C, (b) The three-parameter nonlinear adsorption isotherms for cadmium(II) with CNS at 30 °C.

7. Adsorption Isotherm Models

The analysis of the adsorption isotherms data by fitting them into different isotherm models is an important step to find the suitable

Table 2. Thermodynamic parameters for the adsorption of cadmium(II) ions onto CNS

Initial cadmium(II) conc. (mg/L)	ΔH^o (kJ/mol)	ΔS^o (J/mol/K)	ΔG^o (kJ/mol)			
			30 °C	40 °C	50 °C	60 °C
10	−9.187	−18.726	−3.513	−3.334	−3.109	−2.965
20	−8.068	−17.328	−2.831	−2.631	−2.449	−2.317
30	−7.224	−16.294	−2.285	−2.219	−1.960	−1.798
40	−8.352	−20.641	−2.108	−1.868	−1.684	−1.483
50	−7.689	−19.607	−1.735	−1.563	−1.371	−1.143

model that can be used for design process. It was found that adsorption equilibrium time of cadmium(II) onto CNS was 30 min. Fig. 9(a) and (b) show the plot of q_e versus C_e for the adsorption isotherms of cadmium(II) onto CNS at 30 °C. These curves are convex upward throughout and are designated as favorable type [52,53]. The experimental data were applied to the two-parameter isotherm models: Langmuir [54], Freundlich [55], Temkin [56] and Dubinin-Radushkevich [57], and three-parameter isotherm models: Redlich-Peterson [58], Koble-Corrigan [59], Toth [60] and Sips [61]. The constant parameters of the isotherm equations for this adsorption process were calculated by nonlinear regression analysis using MATLAB 7.1. The constant parameters, correlation coefficients, sum of error squared (SSE) and root mean square error (RMSE) are summarized in Tables 3 and 4.

Table 3. The value of parameters for two-parameter isotherm models used in the studies

Isotherm model	Parameter	R^2	Equation
Langmuir	$q_m=22.11$ $K_L=0.059$ SSE=0.263 RMSE=0.296	0.994	$q_e=\frac{1.304C_e}{1+0.059C_e}$
Freundlich	$K_F=1.741$ n=1.511 SSE=0.098 RMSE=0.181	0.998	$q_e=1.741C_e^{0.662}$
Temkin	A=0.863 B=1.698 SSE=1.676 RMSE=0.748	0.963	$q_e=1.698\ln(0.863C_e)$
Dubinin-Radushkevich	$q_m=10.60$ $\beta=7.23\times10^{-7}$ SSE=8.211 RMSE=1.433	0.816	$q_e=10.6e^{-7.23\times10^{-7}\varepsilon^2}$

Table 4. The value of parameters for three-parameter isotherm models used in the studies

Isotherm model	Parameter	R^2	Equation
Redlich-Peterson	$K_R=3.347$ $\alpha_R=1.096$ $\beta=0.461$ SSE=0.084 RMSE=0.205	0.9981	$q_e=\frac{3.347C_e}{1+1.096C_e^{0.461}}$
Koble-Corrigan model	a=1.663 b=0.024 n=0.739 SSE=0.081 RMSE=0.201	0.9983	$q_e=\frac{1.663C_e^{0.739}}{1+0.024C_e^{0.739}}$
Toth	f=100.00 g=4.528 d=0.406 SSE=0.098 RMSE=0.222	0.9980	$q_e=\frac{100C_e}{[4.528+(C_e)^{0.406}]^{2.463}}$
Sips	$Q_{max}=68.17$ $K_S=0.023$ n=1.353 SSE=0.081 RMSE=0.201	0.9983	$q_e=\frac{1.568C_e^{0.739}}{1+0.023C_e^{0.739}}$

7-1. Two-parameter Isotherm Models

7-1-1. Langmuir Isotherm

The theoretical Langmuir sorption isotherm is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The non-linear equation of Langmuir isotherm model is expressed as follows:

$$q_e=\frac{q_m K_L C_e}{1+K_L C_e} \tag{8}$$

Where C_e is the equilibrium concentration in solution (mg/L), q_m and K_L are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively. The maximum monolayer adsorption capacity was found to be 22.11 mg/g for CNS.

The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using separation factor or dimensionless equilibrium parameter, "R_L", expressed as in the following equation [62]:

$$R_L=\frac{1}{1+K_L C_o} \tag{9}$$

Where K_L is the Langmuir constant and C_o is the initial concentration of cadmium(II) ion. The value of separation parameter R_L provides important information about the nature of adsorption. The value of R_L indicates the type of Langmuir isotherm to be irreversible ($R_L=0$), favorable ($0<R_L<1$), linear ($R_L=1$) or unfavorable ($R_L>1$). The R_L was found to be 0.628 to 0.252 for concentration of 10-50 mg/L of cadmium(II). They are in the range of 0-1, which indicates favorable adsorption [63].

7-1-2. Freundlich Isotherm

The Freundlich isotherm model is the well known earliest relationship describing the sorption process. The model applies to adsorption on heterogeneous surfaces with the interaction between adsorbed molecules, and the application of the Freundlich equation also suggests that sorption energy exponentially decreases on completion of the sorptional centers of an adsorbent. This isotherm is an empirical equation that can be employed to describe heterogeneous systems and is expressed as follows:

$$q_e=K_F C_e^{1/n} \tag{10}$$

Where K_F is the Freundlich constant (l/g) related to the bonding energy. 1/n is the heterogeneity factor and n is a measure of the deviation from linearity of adsorption. This value indicates the degree of non-linearity between solution concentration and adsorption as follows: if n=1, then adsorption is linear; if n<1, then adsorption is a chemical process; if n>1, then adsorption is a physical process. The n value in Freundlich equation was found to be 1.511 for CNS. Since n lies between 1 and 10, this indicates the favorable adsorption of cadmium(II) onto CNS.

7-1-3. Temkin Isotherm

The Temkin isotherm model contains a factor that explicitly takes into account adsorbing species-adsorbate interactions. This model assumes the following facts: (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and then (ii) the adsorption is characterized by a uniform distribution of binding energies, up to a maximum binding energy. The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm has commonly been applied in the following form:

$$q_e=B\ln(AC_e) \tag{11}$$

Where, B=(RT)/b, b is the Temkin constant related to heat of adsorption (J/mol), A is the Temkin isotherm constant (L/g), R is the universal gas constant (8.314 J/(mol K)) and T is the absolute temperature (K). The Temkin isotherm constants A and B were found to be 0.863 and 1.698, respectively.

7-1-4. Dubinin-Radushkevich Isotherm

The Dubinin-Radushkevich isotherm is applied to find the adsorption mechanism based on the potential theory assuming a heterogeneous surface. Dubinin-Radushkevich isotherm is expressed as follows:

$$q_e = q_m e^{-\beta\varepsilon^2} \tag{12}$$

Where q_m is the Dubinin-Radushkevich monolayer capacity (mg/g), β is a constant related to sorption energy, and ε is the Polanyi potential which is related to the equilibrium concentration as follows:

$$\varepsilon= RT\ln\left(1+\frac{1}{C_e}\right) \tag{13}$$

Where R is the gas constant (8.314 J/mol K) and T is the absolute temperature. The constant β gives the mean free energy, E, of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the relationship;

$$E=\frac{1}{\sqrt{2\beta}} \tag{14}$$

The final form of the Dubinin-Radushkevich isotherm is expressed as follows:

$$q_e=q_m\exp(-\beta(RT\ln(1+1/C_e))^2) \tag{15}$$

Dubinin-Radushkevich isotherm constants, monolayer capacity (q_m) and sorption energy (β) were found to be 10.6 mg/g and 7.23×10^{-7} mg^2/J^2, respectively. The magnitude of E is used to determine the type of adsorption mechanism. When one mole of ions is transferred to the CNS surface, its value is less than 8 kJ/mol, which indicates physical adsorption [64]; the value of E is between 8 and 16 kJ/mol, indicates the adsorption process which follows ion-exchange [65]; while its value in the range of 20-40 kJ/mol indicates chemisorption [66]. The calculated value of E for the present study is below 8 kJ/mol, which indicates the adsorption of cadmium(II) onto CNS surface is following physical adsorption type.

7-2. Three-parameter Isotherm Models

7-2-1. Redlich-Peterson Isotherm

The Redlich-Peterson isotherm approximates Henry's law at lower sorbate concentrations, and at higher concentrations it behaves like the Freundlich adsorption isotherm. The Redlich-Peterson isotherm is expressed as follows:

$$q_e=\frac{K_R C_e}{1+\alpha_R C_e^{\beta}} \tag{16}$$

Where K_R is Redlich-Peterson isotherm constant (L/g), α_R is Redlich-Peterson isotherm constant (L/mg) and β is the exponent which lies between 0 and 1. The Redlich-Peterson isotherm constants, K_R and α_R, for the adsorption of cadmium(II) onto CNS were found to be 3.347 L/g and 1.096 L/mg, respectively. The exponent β value was calculated as 0.461.

7-2-2. Koble-Corrigan Isotherm

The Koble-Corrigan isotherm is another three-parameter empirical model which depends on the combination of the Langmuir and Freundlich isotherm equations in one non-linear equation for representing the equilibrium adsorption data. It is commonly expressed as follows:

$$q_e=\frac{aC_e}{1+bC_e^n} \tag{17}$$

Where a and b are the Koble-Corrigan constants and n is the Koble-Corrigan model exponent. The Koble-Corrigan isotherm constants, a and b, for the adsorption of cadmium(II) onto CNS were found to be 1.663 and 0.0244, respectively. The exponent n value was calculated as 0.739.

7-2-3. Sips Isotherm

The Sips isotherm is a combination of the Langmuir and Freundlich isotherm models and it is expected to describe the heterogeneous surfaces much better. At lower sorbate concentration it reduces to the Freundlich isotherm, while at higher sorbate concentrations it approaches to Langmuir isotherm to predict a monolayer adsorption capacity. The sips isotherm has been used in the following form:

$$q_e=\frac{Q_{max}K_S C_e^{1/n}}{1+K_S C_e^{1/n}} \tag{18}$$

Where Q_{max} is the Sips maximum adsorption capacity (mg/g) and K_S is the Sips constant related with affinity constant (mg/L)$^{-1/n}$. According to the Sips isotherm, the sips monolayer adsorption capacity value was found to be 68.17 mg/g for the adsorption of cadmium(II) onto CNS. The exponent 1/n value for CNS was closer to unity. It means that cadmium(II) adsorption data for CNS is more of the Langmuir isotherm form rather than that of the Freundlich isotherm.

7-2-4. Toth Isotherm

The Toth isotherm is a Langmuir-based isotherm that considers a continuous distribution of site affinities:

$$q_e=\frac{fC_e}{[g+(C_e)^d]^{1/d}} \tag{19}$$

Where g is the Toth isotherm constant and d is the Toth exponent ($0<d\le 1$). It is obvious that for d=1 this Toth isotherm reduces to the Langmuir equation. The Toth isotherm constant g and exponent d values were found to be 4.528 and 0.4063, respectively.

7-3. Comparison of Adsorption Isotherms

The experimental data on the effect of an initial concentration of cadmium(II) on the CNS surface of the test medium were fitted to the two-parameter and three-parameter isotherm models using MATLAB 7.1, and the graphical representations of these models are presented in Fig. 9(a) and (b). It was observed that the best fitted adsorption isotherms considering the correlation coefficient were obtained for the two-parameter isotherms to be in the order of prediction precision: Freundlich>Langmuir>Temkin>Dubinin-Radushkevich and for three-parameter isotherms: Redlich-Peterson, Koble-Corrigan, Sips>Toth isotherms. Three-parameter isotherms have higher correlation coefficients than that of the two-parameter isotherms. Comparing the correlation coefficients, sum of error squared (SSE) and root mean square error (RMSE) were obtained from the adsorption isotherms, which shows the best fits to the experimental values using the different isotherm equations, and were also generally very good for all the three-parameter isotherm equations. The applicability of all isotherm equations to the cadmium(II)-CNS system indicates that both the monolayer adsorption and heterogeneous surface conditions exist under the studied experimental conditions. The adsorption of cadmium(II) onto the CNS surface is thus complex, involving more than one mechanism [63]. The comparison of maximum monolayer adsorption capacity of cadmium(II) onto various adsorbents is presented in Table 5. It shows that the CNS studied in this work has larger adsorption capacity. This is due to its high surface area (395 m^2/g).

8. Adsorption Kinetics

Various kinetic models, namely pseudo-first-order, pseudo-second-order, Elovich models and intraparticle diffusion have been used for their validity with the experimental adsorption data for cadmium(II) onto CNS. The study of adsorption kinetics describes the solute uptake rate, and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface, including the diffusion process. The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the mass transfer process. The results obtained from the experiments were used to study the kinetics of metal ion adsorption. The rate kinetics of cadmium(II) ion adsorption on CNS was analyzed using pseudo-first-order [67], pseudo-second-order [68], Elovich models [69] and intraparticle diffusion [70].

Table 5. Comparison of maximum monolayer adsorption of cadmium(II) ions onto various adsorbents

Adsorbents	q_m (mg/g)	Reference
AGCS	22.17	[3]
Cashew nut shell	**22.11**	**This study**
Rice husk	21.28	[21]
Corncob	19.3	[24]
Ceiba pentandre hulls carbon	19.59	[37]
Gracilaria salicornia (red)	17.99	[36]
Chinese herb *Pang Da Hai*	17.50	[35]
Hypnea valentiae biomass	15.785	[42]
Tea-industry waste	11.29	[26]
Olive cake	10.56	[27]
Live *Mucor rouxii*	8.46	[34]
Pretreated *Mucor rouxii*	8.36-20.31	[34]
Carbon F-400	8.00	[39]
Low-grade phosphate	7.54	[30]
Calgon F-400	6.35	[40]
Banana peels	5.71	[43]
Hazelnut shell	5.42	[28]
Oak bark char	5.40	[39]
Pretreated *Aspergillus niger*	3.98-4.38	[33]
Pure smectite	3.87	[41]
RCS	3.81	[3]
Lewatite S100	3.46	[41]
Olive stone carbon	1.56-1.85	[38]
Bagasse fly ash	1.24-2.00	[29]
Wheat bran	0.63-0.70	[32]
Oak wood char	0.37	[39]
Pine bark char	0.34	[39]
Hematite	0.22-0.24	[31]

8-1. The Pseudo-first-order Kinetic Model

The adsorption of cadmium(II) ion from an aqueous solution to CNS can be considered as a reversible process with equilibrium being established between the solution and CNS. Adsorption phenomena can be described as the diffusion control process assuming a non-dissociation molecular adsorption of cadmium(II) on CNS as follows:

$$A+S \Leftrightarrow AS \tag{20}$$

If initially no cadmium(II) ion is present on the CNS (i.e., $C_AS_o=0$ at t=0), and assuming the first-order rate kinetics then, the fractional uptake of the cadmium(II) by the CNS can be expressed as:

$$\frac{q}{q_e}=1-\exp\left[k_AC_S+\frac{k_A}{k_S}\right]t \tag{21}$$

Equation can be transformed as

$$\log(q_e-q_t)=\log q_e-\frac{k_{ad}}{2.303}t \tag{22}$$

Where

$$k_{ad}=\left[\left(k_AC_S+\frac{k_A}{k_S}\right)\right] \tag{23}$$

$q_t=X_{At}$ and $q_e=X_{Ae}$

Where q_t is the adsorption capacity at time t (mg/g) and k_{ad} (min^{-1}) is the rate constant of the pseudo-first order adsorption, which was applied to the present study of cadmium(II) adsorption. The rate constant, k_{ad} and correlation coefficients of the cadmium(II) under different concentrations were calculated from the linear plots of log (q_e-q_t) versus t (Fig. 10) and listed in Table 6. The correlation coeffi-

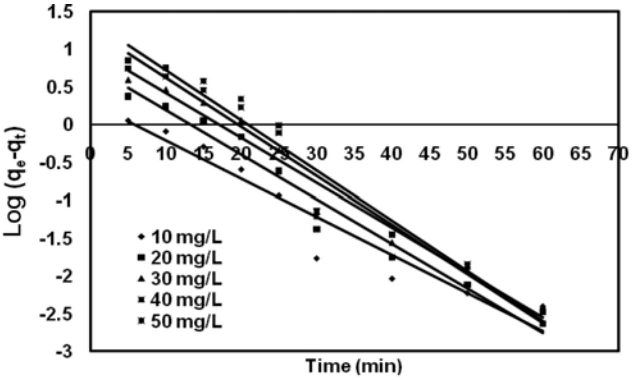


Fig. 10. Pseudo-first-order kinetic fit for adsorption of cadmium(II) onto CNS at 30 °C.

Table 6. Kinetic models and other statistical parameters at 30 °C and at pH 5.0

Kinetic model	Parameters	Concentration of cadmium(II) solution				
		10 mg/L	20 mg/L	30 mg/L	40 mg/L	50 mg/L
Pseudo-first-order equation	k_{ad} (min^{-1})	0.115	0.136	0.136	0.147	0.152
	q_e, cal (mg/g)	1.936	6.026	10.209	18.621	23.768
	R^2	0.925	0.929	0.923	0.924	0.929
Pseudo-second-order equation	k (g mg^{-1} min^{-1})	0.077	0.033	0.019	0.013	0.009
	q_e, cal (mg/g)	2.932	5.549	7.692	9.658	11.357
	h (mg g^{-1} min^{-1})	0.666	1.022	1.127	1.183	1.217
	q_e, exp (mg/g)	2.689	5.053	7.211	9.341	11.165
	R^2	0.997	0.996	0.995	0.992	0.991
Elovich equation	α (mg/g.min)	2.614	3.082	2.553	2.389	2.353
	β (g/mg)	2.012	0.959	0.576	0.399	0.309
	R^2	0.917	0.927	0.929	0.930	0.926
Intraparticle diffusion	k_p (mg/g·min$^{1/2}$)	0.205	0.434	0.724	1.050	1.356
	C	1.332	2.175	2.402	2.356	2.149
	R^2	0.808	0.828	0.834	0.842	0.841

cients for the pseudo-first-order kinetic model are low. Moreover, a large difference in equilibrium adsorption capacity (q_e) obtained from the experimental and calculated values was observed, indicating a poor pseudo first-order fit to the experimental data.

8-2. The Pseudo-second-order Kinetic Model

The kinetic data were further analyzed using Ho's pseudo-second-order kinetic model. This model is based on the assumption that the sorption follows second order chemisorption:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{24}$$

Integrating Eq. (24) and applying the boundary conditions, gives:

$$\left(\frac{1}{q_e - q_t}\right) = \frac{1}{q_e} + kt \tag{25}$$

Eq. (25) can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \tag{26}$$

Where $h=kq_e^2$ (mg g^{-1}min^{-1}) can be regarded as the initial adsorption rate as and k is the rate constant of pseudo-second-order adsorption (g mg^{-1}min^{-1}). The plot of t/q_t versus t (Fig. 11) should give a straight line if pseudo-second-order kinetics is applicable and q_e, k and h can be determined from the slope and intercept of the plot. At all initial cadmium(II) concentrations, straight lines with extremely high correlation coefficients (>0.99) were obtained. In addition, the calculated q_e values also agree with the experimental data in the case of pseudo-second-order kinetics. This suggests that the adsorption data are well represented by pseudo-second-order kinetics, and it supports the assumption [68] that the rate-limiting step of cadmium(II) ion onto CNS may be chemisorption. From Table 6, the values of the rate constant k decrease with increase in initial cadmium(II) concentration for the CNS. The reason for this behavior can be attributed to the lower competition for the sorption surface sites at lower concentration. At higher concentrations, the competition for the surface active sites will be high, and consequently lower sorption rates are obtained.

8-3. The Elovich Kinetic Model

The Elovich kinetic model is also considered where α is the initial adsorption rate in mg/(g·min), and β (g/mg) is the desorption constant related to the extent of the surface coverage and activation energy for chemisorptions. Both kinetic constants (α and β) will be estimated from the slope and intercept from the plot of q_t versus ln t.

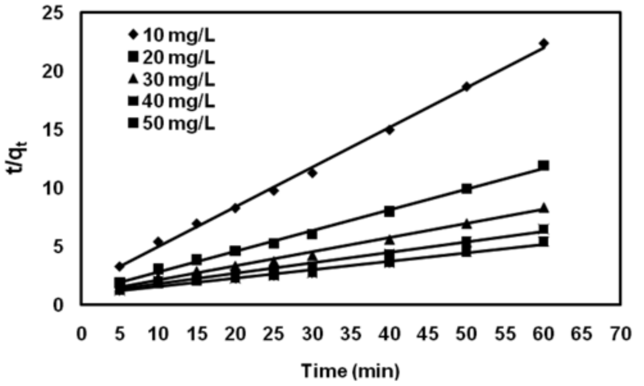


Fig. 11. Pseudo-second-order kinetic fit for adsorption of cadmium (II) ions onto CNS at 30 °C.

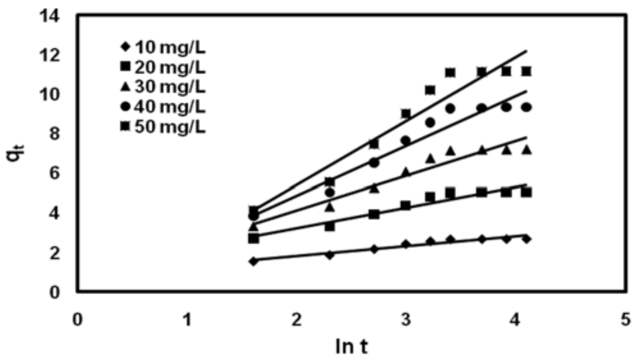


Fig. 12. Elovich kinetic model for adsorption of cadmium(II) ions onto CNS at 30 °C.

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{27}$$

Cadmium(II) ion adsorption kinetics onto CNS was also tested with the Elovich kinetic model by plotting q_t versus ln t as shown in Fig. 12. Recorded R^2 values are low, which indicates that the experimental data do not fit the Elovich kinetic model and cadmium(II) ions removal using CNS under study cannot be described using this model.

8-4. The Intraparticle Diffusion Model

Taking into account that the kinetic results were fitted very well to a chemisorption model, the intraparticle diffusion model was plotted in order to verify the influence of mass transfer resistance on the binding of cadmium(II) to the CNS. The kinetic results were analyzed by the Weber and Morris intraparticle diffusion model to elucidate the diffusion mechanism; the model is expressed as:

$$q_t = k_p t^{1/2} + C \tag{28}$$

Where C is the intercept and k_p is the intraparticle diffusion rate constant, (mg/gmin$^{1/2}$), which can be evaluated from the slope of the linear plot of q_t versus $t^{(1/2)}$ as shown in Fig. 13. The intercept of the plot reflects the boundary layer effect. The larger the intercept is, the greater will be the contribution of the surface sorption in the rate-controlling step. The calculated intraparticle diffusion coefficient k_p values are listed in Table 6. If the regression in the plot of q_t versus $t^{(1/2)}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step. However, the linear plots at each concentration did not pass through the origin. This deviation from the origin may perhaps be due to the difference in the rate of mass transfer in the initial and final stages of adsorption. This indicates some degree of boundary layer control and further shows that the intraparticle diffusion was not only the rate-limiting step, but also be the rate controlling of sorption or all may be operating simultaneously. Thus based on the high co-relation coefficient values (Table 6), it can be inferred that adsorption of cadmium(II) onto CNS followed pseudo-second-order model than that of intraparticle diffusion model, pseudo-first-order model and Elovich kinetic model.

9. Designing Batch Adsorption from Equilibrium Data

Adsorption isotherms can be used to predict the design of single-stage batch adsorption system [71]. The schematic diagram of single-stage batch adsorption system is shown in Fig. 14. The design objective is to reduce the cadmium(II) ion concentration from C_o (mg/L) to C_1 (mg/L) of solution volume V (L). The amount of adsorbent is M (g) and the cadmium(II) ion loading changes from q_o (mg/g) to q_1 (mg/g). At time t=0, q_o=0 as time proceeds the mass balance equates the cadmium(II) ion removed from the aqueous solution to that picked by the CNS. The mass balance for the single-stage batch adsorption system can be given as:

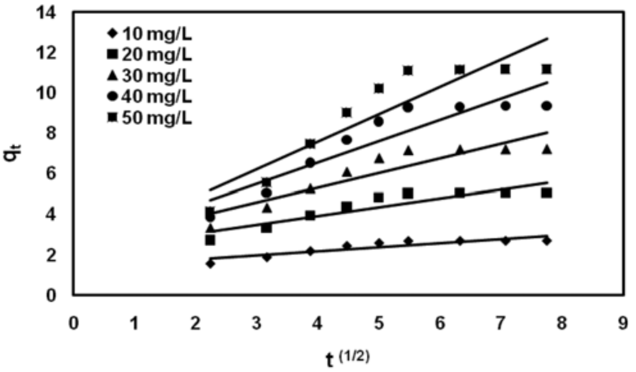


Fig. 13. Intraparticle diffusion model for adsorption of cadmium (II) ions onto CNS at 30 °C.

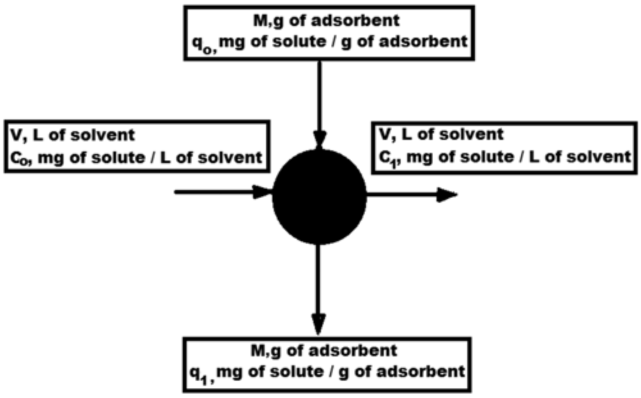


Fig. 14. A single-stage batch adsorber.

$$V(C_o - C_1) = M(q_1 - q_o) = Mq_1 \tag{29}$$

At equilibrium conditions

$$C_1 \rightarrow C_e \text{ and } q_1 \rightarrow q_e$$

Since adsorption isotherm studies fit well in Freundlich adsorption isotherm, it is used for q_1 in equation batch adsorption design.

Rearranging Eq. (29) we get

$$\frac{M}{V} = \frac{(C_o - C_1)}{q_1} = \frac{(C_o - C_e)}{q_e} = \frac{(C_o - C_e)}{K_F C_e^{1/n}} \tag{30}$$

Fig. 15. shows the plot between the calculated amount of CNS required to remove cadmium(II) ion solution of initial concentration 20 mg/L for 50%, 60%, 70% and 80% cadmium(II) removal at different solution volumes (1 to 10 L) for a single-stage batch adsorption system, for which the design procedure is outlined. For example, the amount of CNS required for the 80% removal of cadmium(II) ion from an aqueous solution of 20 mg/L concentration was 3.671,

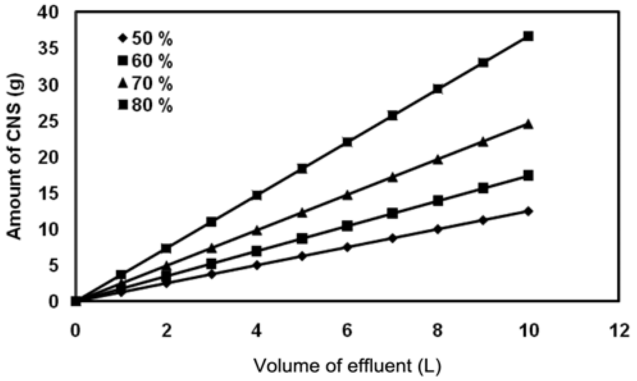


Fig. 15. Design plot generated using Freundlich isotherm for adsorbent mass against volume of effluent treated for various percentage of cadmium(II) removal at 20 mg/L initial cadmium(II) ion concentration.

Table 7. Desorption of cadmium(II) ions from spent CNS using HCl

Initial cadmium(II) concentration (mg/L)	Removal efficiency	Percentage recovery of cadmium(II) ions			
		0.05 M	0.1 M	0.15 M	0.2 M
25	73.84	61.08	66.95	70.26	70.52
50	66.57	53.48	58.48	63.98	64.15

7.342, 11.013, 14.684, 18.355, 22.026, 25.697, 29.368, 33.039 and 36.71 g for cadmium(II) ion solution volumes of 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 L, respectively.

10. Desorption Studies

The desorption study is to elucidate the nature of adsorption and recycling of the spent adsorbent and the cadmium(II) ions. The use of thermal activation method to regenerate the adsorbent could require high energy and 5-10% adsorbent loss in each cycle. Hence, desorption studies were attempted to use the chemical regeneration for cadmium(II) ions desorption from the spent CNS. Desorption results are reported in Table 7. The results show that the concentration of HCl increases with the increase in desorption rate, but it is reached a constant value with 0.15 M HCl.

CONCLUSIONS

The present study evaluates the cadmium(II) removal by the use of agricultural waste such as cashew nut shell. The operating parameters such as solution pH, CNS concentration, contact time, initial cadmium(II) ion concentration and temperature, were effective in the adsorption efficiency of cadmium(II) ions. The maximum cadmium(II) adsorption was obtained at pH 5.0. The monolayer adsorption capacity was found to be 22.11 mg/g. The adsorption of the cadmium(II) ion on CNS reached equilibrium in 30 minutes. The two-parameter (Langmuir, Freundlich, Temkin and Dubinin-Radushkevich) and three-parameter isotherm models (Redlich-Peterson, Koble-Corrigan, Toth and Sips) were used for the mathematical description of the adsorption of cadmium(II) ions onto CNS and the constants were evaluated from these isotherms using MATLAB 7.1. Considering the two-parameter and three-parameter isotherm models, Langmuir, Freundlich, Redlich-Peterson, Koble-Corrigan, Toth and Sips isotherm models best describe the adsorption of cadmium(II) ion onto CNS. The kinetic data showed that the pseudo-second-order kinetic model was obeyed better than the pseudo-first-order, Elovich kinetic and intraparticle diffusion models, which indicates that chemisorption is the rate-limiting step. The thermodynamic calculations indicated the feasibility, exothermic and spontaneous nature of adsorption of cadmium(II) ions onto CNS at 30-60 °C. It can be also concluded that the CNS is an effective and alternative adsorbent for the removal of cadmium(II) ions from an aqueous solutions in terms of high adsorption capacity, natural, abundant availability and low cost.

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