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Kinetic and equilibrium studies of the adsorption of Cd(II) from aqueous solutions by wood apple shell activated carbon

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ABSTRACT

The use of heavy metals along with the associate risks of metal pollution has increased to a great extent over the recent times. Cadmium is one of the most harmful toxic metals. In present study, with the economical and efficient adsorbent, wood apple shell activated carbon (WASAC), removal of the Cd(II) ions was investigated. The WASAC was characterized with modern techniques. Among them, Energy-dispersive X-ray spectroscopy (EDAX) was used to observe the adsorption of Cd(II) on WASAC. The effects of pH, temperature, contact time, initial Cd(II) concentration, and adsorbent dosage on the adsorption yield were studied. The adsorbent exhibited good sorption potential for cadmium at pH 6.5. Langmuir and Freundlich isotherms were used to interpret the adsorption data of the investigated systems. The Langmuir model resulted in the best fit and WASAC had 27.64 mg/g as maximum adsorption capacity for Cd(II). The sorption kinetics of cadmium has been analyzed by Lagergren pseudo-first-order and pseudo-second-order kinetic models. The thermodynamic study was carried out with determination of standard Gibbs energy, standard enthalpy, and standard entropy. This reported study and comparison with reported adsorbents concluded that WASAC was the best adsorbent for removal of Cd(II) ion from the waste water.

Keywords: Wood apple shell activated carbon; Fruit waste; Isotherm; SEM-EDAX study; Kinetic study

1. Introduction

With the rapid increase in population and growth of industrialization, quality of water is deteriorating day by day. Industrial uses of metals have introduced substantial amounts of potentially toxic heavy metals into the environment [1]. Modern societies use many goods and amenities involving an increasing range of metallic products. High consumptions, frequent disposal, and replacement of disposable items are generating diverse types of metallic wastes. These wastes are invariably discharged into the environment and are poisoning the biosphere [2]. Heavy metals are toxic to aquatic flora, animals, and human beings even at relatively low concentrations. Some of them (such as Cd, Hg, Cr, etc.) are capable of being assimilated, stored, and concentrated by organisms. Cadmium is introduced into water from different processes like, smelting, metal plating, Cd–Ni batteries, phosphate fertilizers, mining, paint, pigments, plastics, stabilizers, alloy industries, mining, ceramics, sewage sludge, etc. [3–5].

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Cadmium concentrations in unpolluted natural waters are usually below 1 μg/dm^3. Contamination of drinking water may occur as a result of the presence of Cd(II) as an impurity in the zinc of galvanized pipes or cadmium-containing solders in fittings, water heaters, water coolers, and taps. Food is the main source of Cd(II) intake for non-occupationally exposed people. Crops grown in polluted soil or irrigated with polluted water may contain increased concentration of Cd(II) [6].

The biological half-life of Cd(II) in humans is in the range 10–35 years [6]. The results of studies of chromosomal aberrations in the peripheral lymphocytes of patients with itai-itai disease exposed chronically to Cd(II) via the diet were contradictory. According to IARC (1987), Cd(II) is carcinogenic. Joint FAO/WHO Expert Committee on Food Additives remarked that, if levels of Cd(II) in the renal cortex are not to exceed 50 mg/kg, the total intake of Cd(II) should not exceed 1 μg/kg of body weight per day [6].

Metals cannot be degraded further to nontoxic products or recovered economically from such a contaminated environment. There are different techniques to remove Cd(II) such as ion exchange, coagulation, flotation, co-precipitation, solvent extraction, membrane technology, adsorption, etc. With increasing environmental awareness and legal constraints being imposed on discharge of effluents, a need for cost effective technologies are essential. Among these techniques, adsorption process is a promising technique for the removal of heavy metal ions from waste water, because of its wide range of pollutants, high adsorption capacity, and possibly selective adsorbent; hence, many researchers have shown interest towards the development of many adsorbents which are being good alternatives for commercial adsorbents like activated carbon [1]. Commercially available activated carbon is expensive, so there is need to develop economical alternatives to it. In the present study, wood apple shell activated carbon (WASAC) as an inexpensive, easily available, and effective adsorbent was developed to get maximum adsorption of Cd(II). The developed WASAC has been characterized with modern techniques which gave the information about the properties and surface morphology of it. The isotherm and kinetic study had been done with various models. Along with this, thermodynamic and mechanistic study had been done. The efficiency of the adsorbent has been proved by comparison with reported adsorbents, which concluded that WASAC is the best adsorbent among all those studied.

2. Experimental

2.1. Preparation of materials

The stock solution of Cd(II) of 1,000 ppm was prepared from $CdSO_4{\cdot}8H_2O$. By using this stock solution, dilutions were made and used throughout the study. The waste fruit shell of wood apple was cleaned and dried in oven and crushed. It was treated with Conc. H_2SO_4 in 1:2 ratio for 1 h. The material was thoroughly washed with double distilled water up to get neutral pH. The material was dried in oven at 110˚C for 24 h and sieved through BSS-44.

2.2. Characterization of adsorbent

The developed adsorbent WASAC was characterized with modern techniques such as, Fourier transform infra red spectroscopy (FTIR), scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDAX), BET Surface area etc. and some properties such as moisture, bulk density, etc. were studied (Table 1).

The FTIR (PerkinElmer Spectrum 100) study show the functional groups like O–H, C–H, C=C, S=O, C–C having peak values 3359.52, 2918.72, 1614.94, 1396.66, 1208.28 cm^{-1}, respectively (Fig. 1). On the basis of SEM (Quanta 3D FEI) (Fig. 2(a)–(c)) study, the microporous nature like honey comb was observed. The EDAX (Model-20 ANTAX-200 with X-flash LN2 free detector Model-4010) study confirmed the adsorption of Cd(II) on the WASAC surface. The EDAX before adsorption of the Cd(II) (Fig. 3(A)) showed the absence of the Cd(II) while the success of adsorption could be observed by EDAX after adsorption of Cd(II) (Fig. 3(A)). The surface area and pore size of the adsorbents were measured by means of a NOVA (Quantachrome) surface area analyzer using a Brunauer–Emmett–Teller (BET) nitrogen

Table 1
Characteristics of WASAC

Property	Result
Ash content	8.12%
Bulk density	0.734 gm/cm^3
Moisture content	8.85%
BET surface area	12.07 m^2/g
Average pore diameter	30.13
Total pore volume	27.64×10^{-3} mg/L
Carbon	65.10%
Hydrogen	4.60%
Nitrogen	0.04%
Sulphur	2.35%

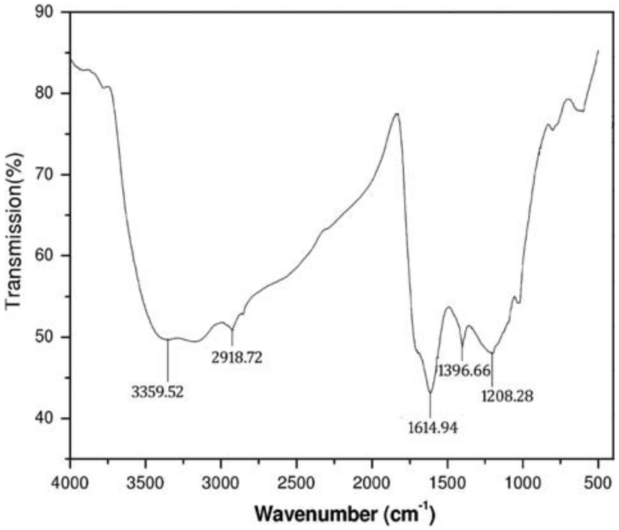

Fig. 1. FTIR spectrum of WASAC.

adsorption technique. The average pore size and total pore volume were also determined (Table 1). The BET surface area analysis indicates the greater adsorbent area which is also one of the vital reasons to better adsorption. The C, H, N, S Elemental analyzer (EA 1108, Carlo Erba) showed that carbon was the major constituent among all of them (Table 1).

2.3. Batch adsorption experiment

Batch-mode adsorption studies were carried out with 400 mg of adsorbent and 50 ml of Cd(II) solution of concentrations at an initial pH of 6.5 in 250 ml Erlenmeyer flasks and agitated at 150 rpm for predetermined time intervals at constant temperature on an orbital shaker. The concentration of free Cd metal ion in the effluent was determined with atomic adsorption spectroscopy (Perkin Elmer A Analyzer 300). Adsorption isotherm study was done with varying concentrations of Cd(II) from 100 to 420 mg/dm^3 at 299 ± 2 K, pH 6.5, and time of contact 4 h at 150 rpm in the Erlenmeyer flasks. For the thermodynamic study, temperature was varied from 303 to 323 K. The equilibrium adsorption capacity was evaluated using the equation

$$q_e = \frac{(C_0 - C_e)V}{M} \tag{1}$$

where q_e (mg/g) is the equilibrium adsorption capacity, C_0 and C_e are the initial and equilibrium concentrations (mg/dm^3) of Cd(II) solution, V is the volume, and M is the weight of adsorbent.

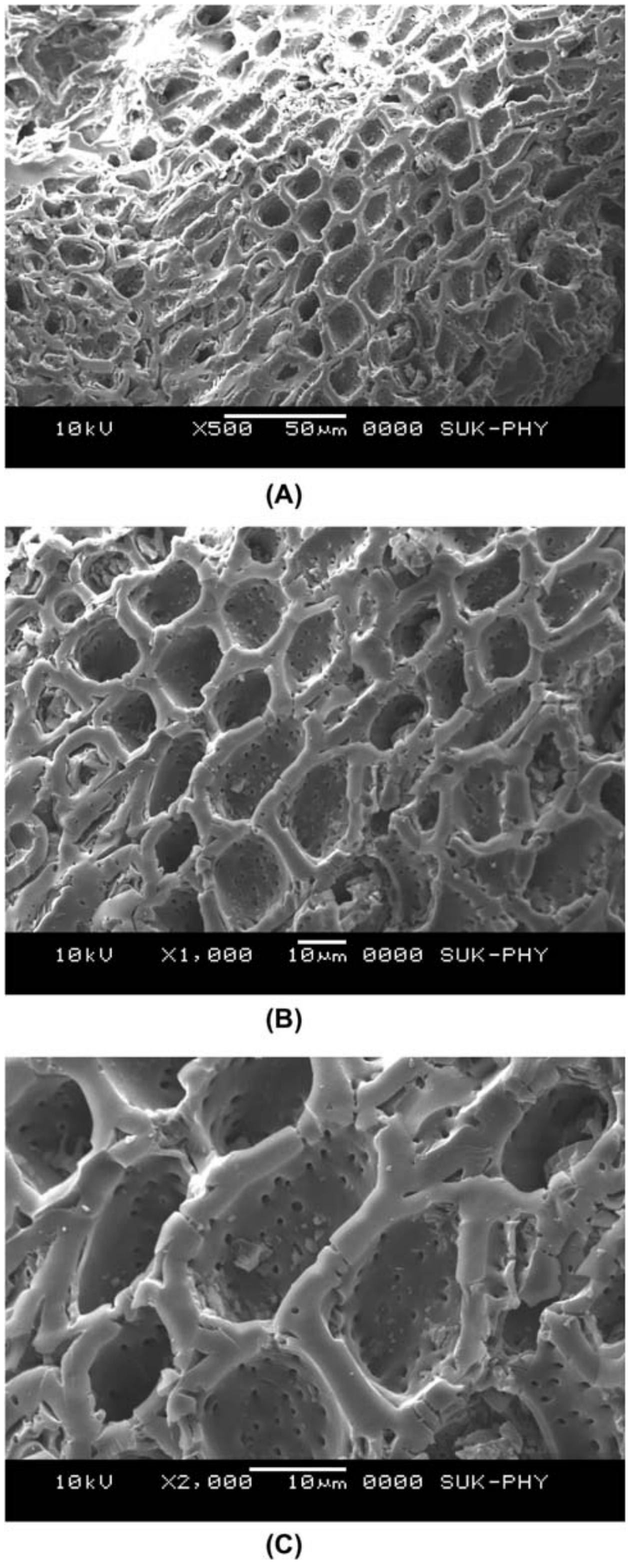

Fig. 2. SEM of WASAC with (A) enlargement with 500×, (B) enlargement with 1,000×, and (C) enlargement with 2,000×.

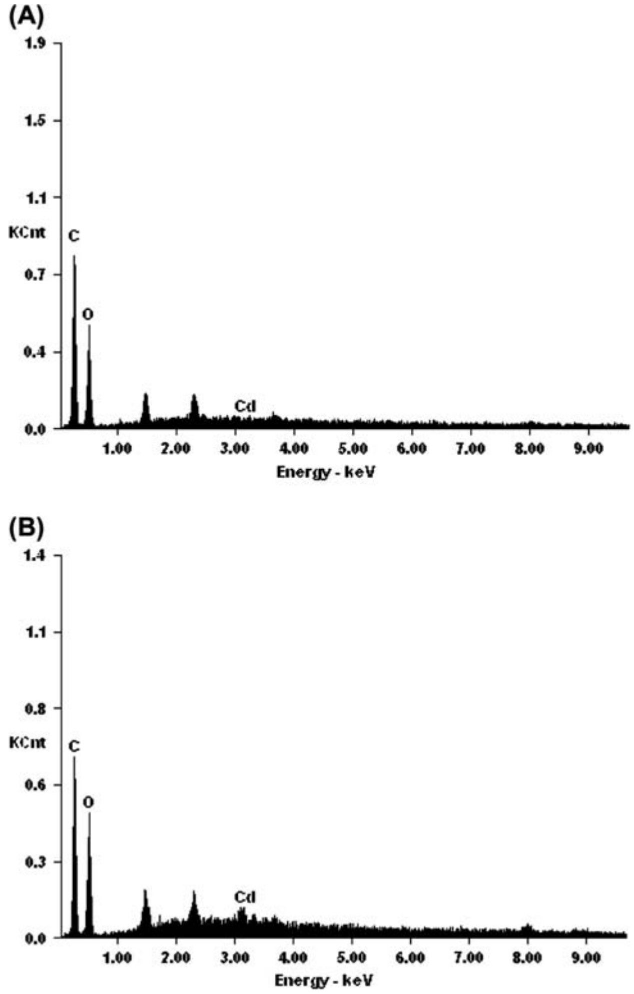

Fig. 3. EDAX of WASAC (A) before adsorption of Cd(II) and (B) after adsorption of Cd(II).

3. Result and discussion

3.1. Effect of pH

The effect of pH on adsorption of Cd(II) was studied by varying the pH from 1 to 7. The concentration of Cd(II) was taken as $100\,mg/dm^3$, while the volume of solution was kept 50 ml, at constant temperature 299 ± 2 K and it was agitated for 4 h at 150 rpm. From Fig. 4, it is clearly indicated that the adsorption was significant above pH 6. For further studies, the pH was maintained at 6.5 because, above neutral pH, the reaction mixture forms a precipitate. The Cd(II) percentage removal and adsorption capacity was 98.80% and 12.35 mg/g, respectively for WASAC.

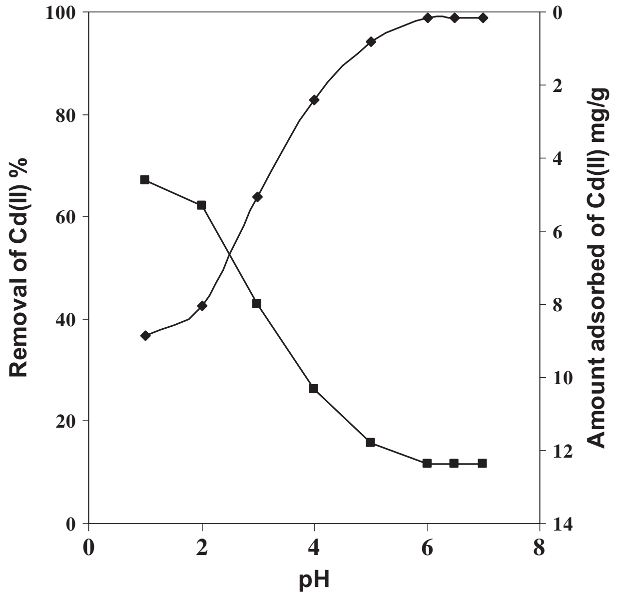

Fig. 4. Effect of pH on removal of Cd(II), % and amount adsorbed, mg/g $Cd(II) = 100\,mg/dm^3$, time = 240 min. $T = 299 \pm 2\,K$, WASAC = 400 mg, agitation speed = 150 rpm.

The pH of the solution was found to have a great effect on the adsorption of Cd(II) ions. Initial pH range was chosen in order to avoid metal solid hydroxide precipitation. The metal hydroxide precipitation was observed from pH 7.5 and the same observation was reported by other researchers [7]. It was observed from the results that negligible precipitations occurred at pH <8.0, but at higher pH (namely pH <10), more precipitation occurred, and the initial concentration ($C_0 = 100\,mg/dm^3$) decreased to $89.4\,mg/dm^3$. This will allow discriminating the importance of Cd(II) adsorption while comparing the precipitation by the pH effect [5].

Lower adsorption capacity observed at low pH may be explained on the basis of electrostatic repulsion forces between positively charged H_3O^+ and Cd(II) ions. At low pH values, the concentration of H_3O^+ is higher than that of Cd(II) ions, and hence, these ions are adsorbed on the active sites of activated adsorbents, leaving Cd(II) ions free in the solution. When pH increased, Cd(II) ions would be replaced with H_3O^+ ions. Competing effect of H_3O^+ decreased with increase of the pH, which increases the adsorption yield of the Cd(II) ions. The adsorption capacity increases with increase in pH value up to 7 and remains constant up to pH 9.0. But we have considered range of pH 6–7 as the removal takes place by adsorption as well as precipitation of Cd(II) ions in the form of $Cd(OH)_2$. The decrease in adsorption yield at alkaline conditions can be attributed to the formation of $Cd(OH)_3^-$ ions taking place as a result of dissolution of $Cd(OH)_2$ due to its amphoteric characteristic. The hydrolysis and precipitation of metal ions affect adsorption by changing the concentration and form of soluble metal species that are available for adsorption. The hydrolysis of Cd(II) ions may be represented by following reaction

$$Cd^{2+} + 2nH_2O \leftrightarrow Cd(OH)n^{2-n} + nH_3O^{+} \qquad (2)$$

Depending upon the pH of the solution, various species of cadmium can be formed during the hydrolysis. The hydrolysis extent of Cd(II) ions is unimportant up to approximately pH 7.5 and cadmium is in the form of Cd^{2+} ions at this pH. For that reason, it can be said that the adsorption mechanisms can be explained on the basis of H_3O^+–Cd^{2+} exchange reaction [8].

3.2. Effect of time

With the increase in the contact time, there is enhancement in the adsorption of adsorbate both in percentage as well as the amount adsorbed. This is probably due to a larger surface area of the WASAC being available, at the beginning, for the adsorption of Cd(II). As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. Effect of shaking period was done at various time intervals from 30 to 360 min. The increase in percentage adsorption from 31.78 to 98.80% (Fig. 5) was observed up to 230 min. After 230 min, there was no significant change observed.

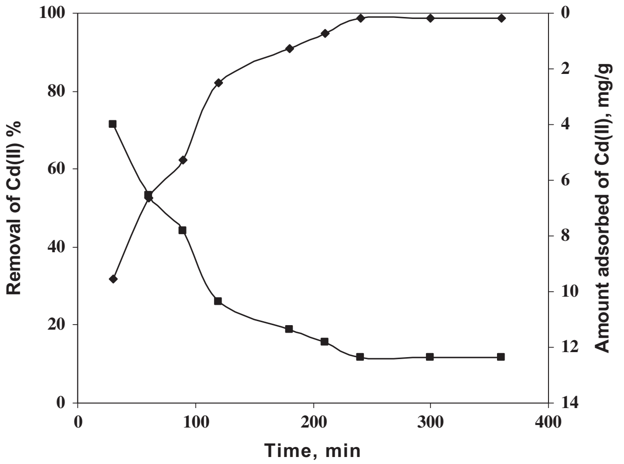

Fig. 5. Effect of shaking period on removal of Cd(II), % and amount adsorbed, mg/g Cd(II) = 100 mg/dm^3, pH = 6.5, T = 299 ± 2 K, WASAC = 400 mg, agitation speed = 150 rpm.

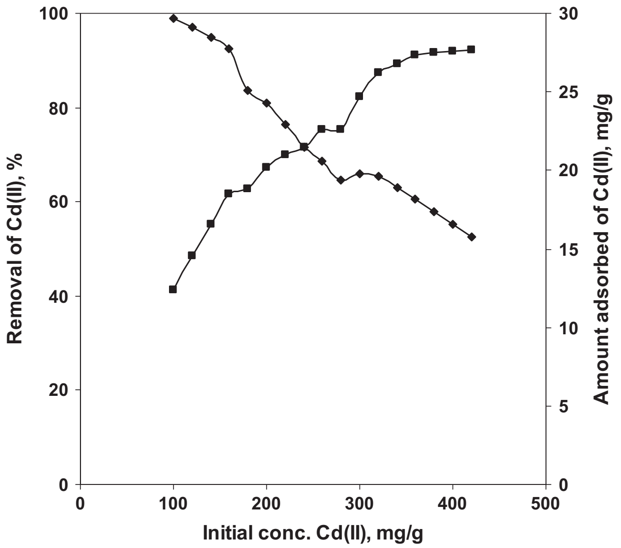

Fig. 6. Effect of initial concentration of Cd(II) on amount adsorbed, mg/g and removal, of Cd(II) on WASAC Time = 240 min, pH 6.5, T = 299 ± 2 K, WASAC = 400 mg, agitation speed = 150 rpm.

3.3. Effect of initial concentration of Cd(II)

The effect of initial Cd(II) concentration in the range of 100–420 mg/dm^3 on adsorption was investigated. Along with pH, all parameters were kept constant in this study. It is evident from Fig. 6 that as the concentration of Cd(II) was increased, the amount adsorbed was increased; but, there was a decrease observed in percentage removal. It is due to the initial Cd(II) concentration providing the necessary driving force to overcome the resistances to the mass transfer of Cd(II) between the aqueous phase and the solid phase. The increase in initial Cd(II) concentration also enhances the interaction between Cd(II) and WASAC i.e. adsorbate and adsorbent. Therefore, an increase in initial concentration of Cd(II) enhances the adsorption uptake of Cd(II) and results in higher adsorption, while the adsorption was carried out for fixed number of active sites, there was a decrease in percentage removal of Cd(II). The amount adsorbed of Cd(II) adsorption was increased from 12.35 mg/g to 27.64 mg/g, as the initial metal ion concentration increased.

3.4. Effect of adsorbent dosage and agitation speed

Adsorption dosage is one of the vital parameters in the study. The adsorbent WASAC was varied from 50–400 mg/dm^3, to study the effect on the adsorption of Cd(II). As the amount of adsorbent was increased (Fig. 7), the amount adsorbed and percentage removal of Cd(II) was increased respectively. The adsorbent dosage affects the adsorption capacity directly, and as there is increase in dosage, more active sites becomes available for adsorbate. The maximum amount 12.35 mg/g of Cd(II) was adsorbed for 400 mg of WASAC and 98.80% removal of Cd(II) was found.

The agitation speed effect on the adsorption amount and percentage removal was investigated. To study this parameter, rpm was varied from 50 to 200 rpm. In the present study, it was observed that the interaction between adsorbate and adsorbent was effective at high speed i.e. 150 rpm and more up to 200 rpm.

3.5. Adsorption isotherm

Adsorption isotherms express the mathematical relationship between the quantity of adsorbate and equilibrium concentration of adsorbate remaining in the solution at a constant temperature. The adsorption data has been analyzed with well-known Langmuir and Freundlich isotherm models.

3.6. Langmuir Isotherm

Langmuir isotherm model is applicable when the extent of adsorbate coverage is limited to one molecular layer at or before a relative pressure of unity is reached. The isotherm assumes a dynamic equilibrium between the adsorbed phase and the vapor/liquid phase. Langmuir described chemisorption as the formation of an ionic or covalent bond between adsorbent and adsorbate. The isotherm equation gives the fractional coverage (θ) in the form

$$\theta = \frac{q_e}{q_m} = \frac{K_L C_e}{1 + K_L C_e} \tag{3}$$

where K_L is k_1/k_d (where k_1 and k_d are rate constants for adsorption and desorption, respectively) and q_m is the quantity of adsorbate required to form a single monolayer and q_e is the amount adsorbed on unit mass of the solid when the equilibrium concentration is C_e. The ratio q_e/q_m can be measured and expressed in different ways. The most widely used form, known as the two-parameter equation for a single solute system, is represented by Eq. (3). It can be rearranged to,

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \tag{4}$$

which shows that a plot of (C_e/q_e) vs. C_e should yield a straight line if the Langmuir equation is obeyed by the adsorption equilibrium (Fig. 8). The slope and the intercept of this line give the values of q_m and K_L. These expressions have been shown to be valid in relatively higher concentration ranges [9].

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium

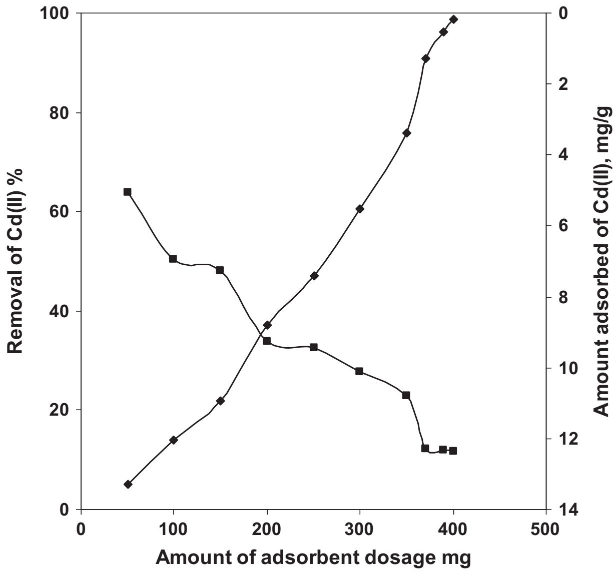

Fig. 7. Effect of adsorbent dosage on Cd(II) removal, % and amount adsorbed, mg/g Cd(II) = 100 mg/dm^3, time = 180 min, pH = 6.5, $T = 299 \pm 2$ K, agitation speed = 150 rpm.

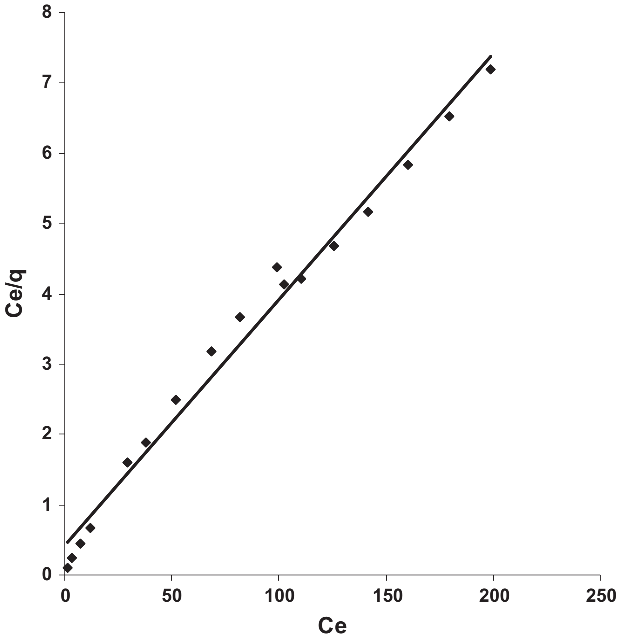

Fig. 8. Langmuir isotherm for adsorption of Cd(II) on WASAC.

parameter, $R_{L,}$ also known as the separation factor, given by

$$R_L = \frac{1}{1 + K_L C_e} \tag{5}$$

where C_e is equilibrium liquid phase concentration of the solute at which adsorption is carried out. The value of R_L lies between 0 and 1 for favorable adsorption, while $R_L > 1$ represents unfavorable adsorption, and $R_L = 1$ represents linear adsorption, while the adsorption process is irreversible if $R_L = 0$ [10].

The Langmuir constants (q_m and K_L) calculated from the plots are presented in Table 2. The data related to the equilibrium obeyed well the Langmuir isotherm model with 28.33 mg/g maximum adsorption capacity of adsorption of Cd(II), which is more agreeable to the calculated value 27.64 mg/g. The value of regression coefficient was also good. The value of R_L was subsist between 0.049 and 0.896, which indicates the favor of adsorption i.e. formation of monolayer of Cd(II) ions on the surface of WASAC.

3.7. Freundlich isotherm

The Freundlich isotherm model is the empirical relationship and an assumption that the adsorption energy of a metal ion binding to a site of an adsorbent depends on whether or not the adjacent sites are already occupied. It has the following form [11],

The Freundlich equation is expressed as

$$q_e = K_F C_e^{1/n} \tag{6}$$

where K_F is the measure of adsorption capacity and n is the adsorption intensity linear form of Freundlich Eq. (6) is

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{7}$$

where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of adsorbate (mg/dm^3), and K_F and n are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. A plot of log q_e vs. log C_e (Fig. 9) gives a linear trace with a slope of $1/n$ and intercept of log K_F (Table 2).

Table 2
Langmuir and Freundlich constant for the adsorption of Cd(II) on WASAC

Langmuir constants			Freundlich constants		
q_m (mg/g)	K_L (1/mg)	R^2	K_f	n	R^2
28.33	0.0967	0.986	11.280	5.935	0.953

From the results, it was observed that both models are suited for adsorption of Cd(II) on WASAC, but on the basis of the regression factor and more correlation of the calculated and experimental values, it was concluded that, Langmuir isotherm model was more suitable for this study. The Cd(II) ions form monolayer on surface of WASAC and the adsorption was chemisorption.

3.8. Adsorption kinetics

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 [12].

The kinetic study for the adsorption of Cd(II) was conducted at optimum pH 6.5 where maximum adsorption takes place. The adsorption study was tested for well-known models i.e. pseudo-first-order and pseudo-second-order model. The experiment was

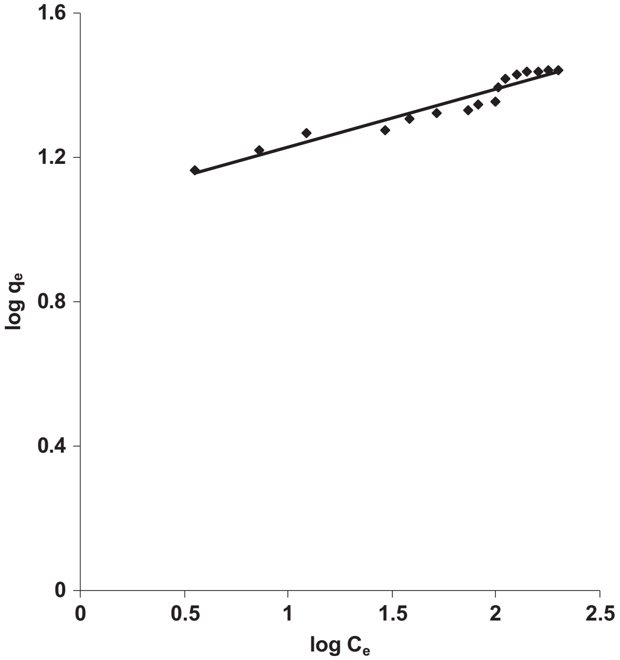

Fig. 9. Freundlich adsorption isotherm for adsorption of Cd(II) on WASAC.

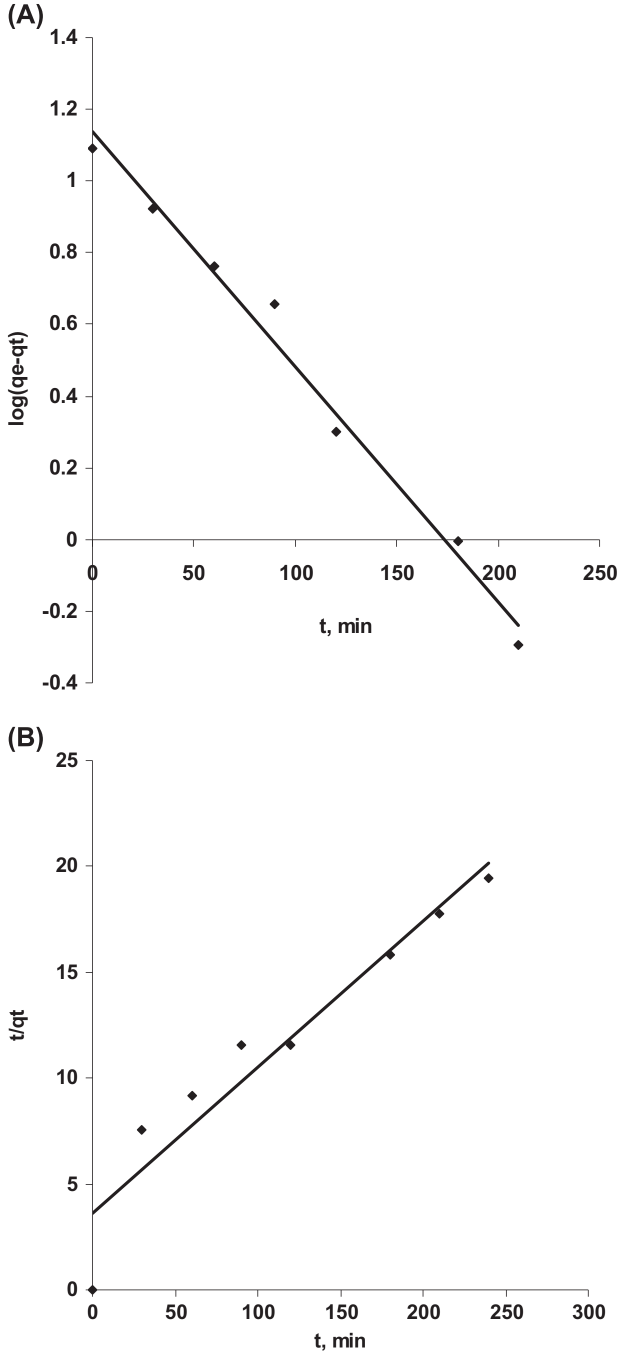

Fig. 10. (A) Pseudo-first-order for adsorption of Cd(II) on WASAC and (B) pseudo-second-order for adsorption of Cd(II) on WASAC.

carried out from 0–240 min. at constant temperature, with 100 mg/dm^3 concentration of Cd(II).

Several kinetic models are in use to explain the mechanism of the adsorption processes. A simple pseudo-first-order equation was used [13].

$$\frac{dq_t}{dt} = k_1(q_e - q_t)^2 \tag{8}$$

where q_e and q_t are the amount of adsorption at equilibrium and at time t (min) respectively, and k_1 is the rate constant of the pseudo-first-order adsorption process. Lagergren plot of the adsorption of Cd(II) by WASAC, for the log of the initial condition of $q_t = 0$ at $t = 0$, becomes easy for graphical representation [14]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{9}$$

Plot of log (q_e−q_t) vs. t (Fig. 10(A)) gives a straight line for pseudo-first-order adsorption kinetics, which allows computation of the adsorption rate constant, k_1. The k_1 and q_e value for the initial concentration of 100 mg/dm^3 are found to be $0.65 \times 10^{-3}\,\text{min}^{-1}$ and 13.652 mg/g. The true value of q_e obtained from experiments is 12.35 mg/g. The value R^2 was 0.982 for pseudo-first-order; so we tried for pseudo-second-order.

The corresponding pseudo-second-order rate equation [15] is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{10}$$

where k_2 is the rate constant for pseudo-second-order adsorption. The rate parameters k_2 and q_e can be directly obtained from the intercept and slope of the plot of t/q_t vs. t (Fig. 10(B)). The values obtained from graph for both adsorption models are given in Table 3. As per the calculated and experimental results concerned, it is clear that, the pseudo-first order-model provided a better approximation to the experimental kinetic data than the pseudo-second-order model.

3.9. Prediction of adsorption rate-limiting step

There are essentially three consecutive mass transport steps associated with the adsorption of solute from the solution by an adsorbent. These are (1) film diffusion, (2) intraparticle or pore diffusion, and (3) sorption into interior sites. The third step is very rapid and hence, film and pore transports are the major steps controlling the rate of adsorption [15,16]. The study tries to use Fick's equation, Eq. (11) [17,18] to describe the diffusion process of Cd(II) ions on the exterior and interior surface.

$$\frac{q_e}{q_t} = \frac{6}{R_a}\sqrt{\frac{D_{et}}{\pi}} \tag{11}$$

Table 3
Kinetic parameters for the adsorption of Cd(II) on WASAC

Pseudo-first-order				Pseudo-second-order			Intraparticle diffusion equation	
q_e exp. (mg/g)	$k_1 \times 10^{-3}$ (min^{-1})	q_e calc. (mg/g)	R^2	$k_2 \times 10^{-3}$	q_e calc. (mg/g)	R^2	k_{id} (mg g^{-1} min^{-1})	R^2
12.35	0.65	13.652	0.982	0.0545	17.762	0.988	0.434	0.997

Plot of q_t/q_∞ (q_∞ was replaced by q_e) vs. $t^{1/2}$ is shown in Fig. 11. This plot represented the different stages of adsorption. The first linear portion related to the film diffusion, the second linear portion represented the intraparticle diffusion, and the last linear portion indicated adsorption–desorption equilibrium. It can be calculated from Fig. 11 that film diffusion took about 120 min while the intraparticle diffusion took 240 min. The ratio of the time taken by film diffusion to intraparticle diffusion was 1:2. The process was jointly controlled by film diffusion and intraparticle diffusion. Here, intraparticle diffusion was predominant over the film diffusion.

Whatever the case, external diffusion will be involved in the sorption process. The adsorption of Cd(II) onto WASAC may be controlled due to film diffusion at earlier stages and later by the particle diffusion. The most commonly used technique for identifying the mechanism involved in the adsorption process is by fitting an intraparticle diffusion plot [18]. The amount of Cd(II) adsorbed (q_t) at time (t), was plotted against the square root of t ($t^{1/2}$), according to Eq. (12) proposed by Weber and Morris and the resulting plot is shown in Fig. 12.

$$q_t = k_{id} t^{1/2} + C \tag{12}$$

where C is constant and k_{id} is the intraparticle diffusion rate constant (mg/g min$^{1/2}$), q_t is the amount adsorbed at a time (mg/g), t is the time (min), and k_{id} (mg/g min$^{1/2}$) is the rate constant of intraparticle diffusion. The rate constant of intraparticle diffusion is shown in Table 3.

The initial curved portion relates to the boundary layer diffusion (film diffusion) and the latter linear portion represents the intraparticle diffusion. The two regions in the q_t vs. $t^{0.5}$ plot suggest that the sorption process proceeds by surface sorption and intraparticle

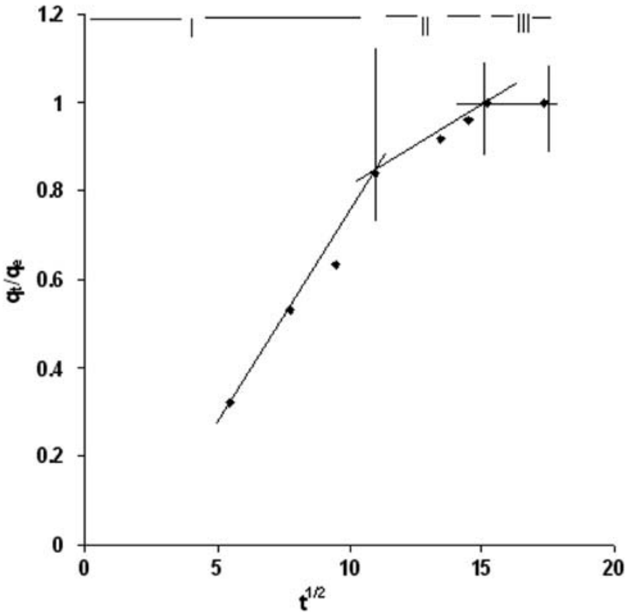

Fig. 11. Diffusion study for adsorption of Cd(II) on WASAC.

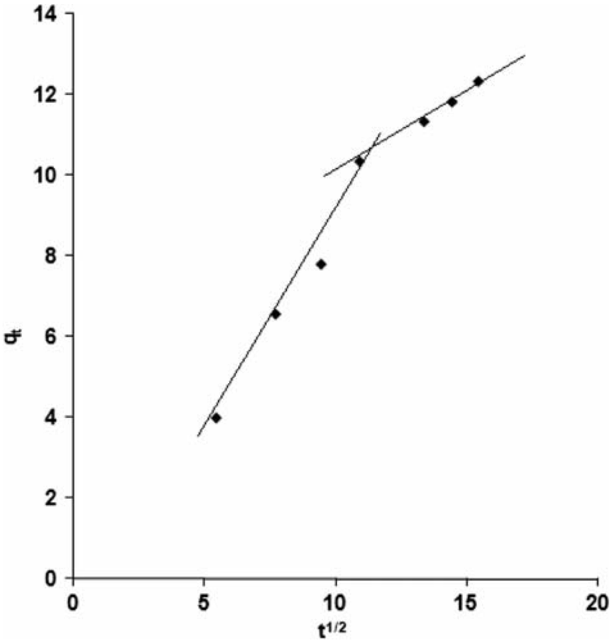

Fig. 12. Intraparticle diffusion plot for adsorption of Cd(II) on WASAC.

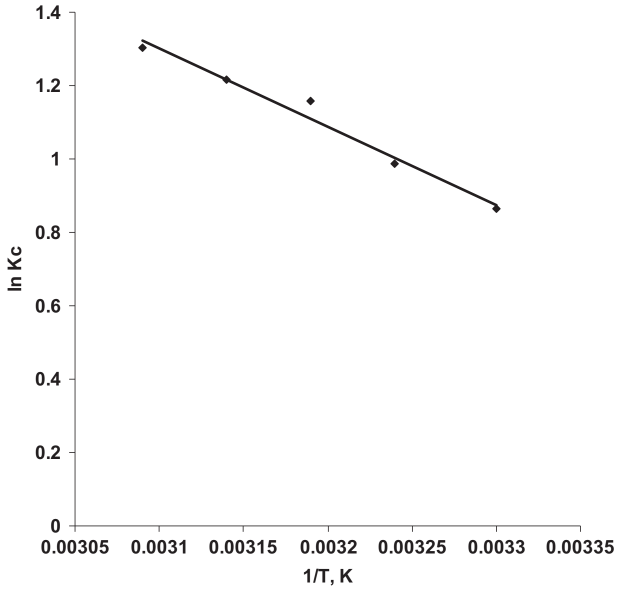

Fig. 13. Van't Hoff plots for adsorption of Cd(II) on WASAC.

Table 4
Thermodynamic parameters adsorption of Cd(II) on WASAC

T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
303	−1.110	1.582	5.707
308	−1.604		
313	−1.824		
318	−1.971		
323	−2.115		

diffusion. The initial curved portion of the plot indicates a boundary layer effect, while the second linear portion is due to intraparticle or pore diffusion. The slope of the second linear portion of the plot has been defined to yield the intraparticle diffusion parameter k_{id} (mg/g min$^{-1/2}$). On the other hand, the intercept of the plot reflects the boundary layer effect. The larger the intercept, the greater the contribution of the surface sorption in the rate-controlling step [18].

3.10. Adsorption thermodynamics

The study was essential as, the theory of adsorption gives the general information that, there is influence of temperature on the adsorption. We have used 420 mg/dm^3 concentration to study with 0.4 g WASAC agitated for 4 h at 150 rpm. The adsorption was increased with increase in temperature. Temperature was increased from 303 to 323 K with 5 K change which shows the swell into the amount adsorbed. This indicates that the adsorption reaction was endothermic in nature. The enhancement in the adsorption capacity may be due to the chemical interaction between the adsorbate and adsorbent, creation of some new adsorption sites or the increased rate of intraparticle diffusion of Cd(II) ions into the pores of the adsorbent at higher temperatures [19].

The standard Gibbs energy was,

$$\Delta G^0 = -RT \ln K_{\mathrm{C}} \tag{13}$$

The equilibrium constant K_{C} was evaluated at each temperature using the following relationship

$$K_{\mathrm{c}} = \frac{C_{\mathrm{Ae}}}{C_{\mathrm{e}}} \tag{14}$$

where C_{Ae} is the amount adsorbed on solid phase at equilibrium and C_{e} is the equilibrium concentration. Other thermodynamic parameters such as change in standard enthalpy (ΔH°) and standard entropy (ΔS°) were determined using the following equations [20]

$$\ln Kc = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{15}$$

ΔH° and ΔS° were obtained from the slope and intercept of the Van't Hoff's plot of ln K_{C} vs. $1/T$ as shown in Fig. 13. Positive value of ΔH° indicates that the adsorption process is endothermic. The negative values of ΔG° reflect the feasibility of the process and the values become more negative with increase in temperature. Standard entropy determines the disorderliness of the adsorption at solid–liquid interface. Table 4 summarizes the results. The positive value of ΔS° shows that increasing randomness at the solid/liquid interface during the adsorption of Cd(II) ions on WASAC.

4. Comparison of adsorption capacity of WASAC with other adsorbents

In present study, the parameters were investigated to get equilibrium as well as to determine the maximum adsorption with isotherm model. This maximum adsorption capacity has been compared with other reported adsorbents given in Table 5 and the results show that, the WASAC has good adsorbent capacity.

Table 5
Comparison of adsorption capacity of WASAC with other adsorbents

Adsorbent	q_{m} (mg/g)	Refs.
Raw corn stalk	3.39	[1]
Acrylonitrile modified	12.73	[1]
Olive stone activated carbons	1.85	[18]
Kaolinite clay		[19][19]
(a) modified	14.03	
(b) unmodified	9.23	
Loess soils	9.37	[20]
Mine tailing	3.52	[21]
Jordanian low grade phosphate	7.54	[22]
Zeolite tuff	5.157	[23]
Granulated activated carbon	17.153	[23]
Duolite ES 467	13.77	[24]
Carbon nanotubes	1.1	[25]
Oxidized with		
(a) H_2O_2	2.6	[25]
(b) $KMnO_4$	5.1	[25]
(c) HNO_3	11.0	[25]
Bagasse fly ash	6.194	[26]
Bagasse fired	1.24	[27]
Coal fly ash pellets	18.98	[28]
Betel nut	1.12	[29]
Pycnoporus sanguineus	3.18	[30]
Brewer's yeast	10.17	[31]
Corncob	4.73	[32]
Raw corn stalk	3.81	[33]
Modified using graft copolymerization	22.17	[33]
Olive cake	10.56	[34]
Rice husk	21.28	[35]
Wheat bran	0.703	[36]
Wheat bran	15.71	[37]
Castor (*Ricinus communis*) seed hull	6.98	[38]
Walnut tree sawdust	5.76	[39]
Jack fruit seed carbon	1.215	[40]
Ceiba pentandra hulls activated carbon	19.5	[41]
Bamboo charcoal	12.08	[42]
Cashewnut shell activated carbon	14.29	[43]
Shellac-coated magnetic nanoparticle	18.80	[44]
Green macroalga	15.53	[45]
Clarified sludge	14.30	[45]
Grafted cellulosic fabrics	13.69	[45]
Lichen ramalina fraxinea	7.00	[46]
Aspergillus niger	2.2	[47]
Granular activated carbon	11.75	[48]
Activated clay	8.718	[48]
Activated sludge biomass	1.95	[49]
Rice bran residue	20.74	[50]
Lentinus edodes mushroom flesh particles	6.45	[51]
Lotus stalks activated carbon	41.79	[52]
Titanium dioxide (Dugussa P25) nanoparticles	11.62	[53]
Loess-modified clay liner	5.17	[54]
Clarified sludge	36.25	[55]
Coal fly ash	35.06	[56]
Activated alumina	35.84	[57]
Rice husk ash	34.12	[58]
WASAC	27.64	Present study

5. Conclusion

This study clearly suggests that the use of WASAC as adsorbent is much economical and effectual as it is abundant. It can be efficiently used to remove Cd(II) ions from aqueous solution. The different operational parameters observed during the process of investigations reveal that the contact time, initial concentration, adsorbent mass, pH of solution, speed, and temperature govern the overall process of sorption. The adsorption constants agree well with the conditions supporting favorable adsorption and regression factor. Among the isotherms, Langmuir model fits better than Freundlich model. The increase in the adsorption capacity observed with increasing temperature showed that the adsorption process was chemical in nature, being feasible, spontaneous, and endothermic as confirmed by the evaluation of the relevant thermodynamic parameters, viz. ΔH°, ΔG° and ΔS° From the kinetic study of the adsorption, it was concluded that, pseudo-first-order agreed better than pseudo-second-order. It could be concluded that with high efficiency of adsorption by the WASAC, we developed very effective, inexpensive method with good capability. Finally, it can be concluded that WASAC could be applied for the removal of Cd(II) ion from waste water effectively and economically.

Nomenclature

C_0 — initial concentration (mg/dm^3) of Cd(II) ions solution
C_e — equilibrium concentration (mg/dm^3) of Cd(II) ions solution
V — volume (L) of the solution
M — weight of adsorbent (g)
q_e — amount adsorbed on adsorbent (mg/g)
k_1 — rate constants for adsorption
k_d — rate constants for desorption
q_m — Langmuir monolayer adsorption capacity (mg/g)
θ — fractional coverage
K_L — Langmuir adsorption intensity constant (l/mg)
R_L — dimensionless equilibrium parameter
R^2 — correlation coefficient
K_F — Freundlich multilayer adsorption capacity (mg/g)
n — Freundlich isotherm exponent
q_t — amount adsorbed at time t (mg/g)
t — time (min)
ΔG° — standard Gibbs energy of adsorption (kJ/mol)
ΔH° — standard enthalpy of adsorption (kJ/mol)
Kc — equilibrium constant
ΔS° — standard entropy of adsorption (J/mol k)
T — temperature (K)
C_{Ae} — amount adsorbed on solid at equilibrium (mg/dm^3)
k_{id} — intraparticle diffusion rate (mg/g min$^{1.2}$)
c — constant

Abbreviations

WASAC — Wood apple shell activated carbon
IARC — International Agency for Research on Cancer
JECFA — Joint FAO/WHO Expert Committee on Food Additives
FTIR — Fourier transform infrared spectroscopy
SEM — Scanning electron microscopy
EDAX — Energy-dispersive X-ray spectroscopy
BET — Brunauer–Emmett–Teller

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