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Adsorption of Cu (II) and Cd (II) onto Activated Carbon Prepared from Pumpkin Seed Shell

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ABSTRACT

Present study discusses the removal of heavy metal contaminants from an aqueous solution using ortho-phosphoric acid activated pumpkin seed shells derived activated carbon (PSS-AC). The activation was done by heating the mixture in an electrical furnace at 800 °C for 3 h. Adsorption experiments were carried out as a function of pH, contact time, initial Cu (II) and Cd (II) ion concentrations, adsorbent dosage and temperature of the solution for the metal ion removal. The equilibrium and kinetic studies data were fitted better for the Langmuir isotherm model and pseudo-second order model respectively. Thermodynamic parameter obtained for Cu (II) and Cd (II) ions adsorption suggests the reaction to be non-spontaneous, feasible; and endothermic between temperatures of 25 °C and 45 °C.

1. Introduction

Water is one of the most vital resources for all living organisms. It is an important component for industrial processes, agricultural production and domestic uses on the Earth. Water has different sources such as groundwater and aquifers, surface water, sea and ocean. In its purest form, water is colorless, odorless and tasteless; and should also be free from hazardous compounds [1,2]. Although water availability is not a problem on a global scale, there might be a problem of finding an adequate supply of fresh water that meets the ever-increasing demand; and maintaining its quality is becoming a great challenge [3].

Water could be exposed to different contaminants on its sources as or its way of the journey with elements created by human activities, effluents from chemical industries, human and animal waste, dissolved gases, etc. In addition, water contains some number of mineral constituents such as iron, magnesium, lithium, zinc, copper, chromium, nickel, cobalt, vanadium, arsenic, molybdenum, selenium, lead and so many other elements [4-7].

Heavy metals enter our body through drinking, eating, inhaling, and skin and eye contact. Once they enter into the body, they can damage at the cellular level by causing hazardous free radicals production that can cause cancer and many other diseases. Unlike organic pollutants, the majority of which are susceptible to biological degradation and do not degrade into harmless end products [8,9]. The removal of heavy metal effectively from water and wastewater is ecologically benign. There are many reported and established conventional methods for the recovery of heavy metal ions from wastewater, which included the chemical oxidation and reduction, ion exchange, filtration, electrochemical treatment, chemical precipitation, and evaporation. However, these hightechnology processes have significant disadvantages, which include incomplete metal removal, expensive equipment and monitoring systems, costly reagents, generation of toxic sludge and other waste products that require proper disposal [10-12].

In recent years, many types of research have been conducted to study low-cost agricultural waste as adsorbents for the removal of heavy metal ions from water sources. The advantage of using agricultural waste as raw materials for the production activated carbon is due to its low cost and renewable in nature [13]. These include peat [14], wood [15], pine bark [16], banana pith [17], soybean hulls [18], peanut shells [19], hazelnut shell [20], compost [21], rice husk and saw dust [22] are used as a precursor to prepare activated carbon.

Pumpkin is one of the most important vegetables grown worldwide. It is a gourd-like squash and belongs to the family of *Cucurbitaceae's* [23]. Pumpkin seeds, also known as pepitas, are flat and variable in size, shape and color. The pumpkin seed has been used for the extraction of oil which has several benefits such as anti-microbial, anti-fungal and anti-viral properties. Survey related to pumpkin seed shell as a potential adsorbent suggest many researchers have worked on preparation and use it for removal of heavy metals [24-28]. But none of these articles reflect its use for the removal of Cu (II) and Cd (II) from aqueous solution. Thus, in the present study we have chosen pumpkin seed shell as a precursor of activated carbon for the removal of Cu (II) and Cd (II) ion.

2. Experimental Methods

2.1 Materials

All chemicals used were of analytical reagent grade and were used as received without any treatment. Distilled water was used for the preparation of the stock solution. Copper sulphate, $CuSO_4 \cdot 5H_2O$ (Riedel-de Haën, Germany) (98% by wt.) and Cadmium chloride, $CdCl_2 \cdot 1/2H_2O$ (Riedel-de Haën, Germany) (99% by wt.) were used to prepare respective stock solutions. Further concentrations were prepared by progressive dilution using distilled water. H_3PO_4 (Riedel-de Haën, Germany) (85% by wt.) was used as the activating agent. The instruments used in this works were: atomic absorption spectrophotometer (AAS) (Model analytic Jenanov AA 300), thermostatic water bath shaker (Model GRANT GLS 400, England), digital pH meter (HANNA instruments, pH 211), electronic balance (ADAM AFP-110), Air drying oven (Model GENLAB WIDNES, England), electrical furnace (Model Nabertherm(R)), Scanning electron microscope (Model JSM 6510LV, JEOL Japan) and FTIR spectrophotometer (Spectrum 65 FTIR, Perkin Elmer model).

2.2 Adsorbent Preparation and Activation

Raw pumpkin seed shells were washed first with tap water and then with distilled water to remove the attached dust and other impurities. Washed PSS was dried at 105 °C for 12 h, and grinded to powder. The powdered pumpkin seed shells were soaked with ortho-phosphoric acid (85% by v/v) by using the weight ratio of raw material and the acid at 1:1 w/v. The mixture was dried in an air-drying oven at 105 °C for 24 h. The dried PSS/H_3PO_4 mixture was then put on to a crucible and placed in an electrical furnace for carbonization. The heating rate of carbonization was 10 °C/min and continues until the final temperature of 800 °C was attained and it was kept at this temperature for 3 h. The produced activated carbon was then cooled down to room temperature, washed with 5% aqueous NaOH solution followed by distilled water several times until the pH of the

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washing becomes neutral. Finally, the activated carbon prepared was dried at 105 °C for 12 h and grinded to powder into 150 µm sieve size and kept it in an air tight container for further use in adsorption experiments.

2.2 Batch Adsorption Experiments

Batch adsorption experiments were carried out using a set of volumetric flask. A known amount of PSSAC (0.2 g) was kept into flasks containing various concentrations of Cu (II) and Cd (II) aqueous solutions. pH of the solution was adjusted to the desired value by adding HCl or NaOH. The flasks were then shaken at room temperature using a shaker for a certain period so that the equilibrium is attained. The solutions were filtered and metal ion concentrations were determined by AAS method. Contact time (10 – 90 min), solution pH (1– 9), adsorbent dose (0.05 – 0.30 g), and effects of initial concentration (0.002 - 5 mg/L) for both Cu (II) and Cd (II) were studied.

2.3 Adsorption Experiments

The adsorption process provides vital information about the mechanism of reaction between adsorbate and adsorbent. Equilibrium adsorptions are described by isotherms governing the distribution of a given adsorbate between the liquid phase and the adsorbent where, Freundlich and Langmuir models were developed and used to analyze the data for the adsorption of the ions by pumpkin seed shell activated carbons. A kinetics study was carried out using Lagergren pseudo-first order and pseudo second order kinetic models to determine the equilibrium time required for the uptake of metals from a liquid solution [29]. Thermodynamic parameters such as Gibbs free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) of adsorption were evaluated. The amount of Cu (II) and Cd (II) adsorbed at a time t, q_t (mg/g) was calculated using Eq.(1).

$$q_t = \frac{(C_o - C_t)V}{W} \quad (1)$$

where C_t (mg/L) is the liquid phase concentrations of metal ion at any time, C_0 (mg/L) corresponds to the initial concentration of each metal ion. V (L), volume of the solution and W (g), mass of the adsorbent. Under the experimental conditions, the adsorption capacity (q_e), of the adsorbent for each concentration of Cu (II) and Cd (II) ions at equilibrium were calculated using Eq.(2),

$$q_e = \frac{(C_o - C_e)V}{W} \quad (2)$$

where C_0 (mg/L) corresponds to the initial concentration of each metal ion, and C_e (mg/L) to the concentration at equilibrium. The removal efficiency percentage of Cu (II) and Cd (II) ions was calculated for each run by using Eq.(3),

$$Removal\ (\%) = \frac{(C_o - C_e)}{C_o} \times 100 \quad (3)$$

3. Results and Discussion

3.1 Characterization of The Activated Carbon

The proximate analyses of PSS-AC as presented in Table 1 showed a lower amount of moisture, ash and volatile matter, indicating that the particle density is relatively small and that the biomaterial should be an excellent raw material for adsorbents to be used in the adsorption process. Ash content can also affect activated carbon i.e. it reduces the overall activity of activated carbon. It also reduces the efficiency of reactivation, the lower the ash value therefore the better the activated carbon for use as an adsorbent. Higher percentage adsorption for adsorbents having smaller particle size is due to the availability of more surface area [30].

Table 1 Proximate analysis of PSS-AC

Parameter	Value
Moisture content (%)	10.06
Volatile matter (%)	4.89
Ash content (%)	21.01
Fixed carbon (%)	74.1
Mesh size (µm)	150
pH	6.5±1

3.1.1 Fourier Transforms Infrared Characterization

Fourier transforms infrared (FT-IR) spectrum analysis is one of the essential methods for the identification of the surface functional groups which can significantly enhance the adsorption efficiency of the prepared activated carbon by surface complexation. The spectrum in the near IR region (wave number: 4000-400 cm^{-1}) of PSS-AC exhibits different absorption peaks indicating the presence of different functional groups. A peak around 2935 cm^{-1} was attributed to aliphatic methyl C-H stretching. The peak observed around 1465 cm^{-1} can be attributed to the CH_3 bending and that observed around 1358 cm^{-1} was due to in-plane C-H bending. The very weak absorption band which was observed at around 725 cm^{-1} was attributed to the long chain band of an aliphatic alkane. Fig. 1 and Table 2 below shows the FT-IR spectra of the activated carbon prepared from PSS-AC before and after adsorption of Cu (II) and Cd (II) ions.

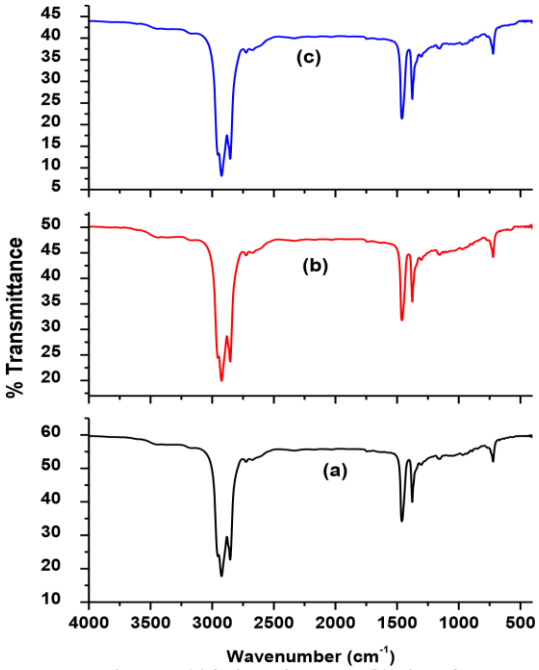

Fig. 1 FT-IR spectra of PSS-AC (a) before adsorption, (b) after adsorption of Cd (II) and (c) Cu (II) ions

Table 2 The FT-IR Spectral Characteristics of PSS-AC before and after adsorption of Cd (II) and Cu (II)

Metal ion	Before	After	Difference	Functional groups
Cu (II)	2935	2924	11	C-H stretching
Cd (II)		2924	11	
Cu (II)	1465	1461	4	CH_3 bending
Cd (II)		1462	3	
Cu (II)	1358	1356	2	in-plane C-H bending
Cd (II)		1356	2	
Cu (II)	725	722	3	long chain band of
Cd (II)		722	3	aliphatic alkane

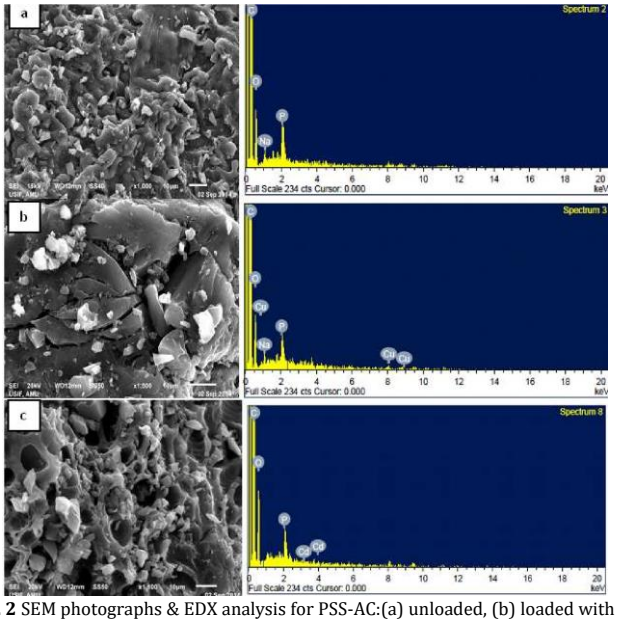

Fig. 2 SEM photographs & EDX analysis for PSS-AC:(a) unloaded, (b) loaded with Cu (II) and (c) loaded with Cd (II)

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3.1.2 Scanning Electron Microscope (SEM) and EDX Analysis

The SEM micrographs of PSS-AC, Figs. 2(a-c), shows the surface having small cavities, pores and more rough surfaces indicating the presence of the interconnected porous network.

SEM micrographs of Cu (II) loaded PSS-AC shows that the surface is pitted and fragmented due to the Cu (II) uptake. The surface areas of Cd (II) loaded PSS-AC is found to be enhanced by the presence of more porosity, which can hold more solute from solution during adsorption. Figs. 2(a-c) EDX analysis was performed to determine the elemental composition of the activated carbon before and after metal ion adsorption implies the ability of the PSS-AC for Cu (II) and Cd (II) ions binding.

3.2 Adsorption Experiments

3.2.1 Effect of Initial Metal Ion Concentration

This effect was conducted to find the optimum concentration for the removal of metal ions from solutions. To find the optimum concentrations and time for the removal of the Cu (II)and Cd (II) ions, ten conical flasks containing 0.2 g of PSS-AC within 25 mL (0.01 mg/L, 0.05 mg/L, 0.2 mg/L, 2 mg/L and 5 mg/L) of Cu (II) and (0.002 mg/L, 0.005 mg/L, 0.04 mg/L, 0.2 mg/L and 1 mg/L) of Cd (II) solutions were taken. The result of initial metal ion concentrations for the removal of Cu (II) and Cd (II) from aqueous solution is demonstrated in Fig. 3 below. It clearly indicates the percent adsorption was increased from 90.58% to 98.81% for Cu (II) with an increase of initial metal ion concentration from 0.01 mg/L to 5 mg/L; and it increased from 93.52% to 98.99% for Cd (II) with increasing initial metal ion concentration from 0.002 mg/L to 1 mg/L. It also depicts that the adsorption equilibrium was reached for Cu (II) at the optimum time of 70 min at 0.2 mg/L and for that of Cd (II) the optimum time was of 50 min at 0.005 mg/L. It should be attributed to the fact that at lower concentrations, the metal-ions adsorption occurred a slow and further increase in concentration initiates a competition for available bonding sites on the PSS-AC surface by the metal ions and thus increased the adsorption [31].

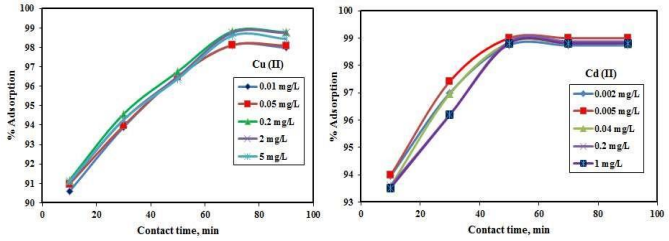

Fig. 3 Effect of initial metal ion concentration on the adsorption of Cu (II) and Cd (II) using PSS-AC

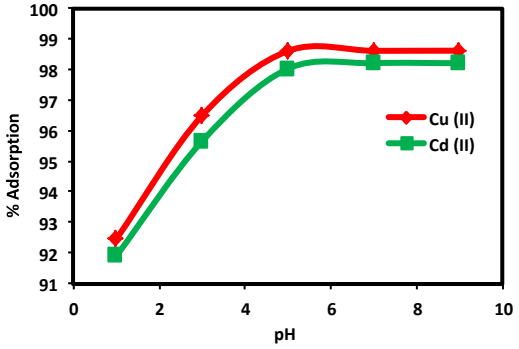

Fig. 4 Effect of pH on the adsorption of Cu (II) and Cd (II) using PSS-AC

3.2.2 Effect of pH

pH is one of the important controlling parameters for the removal of heavy metal ions from solutions because it affects the solubility of the metal ions, concentration of the counter ions on the functional group of the adsorbent and the degree of ionization of the adsorbate during the reaction process. The effect of pH on the adsorption of Cu (II) and Cd (II) from solution containing 0.2 g PSS-AC was studied by taking optimum concentrations of the metal ion (0.2 mg/L at 70 min for Cu (II) and 0.005 mg/L at 50 min for Cd (II)) shaking at 140 rpm by varying the pH of the system between 1 to 9. Desired value of pH was adjusted by drop wise addition of aqueous 5% NaOH (w/v) and/or 5% HCl (v/v). Fig. 4 below shows the effect of pH on adsorption percentage of Cu (II) and Cd (II) using PSS-AC. It can be seen from the figure that the percent adsorption of Cu (II) increases from 92.45% to 99.85% with increasing pH from 1 to 5. After that it reaches equilibrium and it had a fractional deviation from one another. It can also be seen from Fig. 4 that the percent adsorption for Cd (II) increases from 91.9% to 98.9% with increasing pH from 1 to 5. The maximum adsorption percentage obtained was 98.9% at pH 5.

3.2.3 Effect of Adsorbent Dose

The removal efficiency and specific uptake of metals depend on the type and quantity of the adsorbent. The dosage of adsorbent is a key parameter to control both availability and accessibility of adsorption sites. Raise in quantity of AC increases the deduction percentage of both Cu (II) and Cd (II). This was due to extra surface area existing on the adsorbent and thus makes the penetration of the ions easier to the adsorption sites [32]. The effect of adsorbent dosage on the removal of Cu (II) and Cd (II) has been presented in Fig. 5 below. It is clear from the figure that the percent removal increases with a rise in the carbon dosage. After a certain dose it was found that it reaches equilibrium and had a fractional deviation from one another. It also depicts that the percent adsorption was increasing from 97.405% to 98.995% for Cu (II) and from 97.42% to 98.96% for Cd (II) at 0.2 g of carbon dose; the percent adsorption was insignificant around 98.99% for Cu (II) ion and around 98.96% for the Cd (II) ion.

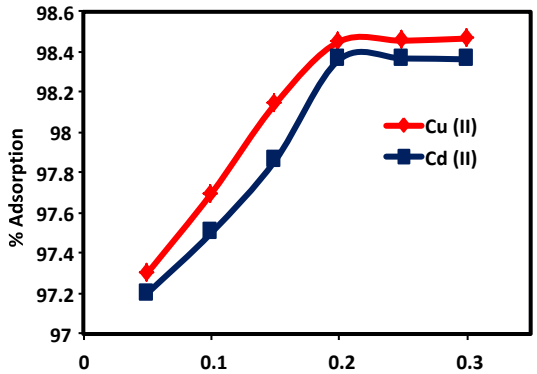

Fig. 5 Effect of adsorbent dose on the removal efficiency of Cu (II) and Cd (II) using PSS-AC

3.2.4 Effect of Temperature

In order to investigate the effect of temperature on the adsorption process, the batch adsorptions were done at different temperatures (from 25 °C – 45 °C) by mixing 0.2 g of activated carbon with 25 mL of 0.2 Cu (II) mg/L and 0.005 mg/L of Cd (II) solution at the optimal pH. From the results in Fig. 6, it is noted that the Cu (II) and Cd (II) adsorption has a steady increase with increasing solution temperature from 25 °C to 45 °C, indicating that the adsorption is an endothermic process. Percentage adsorption for both Cu (II) and Cd (II) ions was optimum at 30 °C and it had insignificant increase above this temperature.

This implies that increasing temperature creates a wider surface area for adsorption at the adsorbent. In addition, at high temperature due to bond rupture of functional groups on the adsorbent, be an increase in a number of active adsorption sites, which may also lead to enhanced adsorption with the rise in temperature [33].

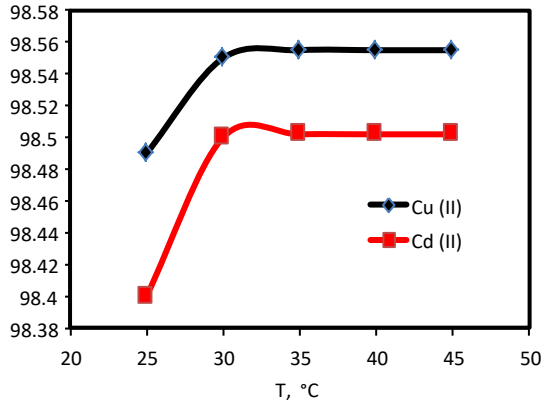

Fig. 6 Effect of temperature on removal efficiency of Cu (II) and Cd (II) ions using PSS-AC

3.3 Adsorption Isotherms

Adsorption isotherm is an important requirement for the design of an adsorption system that can provide information on the capacity of the adsorbent. The equilibrium study for the present work has been conducted based on the early and commonly used monolayer and

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multilayer adsorption isotherm models called Langmuir model and Freundlich model respectively.

3.3.1 Langmuir Isotherm Model

The Langmuir adsorption isotherm model is the best known of all other isotherm models that describe the adsorption process and it has been successfully applied to many adsorption processes. Weber and Chakravorti [34] expressed the Langmuir equation with its essential characteristics and the feasibility of the process in terms of a dimensionless constant separation factor or equilibrium parameter R_L obtained from Eq.(4); the Langmuir equation was modeled equation,

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b_L} \quad (4)$$

where C_e (mg/L) is the equilibrium concentration of Cu (II) and Cd (II) in solution, q_e(mg/g) is the amount each ion adsorbed at equilibrium from the solution on the adsorbent. Linear plots of C_e/q_e versus C_e for Langmuir model with a straight line of slope $1/q_m$ and intercept of $1/q_m b_L$ is obtained as shown in Fig. 7 where it is clearly seen that an excellent linear relationship exists for both metals indicating that the copper and cadmium adsorption on the PSS-AC follow the Langmuir adsorption isotherm. The values of q_m and b_L were calculated from the slopes and the intercepts of lines in Fig. 7, shown in Table 3. The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless factor, R_L,

$$R_L = \frac{1}{1+b_L C_o} \quad (5)$$

where R_L values indicate the type of adsorption either unfavorable (R_L>1), linear (R_L =1), favorable (0< R_L<1) or irreversible (R_L=0).

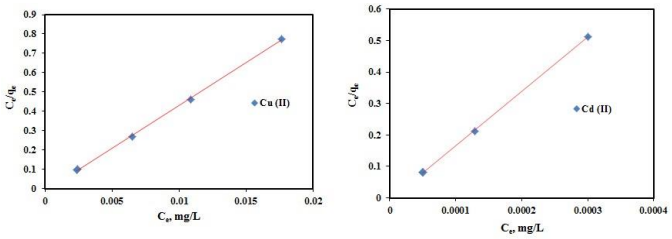

Fig. 7 Langmuir plot for adsorption of Cu (II) and Cd (II) using PSS-AC

3.3.2 Freundlich Isotherm Model

Freundlich isotherm gives the relationship between equilibrium liquid and solid phase capacity based on the multilayer adsorption properties consisting of a heterogeneous surface of the adsorbent. This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption [35]. Freundlich equation does not consider all sites on the adsorbent surface to be equal rather it assumes that, once the surface is covered, additional adsorbed species can still be accommodated [36]. The Freundlich equation is,

$$\log q_e = \log K_f + \frac{1}{n} log C_e \quad (6)$$

where K_f (mg/g) and n are Freundlich constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity of the adsorption.

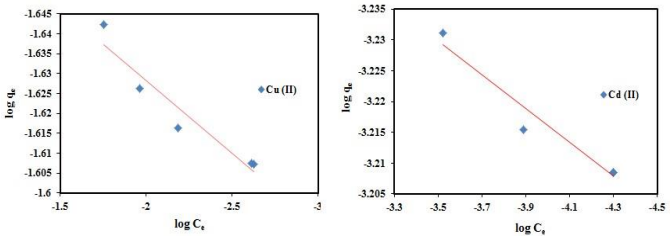

Fig. 8 Freundlich plot for Cu (II) (a) and Cd (II) (b) removal using PSS-AC

The Freundlich isotherm plot, log q_e versus log Ce, is shown in Fig. 8 below. K_f and 1/n values can be obtained from the intercept and slope of the straight line. The exponent (n) is an index of the diversity of free energies associated with the sorption of the solute by multiple components of a heterogeneous sorbent. When n < 1, the isotherm is concave and adsorbates are bound with weaker and weaker free energies, n > 1, the isotherm is convex and more sorbate presence in the sorbent enhance the free energies of further sorption and n=1, the isotherm is linear and system has a constant free energy at all adsorbate concentrations.

In the present study, the value of *n* at equilibrium was below unity, suggesting favorable adsorption. Furthermore, the values of the dimensionless factor, R_L, were between 0 and 1. This also suggested favorable adsorption of Cu (II) and Cd (II) ions using PSS-AC.

Table 3 Results of isotherm models for the removal of Cu (II) and Cd (II) ions using PSS-AC at 30 °C

Heavy metal ion	Langmuir isotherm q_m (mg/g)	b_L (dm^3/g)	R^2	Freundlich isotherm K_f (mg/g)	1/n (L/mg)	R^2	R_L
Cu (II)	43.48	76.56	0.9997	-0.0365	0.588	0.961	0.061
Cd (II)	172	1656	0.9999	- 0.027	0.300	0.976	0.11

3.4 Adsorption Kinetic Studies

The adsorption kinetics describing the contact time in the removal of Cu (II) and Cd (II) is one of the characteristics defining efficiency of the adsorption. The adsorption kinetics of adsorbent depends on the properties of the adsorbate, the experimental conditions, temperature, concentrations and pH values. Each combination of adsorbent and adsorbate has a unique metal ion-adsorbent interaction. To explain adsorption kinetics of Cu (II) and Cd (II) ions by PSS-AC at 30 °C both pseudo-first order and pseudo-second order kinetic models were adopted.

3.4.1 Pseudo-First Order

The values of q_e and K_1 for the pseudo-first order kinetic model was determined from the intercepts and the slopes of the plots of log (q_e - q_t) versus time, respectively from Figure 9. The linear form of the pseudo-first order equation was generally expressed as Eq.(7),

$$\log(q_e - q_t) = \log q_e - \frac{K_f}{2.303} t \quad (7)$$

where q_e and q_t are the values of amount adsorbed per unit mass (mg/g) at equilibrium and at any time t respectively, and K_f is the pseudo first order sorption rate constant (min^{-1}). The K_f value could be obtained by plotting log (q_e - q_t) versus t. In order to find a more reliable description of the kinetics, second order kinetic equation was applied as the linear [37].

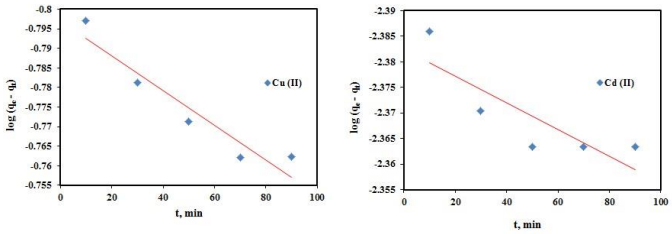

Fig. 9 Pseudo-first order sorption kinetics of Cu (II) and Cd (II) using PSS-AC

3.4.2 Pseudo-Second Order

The procedure for the pseudo-second order is more likely to predict the behavior over the whole range of adsorption process which was based on the assumption that the rate limiting step may be physisorption due to the presence of weak forces of attraction between adsorbent and adsorbate.

$$\frac{t}{q_t} = \frac{1}{k q_e^2} + \frac{t}{q_e} \quad (8)$$

where $\mathbf{k_s}$ is rate constant for the second order kinetics (g mg/min).

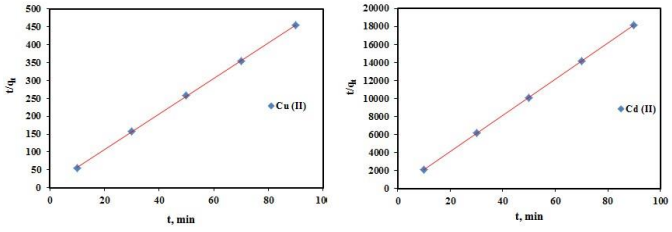

Fig. 10 Pseudo-second order sorption kinetics of Cu (II) and Cd (II) using PSS-AC

The pseudo-second-order plot of t/q_t versus t is a straight line as shown in Fig. 10. K_2 and q_e values determined from the slopes and intercepts of the plot respectively are presented in Table 4. The results indicate that the

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kinetic behavior of Cu (II) and Cd (II) adsorption on activated carbon from pumpkin seed shells can be satisfactorily explained with the pseudo-second order adsorption equation.

Table 4 Kinetics parameters for the adsorption of Cu (II) and Cd (II) using PSS-AC at 303 K

	Pseudo-first order				Pseudo second order		
Heavy metal ion	q_e exp. (mg/L)	$q_e$cal (mg/L)	K_1 ($\times 10^{-4}$ min^{-1})	R^2	$q_e$cal (mg/L)	K_2 (g/mg min)	R^2
Cu (II)	2.5	0.0227	4.438	0.952	2.45	4.985	0.9999
Cd (II)	6.19	0.054	2.61	0.841	5.58	200.46	0.9999

exp. (Experimental result), cal. (Calculated values)

3.5 Thermodynamic Study

The thermodynamic parameters that help us to understand the nature of the adsorption process of the heavy metals, such as standard Gibbs free energy change (ΔG°), enthalpy changes (ΔH°) and entropy change (ΔS°) were calculated to evaluate thermodynamic feasibility to confirm the nature of the adsorption process. The enthalpy value for adsorption process may be used to distinguish between chemical and physical adsorption. For chemical adsorption, values of enthalpy change range from 83 to 830 kJ/ mol, while for physical adsorption they range from 8 to 25 kJ/ mol [38].

$$\mathbf{\Delta G^{\circ} = -RT \ln K_c} \quad (9)$$

The values of ΔH° (kJ/mol) and ΔS° (kJ/mol/K) were calculated from the slope and intercept of the linear plot of ln K_c versus reciprocal of temperature 1/T Eq.(10).

$$\mathbf{\ln K_c = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}} \quad (10)$$

where R is the gas constant (8.314 J/ mol. K), T is the absolute temperature in Kelvin (K) and K_c (L/g) is the standard thermodynamic equilibrium constant defined as q_e/c_e. The magnitude of Gibbs free energy change, obtained is negative demonstrating that the adsorption is rapid and spontaneous. The negative value of ΔG° ensures the feasibility of the process. Generally, ΔG° values range from 0 to -20 KJ/mol for physical adsorption and -80 to -400 KJ/mol for chemical adsorptions [39]. Thus, in this study the ΔG° values are a negative number indicating that the adsorption is mainly physical. The values of ΔS° and ΔH° were obtained from the slope and intercept of a linear plot of lnK_c against 1/T, shown in Table 5.

The low values of ΔH° give clear evidence that the interaction between the metal ions and the PSS-AC was weak. On this basis, the adsorption concluded by Cu (II) and Cd (II) with PSS-AC is a physical adsorption process. The positive value of entropy, ΔS° represents an increase in the degree of freedom of the adsorbed species and some changes that occur in the internal structure of PSS-AC during the adsorption process [40].

Table 5 Thermodynamic parameters for the adsorption of Cu (II) and Cd (II) using PSS-AC at different temperatures

Heavy metal	T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol.K)
Cu (II)	298	-5.309	2.595	70.886
	303	-5.398		
	308	-5.487		
	313	-5.576		
	318	-5.665		
Cd (II)	298	-5.052	0.3608	16.956
	303	-5.136		
	308	-5.222		
	313	-5.306		
	318	-5.391		

3.6 Desorption Study

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent. This process has been carried out by reagents as an extractant like H_2SO_4, HNO_3, acetic acid and HCl. Desorption process performed by mixing an appropriate amount of solvent along with the spent adsorbents and shaken together for a fixed time and then filter to separate the adsorbent and adsorbate.

In this study HCl a comparatively inexpensive solvent was used to perform desorption process. Various concentration of HCl (0.5, 1, 2 and 3 mol/L) was mixed with the spent adsorbent loaded with copper and cadmium ions and agitated for half an hour. After that the solution was filtered to separate the adsorbent and adsorbate. The concentration of the filtrate was measured and desorption efficiency was calculated using the given formula. Data obtained are reported in Table 6 given below.

$$\textit{Desorption Efficiency}\ (\%) = \frac{\textit{released metal concentration}}{\textit{initially sorbed metal concentration}}\, x100 \quad (11)$$

Table 6 Desorption of Cu (II) and Cd (II) from loaded PSSAC

Metal Ions	Removal efficiency	HCl Concentration (mol/L)			
		0.5	1	2	3
Cu (II)	98.81	70	80	85	82
Cd (II)	98.99	65	75	80	78

The result of the desorption study suggests that the reuse pertaining to PSSAC increases with increasing concentration of HCl until 2 mol/L beyond this decrease is observed in desorption efficiency for the metal ions.

4. Conclusion

It is concluded from this study that adsorption is a valuable tool for controlling the level of aqueous Cu (II) and Cd (II) pollution. Characterization of H_3PO_4 activated pumpkin seed shells using FT-IR showed slight differences in the peaks due to the presence of functional groups before and after adsorption of Cu (II) and Cd (II) ions. The majority of the functional groups were aromatic carbon containing in both the cases. The SEM analysis clearly indicates significant changes to the surface morphology; and EDX analysis determines the elemental composition of the adsorbent before and after adsorption of the metals. The adsorption of Cu (II) and Cd (II) using PSS-AC is found to be contact time, initial metal ion concentration, pH and adsorbent dose dependent. The adsorption kinetics provides a better correlation of the sorption data by a pseudo-second order kinetic model than the pseudo-first order model for both metals; this suggests that the pseudo-second order model satisfactorily describe the adsorption process. The Langmuir adsorption isotherm model was better used to represent the experimental data. Adsorption was increased with increasing initial metal ions concentrations and adsorbent. The thermodynamic parameters ΔG°, ΔH° and ΔS° showed a chemically favoured, spontaneous and endothermic adsorption.

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