Enhanced sorption of aqueous cadmium (II) ions on phenylalanine modified activated carbon

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Abstract. Phenylalanine modified activated carbon sorbent (PAAC) was prepared and characterised using FTIR and XRD spectroscopic studies and scanning electron microscopy. The potential removal of Cd (II) ions from aqueous solutions using this sorbent was investigated through adsorptive experiments. The parameters evaluated in the batch studies included pH (2-9), PAAC dosage (0.1–1.2 g L^{-1}), contact time (1–240 min), initial Cd (II) ion concentration (5-60 mg L^{-1}) and temperature (10–50 ^{o}C). A dosage of 1.0 g L^{-1} of PAAC showed a near complete removal of 25 mg L^{-1} of the initial Cd (II) ion concentration from aqueous solution at pH 6 and a temperature of 25 ^{o}C. The equilibrium studies revealed that the experimental data fitted very well into the Langmuir isotherm model. Kinetic studies showed that the adsorption process followed pseudo-second-order and the thermodynamic parameters indicated that adsorption was spontaneous and endothermic in nature. Sorption results reveal that the PAAC is an efficient sorbent for the removal of Cd(II) ions from aqueous media.

Keywords: Activated carbon, sorption, cadmium, phenylalanine

1 Introduction

The accumulation of heavy metals in the environment poses undesirable effects to the ecosystems and the major sources of contamination include municipal and industrial wastewater, battery recycling, military facilities, landfill leachate and urban rainwater runoff [1–3] Metals such as cadmium damage the brain and internal organs like the liver [4], hence the need to remove them from the environment. Carbonaceous materials like graphene and its oxides, activated carbon (AC) and carbon nanotubes are effective adsorbents for the decontamination of metal ions as well as their complexes [5–7]. Oxidized multiwalled carbon nanotubes have been used as adsorbents in the removal of 5-(4-Dimethyl Amino Benzylidene) Rhodanine and bromothymol blue [8,9] due to their high sorption capacities.The adsorbents are associated with the large surface areas and the availability of surface functional groups [5,10]. AC has shown to be a very efficient adsorbent in the removal of heavy metal ions [11]. Modifying AC with compounds containing amine (like phenylalanine, PA, Fig. 1) groups improves their adsorption capacities [12]. These modifiers have excellent thermal, chemical and mechanical stability, making them less vulnerable to swelling and shrinking [13]. Apart from the stated advantages, PA modified AC provides amide and free carboxylic acid functionalities that enhance adsorption of metal cations [14].

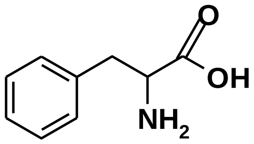


Fig. 1. Representative structure of phenylalanine (PA)

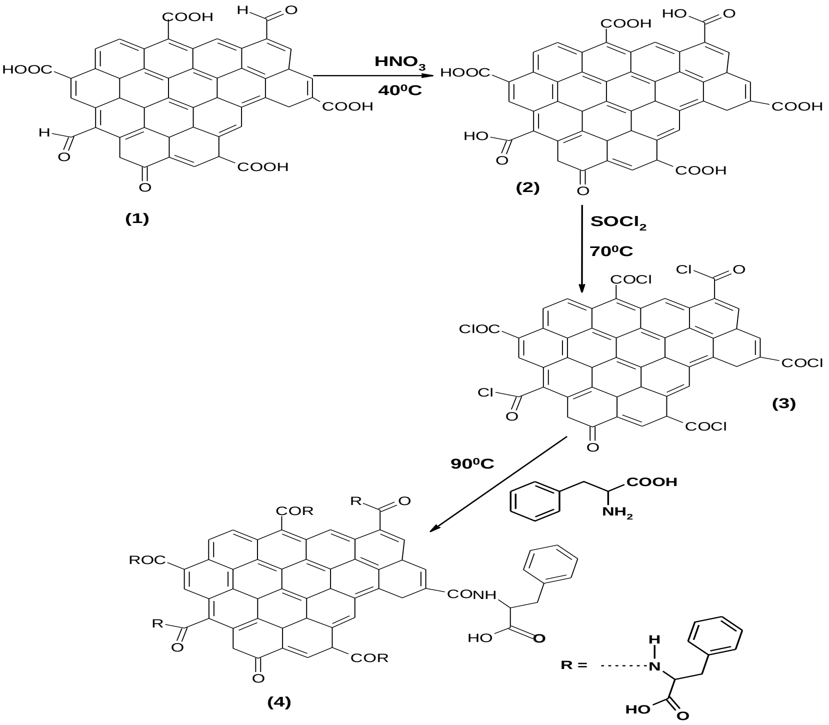
2. Materials and methods

2.1 Chemicals and reagents

Phenylalanine (0.05 M, Cosmo Chemicals), cadmium (II) nitrate (Cosmo Chemicals), thionyl chloride (Associated Chemical Enterprise), ethanol(Associated Chemical Enterprise), Nitric acid (Skylabs), potassium bromide (Skylabs), hydrochloric acid (Skylabs), sodium hydroxide (Saarchem). All the chemicals used were of analytical grade and were used as received. Aqueous solutions were prepared using double distilled water.

2.2 Preparation of Phenylalanine Modified Activated Carbon (PAAC) adsorbent

Maize tassel based activated was prepared as reported in our earlier work [15] and was designated AC (1). The AC was subjected to surface modification according to the procedures reported elsewhere with slight modifications [15, 16]. Scheme 1 summarises the synthesis of PAAC. A mass of 15 g of activated carbon **(1)** was oxidized with 100 mL of 5 M HNO_3 solution for 5 h at 40 °C to give compound **(2)** which was designated AC_a. The oxidized carbon was filtered, washed with deionised water to pH 7 and dried at 120 °C for 24 h. The surface carboxylic acid groups were then converted to acyl chloride functionalities **(3)** by mixing 12 g of the dried oxidized carbon with 40 mL of 5% thionyl chloride in toluene for 5 h at 70 °C [18] to give **(3)**. To the resultant product **(3)**, toluene (40 mL) and phenylalanine (100 mL, 0.05 M) were added and reacted for 24 h at 90 °C under a nitrogen atmosphere [17] giving compound **(4)** which was designated PAAC.



Scheme 1. Synthesis of PAAC

2.3 Characterisation of the samples

Moisture and ash content of AC were determined using standard procedures, ASTND3173-03 and ASTND3174-04, respectively. Thermo Scientific Nicolet 6700 Fourier Transform Infrared (FTIR) spectrometer was used to record the FTIR spectra of the samples. The final product was characterised using Bruker D8 Scanning Electron Microscope (SEM), and the Bruker Advance X-Ray Diffraction (XRD) spectrometer. Elemental analysis of AC and PAAC was done by elemental analyser (CHN, Perkin Elmer 2400). The surface functional groups of AC and AC_a were determined by Boehm titration [16].

2.4 Preparation of stock solution

1000 mg $L^{-1}$of cadmium (II) nitrate ($Cd(NO_3)_2.4H_2O$) solution was prepared using deionised water. The working standards were made through serial dilutions.

2.5 Sorption experiments

The experiments were conducted by placing 1.0 g of PAAC into a 500 mL polythene bottle containing 100 mL of 25 mg L^{-1} cadmium (II) nitrate solution. The pH of the solutions was adjusted to desired levels using 0.1 M HNO_3 and 0.1 M NaOH. The samples were allowed to equilibrate at room temperature on a temperature controlled shaker before filtration of the suspensions and analysis using Shimadzu AA-6800 Flame Atomic Absorption Spectrophotometer (FAAS). The adsorption capacity (q_t, mg g^{-1}) of Cd (II) ions at any given time on the PAAC sorbent was calculated using the mass balance relationship, Equation (1).

$$q_t = \frac{v(C_0 - C_e)}{m} \qquad (1)$$

where q_t is the Cd (II) ion concentration on PAAC (mg g^{-1}) at equilibrium, C_e is the Cd (II) ion concentration in solution (mg L^{-1}) at equilibrium, C_0 is the initial Cd (II) ion concentration in solution (mg L^{-1}), v is the initial volume of Cd (II) ion solution used (L), and m is the mass of PAAC used (g).

2.6 Desorption studies

An investigation on the regeneration of the spent PAAC was done by looking at the liberation of adsorbed Cd (II) ions after adsorption at optimum conditions of pH, contact time, initial concentration and temperature. Masses of 1.0 g of the loaded PAAC samples were desorbed by washing three times with distilled water to remove residual Cd (II) ions on the surface before subjecting them to 0.05 M – 3.0 M concentrations of HCl. The mixtures were shaken for 120 min and the filtrates were analysed to determine the liberated cadmium [15].

3. Results and Discussion

3.1 Characterization of AC, AC$_a$, PA and PAAC

The prepared activated carbon (AC) had the following physicochemical characteristics: pH 6.9, ash (3.2%), and moisture content (4.8%). Elemental analysis showed that AC contains 24.46% O giving evidence as supported by the FTIR spectrum that it has oxygen functional groups. Elemental analysis results showed a decrease in carbon content from 75.29 to 54.86% and an increase in oxygen content from 24.46 to 37.52% for AC and PAAC, respectively (Table 1). Furthermore, AC had oxygen content of 0% whereas PAAC had 6.38% N. This provides evidence for structural changes in the surface of activated carbon. Further evidence for structural changes is given by Boehm titration which detects oxygen functionalities. AC had no phenolic and carboxylic groups but a higher lactonic group amount relative to the oxidised activated carbon (AC$_a$) as shown in Table 2. FTIR was used to determine the available functional groups in PA, AC and PAAC as well as to confirm the success of the modification processes. SEM and XRD were used study the morphologies of both AC and PAAC.

Table 1. Elemental analyses of AC and PAAC

	Elemental analysis (wt%)			
Sample	**C**	**H**	**N**	**O**
AC	75.29	0.25	0	24.46
PAAC	54.86	1.24	6.38	37.52

Table 2. Determination of acidic functional groups

	Acidic group (mmol/g)		
Sample	**Phenolic**	**Carboxylic**	**Lactonic**
AC	0	0	0.8721
AC$_a$	0.7235	0.5424	0.7806
PAAC	0.8652	0.6599	0.7483

3.2 FTIR spectroscopic studies

FTIR spectroscopy identified the functional groups present [19,20] and was used to confirm the formation of PAAC. The comparative FTIR analysis for PA, AC and modified AC (Fig. 2 (a-c)), shows successful phenylalanine modification process. The bands from 2900 to 3000 cm^{-1} represent C-H stretching vibrations, while hydroxyl groups and amide linkages are found around 3500 and 1650 cm^{-1}, respectively, as observed elsewhere [21,22]. The new peak formed at 3415.92 cm^{-1} (Fig. 2c), confirms the presence of amide N-H stretching vibrations of PAAC and is in agreement with other studies [22].

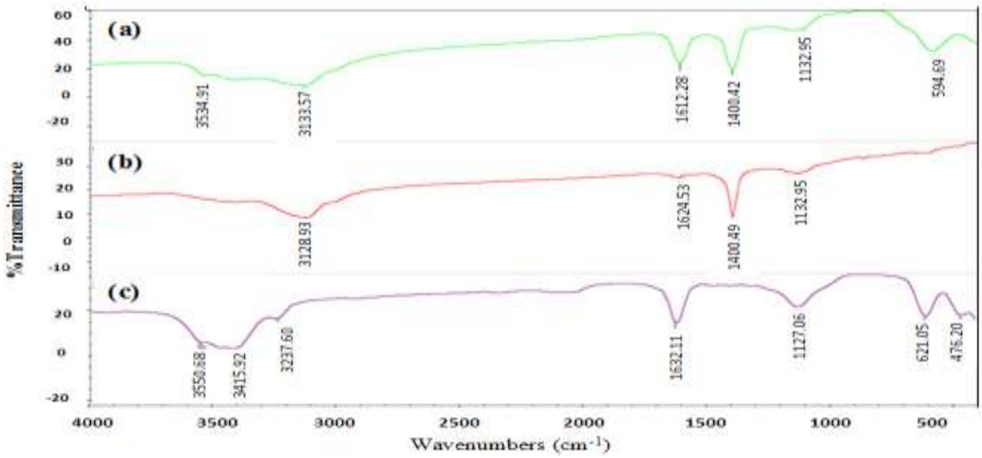


Fig. 2. FTIR spectra of (a) Phenylalanine, (b) Activated Carbon and (c) PAAC

The C=O band was observed at 1624.53 cm^{-1} in AC and shifted to a very sharp and pronounced peak at 1632.11 cm^{-1} in PAAC, confirming formation of a new surface structure. This band in PAAC has been observed before for amides [22]. The NH_2 of PA at 3534.91 cm^{-1}, Fig. 2a, became a broad band ranging from 3237.60 – 3550.68 cm^{-1} for PAAC (Fig. 2c), again confirming surface modification. The broad band can be attributed to the combination of OH stretches of carboxylic acid groups of PA and the NH stretches of the amide groups of PAAC. The peak at 1400 cm^{-1} indicates the aromatic C=C stretching vibration of PA and the modified activated carbon sorbent. According to literature, it results from the nature of substituents of bonded groups including extensive inter hydrogen bond formation between the amine and acidic groups in the modified carbon sorbent [23].

3.3 Scanning Electron Microscopy studies

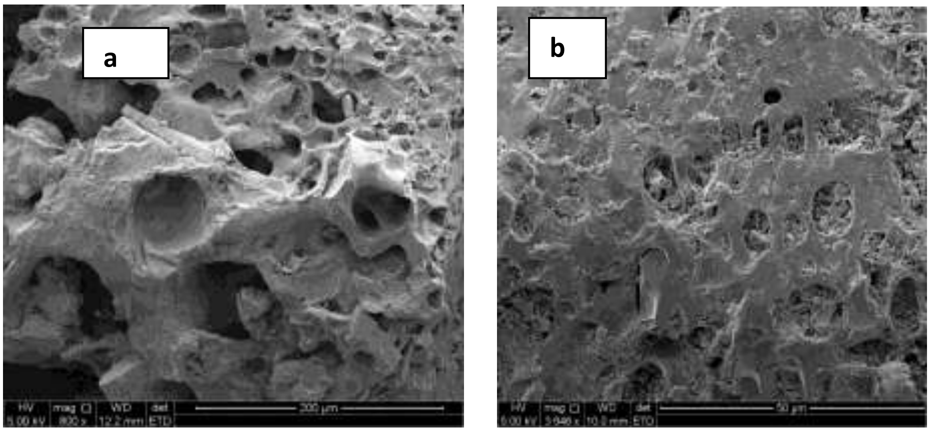


Fig. 3. SEM images for PAAC (a) before (b) after Cd^{2+} adsoption

The images for PAAC before (unloaded) and after (loaded) Cd^{2+} adsoption are shown in Fig.s 3a and 3b, respectively. The unloaded PAAC (Fig. 3a) shows an external surface with rough extensive pores and irregular cavities as observed in other studies [21]. These could have been formed during the acidification of AC. A similar structure and morphology has been revealed in other studies [17,21]. The observed surface texture and porosity of the sorbent, Fig. 4a, confirms the availability of a large surface area [24] that is readily available for the adsorption of Cd (II) metal cations. The SEM image for loaded PAAC (Fig. 3b) shows the presence of a glossy surface film layer, which is most likely a result of adsorption of Cd (II) ions.

3.4 XRD characterisation

XRD spectroscopy was used to determine surface characteristics of the samples. Fig.s 4a and 4b show the XRD spectra for the dry unloaded and loaded PAAC, respectively. These spectra gave the major peaks for the components present in the PAAC sorbent as observed in other studies [17,22].

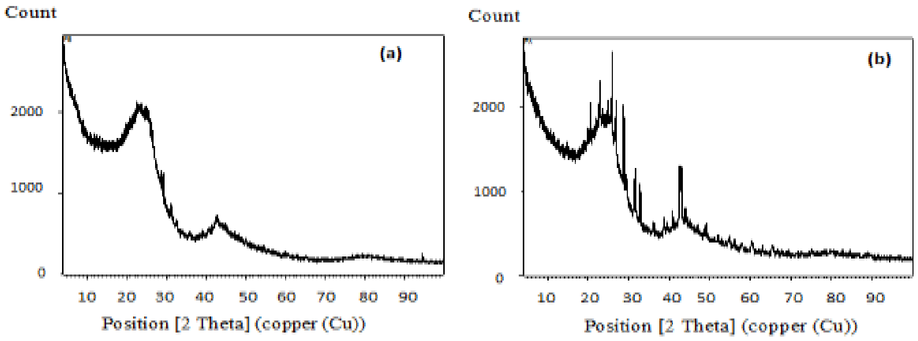


Fig. 4. Powder XRD spectra for PAAC (a) before (b) after Cd^{2+} adsoption

The PAAC sorbent was found to be highly amorphous due to broad peaks at $2\theta = 23^0$ and 43^0 and these are due to carbon [21]. The sharp peaks imbedded on the broad peaks around $2\theta = 25^o$, 28^o, 31^o and 43^o shows a change in the crystalline nature of the loaded PAAC (Fig. 4b). Emergence of sharp peaks (Fig. 4b) and peak shifts (from 23^0 (Fig. 4a) to 25^0 (Fig. 4b)), confirms the formation of a crystalline surface as already observed from the glossy surfaces from SEM studies (Fig. 3b). Sharp peaks could confirm the chemical interactions between PAAC and Cd (II) metal ions [21].

3.5 Batch studies

3.5.1 Effect of pH.

Fig. 5 shows the effect of pH on Cd (II) ions uptake by PAAC sorbent. The results indicate a general increase in the removal of Cd (II) ions by PAAC with increase in pH. These findings are consistent with those observed in other studies [19]. The increasing efficiency of adsorption on PAAC with increase in pH (3-6) is due to a decrease in competition between the protons and the Cd (II) ions for the available surface sites [25,26]. As pH increased, the sorbent surface became less occupied with protons and thus more negatively charged making it more possible for the uptake of Cd (II) ions [27]. Constant adsorptivity was observed from pH 7-10 and this could be due to sorption of Cd (II) ions and the formation of hydroxide precipitates [28,29]. Thus at pH greater than 6, removal of Cd (II) ions does not solely depend on its adsorption on PAAC but also on the precipitation of its hydroxides [28]. Cd(II) ions and thus all further studies were carried out at pH 6.

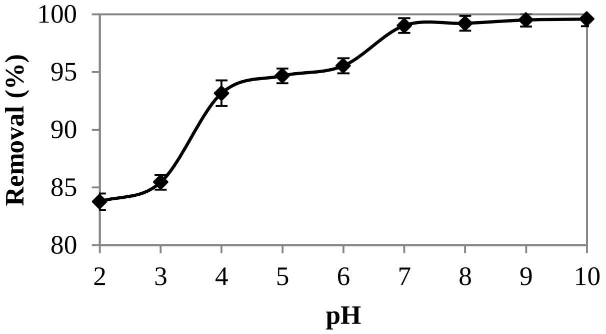


Fig. 5. Effect of pH on Cd (II) ions uptake by PAAC

3.5.2 Effect of contact time. The effect of contact time on sorption proficiency of PAAC is shown in Fig. 6. The results indicate that adsorption of Cd (II) ions increased with increase in contact time as already observed [30]. Equilibrium was reached around 120 min after which sorption became constant. There is rapid initial sorption rate in the interval 1-5 min (Fig. 6) due to the steep charge gradient between the unoccupied negatively charged surface and the positively charged Cd^{2+} ions. The high affinity binding sites on the surface were first occupied leading to rapid adsorption as observed elsewhere [31]. Beyond 120 min, no more cations could be adsorbed and similar findings were reported for the adsorption of heavy metals by microbial and plant derived biomass [30,32].

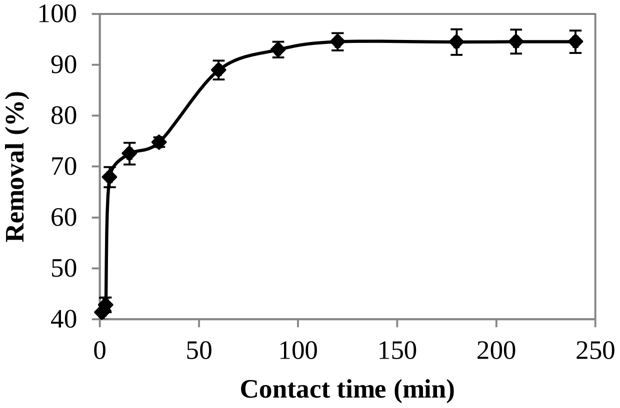


Fig. 6. Effect of contact time on Cd (II) ions uptake by PAAC.

3.5.3 Effect of PAAC dosage.

The investigation of the effect of PAAC dosage aided to determine the quantity of sorbent required per given concentration of metal to be determined as previously observed [15,33,34]. Fig.7 shows the effect of PAAC dosage on the Cd (II) ions removal percentage. The percentage removal of Cd (II) ions increased from 91.5 to 98.8% with increasing dosage from 0.1 to 1.0 g/0.1 L, respectively. Beyond the 1.0 g dosage, the percentage removal became constant indicating point of equilibrium [35]. The general increase in Cd (II) ion removal with dosage can be explained in terms of the increasing availability of active binding sites [15]. At equilibrium, the available receptor sites on the sorbent are by far greater than the concentration of Cd (II) ions that are being adsorbed and therefore the adsorption capacity becomes constant. These results are in agreement with reports from related work [15].

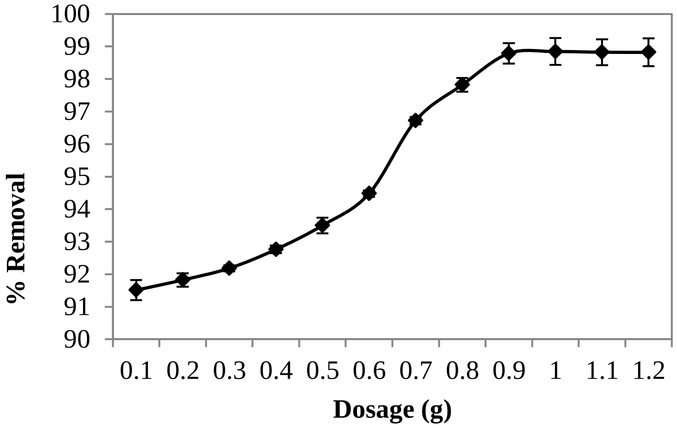


Fig. 7. Effect of PAAC dosage on Cd (II) ions uptake by PAAC

3.5.4 Effect of initial metal concentration

The uptake of Cd(II) ions by PAAC was found to be dependent on the initial Cd(II) ion concentration. Adsorption was observed to decrease with increase in Cd(II) ion concentration due to the filling up of the binding sites on the external and pore surfaces of the sorbent. The saturation point of adsorption sites was 92.6% at an initial concentration of 25 ppm. Similar trends have been observed elsewhere [36].

3.5.5 Effect of temperature

An investigation on the effect of temperature on adsorption was carried out to determine the nature of binding on the PAAC surface. A steep increase in percentage removal of Cd (II) ions by PAAC was observed from 10 to 25 ^{o}C and this was due to the increase in particle kinetic energy that encouraged diffusion of solutes from the solution to the binding sites. There is also a possibility that part of this energy was used to activate the binding sites [37]. The optimum adsorption temperature was found to be 25 ^{o}C.

3.6 Thermodynamic studies

Thermodynamic studies enabled the calculation and inference of parameters that define temperature effect on adsorption [37]. Equation (2) shows the relationship for the partition coefficient (equilibrium constant), $K_{o.}$

$$K_o = \frac{C_{ad}}{C_e} \qquad (2)$$

where C_{ad} (mg L^{-1}), is the concentration of the analyte on the solid phase and C_e (mg L^{-1}) is the concentration of the analyte in the liquid phase at equilibrium, respectively. The Gibbs free energy is related to the equilibrium constant by Equation (3).

$$\Delta G^o = -RTlnK_o \qquad (3)$$

where R is the universal gas constant and T is the temperature.

$$InK_0 = \; - \; \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \qquad (4)$$

The Van't Hoff relationship, Equation (4), shows the relationship between the equilibrium constant (K_0), the enthalpy change (ΔH^0) and entropy change (ΔS^0). Using Equation (4) a plot of InK_o versus $1/T$ gave a linear relationship (Figure not shown) with an R^2 value of 0.9982. The values of ΔG° (kJ mol^{-1}), ΔH^o (kJ mol^{-1}) and ΔS^o(kJ mol^{-1} K^{-1}) calculated from the slope ($-\frac{\Delta H^0}{R}$) and intercept $\left(\frac{\Delta S^0}{R}\right)$, are given in Table 3.

Table 3 Thermodynamic parameters for Cd (II) adsorption on PMAC

T(K)	ΔG°(KJmol^{-1})	ΔH°(KJ mol^{-1}	ΔS°(KJ mol^{-1})
283	-0.679	+73.8	0.2633
288	-2.089		
293	-3.310		

The ΔH^ovalue of +73.8 kJ mol^{-1} is typical of chemisorption process [37]and is endothermic in nature. The Gibbs energy values (ΔG^o kJ mol^{-1}, Table 1) became more negative with increase in temperature indicating that the process is feasible and spontaneous[37]. A small positive ΔS^o value (Table 3) was obtained revealing a decrease in randomness at the solid solution interface during adsorption of Cd (II) ions onto PAAC sorbent as observed elsewhere [38].

3.7 Equilibrium studies

Equilibrium sorption studies of Cd (II) ions onto PAAC were modeled using two adsorption isotherms: Freundlich and Langmuir

3.7.1 Langmuir isotherm.

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites [39] as represented by Equation (5), with no further sorption taking place at the site once it is filled.

$$\frac{1}{q_e} = \frac{1}{bq_{max}} + \frac{1}{q_{max}C_e} \qquad (5)$$

where q_e is the quantity of adsorbed cadmium per unit weight the sorbent at equilibrium (mg g^{-1}), C_e is the concentration of the Cd (II) ions in solution (mg L^{-1}) at equilibrium, b is the Langmuir constant correlating to the affinity of binding sites (L/mg) and q_{max} is the adsorption capacity (mg g^{-1}) [37].

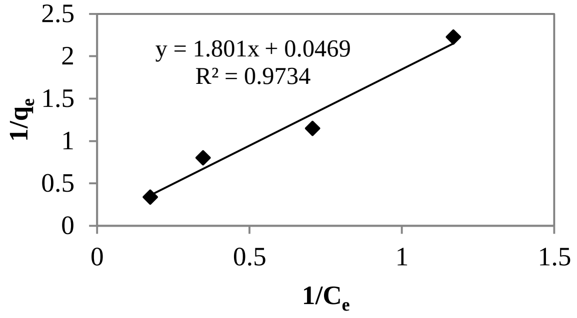


Fig. 8. Langmuir adsorption isotherms for Cd (II) ions onto PAAC

The plot of $1/q_e$ versus $1/C_e$ (Fig. 8) produced a linear relationship. The different isotherm parameters are summarised in Table 4. A fairly high correlation coefficient value of 0.973 for the Langmuir isotherm is in agreement with monolayer adsorption [40,41]. The Cd (II) metal ions would bind onto specific sites on the surface of PAAC and the obtained results are consistent with what has been observed in other studies [15]. The q_{max} value was found to be 21.739 mg g^{-1} and this shows that PAAC is highly efficient sorbent (Table 4). The separation factor (R_L) values were found to be in the range 0.39 - 0.87 for the Cd (II) ion concentration range of 5-60 mg L^{-1}, which is in the range of $0 < R_L < 1$. This indicates favourable adsorption of Cd (II) ions onto PAAC as observed in other studies [40].

Table. 4 Equilibrium parameters for Cd (ll) adsorption on PAAC sorbent

Adsorption isotherm	**Parameter**	**Value**
	q_{max} (mg g^{-1})	21.739
Langmuir	b (mg L^{-1})	0.026
	R^2	0.973
Freundlich	K_f (mg g^{-1})	1.916
	n	0.962
	R^2	0.972

Table 5 compares the uptake of Cd(II) ions on PAAC with sorbents used in other studies. It can be shown that PAAC is very efficient relative to Arundo donnax root carbon and cellulose [13] but lower than modified rice straw [42] which has a cumulative contact time of 10 h. This reveals the effectiveness of PAAC in adsorption processes relative to other sorbents.

Table 5. Comparison of PAAC adsorption of Cd (II) with other sorbents

Adsorbent	q_{max} (mg g^{-1})	Reference
Bamboo charcoal	12.08	[43]
Hazelnut shell	5.42	[44]
Almond shell	3.18	[44]
Rice husk	8.58	[45]
Oak wood char	0.37	[46]
Pine bark char	0.34	[46]
Oak bark char	5.4	[46]
Carbon F-400	8	[46]
Mungbean husk	35.41	[47]
AC	11.20	This study
PAAC	21.7	This study

3.7.2 The Freundlich Isotherm.

Values of K_f and $1/n$ were calculated from Equation (6) which represents the linearized Freundlich Isotherm.

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

where K_f (mg g^{-1}) is the Freundlich constant (related to the bonding energy), $1/n$ (L mg^{-1}) is the heterogeneity factor and n (L g^{-1}) is a linearity deviation measure of the adsorption. The isotherm is an empirical model applicable to both chemisorption and physisorption.

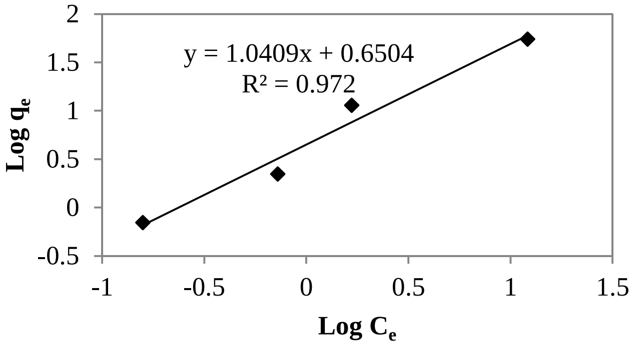


Fig. 9. Freundlich adsorption isotherm of Cd (II) ions onto PAAC

The plot of $log q_e$ versus $log C_e$ gave a linear relationship (Fig. 9). The calculated constants K_f (mg g^{-1}) and $1/n$ are shown in Table 2. A value of $1/n$ greater than 1 indicates an unfavourable adsorption process. The Freundlich constant n which illustrates the degree of non-linearity between the metal concentration and adsorptivity was also found to lie within the range of $n < 1$ (Table 2), indicating that adsorption is a chemical process [37,40,41]. The correlation coefficient of Freundlich isotherm was found to be slightly lower that of Langmuir isotherm which shows that the Langmuir isotherm better describes the adsorption process than the Freundlich. A K_f value of 1.9163 mg g^{-1} was obtained representing a relatively low adsorption capacity and affinity for Cd (II) ions.

3.8 Adsorption kinetics

One mole of the solute is assumed to adsorb onto one and specific sorption site on the sorbent surface. The pseudo first order linear model is shown by Equation (7).

$$log(q_e - q_t) = \log q_e - t\left(\frac{k_1}{2.303}\right) \qquad (7)$$

where q_e and q_t (mg g^{-1}) are the adsorption capacities at equilibrium and time t (h), respectively. The plots of $log(q_e - q_t)$ versus t were used to determine k_1 and q_e and results are shown in Table 4. The observed low correlation coefficient value of 0.967 showed that sorption onto the PAAC sorbent does not follow pseudo first order as observed in other studies [41].

The pseudo second order model can be linearly expressed as in Equation (8):

$$\frac{t}{q_t} = 1 + \frac{1}{k_2 q_e^2}\, t\left(\frac{1}{q_e}\right) \qquad (8)$$

where t is the contact time (min), q_e (mg/g) and q_t (mg/g) are the amount of the solute adsorbed at equilibrium and at any time, *t*. The plot of *t/q_t* versus *t* gave a linear relationship (Fig. 10). Results are summarized in Table 4. A higher regression value of 0.9957 reflected that adsorption process followed pseudo second order kinetics as reported in other studies [41].

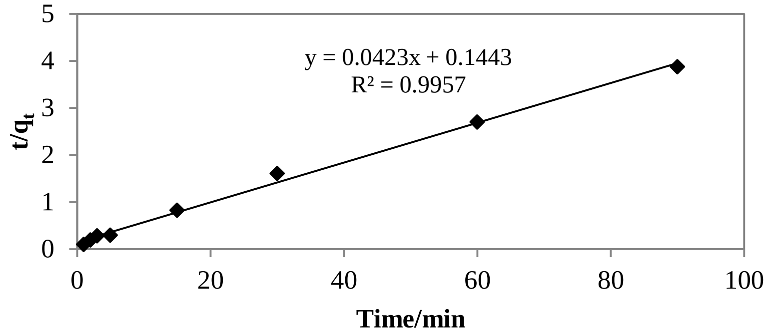


Fig. 10. Ho pseudo-second order kinetics plot

Table 4 Adsorption kinetic model parameters for Cd(II) ions on PAAC

T(298 K)	Pseudo First Order			Pseudo First Order		
	k_1	q_e	R^2	k_2	q_e	R^2
Cd(II)	0.03685	12.246	0.967	0.01225	23.81	0.996

The credibility of the findings was validated using a chi square (χ^2) test [33] that gave a value of 1.036 for the pseudo second order kinetics versus 2.197 for the pseudo first order kinetics. A lower χ^2 value indicates a favourable process, in this case, second order kinetics.

3.9 Desorption

The regeneration of PAAC after use was examined using HCl and it was observed that desorption increased with increase in HCl concentration upto a concentration of 0.2 M. Normally such high acid concentrations are found in natural aquatic system and as such PAAC is a very good sorbent for the removal of Cd (II) ions since it does not readily release the attached ions.

4. Conclusion

The modification of activated carbon with phenylalanine to give PAAC was successful and the modified sorbent was found effective in the removal of Cd (II) ions from aqueous solutions. The potential PAAC for the removal of Cd(II) ions from aqueous solutions depends on sorption processes such as pH, initial metal ion concentrations, sorbent dose, contact time, and temperature. The Langmuir isotherm provided the best correlation for the sorption of Cd(II) ions onto PAAC. The maximum adsorption capacity (q_{max}) was found to be 21.7 and the separation factor R_L was in the range (0-1) for favourable adsorption process. The Temkin isotherm also confirmed chemisorption process and adsorption occurred readily at room temperature. The pseudo second order perfectly described the kinetics of the adsorption. The thermodynamics parameters $\Delta G^o, \Delta H^o$ and ΔS^o revealed that the adsorption process was feasible, endothermic and spontaneous, respectively.

Acknowledgements

In loving memory of Dr Tawanda Mugadza. You will be greatly missed.

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