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Title: Sorption of cadmium (II) ion from aqueous solution onto sweet potato (*Ipomoea batatas* L.) peel adsorbent: characterisation, kinetic and isotherm studies.

Article Type: Research Paper

Keywords: sweet potato adsorbent, heavy metal, kinetics, isotherm, sorption, cadmium, kinetic modelling, equilibrium modelling, agricultural residue

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Abstract: Sweet potato peels was used for the removal of Cd (II) from aqueous solutions. The residue was characterised using SEM, EDX, XRF, N₂ BET, TGA and ATR-FTIR. Sorption of Cd (II) was carried out by varying pH, contact time and initial ion concentration at 25 °C and the results showed a strong dependence of the ion removal on the adsorbate pH with optimum observed at pH 7. Kinetics of Cd (II) sorption indicates optimum time of 180 minutes and the removal of Cd (II) occurred via a fast initial uptake. This was modelled using the pseudo first, pseudo-second and intraparticle diffusion models. The pseudo-first order gave a better description of the uptake kinetics than the pseudo-second order model with an r² value of 0.99. The intraparticle-diffusion model showed that sorption had multi-linear steps indicating that the intraparticle-diffusion is not the only rate controlling step in Cd (II) sorption. FTIR analysis of the PTPS before and after adsorption of Cd (II) indicates that some functional groups such as hydroxyl, carbonyl and carboxylate groups may be involved in metal ion sorption. Isotherm modelling of Cd (II) sorption was carried out using the Langmuir and Freundlich isotherms using a non-linear optimisation. The Langmuir isotherm gave a better fit for Cd (II) sorption and maximum loading capacity (q_{max}) was 18mgg⁻¹ with an isotherm constant of 5.21×10⁻³ Lmg⁻¹ and r² value of 0.99 at 25 °C. Hence, the PTPS residue was found to be a promising adsorbent for Cd (II) removal from aqueous streams.

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18th August, 2016

The Editor
Journal of Environmental Chemical Engineering

Re-Submission of Manuscript

Dear Sir/Madam,

We hereby re-submit the manuscript titled: *sorption of cadmium (II) ion from aqueous solution onto sweet potato (Ipomoea batatas L.) peel adsorbent: characterisation, kinetic and isotherm studies* to your journal for publication. The authors are grateful to the Editor for giving us an opportunity to re-submit the manuscript after revision. The points mentioned by the editor and the reviewers have been taken care of while preparing the revised version. In addition new references have been only added to substantiate points in the responses to the comments and for overall improvement of the technical quality of the manuscript. The changes in the revised manuscript are highlighted for your information.

The authors want to draw your attention to the first and second comments of reviewer #1 and we want to indicate our displeasure at the attitude of recommending reference in the comment for inclusion the manuscript that are not relevant to the subject of discussion. This has made us presume that the reviewer in question want to carry out reviews for the purpose of increasing his citation and H-index and this should not be encouraged by this Journal. Thus, we will request the editor not to send any further manuscripts that we submit in future to this Journal to this reviewer.

I hope the manuscript will be considered for publication.

Yours faithfully

Edidiong Asuquo
Corresponding author

Response to Reviewers comments

Reviewer #1: Thanks for the revisions thus far. The paper has improved considerably. However, there are still some items that must be accounted for, and revisions are needed.

Response: The authors are grateful to the reviewers for their corrections that have been used to improve the quality of the manuscript. The comments below have also been used to update the manuscript and we are grateful to the Editor and reviewers for their meaningful contributions.

Comment

1. The resolution of the figures should be improved; for example figure 7.

Response: The resolutions in the figures have been improved.

2. Peaks of Fig. 4 , 5 should be properly indexed.

Response: Both Figs. 4 & 5 have been indexed based on their composition as obtained from the EDAX genesis software used to obtain the EDAX spectra.

3. Peaks and bands of Fig. 7, 8, should be labelled.

Response: The peaks and bands discussed in the FTIR of the adsorbent (Section 3.1.6) have been labelled on both figures.

4. Page 15; "The result shows that the surface area of the PTPS adsorbent was 1.91m²g⁻¹. This indicates that the adsorbent did not have any significant surface area". This discussion requires to be completed, if the materials have no sig. surface area, then, what is make it good in your applications; pores, structure, etc. Please add the discussion to complete the idea

Response: The discussion has been improved to convey the information obtained from the results and the trend in properties observed from previous studies as stated below:

The result shows that the surface area of the PTPS adsorbent was $1.91\text{m}^2\text{g}^{-1}$. This indicates that the PTPS adsorbent did have a low surface area and this is similar to what has been reported in previous studies for some agricultural residues. These lignocellulosic residues are known to have low surface areas due to the nature of the cellulose, hemicellulose and lignin content in them. These results in these residues having wide pore size distributions due to the high percentage of mesopores/macropores within their network compared to micropores as can be observed in the pore size distribution in Fig.1. Furthermore, these wide pore size distributions of mesopores/macropores in the lignocellulosic materials make them suitable for liquid phase sorption as it facilitates diffusion of the adsorbate into the adsorbent structure (Ribeiro *et al.*, 2015; Menendez-Diaz and Martin-Gullon, 2006). However, it should be noted that the sorption properties of these residues are not only dependent on the possession of large surface areas as since porosity alone is not the only criteria required for good adsorbents. In addition to porosity, the nature and types of functional groups on these materials which serve as active sites for sorption contributes significantly to their adsorption potential for target pollutants (organic or inorganic). Thus, lignocellulosic residues have been reported to possess a number of different functional groups on their surface such as phenolic, carboxylic, hydroxyl, amines and ether groups which act as sources of physical and chemical interactions that facilitates adsorption via a number of mechanisms that include; hydrogen bonding, electrostatic interactions and surface complexation (Tan *et al.*, 2015; Nguyen *et al.*, 2013; Barkar *et al.*, 2013; Bailey *et al.*, 1999). Martin-Lara *et al.*, (2013) in their study on the development and characterisation of biosorbents to remove heavy metals from aqueous solutions by chemical treatment of Olive stone observed that the Olive stone residue had a BET surface area of $0.163\text{m}^2\text{g}^{-1}$ and a Pb^{2+} loading capacity of 6.32mgg^{-1} , thereby indicating that surface area alone is not the only indicator of a good adsorbent.

5. Being in line with what has been reported in previous studies is not enough; you please add scientific discussion of your finding as well.

Response: The discussion has been updated: See-

The small pore volume of the PTPS residue may be due to the nature of arrangement of cellulose, hemicellulose and lignin structures within the lignocellulosic framework of the material which may lead to the development of few number pores or blocked pores if they exist (Bota *et al.*, 1996).

6. Same for other characterization sections / results

Response: The characterisation was discussed based on the results obtained and the use of previous studies in the discussion is to place the material in the context of similar research which confirms the trend observed.

7. Why is it important to have the 3.1.3 Chemical composition of adsorbent; for the application in adsorption?

Response: The adsorbent chemical composition is important as it gives information on the chemical species within the material which is useful in the discussion of the material behaviour during sorption- See- Martin-Lara *et al.*, (2013) Development and characterisation of biosorbents to remove heavy metals from aqueous solutions by chemical treatment of Olive stone. *Industrial & Engineering Chemistry Research*, 52: 10809-10819.

8. As shown in Fig 7,8, are these functional groups indicating the chemisorption or physisorption

Response: The functional groups both indicate that the PTPS adsorbent may have possibly interacted with the Cd(II) ions via chemical and physical sorption. This is based on presence of the functional groups- C=O, C-O, NH₂ and O-H groups and their variations after adsorption which may be used to infer hydrogen bonding and

electrostatic interactions as well as complexation reactions as discussed in section 3.2.5- “mechanism of Cd(II) ion sorption” in the manuscript.

9. Why there a decrease in acidity (Table 3).

Response: The explanation is presented below;

The sorption of Cd(II) by the PTPS adsorbent may occur via a process that starts by the deprotonation of groups such as -COOH, -NH₂ leading to release of H⁺ into the adsorbate system. The Cd(II) ions which are positively charged are thereafter attracted to the active adsorption sites- which are negatively charged (COO⁻, NH₂ groups) and becomes coordinated with the deprotonated functional groups via coordinating bonding to the form an adsorbent metal complex. This scenario has been illustrated by Vaghetti *et al.*, (2009). Pecan nutshell as biosorbent to remove Cu (II), Mn (II), and Pb (II) from aqueous solutions, *Journal of Hazardous Materials*, 162: 270-280. This mechanism of proton release during the surface complexation step may account for the decrease in the pH of the adsorbate after sorption between the pH 6-8 where there was substantial Cd(II) sorption which reduces as the pH further increases up till pH 10.

10. Table 6 is to be updated; Journal of Molecular Liquids (2013) 188, 136-142

Response: Table 6 has been updated with q_{max} parameter values from previous studies based on cadmium sorption on lignocellulosic materials to provide a similar basis for direct comparison.

11. Page 6, introduction, "These approaches have 12 been reported to either be too expensive for the treatment and disposal...." Please add Environmental Science and Pollution Research (2013) 20 (5), 2828-2843

Response: The references cited in that paragraph are sufficient for the information it conveys.

12. Page 6 after "that can be used as alternatives to activated carbon that are less expensive and readily" pls add Advances in colloid and interface science (2014) 211, 93-101.

Response: The authors wish to observe that the references cited in the aforementioned paragraph are sufficient for the discussion. In addition, the referred reference by the reviewer (Advances in colloid and interface science (2014) 211, 93-101) is a review relating to the "Processing methods, characteristics and adsorption behaviour of tire derived carbons" and is not relevant to the context of the study reported in this manuscript which relates to lignocellulosic derived adsorbents.

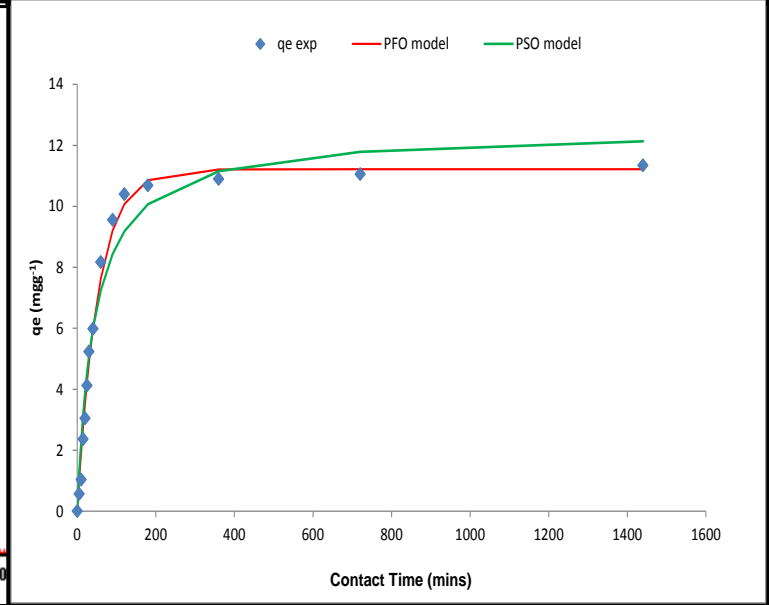
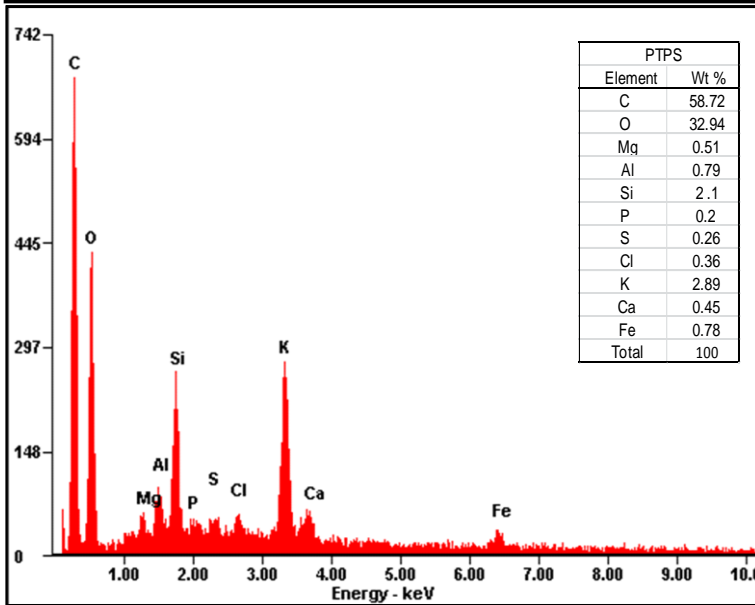
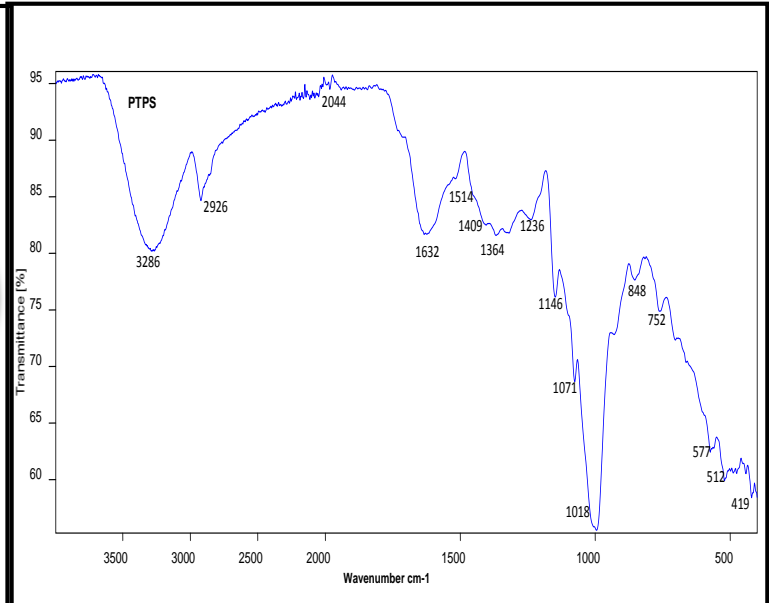
13. The MS requires refine for errors, typos, like missing full-stop, using of correct verbs, etc

Response: The manuscript has been updated to correct errors.

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Reviewer #4: The revised manuscript deems to be convincing in the present work. I recommend the manuscript to be accepted.

Response: The authors are grateful to the reviewer for the contributions that were used to improve the quality of the manuscript.



Highlights

- Cheap and available resource for heavy metal pollution remediation
- Characterisation of Cd(II) ion removal using waste as adsorbent
- Dependence of metal ion sorption on adsorbate pH
- Intraparticle-diffusion modelling indicated multi linear rate controlling diffusion steps
- Isotherm modelling using non-linear optimisation technique was used to obtain the maximum loading of the metal ion.

**Sorption of cadmium (II) ion from aqueous solution onto sweet potato (*Ipomoea batatas*
L.) peel adsorbent: characterisation, kinetic and isotherm studies.**

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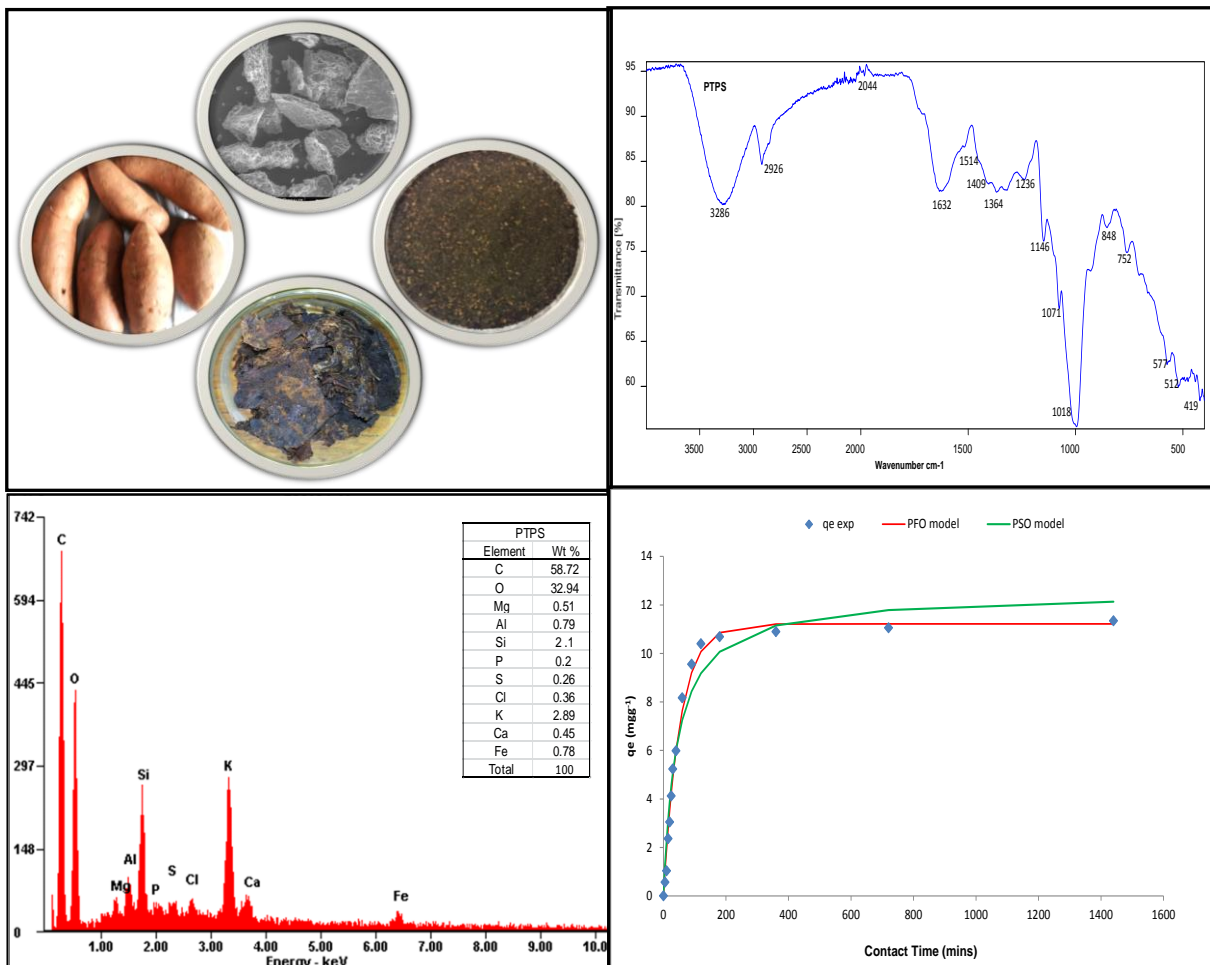
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Highlights

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Graphical Abstract



Abstract

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2 was characterised using SEM, EDX, XRF, N₂ BET, TGA and ATR-FTIR. Sorption of Cd (II)
3 was carried out by varying pH, contact time and initial ion concentration at 25 °C and the
4 results showed a strong dependence of the ion removal on the adsorbate pH with optimum
5 observed at pH 7. Kinetics of Cd (II) sorption indicates optimum time of 180 minutes and the
6 removal of Cd (II) occurred via a fast initial uptake. This was modelled using the pseudo first,
7 pseudo-second and intraparticle diffusion models. The pseudo-first order gave a better
8 description of the uptake kinetics than the pseudo-second order model with an r² value of
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10 that the intraparticle-diffusion is not the only rate controlling step in Cd (II) sorption. FTIR
11 analysis of the PTPS before and after adsorption of Cd (II) indicates that some functional
12 groups such as hydroxyl, carbonyl and carboxylate groups may be involved in metal ion
13 sorption. Isotherm modelling of Cd (II) sorption was carried out using the Langmuir and
14 Freundlich isotherms using a non-linear optimisation. The Langmuir isotherm gave a better fit
15 for Cd (II) sorption and maximum loading capacity (q_{max}) was 18mgg⁻¹ with an isotherm
16 constant of 5.21×10⁻³ Lmg⁻¹ and r² value of 0.99 at 25 °C. Hence, the PTPS residue was found
17 to be a promising adsorbent for Cd (II) removal from aqueous streams.
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39 **Keywords:** sweet potato adsorbent, heavy metal ion, kinetics, isotherm, sorption, cadmium
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Nomenclature

1	C_i	Initial metal ion concentration (mg l^{-1})
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3	C_t	Metal ion concentration at time t (mg l^{-1})
4		
5	SEM	Scanning electron microscopy
6		
7	q_{max}	Langmuir isotherm maximum adsorption capacity (mg g^{-1})
8		
9	q_t	Metal ion loading at time t (mg g^{-1})
10		
11	R_L	Langmuir separation factor
12	r^2	Co-efficient of determination
13		
14	t	Contact time
15		
16	m	Mass of adsorbent
17		
18	V	Volume of adsorbate
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20	PTPS	Sweet potato peel residue
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22	K_2	Pseudo-second order rate constant
23		
24	K_{id}	Intraparticle diffusion rate constant
25		
26	Cd	Cadmium
27		
28	H	Pseudo-second order initial adsorption rate
29		
30	K_1	Pseudo-first order rate constant
31		
32	q_e	Equilibrium adsorption loading
33		
34	χ^2	Chi-square test
35		
36	RMSE	Root mean square error
37		
38	CHNS/O	Carbon, hydrogen, nitrogen, sulphur and oxygen
39		
40	XRF	X-ray fluorescence
41		
42	EDAX	Energy dispersive X-ray analysis
43		
44	pHpzc	pH point of zero charge
45		
46	N	Freundlich isotherm parameter
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48	K_F	Freundlich isotherm constant (mg g^{-1})
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50	K_L	Langmuir isotherm constant (l mg^{-1})
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52	ATR-FTIR	Attenuated total reflectance Fourier transform infra-red

1. Introduction

1
2 Environmental pollution, food poverty, climate change and fossil fuel depletion are some of
3 the most pressing challenges facing humanity in this century. These issues are generating
4 interest globally as the race to find solutions that will sustain our continued human existence
5 gathers momentum. The development of 21st century solutions to these challenges have also
6 brought about pollution incidences as environmental pollution is increasing at great
7 proportions due to rapid industrialisation that is expanding to previously less developed
8 Countries and cities. This has resulted in the rapid and indiscriminate use and disposal of
9 resources that pose significant threat to the human and environment such as heavy metals
10 (Jiang *et al.*, 2015). Heavy metal ions are ubiquitous in the environment but their increased
11 levels in air, water and land resources are consequences of man-made activities. One of the
12 most toxic metal ions in our environment that has raised global concern is cadmium and this
13 element together with other heavy metal ions like lead, mercury, and chromium are not only
14 toxic but are non-biodegradable making them able to accumulate and persist in the food chain
15 (Ceribasi and Yetis, 2001). This has led to toxic incidences that have been reported in
16 literature such as the “itai-itai” disease, which arose due to cadmium poisoning in the Jinzu
17 river area of the Toyama prefecture in Japan. The implication of the cadmium toxicity
18 resulted in the softening of bone (osteoporosis) and kidney failure which affected the
19 inhabitants of the area due to the consumption of cadmium contaminated fish (Siswoyo *et al.*,
20 2014; Giwa *et al.*, 2013).

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39 The pollution of aquatic ecosystems with heavy metal ions such as cadmium is one of the
40 major outlets of metal ion toxicity affecting humans because a large number of number of
41 aquatic resources are used by man for different activities therefore raising the possibility of
42 potential health risk from the contamination of this resource (Hossain *et al.*, 2015). For
43 example wastewater discharges from industrial activities has been reported as one of the main
44 outlets of aquatic pollution from heavy metals. Cadmium can be detected in a number of
45 untreated effluents from a number of processes in the electroplating industry, nickel-cadmium
46 battery manufacture, fertilizer, pesticides, pigments and dyes as well as textile production
47 industries (Salim *et al.*, 1992; Cheung *et al.*, 2000; Perez-Marin *et al.*, 2007). These beneficial
48 uses of cadmium in industrial processes have led to increased cadmium transport within the
49 proximity of man’s environment. However, poor environmental practices has led to their
50 introduction into the food web at magnified levels resulting in cadmium interfering with the
51 physiological, behavioural and biochemical processes in man (Prapagdee *et al.*, 2014;
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1 Bernard, 2008; Johri *et al.*, 2010; Hossain *et al.*, 2015). The significance of this problem has
2 led to the inclusion of cadmium as one of the priority pollutants that should be eliminated
3 from drinking water and discharged effluents by the United States Environmental Protection
4 Agency (USEPA) and the World Health Organisation (WHO). According to the USEPA the
5 recommended maximum contaminant level (MCL) and maximum contaminant level goal
6 (MCLG) of cadmium in drinking water is 0.005mgL^{-1} (Meitei and Prasad, 2013; Amouei *et*
7 *al.*, 2013). Hence, there is need to remove this toxic metal ion from aquatic resources to
8 protect our environment as well as flora and fauna.
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14 A number of conventional techniques have been used to remove heavy metal ions such as
15 cadmium from effluents and aqueous systems and these include; coagulation, foam floatation,
16 precipitation, ion exchange, reverse osmosis, solvent extraction, chelation, electrolysis,
17 chemical oxidation and membrane technology (Sen, 2012; Tyowua *et al.*, 2013; Sari and
18 Tuzen, 2009; Meitei and Prasad, 2013; Alimohammadi *et al.*, 2013). These approaches have
19 been reported to either be too expensive for the treatment and disposal of the secondary toxic
20 sludge or ineffective/expensive when heavy metal ions are dissolved in large volumes of
21 solution at relatively low concentrations (Rao *et al.*, 2009; Volesky, 1990; Basso *et al.*, 2002;
22 Saleh, 2010). These limitations have made a lot of focus to turn to the application of
23 adsorption technology for the removal of these metal ions from effluents. Adsorption has a
24 number of advantages such as ease of availability and operation, low cost of operation and the
25 possibility of utilising it in a variety of industrial and domestic wastewater systems. It has also
26 been reported to have the capability to remove complex forms of heavy metals and can be
27 operated over a range of pH (Rao *et al.*, 2010; Prapagdee *et al.*, 2014). Activated carbon is the
28 most common adsorbent used in adsorption applications in many countries but the high cost
29 of activated carbon especially in developing (where industrialization is increasing with high
30 pollution related activities associated with heavy metal ions) has led to the quest for materials
31 that can be used as alternatives to activated carbon that are less expensive and readily
32 available (Mishra and Patel, 2009; Tyowua *et al.*, 2013; Siswoyo *et al.*, 2014; Wasewar *et al.*,
33 2010).
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52 In response to this, a number of studies have been reported on the use of agricultural residues,
53 waste materials and other low cost non-conventional materials as adsorbents for heavy metal
54 ions. These include; canola residue (Amouei *et al.*, 2013); melon seed husk (Giwa *et al.*,
55 2013); fluted pumpkin (Horsfall and Spiff, 2005); cassava waste (Abia *et al.*, 2003);groundnut
56 husk (Dubey and Gopal, 2006); maize cob (Igwe and Abia, 2007) and orange waste (Perez-
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1 Marin *et al.*, 2007); Manihot sculenta cranz waste (Augustine *et al.*, 2007; Abia *et al.*, 2006);
2 rape straw (Gong, 2013); canola and walnut shell residues (Feizi and Jalali, 2015); oil palm
3 fruit fibre (Abia *et al.*, 2007; Abia and Asuquo, 2007); macro algae *Caulerpa fastigiata*
4 (Sarada *et al.*, 2014) and rice husk (Krishnani *et al.*, 2008). These materials have been
5 reported to possess good adsorption capability for metal ions and organic pollutants from
6 wastewater and aqueous systems. The use of these waste materials as adsorbent also reduces
7 the cost of the heavy metal treatment process and makes the application of adsorption
8 technology adaptable for the developing countries such as Nigeria where these is rapid
9 industrialization.
10

11 Sweet potato (*Ipomoea batatas L.*) is a crop that is native to tropical America and its one of
12 the major root and tuber crops in the tropical regions of the world. It is widely grown and
13 consumed as a staple food in many parts of Africa, Latin America, Asia and the Pacific
14 Islands (FAO, 1998). It is the tenth major crop in world with a global output of about 100
15 million tonnes per year (UNCTAD, 2012). Nigeria is second largest producer after China with
16 a reported annual output of 2.83 million tonnes in 2010 (UNCTAD, 2012) and 3.45 million
17 tonnes in 2013 (FAOSTAT, 2015). In Nigeria, sweet potato is grown for both human and
18 animal consumption and it is consumed in the boiled form after it has been peeled (Olagunju
19 *et al.*, 2013 ; Egbe *et al.*, 2012). The peel has no significant application and is mainly used as
20 animal feed though the generation capacity outstrips animal consumption in many areas of the
21 country thereby leading to a waste management problem.
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38 Activated carbon has been used for treatment of municipal and industrial wastewaters in
39 many countries and has developed rapidly on a much larger scale than ever before. However,
40 the deployment of activated carbon produced from developed countries in the treatment of
41 wastewaters in developing countries has significant financial implications and this has limited
42 their use especially in small scale industries in developing countries where cost of wastewater
43 treatment plays a fundamental role in the decisions of whether the process is carried out or
44 not. Due to this constraint, the utilisation of readily available materials like agricultural
45 residues in these developing countries has become the focus of research for use in wastewater
46 treatment. The novelty of this work is based on the potential of using of a waste material to
47 treat heavy metal effluents at a low cost that will make the remediation of wastewater in the
48 developing countries more viable and environmentally friendly. Based on the aforementioned
49 waste challenge posed by this food crop, the present study examines the potential of using this
50 common agricultural residue in Nigeria as an adsorbent for the removal of Cd (II) ions from
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aqueous solution. Consideration was also given to the examination of the influence some parameters such as pH, contact time and initial concentration of Cd (II) ion on the sorption process. Physical and chemical characterisation of the sweet potato peel agricultural residue was also carried out to determine its intrinsic characteristics and their effect on sorption.

2. Materials and methods

2.1 Chemicals and adsorbent preparation

A standard stock solution of 1000 mgL^{-1} of Cd(II) ion was prepared by dissolving an appropriate amount of analytical grade reagent [cadmium nitrate tetrahydrate- $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich) (99% assay)] in deionised water using a 1000 ml volumetric flask ($\pm 0.8 \text{ ml}$ MBL Boro England). The stock solution was acidified to prevent hydrolysis by adding 5ml HNO_3 and the volume was made up to the 1000 ml mark. The content of each volumetric flask was agitated in a Heidolph Unimax instrument 1010 shaker at 300 rpm for 3 h to ensure complete dissolution at room temperature (25°C). Potato peels were obtained from an agricultural farm in Uyo, Akwa Ibom in Nigeria. The peels were washed with hot deionized water to remove dirt and colour and oven dried at 110°C for 24 hours. The dried residue was thereafter pulverized using a Coors porcelain mortar and pestle. Particle size separation of the residues was carried out by sequential sieving wherein 500g of the pulverized residue was sieved using a laboratory test sieve shaker model E.V.L.1. (Endecott's Limited London). After the sieving, the residues in the $140 \mu\text{m}$ sieve tray were taken off and put in new and clean polypropylene bottles and labelled unmodified residues and stored at room temperature for further use in the adsorption studies. This sample was labelled as the unmodified Sweet potato peel residue (PTPS) and used for Cd(II) ion sorption studies.

2.2 Adsorbent Characterisation

Characterisation of the physical and chemical properties of the PTPS residue adsorbent was carried out using a number of techniques which are subsequently described in this study.

2.2.1 Fourier-Transform infra-red spectroscopy -FTIR

Fourier transform infra-red spectroscopy was used to evaluate the functional groups in the PTPS adsorbent. Prior to the analysis, the adsorbent was dried in an air oven for 24 h at 110°C

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to remove the moisture contents of the sample. This was to eliminate any interference in the spectrum arising from H₂O content in the samples. The infra-red spectrum of the PTPS before and after Cd(II) adsorption were then collected using an attenuated total reflectance FT-IR spectroscopy (ATR-FT-IR). The instrument used was the Smart Golden Gate Thermo Nicolet Avatar 360 FT-IR with ATR probe. The spectra range was from 4000 – 400 cm⁻¹ and the spectra were collected using the FTIR-ATR spectrometer using a total average of 32 co-added scans and a spectral resolution of 4 cm⁻¹ with background subtraction. All the measurements were performed at room temperature and the spectra were recorded using transmittance mode.

2.2.2 *Elemental composition analysis-CHNS/XRF*

The carbon, hydrogen, nitrogen and oxygen content of the PTPS adsorbent were determined using a Flash 2000 CHNS/O automatic elemental analyser (Thermo Fisher Scientific). The sample was weighed and the weight recorded and the samples were then put into tin capsules and placed inside the Thermo-Fisher MAS 200R auto-sampler for analysis. After analysis, the C, H, S and N content of the PTPS adsorbent was calculated by the instrument and the oxygen content was determined by difference. X-ray fluorescence spectroscopy was also used to determine the inorganic composition of the PTPS adsorbent. The XRF instrument used was a wave-length dispersive XRF (WDXRF) model AXIOS (PANalytical). Samples were pelletized to 6mm masks using wax as binder with a powder to wax ratio of 10 g to 3 g and analysed to determine the chemical composition of the PTPS adsorbent.

2.2.3 *SEM and EDAX Analysis*

The surface morphology of the PTPS adsorbent before and after Cd(II) ion adsorption as well as the chemical composition were analysed by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX) respectively. The equipment used for the SEM and EDAX analysis was a FEI Quanta 200 Environmental Scanning Electron Microscope. The PTPS adsorbent was placed and pressed onto a carbon tab (Agar Scientific) and mounted on a 0.5” SEM pin stubs (Agar Scientific). The samples were preconditioned for analysis by coating using an EMITECH K550X sputter gold coater and coating was carried out for 15 minutes and thereafter analysed in the vacuum chamber at 30.kV and 0.75 Torr.

2.2.4 BET surface area, porosity and density analysis

1 The surface area and porosity of the PTPS adsorbent was determined using a Micromeritics
2 Tristar 3000 Surface Area and Porosity Analyzer. The PTPS adsorbent was pre-conditioned
3 by drying in an oven for 24 h at 110°C after which 1.033g was weighed into the BET sample
4 tube and conditioned (degassed) for 2 1hr at 200°C under nitrogen flow in order to eliminate
5 moisture and other gases on the adsorbent using the *Micromeritics Flow prep 060 sample*
6 *degas system*. Thereafter it was cooled under nitrogen flow for 5mins in the cooling section of
7 the Flow prep system and when it had cooled it was then weighed again to determine the
8 actual weight of sample to be analysed. The sample (inside) the BET tube was thereafter
9 exposed to nitrogen at 77 K, whereby the gas pressure in the tube with the sample was
10 allowed to reach equilibrium before subsequent dosing where a series of successive
11 incremental pressures of nitrogen doses were done in order to obtain an adsorption isotherm.
12 The density of the PTPS adsorbent was determined using helium pycnometry. The instrument
13 used for the analysis of the residues was the Accu Pyc 11 1340 Helium pycnometer
14 manufactured by Micromeritics. A weighed amount of sample to be analysed was dried in an
15 oven for 24h before analysis. Pressure and volume calibration of instrument was first carried
16 out before analysis of the samples. The calibration standard was placed in the propylene cup.
17 Thereafter the two bulbs were put into the cup gently and the instrument calibrated. The
18 weighed sample was then placed into the propylene cup and the analysis using helium gas
19 was carried out at 5 purges and 5 cycles.
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2.2.5 pH point of zero charge (pHpzc) determination

38 The point of zero charge (pHpzc) of the PTPS adsorbent was determined using a Malvern
39 Zetasizer 3000 HSA (Malvern Instruments). The PTPS adsorbents were prepared by weighing
40 0.1 g of sample into 20 ml of 0.01 M NaCl solution at pH range of 2 – 12 and agitating it at
41 300 rpm in a shaker for 24 h. After which it was filtered and 10ml of each of sample was
42 taken into labelled polypropylene bottles for analysis. The Zetasizer syringe was cleaned and
43 the analysis cell purged with deionized water using the syringe. The samples of each of the
44 adsorbents at different pH were inserted into the Zetasizer electrophoresis cell (a 3ml
45 polystyrene curvette with a light path of 10 mm) using a syringe. The zeta potential at each
46 pH was measured and recorded. Three measurements were carried out and an average zeta
47 potential for each adsorbent suspension at the different pH values were recorded.
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2.2.6 Thermogravimetric analysis

1 The Thermogravimetric analyzer (TGA) used in the analysis of the PTPS adsorbent was the
2 TGA Q5000 (TA instrument). 28.25mg of the sample was weighed onto a ceramic pan and
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4 subjected to temperature profile analysis from 20°C to 500°C under nitrogen atmosphere to
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6 monitor the thermal degradation at a heating rate of 10 °C min⁻¹. The nitrogen flow rate was
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8 maintained at 50 ml min⁻¹ and the temperature was equilibrated at 25°C and maintained for 5
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10 minutes. Thereafter it was increased to 100 °C at a rate of 10 °C min⁻¹ and maintained for 60
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12 minutes. After this time interval it was ramped at 10 °C min⁻¹ up to 500 °C and maintained for
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14 60 minutes. Subsequently, air was selected to burn off the residue at a flow rate of 50ml min⁻¹
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16 up to 600°C for 30 minutes. The thermal degradation profile of the sample gives information
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18 on the weight loss (%) with temperature and time using a single thermogravimetric curve.
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20 From the TG profile, information of the different components of the sample like the moisture
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22 content, volatile content, fixed carbon and ash composition were obtained using the TA
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24 Instruments Universal Analysis 2000 software.
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2.3 Batch sorption experiments

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31 Standard stock solution of 1000 mg l⁻¹ of Cd(II) ion from the reagent- cadmium nitrate tetra
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33 hydrate-Cd (NO₃)₂·4H₂O (Sigma-Aldrich) (99% assay) was prepared by dissolving
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35 stoichiometric amounts of the analytical grade reagent in deionised water using a 1000 ml
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37 volumetric flask. The working solutions for individual sorption experiments were prepared by
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39 serial dilution of aliquots of the stock solution. Batch sorption experiments for the equilibrium
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41 adsorption experiments were carried out by agitating known weights (2.0g) of the PTPS
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43 adsorbents with 100 ml of adsorbate solutions of different initial concentrations (50, 100, 150,
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45 200, 250, 300, 350, 400, 450 and 500mg l⁻¹). The pH 6.5 and a contact time of 180 minutes
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47 were used for the adsorption studies for initial concentration studies, while 1440 minutes was
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49 used for the contact time studies. The pH for each experiment was modified using NaOH and
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51 HCl. For the study of the effect of adsorbate pH on the removal of Cd(II) PTPS) the range of
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53 pH was from 2 – 10, while the other parameters used were: initial metal ion concentration of
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55 500 mg l⁻¹, temperature of 25 °C ± 0.5 and a reaction volume of 0.1 L. The amount of adsorbent
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57 used was 2.0 g and HCl and NaOH were used to vary the different adsorbate pH. The effect of
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59 contact time on the sorption processes was studied using 5 minutes to 72h (1440min)
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61 intervals. The reaction vessel for each adsorption experiment was a 250 ml conical flask and
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63 the sorption was carried out at a laboratory temperature of 25 °C ± 0.5. Each conical flask with
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1 the adsorbate and adsorbent was agitated for a specified contact time in a Heidolph MR 3001
2 magnetic stirrer with speed and temperature controls at a speed of 200 rpm. At the end of each
3 experiment, the resulting solution was separated from the adsorbent. The metal ion
4 concentrations of the adsorbate solution were determined spectrophotometrically using ICP-
5 OES. For the determination of metal ion loading after sorption, the amount of metal ion
6 adsorbed (q_e) was calculated using eqn. (1).
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$$10 \quad q_e = \frac{(C_i - C_t)V}{w} \quad (1)$$

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15 Where C_t (mg l^{-1}) is the metal ion concentration at time t , q_e (mg g^{-1}) is the loading of the metal
16 ion at time t , C_i is the initial metal ion concentration, w is the weight of the adsorbent (g) and
17 V is the volume of the aqueous system.
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22 *2.3.1 Data quality evaluation*

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25 All adsorption experiments were carried out in triplicates to ensure reproducibility and
26 accuracy of results. The relative standard deviation was used as the error parameter for all
27 analysis and the value for each set of measurements was $< 5\%$. Each experimental set was
28 carried out using blanks to ensure the elimination of errors associated with experimental
29 conditions. For each experimental analysis procedure, blanks were prepared using deionized
30 H_2O and the blank samples were subjected to the same treatment process using the same type
31 of experimental vessel. In the analysis of Cd(II) metal ion in solution, the blank samples were
32 also analysed first in the Inductively coupled plasma optical emission spectrometer (ICP-
33 OES)-Vista-MPX instrument prior to analysis of the standards and the samples. The metal ion
34 concentration in the stock solution and prepared aqueous solution before adsorption were also
35 analysed to ensure the correct concentration was prepared and used for adsorption. The
36 instrument was programmed to take into account any blank concentration and the actual metal
37 ion concentration of Cd(II) ion.
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50 **3. Results and Discussions**

51 **3.1 Adsorbent characterisation**

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58 The physical and chemical characteristics of the PTPS adsorbent are presented in Table 1. The
59 ultimate and proximate analysis of the adsorbent indicates that it is mainly organic in nature
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with some inorganic constituents as shown by the ash content. The organic content (carbon, nitrogen hydrogen and oxygen) of the PTPS residue adsorbent is consistent with what has been reported in literature for other types of dried biomass (Chang *et al.*, 2015). The ash content was determined by two methods- using thermogravimetric analyser and using the procedure described in AOAC (2000) in which 1g of the adsorbent was carbonised at 600°C for 6h and the weight difference determined as a percentage. The two values obtained from these different methods are shown in Table 1 and are comparable; it indicates that the PTPS adsorbent had a high percentage of ash that is due to its inorganic composition.

Table 1: Physical and chemical characteristics of PTPS adsorbent

Characteristics	PTPS
Ultimate Analysis (wt%) ^a	
Carbon	40.1
Hydrogen	5.87
Nitrogen	1.66
Oxygen ^c	46.3
Sulphur	0.30
Proximate Analysis (wt%) ^b	
Fixed carbon	20.5
Volatile matter	62.4
Moisture	4.90
Ash	11.2
Ph	5.70
pHpzc	6.30
BET surface area (m ² g ⁻¹)	1.91
Total pore volume (cm ³ g ⁻¹)	4.87 x 10 ⁻³
BJH desorption average pore diameter (nm)	22.3
Ash content (%) ^d	10.6
Helium density	1.51
^a Ultimate analysis using CHNS analyser	
^b Proximate analysis using thermogravimetric analyser	
^c Obtained by difference	
^d Using AOAC (2000) method	

1 The ash content of agricultural residues is an important parameter in the adsorption studies as
2 it gives information on the inorganic component of residues when they are used as adsorbents
3 or are transformed via thermochemical methods into other types of adsorbents as these can aid
4 heavy metal removal via ion-exchange processes (Sardella *et al.*, 2015). The composition of
5 the PTPS adsorbent is similar to what has been reported for some lignocellulosic adsorbents
6 obtained in Nigeria such as coconut husk (*Cocos nucifera*), cocoa pods (*Theobroma cacao*),
7 kola nut pods (*Cola nitida*) and plantain peels (*Plantago major*) (Oladayo, 2010). The ash
8 content and moisture content of these residues reported by Oladayo (2010) were; 3.95, 12.67,
9 7.76 and 6.06 (% ash content) and 5.34, 10.04, 11.99 and 8.71(% moisture) for coconut husk,
10 cocoa pods, kola nut pods and plantain peels respectively. Also the moisture content, ash
11 content and pH_{pzc} of the PTPS adsorbent are similar to those reported by Pandey *et al.*,
12 (2015) for Kush grass and bamboo leaves adsorbents. The PTPS adsorbent has a high volatile
13 matter content which is characteristics of the organic nature of the lignocellulosic biomass
14 which contains cellulose, lignin and hemicellulose (Khor *et al.*, 2009). Odetoye *et al.*, (2014)
15 in their study on the thermochemical characterisation of *Parinari polyandra* Benth fruit shell
16 reported a 78% volatile matter content for this biomass thus indicating its high organic matter
17 content compared to that of the PTPS residue adsorbent.
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31 The density of the PTPS adsorbent was also determined as described in the materials and
32 methods section. Adsorbents with high solid density are desirable for industrial applications
33 to ensure high structural strength in water treatment processes and the density of porous
34 materials is also an important parameter in the study of the structure and properties of
35 adsorbents (Malbrunot *et al.*, 1997; Guo and Lua, 2002). The helium density of the PTPS
36 residue obtained based on the helium pycnometry method is presented in Table 1. The value
37 obtained (1.51) indicates that the adsorbent had a low solid density meaning that its
38 mechanical or structural strength is poor. The density of residues also has implications on the
39 mechanical strength of adsorbents prepared from them especially those of activated carbon
40 adsorbents (Guo and Lua, 2000; Wan *et al.*, 2014).
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51 The pH is an important variable in the adsorption process involving metal ions as it can
52 influence the type of speciation, degree of ionization of adsorbate and the nature of functional
53 groups on the surface of an adsorbent (Sardella *et al.*, 2015). The effect of pH of the adsorbent
54 and the solution on the adsorption process can be studied using a plot of the zeta potential
55 against the pH to determine the pH at which the charge on the surface is zero (pH_{pzc})
56 (Gautam *et al.*, 2014). This is an important parameter as it gives information on the pH that
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can be used for adsorption of cations and anions; due to the understanding of the regions within the pH window that is dominated with basic or acidic functional groups (Fernandez *et al.*, 2015). The pH of the PTPS was 5.70 and the pH point of zero charge was 6.32 as shown in Table 1. From the value of the pH and pH_{pzc} of the adsorbent, it was observed that the adsorbent was mainly acidic in nature and the pH of 6.5 was chosen for the adsorption studies as the target ions was positive, hence a pH that is above the pH_{pzc} has to be chosen to facilitate the adsorption of the positive Cd(II) by the PTPS adsorbent.

3.1.1 BET Surface area and porosity

The Brunauer-Emmett-Teller (BET) surface area and pore characteristics of the PTPS adsorbent obtained using Nitrogen adsorption-desorption shown in Figure 1 are presented in Table 1. The result shows that the surface area of the PTPS adsorbent was 1.91m²g⁻¹. This indicates that the PTPS adsorbent did have a low surface area and this is similar to what has been reported in previous studies for some agricultural residues. These lignocellulosic residues are known to have low surface areas due to the nature of the cellulose, hemicellulose and lignin content in them. These results in these residues having wide pore size distributions due to the high percentage of mesopores/macropores within their network compared to micropores as can be observed in the pore size distribution in Fig.1. Furthermore, these wide pore size distributions of mesopores/macropores in the lignocellulosic materials make them suitable for liquid phase sorption as it facilitates diffusion of the adsorbate into the adsorbent structure (Ribeiro *et al.*, 2015; Menendez-Diaz and Martin-Gullon, 2006). However, it should be noted that the sorption properties of these residues are not only dependent on the possession of large surface areas as since porosity alone is not the only criteria required for good adsorbents. In addition to porosity, the nature and types of functional groups on these materials which serve as active sites for sorption contributes significantly to their adsorption potential for target pollutants (organic or inorganic). Thus, lignocellulosic residues have been reported to possess a number of different functional groups on their surface such as phenolic, carboxylic, hydroxyl, amines and ether groups which act as sources of physical and chemical interactions that facilitates adsorption via a number of mechanisms that include; hydrogen bonding, electrostatic interactions and surface complexation (Tan *et al.*, 2015; Nguyen *et al.*, 2013; Barkar *et al.*, 2013; Bailey *et al.*, 1999). Martin-Lara *et al.*, (2013) in their study on the development and characterisation of biosorbents to remove heavy metals from aqueous solutions by chemical treatment of Olive stone observed that the Olive stone residue had a

BET surface area of $0.163\text{m}^2\text{g}^{-1}$ and a Pb^{2+} loading capacity of 6.32mgg^{-1} , thereby indicating that surface area alone is not the only indicator of a good adsorbent.

Furthermore, Wan *et al.*, (2014) have reported the BET surface area of $0.86\text{m}^2\text{g}^{-1}$ for tea waste adsorbent used for the sorption of lead (II), cadmium (II) and copper (II) ions from aqueous solution. The surface area of meranti sawdust reported by Rafatullah *et al.*, (2009) in their study was $0.62\text{m}^2\text{g}^{-1}$. Lacerda *et al.*, (2015) has also reported on the BET surface areas of some lignocellulosic biomass, in their study the surface area obtained for the residues were; $0.85\text{m}^2\text{g}^{-1}$ (carnauba palm leaves); $0.60\text{m}^2\text{g}^{-1}$ (macauba seed endocarp) and $0.86\text{m}^2\text{g}^{-1}$ (pine nut shell). The Nitrogen adsorption-desorption isotherm has been classified according to the Brunauer, Deming, Deming and Teller (BDDT) method (Sing, 1982; Sing, 2001) and based on this approach the nitrogen isotherm plot for the PTPS adsorbent is classified as a type II isotherm, which describes nonporous materials or those with macropores/open voids (Tsai *et al.*, 2006).

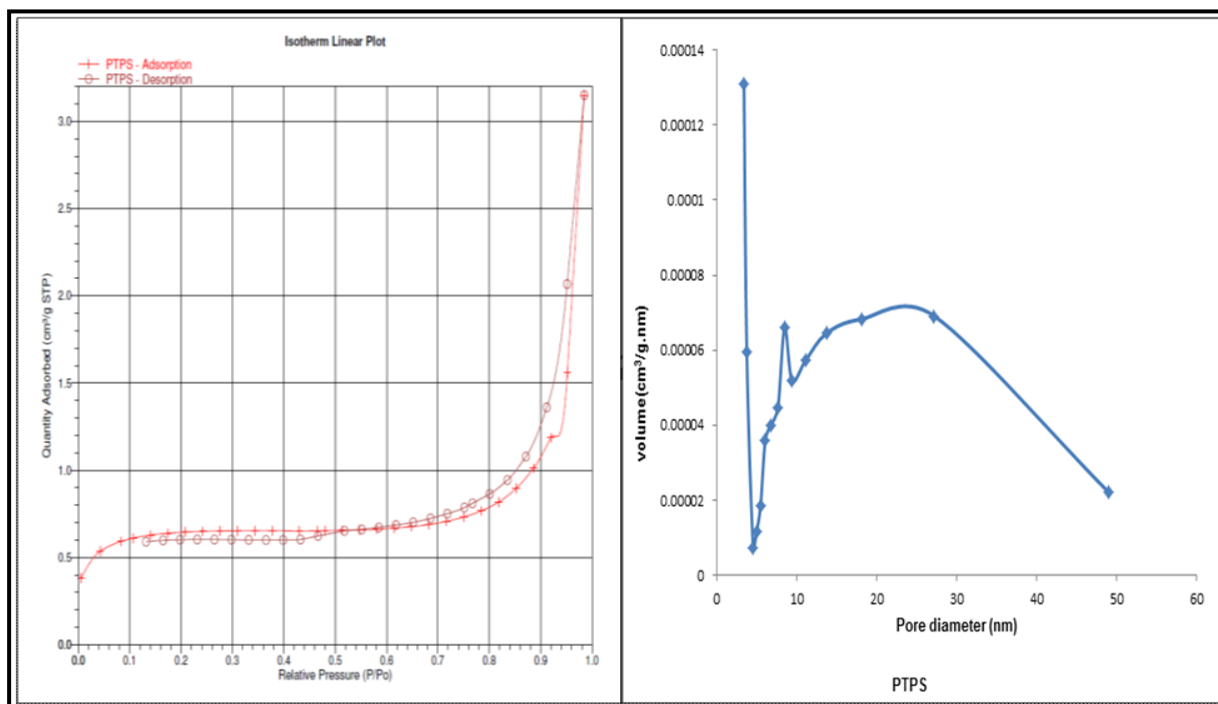


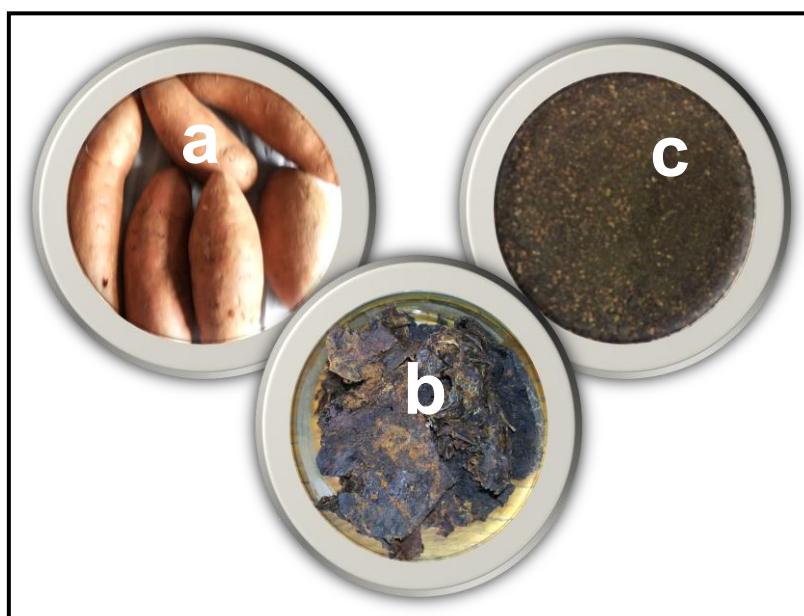
Figure 1: N_2 adsorption-desorption isotherm and pore size plot of PTPS residue adsorbent

The total pore volume of the PTPS residue adsorbent is $4.87 \times 10^{-3}\text{cm}^3\text{g}^{-1}$ as presented in Table 1 and this indicates that the volume of pores is small. The small pore volume of the PTPS residue may be due to the nature of arrangement of cellulose, hemicellulose and lignin structures within the lignocellulosic framework of the material which may lead to the development of few number pores or blocked pores if they exist (Bota *et al.*, 1996). This

1 observation is similar what has been reported in previous studies for lignocellulosic residues.
2 Lacerda *et al.*, (2015) has reported on the total pore volume of some lignocellulosic biomass
3 and in their study the total pore volumes obtained for the residues were; $3.59 \times 10^{-4} \text{ cm}^3 \text{ g}^{-1}$
4 (carnauba palm leaves); $2.01 \times 10^{-3} \text{ cm}^3 \text{ g}^{-1}$ (macauba seed endocarp) and $3.16 \times 10^{-3} \text{ cm}^3 \text{ g}^{-1}$
5 (pine nut shell). The average pore diameter of the PTPS adsorbent based on an analysis of the
6 desorption branch of the N_2 adsorption-desorption isotherm plot (Figure 1) was 22.3nm
7 indicating that the adsorbent is mesoporous according to the IUPAC classification of porous
8 materials (Sing, 1982, Sing 2001). The pore diameter plot of the PTPS adsorbent is shown in
9 Figure 1 and the nature of the plot indicates that the adsorbent had a trimodal pore size
10 distribution with peaks at 2-30nm.
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18 3.1.2 Adsorbent Morphology

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21 Photographs of the raw potato peel and that of the pulverised and dried PTPS adsorbent are
22 shown in Figure 2 and the images indicate a slight colour change after the drying and
23 pulverising of the residue. This may be due to the elimination of some tannin components on
24 the adsorbent surface during the pre-treatment process (Ojedokun and Bello, 2015). The
25 surface characteristics of the PTPS adsorbent were further examined using scanning electron
26 microscopy. The SEM micrograph of the PTPS adsorbent is shown in Figure 3a. The figure
27 indicates the presence of rough crevices on the adsorbent which can be presumed to play a
28 major role in the transport of the Cd(II) ions during sorption (Wahab *et al.*, 2012).
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59 Figure 2: Photograph of sweet potato (a) dried sweet potato peel (b) and pulverised sweet
60 potato residue adsorbent-PTPS (c).
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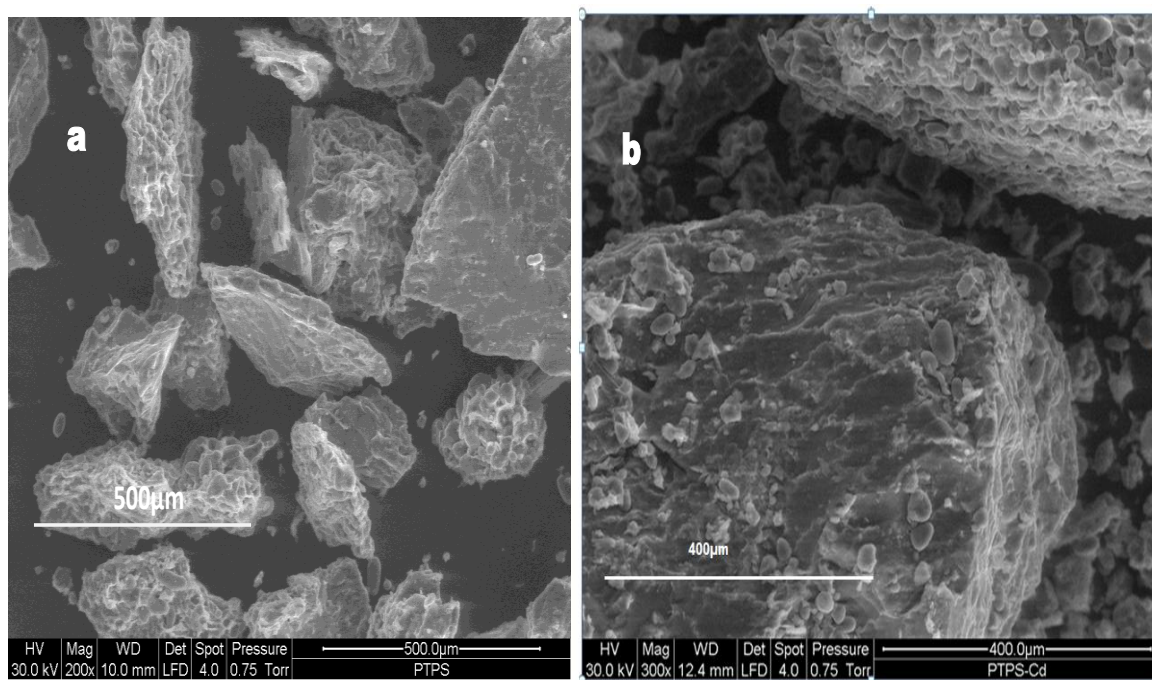


Figure 3: Electron micrograph of PTPS adsorbent (a), PTPS after Cd(II) sorption (b)

Scale bar: 300/200 μm

It can also be observed from Figure 3a, that there are no well-defined pore structures on the residue surface thereby indicating that the PTPS adsorbent does not have porosity (Tsai *et al.*, 2006). This observation also confirms the inference made from the results of the surface area characterisation of the adsorbent using the shape of the nitrogen adsorption-desorption isotherm. The morphology of the PTPS adsorbent was further examined after Cd(II) ion sorption and the electron micrograph is shown in Figure 3b. An examination of this image indicates that the morphology of the PTPS adsorbent was not altered after metal ion sorption. However, the surface roughness seen in the SEM of the PTPS adsorbent (Figure 3a) was reduced on the PTPS-Cd adsorbent (Figure 3b). This may be associated with the effect of the impregnation of the Cd(II) ions on the PTPS adsorbent surface during sorption.

3.1.3 Chemical composition of adsorbent

The chemical composition of the PTPS adsorbent was determined using a number of techniques; the carbon, hydrogen, nitrogen, sulphur and oxygen content were determined using the CHNS elemental analyser (oxygen content obtained by difference) (Table 1), while the inorganic content were determined using X-ray fluorescence spectrometry (XRF) and the results are shown in Table 2. In addition the semi-qualitative chemical composition of the PTPS adsorbent was also obtained using energy dispersive X-ray analysis (EDAX) which is

coupled to the scanning electron microscope (SEM) used for examination of the morphology of the adsorbent.

Table 2: XRF of PTPS residue adsorbent

Element (%)	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO	Fe ₂ O ₃
PTPS	0.05	0.22	0.32	1.32	0.40	0.30	0.39	2.65	0.16	0.12

From the analysis, the chemical composition of the residues indicates that carbon, oxygen and inorganic compounds were the main chemical species present in the residue as this is a lignocellulosic material of plant origin. The percentage carbon, hydrogen, nitrogen, oxygen and sulphur content of the PTPS adsorbent is similar to what has been also been reported by Odetoye *et al.*, (2014) in their study on the thermochemical characterisation of *Parinari polyandra* Benth fruit shell. In their study the percentage carbon, hydrogen, nitrogen, oxygen and sulphur content of the agricultural biomass was 48.04, 5.76, 2.13, 43.5 and 0.10 respectively. The oxygen and carbon content of plant based residues are the main contributors to their high volatile content.

X-ray fluorescence was used to obtain information on the inorganic chemical composition of the PTPS adsorbent considering its high ash content ($\geq 10\%$ of the residue). The X-ray fluorescence (XRF) analysis is shown in Table 2 and it can be observed that the composition of the PTPS residue adsorbent is represented as oxides. It can also be inferred from the table, that the amount of silicon and potassium in the PTPS residue were significant [K₂O (2.65%) and SiO₂ (1.32%)] compared to those of the other inorganic constituents. The other species that also had considerable composition in the adsorbent were magnesium, phosphorus, aluminium and chloride. The elemental composition of the PTPS residue adsorbent is similar to what has been reported in literature for biomass adsorbents. The sodium and magnesium content in the PTPS residue was higher than that of the rice husk adsorbent reported by Zhang *et al.*, (2014) for Cu (II) adsorption. However, the percentage silica content of the rice husk (15) was higher than that of the PTPS residue adsorbent. The presence of these inorganic elements in the adsorbent also confirms the high ash content of the PTPS adsorbent and may

contribute to the type of mechanism for cadmium (II) ion removal onto the adsorbent such as ion-exchange or complexation.

3.1.4 Energy dispersive X-ray analysis (EDAX)

The presence of chemical elements in an adsorbent and their relative compositions can also be determined using the energy dispersive X-ray coupled on the SEM instrument. The EDAX was carried out as a spot size analysis wherein the spot of interest was examined for chemical information. The EDAX spectrum and the relative elemental composition of the PTPS adsorbent are presented in Figure 4. From the Figure, the chemical composition of the PTPS residue adsorbent indicates that carbon, oxygen and inorganic compounds were present in the residue. Some of these inorganic compounds include magnesium, aluminium, silicon, phosphorus, sulphur, chloride, potassium, calcium and iron. From the EDAX spectrum, it can be observed that amongst the inorganic elements potassium and silicon were the most abundant in the PTPS residue adsorbent. This trend was also observed from the X-ray fluorescence data previously discussed (Table 2).

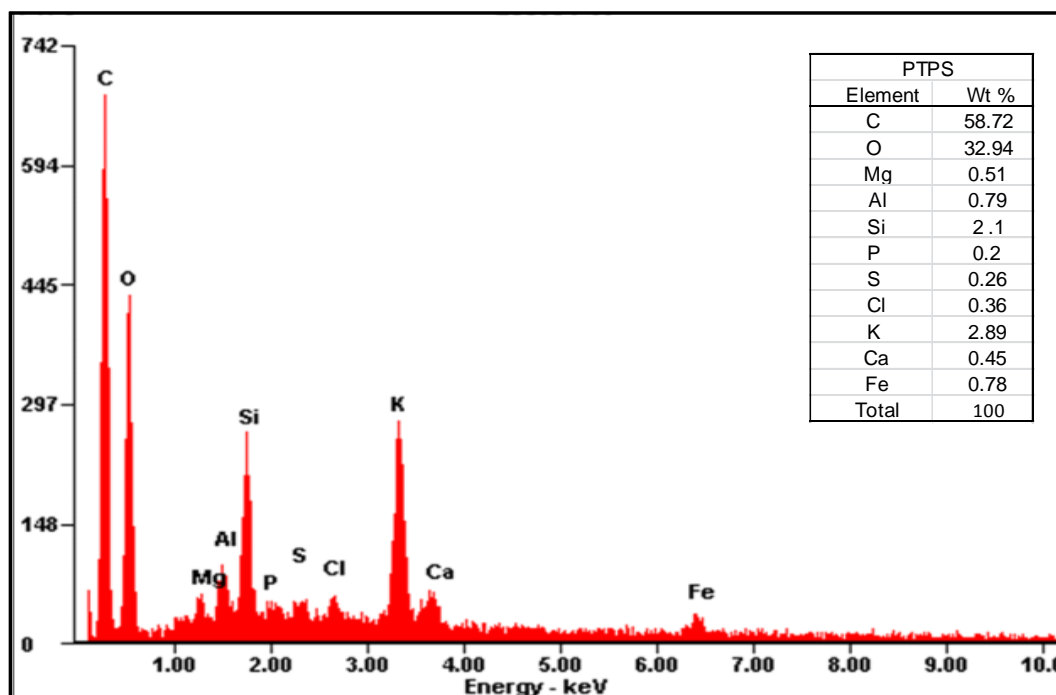


Figure 4: EDAX spectrum of PTPS residue adsorbent

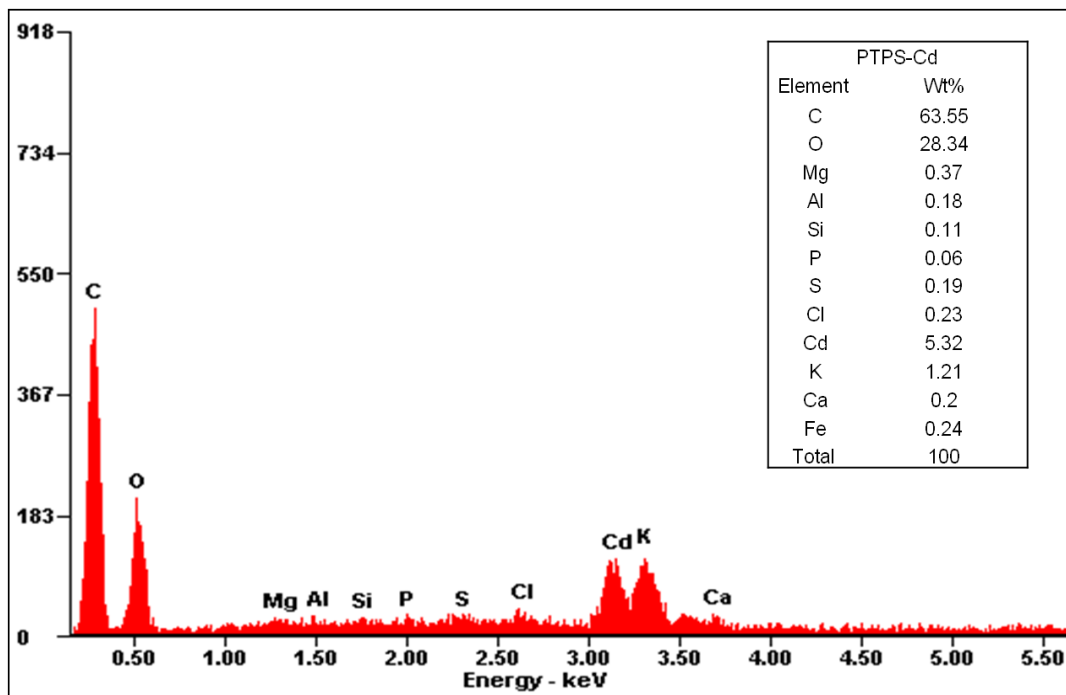


Figure 5: EDAX spectrum of PTPS residue after Cd(II) adsorption

The PTPS residue used for adsorption of Cd(II) was further subjected to EDAX analysis to confirm the presence of the adsorbed Cd(II) ions and is presented in Figure 5. An examination of the EDAX spectra after Cd(II) ion sorption (Figure 5) indicates that the PTPS residue adsorbent had the characteristic peak associated with Cd(II) ions thus confirming the possibility that Cd(II) metal ion sorption had occurred on the surface of these residue adsorbents. This identification of adsorbed metal ion on an adsorbent after sorption using EDAX has been used to confirm the mechanism of metal ion sorption. Iqbal *et al.*, (2009) reports on the use of the EDAX analysis of grapefruit peel to confirm the mechanism of ion-exchange for the removal of Zn(II) from aqueous solutions. The report also noted that the calcium and potassium ions identified in the EDAX spectrum of the fresh grapefruit peel were absent in the peel used for Zn(II) ion adsorption, thus suggesting that these ions may be involved in the ion-exchange with the Zn(II) ions. From the results of the EDAX analysis of the PTPS adsorbent it is observed that the spectrum shows a reduction in the amount of divalent elements such as magnesium and calcium ions on the PTPS adsorbent after sorption (Figure 5) when compared to that of the fresh adsorbent (Figure 4). This may suggest that one of the mechanisms of Cd(II) ion uptake from the aqueous metal ion solution onto the adsorbent surface is via ion-exchange between these divalent metal ions on the PTPS surface and the Cd(II) ions in the adsorbate. This assumption is similar to what was observed by Iqbal *et al.*, (2009).

3.1.5 Thermogravimetric analysis

1 Thermogravimetric analysis (TGA) was used to obtain information on the thermal
2 decomposition behaviour of the PTPS residue the thermal degradation profile was used to
3 obtain the proximate composition of the PTPS residue. TGA pyrolysis (under nitrogen) was
4 set to operate from 20-500°C, while combustion (in air) took place from 500-600 °C. The
5 thermogravimetric (TG) and the derivative thermogravimetric (DTG) plots of the PTPS
6 residue adsorbent are shown in Figures 6(a) and (b) respectively. Cellulose and hemicellulose
7 are the major components of the volatile matter, while the lignin is a main component in the
8 formation of chars (Sanchez-Silva *et al.*, 2012). These components have different initial
9 decomposition temperatures due to their composition and this can be used to indicate the
10 temperatures and regions of their elimination from the sample under investigation. Previous
11 studies carried out by Stefany *et al.*, (2005) observed that the sequence of degradation in
12 lignocellulosic materials commences with the decomposition of hemicellulose between the
13 temperature ranges (150 – 350°C). The cellulosic material is the second component that
14 degrades between the range 275 – 380°C and lignin degrades between 300 – 500 °C. The third
15 stage of weight loss is the oxidation of the fixed carbon occurring from 500°C to 600°C with
16 the resulting ash residue and this can be used to characterise the degradation profile of the
17 PTPS residue. Examination of Figures 6(a) and (b) shows that there were 4 regions (each
18 with an exothermic peak) with differential quantities of components eliminated by the thermal
19 degradation process and these can be related to the different components on the PTPS residue.
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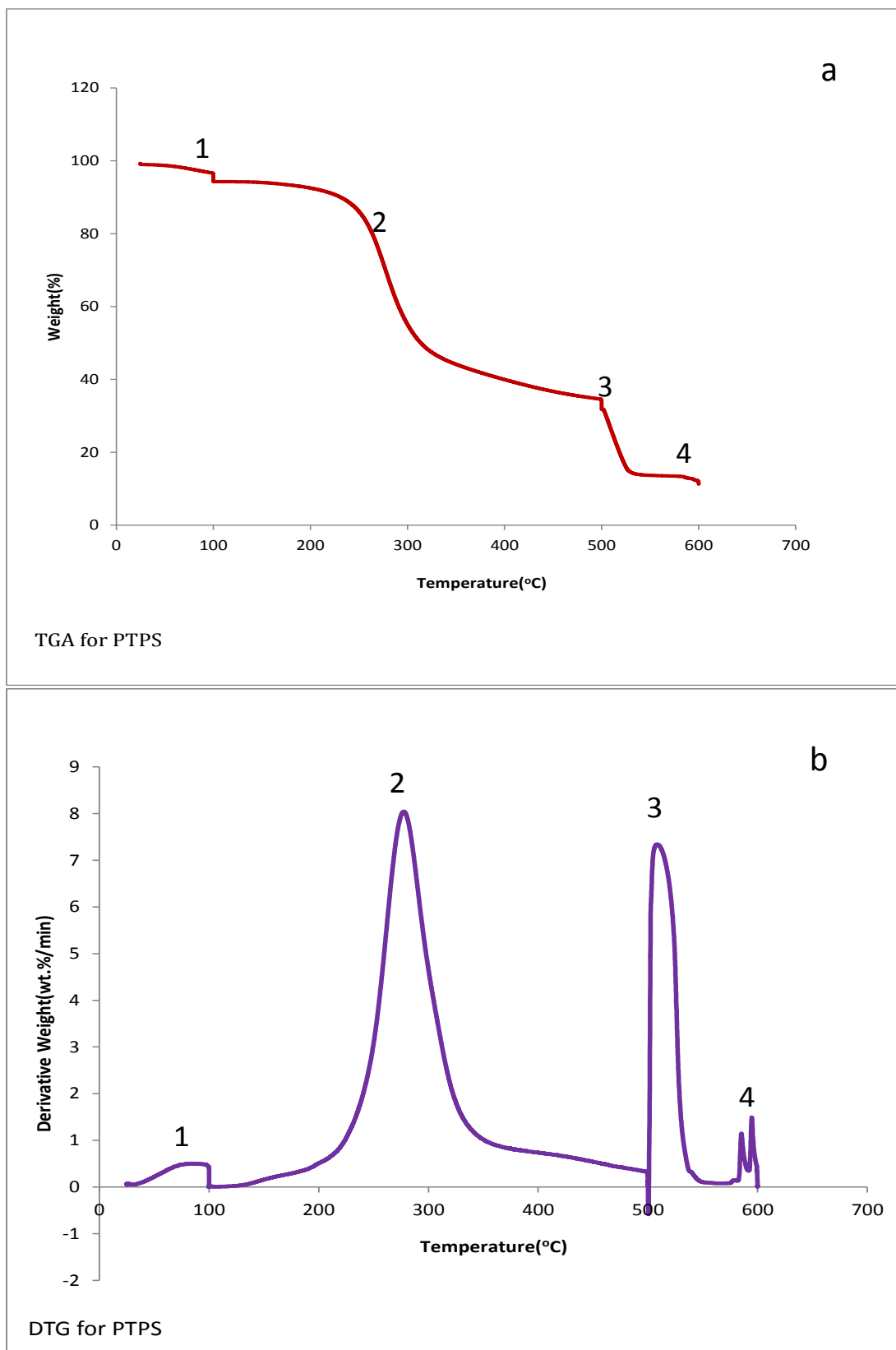


Figure 6: Thermogravimetric (a) and derivative thermogravimetric (b) plots of PTPS in N₂ (20-500 °C) & air (500-600 °C)

1 The weight loss in the first stage (1) (moisture evolution) was 4.9% and this was as a result of
2 keeping the residue at this stage (20-100°C) for 60 minutes to eliminate all moisture, the
3 second stage (2) of the weight loss regime (evolution volatile component) was 62.4% with a
4 maxima in the DTG plot (Fig. 6b) that can be associated with hemicellulose and cellulose
5 decomposition between 180 and 380°C. The third stage (3) is that of the oxidation of fixed
6 carbon on the residue (20.5%) and occurs between 500 and 600°C with final stage (4) being
7 the ash component as the final residue which is composed of the inorganic elements (11.2%).
8 The degradation profile of the different components in the PTPS residue adsorbent is similar
9 to profiles that have been reported in literature as noted by Titiloye *et al.*, (2013) on the
10 evaluation of the thermo-chemical characteristic of some agricultural waste from West Africa.
11 Comparing the results in their study to the PTPS adsorbent, it is observed that the percentage
12 moisture content of the PTPS adsorbent (4.9%) was lower than that reported for the various
13 agricultural wastes such as corn straw (9.15), corn cob (8.72), rice straw (7.23), rice husk
14 (8.59), cocoa pod (10.29), Jatropha cakes (10.03), moringa cakes (10.38) and sugar cane
15 bagasse (8.52). However, the moisture content of the PTPS residue was higher than that of
16 *Parinari* fruit shell (2.65) also reported in the study. Also the percentage volatile matter
17 component of the PTPS (62.4%) was lower than those of the corn straw (75.02), corn cob
18 (80.72), cocoa pod (68.47), Jatropha cakes (72.53), moringa cakes (75.08) *Parinari* fruit shell
19 (78.17) and sugar cane bagasse (79.45). However, the volatile content of the PTPS residue
20 was higher those of rice straw (45.68), rice husk (58.22) (Titiloye *et al.*, 2013). The
21 percentage fixed carbon of the PTPS residue (20.5) was higher than those of all the
22 agricultural residues - corn straw (9.70), corn cob (7.60), cocoa pod (10.43), rice straw (1.33),
23 rice husk (8.48), Jatropha cakes (10.97), and moringa cakes (8.26), *Parinari* fruit shell (14.51)
24 and sugar cane bagasse (8.12) reported by Titiloye *et al.*, (2013). Finally it was also observed
25 that the percentage ash content of the PTPS residue (11.2) was higher than those of corn straw
26 (6.13), corn cob (2.93), cocoa pod (10.81), Jatropha cakes (6.47), moringa cakes (6.28),
27 *Parinari* fruit shell (4.67) and sugar cane bagasse (3.91) with exception of those of rice straw
28 and rice husk which were 45.76 and 24.71 respectively.
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51 3.1.6 Fourier transform infrared (FTIR) spectroscopy

52 The FTIR spectrum of the PTPS residue adsorbent was used to determine the functional
53 groups present based on their characteristic vibrations. It is also used to confirm sorption
54 mechanism as the vibrations associated with the functional groups present in lignocellulosic
55 adsorbents will have shifts if they are involved in interactions with metal ions either as
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covalent, complexation, hydrogen bonding or other electrostatic interactions. The infrared spectrum of the PTPS adsorbent is shown in Figure 7, while that after Cd(II) ion sorption is presented in Figure 8.

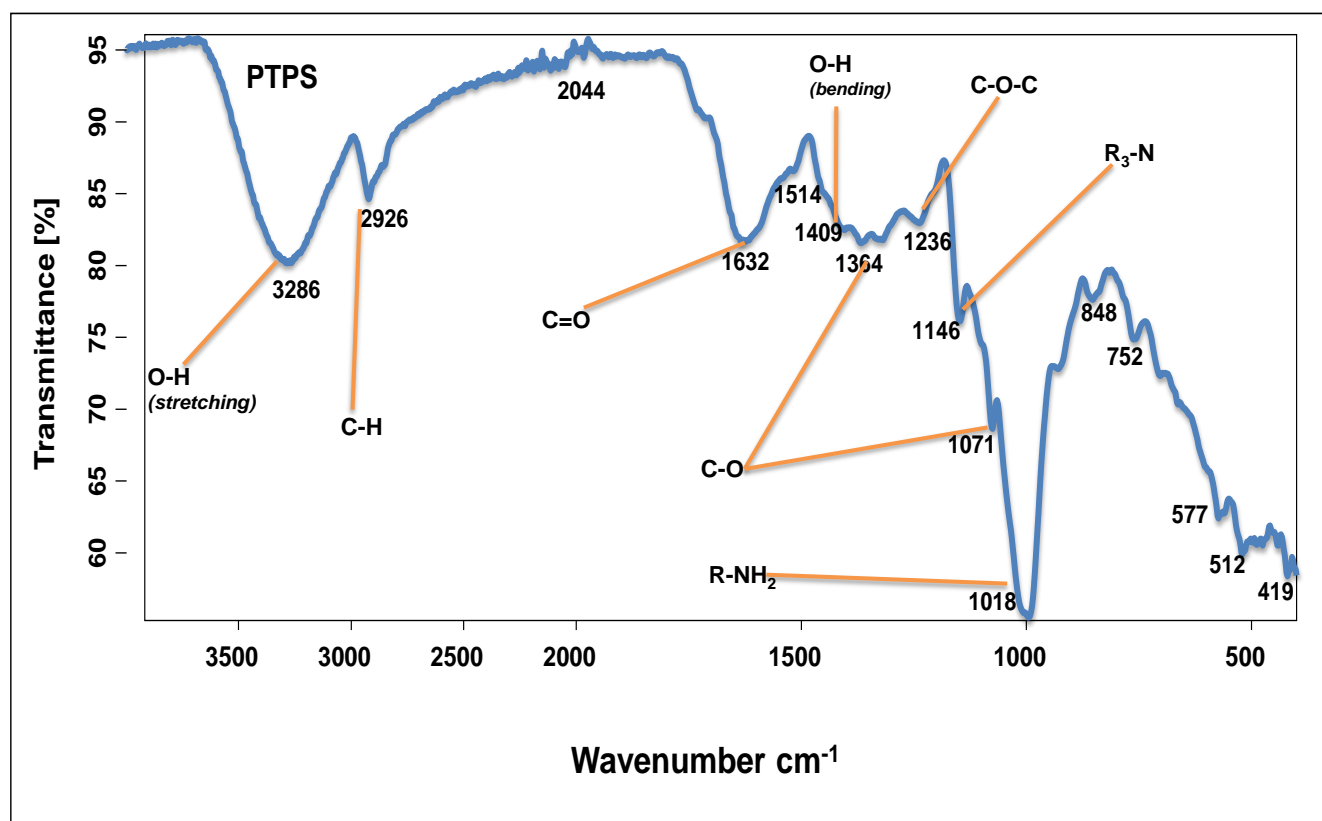


Figure 7: ATR-FTIR spectrum of Sweet potato adsorbent PTPS

The FT-IR spectrum in Fig. 7 indicates a strong broad peak at 3286 cm^{-1} which confirms the presence of free and H-bonded -OH stretching vibration of the hydroxyl group within the cellulose, hemicellulose and lignin in the adsorbent structure (Ahmed *et al.*, 2014). This can also be associated with the presence of water molecules adsorbed onto the adsorbent surface (Rao *et al.*, 2006). The vibration observed at 2926 cm^{-1} corresponds to the C-H stretching of the methyl and methylene groups in the polymers in the adsorbent such as lignin, cellulose and hemicellulose (Farooq *et al.*, 2011). The carbonyl-C=O stretching vibration of aldehydes and ketones and the C=C of the benzene ring stretching is indicated at 1632 cm^{-1} which is indicative of the aromatic compounds in the lignin components of the PTPS adsorbent (Farooq *et al.*, 2011; Yang *et al.*, 2007; Johari *et al.*, 2015). The peaks at 1071 and 1364 cm^{-1} were assigned to the stretching vibrations of the hydroxyl and C-O stretching vibrations of the carboxylate group in the lignin, hemicellulose and cellulose (Naiya *et al.*, 2011; Bodirlau *et al.*, 2009; Fan *et al.*, 2012). The O-H bending vibration peak is observed at 1409 cm^{-1} and the

peak at 1236 cm^{-1} can be associated to the C-O-C stretching vibration of the aryl-alkyl-ether linkages and phenolic O-H plane deformation in the cellulose and hemicellulose components of the lignocellulosic structure of the adsorbent (Yang *et al.*, 2007; Bodirlau *et al.*, 2009; Fan *et al.*, 2012). Furthermore, the primary amine functional groups can be associated to the vibrations observed at 1018 cm^{-1} , while the vibration at 1146 cm^{-1} may be associated to the tertiary amine stretching on the adsorbent surface (Ahmed *et al.*, 2014). The carboxylate and hydroxyl groups on lignocellulosic materials have been reported to have the potential to interact with metal ions during adsorption (Naiya *et al.*, 2011) and since the PTPS adsorbent had these groups, their role in adsorption of metal ions was examined by characterising the PTPS-Cd adsorbent using FT-IR after Cd (II) adsorption and this is presented in Figure 8.

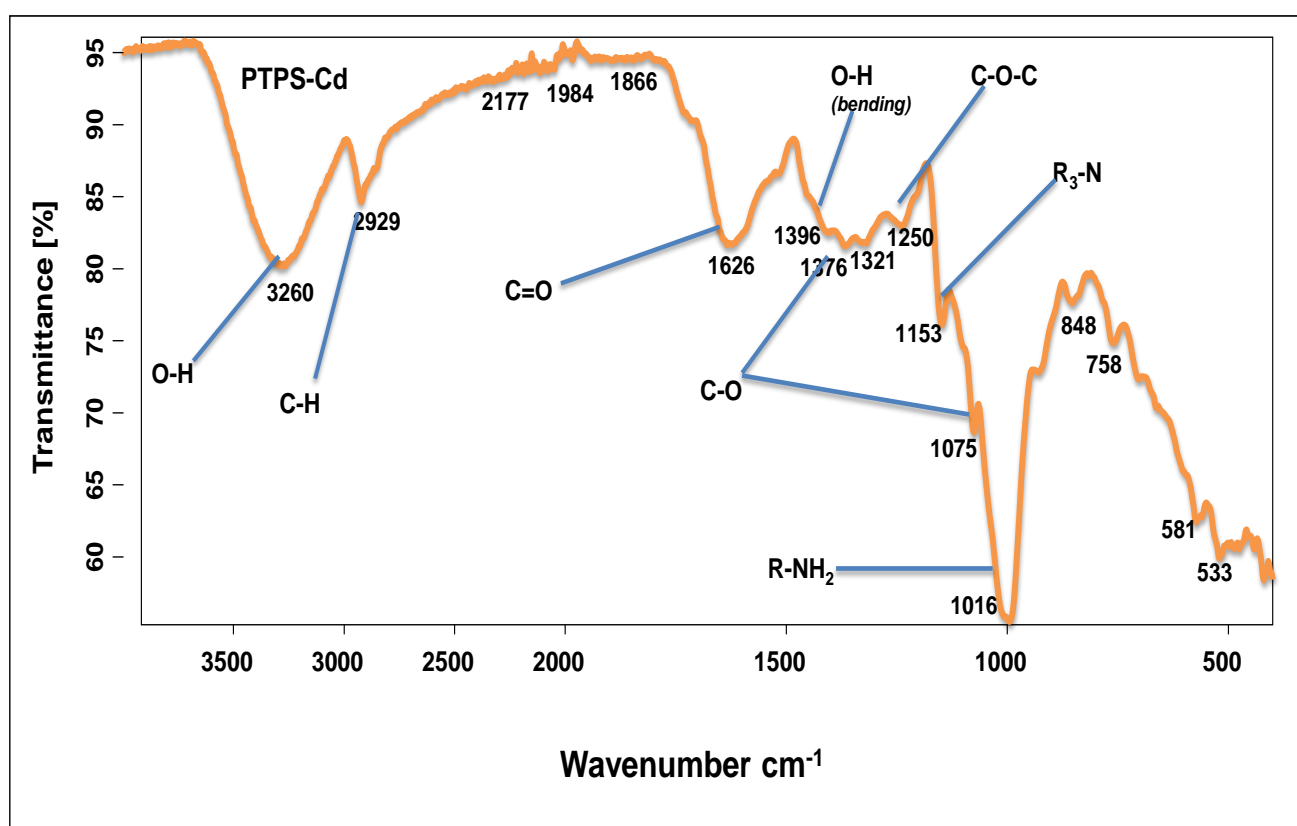


Figure 8: ATR-FTIR spectrum of PTPS adsorbent after Cd(II) adsorption

From Figure 8 it can be observed that spectrum of loaded adsorbent has some characteristic frequency shifts in vibration intensity on some of the bands. One prominent band is the OH-stretching and bending vibrations which confirms the participation of these groups on the residue surface in adsorption interactions. The O-H group vibration present at 3286 cm^{-1} in Figure 7 was observed to shift to 3260 cm^{-1} after the adsorption of Cd(II) ions -PTPS-Cd (Figure 8) due to interactions with the metal ions. The band representing the carboxylate functional group stretching vibrations was also observed to shift from 1364 cm^{-1} to 1376 cm^{-1}

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in the adsorbent after Cd (II) ion sorption. These shifts in vibrations presupposes that the hydroxyl and carboxylate groups on the PTPS adsorbent had chemical interactions with the Cd(II) ion which may be due to surface adsorption and complexation resulting in the decrease in the frequency of the vibrations (Naiya *et al.*, 2011). Furthermore, from Figure 8 it can be observed that there were shifts in vibrations associated with the O-H bending vibrations (1409 to 1396 cm^{-1}), C-O-C stretching of the alkyl ether groups (1236 to 1250 cm^{-1}) and the disappearance of the carboxyl (C=O) vibration observed at 1514 cm^{-1} . These shifts in the vibrations associated with these functional groups indicated that inference can also be made that the Cd(II) bonding on the PTPS adsorbent were to functional groups such as carboxylate groups in (cellulose, hemicellulose and lignin), phenolic groups in (lignin and extractives) and hydroxyl groups associated with cellulose, lignin, hemicellulose, extractives and pectin (Pandey *et al.*, 2015). The shift in the vibrations of the functional groups after metal ion sorption as observed in FTIR spectrum of the PTPS adsorbent after Cd(II) adsorption can be explained based on the change in coordination sites of the functional groups due to the interactions with the Cd(II) ion. This observation has also been reported by Thirumavalavan *et al.*,(2011) in their study on the Fourier Transform spectroscopic analysis of fruit peels before and after adsorption of heavy metal ions from aqueous solution. In their study, it was observed that the C-H peak intensity was reduced on the fruit peels after adsorption, while on some peels the peaks were absent.

3.2 Metal ion sorption studies

From the characterisation of the residue adsorbents a number of parameters were chosen to evaluate their impact on the removal of Cd(II) using the PTPS residue adsorbent. From the results of the zeta potential and pHpzc characterization of the residue, the pH of 6.5 was chosen for Cd (II) ion sorption studies as the results from the pHpzc characterisation previously described indicated that the pHpzc of the PTPS adsorbent was 6.3. Thus for an adsorption system designed for the removal of positive species {Cd(II)} to be effective, the pH of the adsorbate must be higher than the pHpzc (Noamanbhay and Palanisamy, 2005), hence the pH of 6.5 was chosen. This pH is also within the window of pH for discharged effluents (6.5-9.5) based on the WHO standard guidelines (Ipeaiyeda and Onianwa, 2011). The parameters studied were contact time, pH and in addition equilibrium sorption studies was also carried out to evaluate the metal ion loading for the adsorbent. For the determination of

metal ion loading after sorption the amount of metal ion adsorbed was computed based on eqn.1.

3.2.1 Effect of Adsorbate pH

The pH of an aqueous solution is a fundamental parameter that influences the sorption of metal ions due to its effect on the speciation of ions in solution and hence the types of ions that are available at particular hydrogen or hydroxyl ion concentrations to facilitate their removal by the adsorbents (Teker *et al.*, 1999; Antunes *et al.*, 2003). The effect of pH was studied based on the procedure described previously in this study. pH 2 – 10 was taken as the window for analysis for all adsorbents as the pH of range for discharged effluents based on WHO standard guidelines (6.5 – 9.5) is within this window (Ipeaiyeda and Onianwa, 2011). In addition, metal ion precipitation has been reported for both Cd(II) ions as the pH increases from 10 to 12 and this was also observed to occur during the evaluation of these heavy metal ions using natural adsorbents (Ho *et al.* 2002). The effect of pH on Cd(II) ion sorption is shown in Figure 9 and from the figure, it is observed that the optimum pH for Cd(II) ion removal using the PTPS adsorbent was 7. The initial and final pH of the adsorbate solution during the sorption of Cd(II) ions is also presented in Table 3. From Figure 9, it can be observed that the amount of Cd(II) ions adsorbed increased slowly at first with increase in initial pH from 2 to 4, reached a maximum value at pH 7.0 for Cd(II) and thereafter gradually decreased as the pH increased up to pH 10. At pH 2, the amount of Cd(II) adsorbed ions was least when compared to the other pH values and it is presumed that the amount adsorbed at pH 2 was low due to the influence of protons in solution leading to a charge reversal on the adsorbent surfaces which favours the repulsion of the metal on ions ultimately leading to a reduction in the binding ability of the adsorbent.

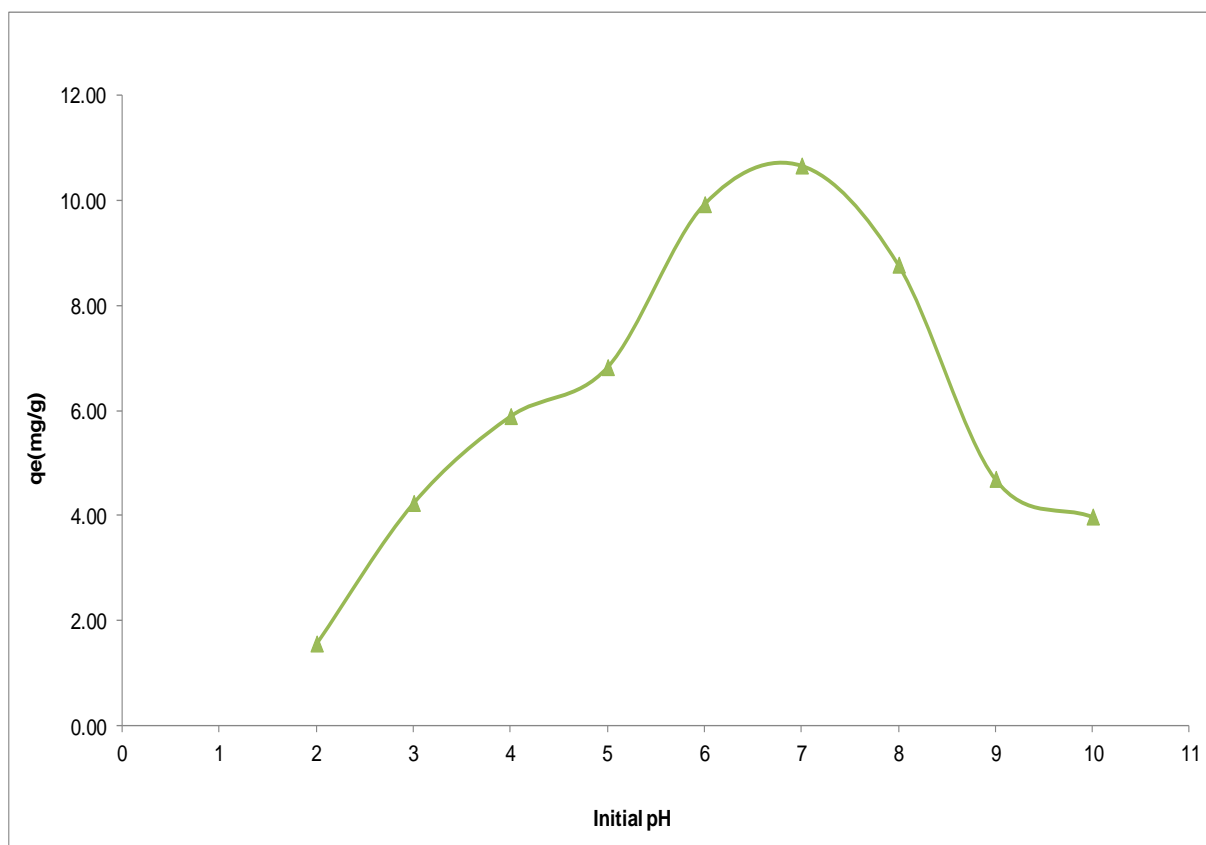


Figure 9: Effect of pH on the sorption of Cd(II) ion onto PTPS adsorbent-Initial conc-500mgL⁻¹, 180 mins and 2.0g of adsorbent.

Table 3: Initial and final pH of adsorbate solution for PTPS sorption of Cd(II)

Initial	2	3	4	5	6	7	8	9	10
Final	2.4	3.3	5.2	5.2	5.3	5.4	7	7.8	9.8

This can be explained based on the surface complexation theory which states that the increase in metal removal as pH increases can be associated to a decrease in competition between protons and metal species for the surface of active sites and by a decrease in positive charge (Krishnani *et al.*, 2008). Hence low pH values would favour protonation of the groups at the binding sites (hydroxyl, carboxyl, phenolic) and high pH values on the other hand would lead to the precipitation of metals especially at alkaline medium (pH 9 to 10) thereby reducing the amount of metal ions adsorbed by the PTPS adsorbents as can be observed in Figure 9. It was also observed from Table 3, that the final pH after metal ion sorption was lower than the initial pH between pH 6-8 where maximum sorption of the Cd(II) existed as observed in Figure 9. This can be related to the mechanism of Cd(II) uptake onto the adsorbent which may

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cause the displacement of hydrogen ions (H^+). Furthermore, the sorption of Cd(II) by the PTPS adsorbent may occur via a process that starts by the deprotonation of groups such as -COOH, $-NH_2$ leading to release of H^+ into the adsorbate system. The Cd(II) ions which are positively charged are thereafter attracted to the active adsorption sites- which are negatively charged (COO^- , NH_2 groups) and becomes coordinated with the deprotonated functional groups via coordinating bonding to the form an adsorbent metal complex. This scenario has been illustrated by Vagheti *et al.*, (2009). This mechanism of proton release during the surface complexation step may account for the decrease in the pH of the adsorbate after sorption between the pH 6-8 where there was substantial Cd(II) sorption which reduces as the pH further increases up till pH 10.

Sari *et al.*, (2008) reports that metal ion removal by sorbents often involves complex mechanism such as ion exchange, chelation, adsorption by physical forces, ion entrapment in the intrafibrillar capillaries and spaces of the adsorbents and since the adsorbent surface is composed of functional groups such as carbonyl, hydroxyl, and amine these group will be involved in all potential metal ion binding mechanism. The processes may result in the elimination of H^+ from the adsorbent surface onto the adsorbate thereby increasing the pH of the adsorbate after sorption.

3.2.2 Sorption Kinetics

The effect of contact time on the removal of Cd(II) metal ion from an aqueous solution using the PTPS adsorbent is an important characteristic of an adsorption system as it gives insight into the nature of adsorbent – adsorbate interactions as well as the transport profiles during metal ion uptake. The effect of contact time on Cd(II) ion uptake using the PTPS adsorbent was studied at pH 6.5 with initial metal ion concentration of 500 mg l^{-1} temperature of 25°C and a volume of 0.1 L. The amount of the PTPS adsorbent used was 2.0 g and the duration of kinetic studies was from 5 to 1440 minutes (72 h). The kinetic profile for Cd(II) is shown in Figure 10 .

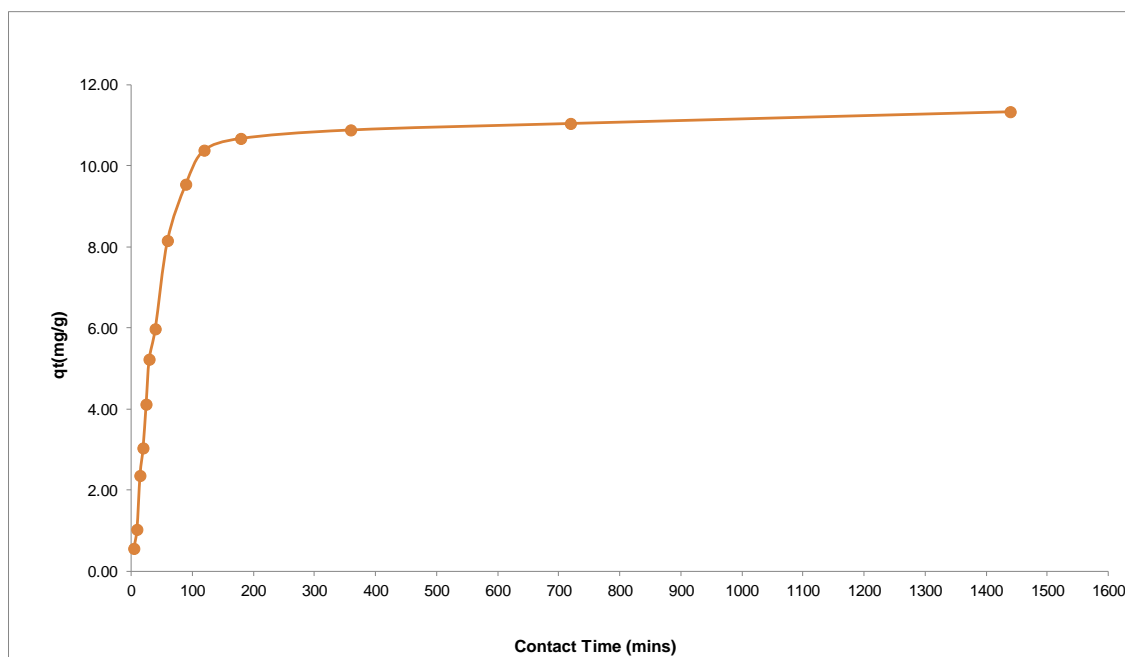


Figure 10: Effect of contact time on Cd(II) ion sorption on PTPS adsorbent Initial conc- 500mgL^{-1} , pH-6.5 and 2.0g of adsorbent.

From Figure 10, it is observed that there was a rapid uptake of metal ions by the adsorbents up to 180 minutes and a gradual loading up to 1440 minutes. The Cd(II), ion maximum loading at attainment of equilibrium time for the PTPS adsorbent was 11.34 mgg^{-1} . An examination of Figure 10 indicates that the metal ion loading on the adsorbent occurred in two stages over the duration of contact. The first stage was characterised by a fast uptake lasting up to 180 minutes for all the residues and the second stage proceeded slowly from 180 minutes up till 1440 minutes where equilibrium was attained. This two stage process can be explained based on the availability of active sites on the PTPS adsorbent for Cd(II) ion loading. At inception of the metal ion-adsorbent contact, there are a number of readily accessible active sites on the adsorbent surface making the uptake of the Cd(II) ions onto these sites rapid. The shape of the curve is due to a combination of two processes, a rapid process and a slow process. The rapid process could be due to primary attachment to “exposed” sites, while the slow process could be due to the re-arrangement of attached Cd (II) to hidden active sites. Alternatively the rapid process could be viewed as a result of the attachment to “exposed” sites with a slow pore diffusion process occurring in parallel as Cd(II) diffuses along the pores to “enclosed” active sites leading to the slow process. (Sarada *et al.*,2014). Krishnani *et al.*, (2008) also reports a two stage metal ion sorption for rice husk for the removal of a number of heavy metal ions in which the first stage was within 90 – 120 minutes after which equilibrium was reached at 150 minutes contact time. It is pertinent to note that the maximum loading for the Cd(II) ion for the adsorbent after 1440 minutes (72h)

(11.3mgg⁻¹) was close to the values after 180 minutes (10.6mgg⁻¹). Hence from the metal ion kinetic results, the time 180 minutes was taken as the time for further sorption experiments. This was because in the design of sorption systems, the attainment of rapid kinetics for metal ion sorption is an important parameter as it facilitates the utilization of smaller reactor volumes thereby ensuring high sorption efficiency and improves the economics of the adsorption process, which is a fundamental parameter in the scale-up of batch adsorption systems (Loukidou *et al.*, 2004; Perez-Marín *et al.*, 2007).

3.2.3 Kinetic Modelling

The kinetics of metal ion sorption processes in a batch system is also used to determine the type of processes that govern the mechanism of sorption. Kinetic data for metal ion sorption can be used to determine the type of mechanism governing the process and possibly also the potential rate controlling step of the adsorption process. The mechanism of an adsorption process depends on the physical and chemical characteristics of the adsorbent as well as the mass transfer process from the adsorbate onto the adsorbent (Kumar *et al.*, 2014). Hence the discrimination of an adsorption mechanism may often involve the use of kinetic models that ascertain the mechanism governing the metal ion sorption based on shapes and fitting of kinetic plots which have fundamental assumptions in their design that can be extrapolated to the system under investigation. The information from the kinetic modelling can be used to interpret the type of transport mechanism and the description of the sorption process can therefore be carried out (Farooq *et al.*, 2011; Kakalanga *et al.*, 2012; Perez-Marín *et al.*, 2007). In this study, two adsorption reaction kinetic models {pseudo-first order (PFO) and pseudo-second order (PSO)} and one adsorption diffusion model (intraparticle diffusion model) were applied to investigate the kinetics of Cd(II) ion adsorption onto the PTPS adsorbent.

Pseudo first order model

In 1898, Lagergren presented the first order rate equation for the adsorption of oxalic acid and malonic acid onto charcoal to explain the kinetics of adsorption on solid surfaces. In order to distinguish the kinetic processes based on concentration of solution and adsorption capacity of solid, this Lagergren equation is called the pseudo-first order equation (Lagergren, 1898; Ho, 2004a) was the first rate equation developed for sorption in liquid/solid systems and it is based on solid capacity (Ho, *et al.*, 2004). It is one of the most widely used rate equations reported in adsorption kinetic literature. Assuming that in a solid liquid adsorption system, the

adsorption rate was proportional to the number of effective adsorption sites and then the rate of adsorption would be expressed as eqn (2):

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad (2)$$

where q_e and q_t are the sorption capacities, at equilibrium and at time t , respectively ($\text{mg}\cdot\text{g}^{-1}$), while K_1 is the rate constant of the pseudo-first order sorption (lmin^{-1}). After integration and applying boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of eqn (3) is expressed as:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (3)$$

Equation 3 is the linear form of the equation and the most common form of the pseudo first order (PFO) equation reported in literature for the description of sorption. Xuan *et al.*, (2006) used the linear pseudo first order equation to describe the kinetics of Pb(II) biosorption onto pre-treated chemically modified orange peel. Ho *et al.*, (2004) has also reported on the sorption of Pb(II) from aqueous solutions using tree fern adsorbent in which the linear form of the PFO equation was used. However, a number of studies have reported that the linear form of the PFO equation may lead to error propagation in the results due to the transformation of the PFO equation which is in a non-linear form to a linear form thereby implicitly altering the error structure in the determination of the model parameters (Ho, 2004b; Lin and Wang, 2009). The non-linear form of the PFO is given as eqn (4) as:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (4)$$

The non-linear form of the PFO will be used to model the kinetics of sorption of Pb(II) and Cd(II) onto the different adsorbents developed in this study and eqn. 4 represents the reversible interaction between the adsorbate and adsorbent and is used for the prediction of the physisorption of the adsorbates onto the adsorbents in the system under consideration.

Pseudo second order model

The reaction kinetics of adsorption is the basis of the adsorption reaction models used in kinetic modelling and one of the most commonly used reaction models for the description of the kinetics of adsorption is the pseudo-second order model proposed by Y.S. Ho in Ho, (2006). This model was proposed in an attempt to present the equation that represents the

adsorption of divalent metals onto sphagnum moss peat during agitation. An assumption was made that the process may be second-order and that sorption depends on the adsorption capacity of the adsorbent which is associated with the number of available active sites. This pseudo second order kinetics is presumed to proceed via chemisorption which involves valence forces through the sharing or exchange of electrons between the peat and the divalent metal ion as covalent forces (Ho, 2006). In the work of Ho (2006), the adsorbent used was peat which has a number of polar functional groups and these include ketones, phenolic acids and aldehydes. These chemical species on the surface of the peat are active sites that can be interact via chemical bonding. These groups are therefore the sites for the cation exchange capacity of the peat. Based on the above process and according to Coleman *et al.*, (1956), the peat–copper reaction may be represented in two different forms as shown in the equations below:



where P^- and HP are polar sites on the peat surface.

Here the rate of the second order reaction may be dependent on the amount of the divalent metal ions on the surface of the peat at time “t” and the amount of the divalent metal ions adsorbed at equilibrium, the assumption is also may that the adsorption follows the Langmuir equation (Ho and McKay, 2000; Ho, 2006; Qiu *et al.*, 2009). Hence, the rate expressions for the adsorption according to Ho and McKay, (2000) can be described by eqns. (7) and (8) as:

$$\frac{d(P)_t}{dt} = K[(P)_0 - (P)t]^2 \quad (7)$$

or

$$\frac{d(HP)_t}{dt} = K[(HP)_0 - (HP)t]^2 \quad (8)$$

Where $(P)_t$ and $(HP)_t$ are the number of active sites occupied on the peat at time t, and $(P)_0$ and $(HP)_0$ are the number of equilibrium sites available on the peat. Therefore the driving force $(q_e - q_t)$ is proportional to the available fraction of active sites. Thus from the above, the kinetic rate equation can be written as follows (Ho and McKay, 2000; Ho and Chiang, 2001; Ho, 2006):

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad (9)$$

Where q_e and q_t are the sorption capacities at equilibrium and at time t , respectively (mg g^{-1}) and K_2 constant is the rate constant of the pseudo-second order sorption ($\text{g mg}^{-1} \text{min}^{-1}$). For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of eqn. (9) becomes (Ho and McKay, 2000):

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + K_2 \cdot t \quad (10)$$

This is the integrated rate law for a pseudo-second order reaction. Eqn. (10) can be rearranged to obtain:

$$q_t = \frac{t}{\frac{1}{K_2 q_e^2} + \frac{t}{q_e}} \quad (11)$$

Eqn (11) has the linear form:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (12)$$

Where h ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$) can be regarded as initial sorption rate as $q_t/t \rightarrow 0$, hence:

$$h = K_2 \cdot q_e^2 \quad (13)$$

Equation (13) can be written as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (14)$$

Equation (14) is the linear form of the pseudo second order equation (PSO) that is commonly reported in literature. This linear form causes distortion in the error structure when used to plot the PSO model leads to differences in model data between the non-linear and linear techniques in modelling the pseudo second order equation (Ho, 2004b; El-Khaiary et al., 2010). Hence, the better option is the use of the non-linear method as the pseudo second order equation is a non-linear equation and the numerical optimization used to determine parameters will provide a more accurate representation of the model and the parameters

within it than a linearization plot which often leads to propagation of errors in a model, (El-Khaiary *et al.*, 2010). This non-linear approach will be applied for the modelling of the sorption kinetics of Cd(II) ion sorption onto the PTPS adsorbent and the non-linear PSO equation that will be used for the kinetic modelling is given by Lin and Wang, (2009) as:

$$q_t = \frac{K_2 \cdot qe^2 t}{1 + K_2 qe t} \quad (15)$$

Thus, equation (15) was used to model the non-linear pseudo second order kinetics for the sorption reported in this work and it assumes a stronger interaction between the adsorbate and adsorbent based on the chemisorption of the adsorbates onto the adsorbents in the system under consideration. One advantage of using the pseudo second order equation for the modelling of adsorption kinetics is that there is no need to know the equilibrium capacity from the experiments, as this value, the pseudo second order rate constant and the initial adsorption rate can be calculated from the model (Ho, 2006).

The co-efficient of determination (r^2) and two non-linear error parameters the chi-square test (χ^2) and the root mean square error (RMSE) were used to analyse the two kinetic models (Basha *et al.*, 2009; Hossain *et al.*, 2013). The coefficient of determination (r^2) formula is given in Eqn. 16 as follows:

$$r^2 = \frac{\sum(qe_{model} - qe_{av})^2}{\sum(qe_{model} - qe_{av})^2 + \sum(qe_{model} - qe_{exp})^2} \quad (16)$$

The non-linear error functions of Chi-square test (χ^2) and the root mean square error (RMSE) were used to evaluate the model and these are given in eqns. 17 and 18 as follows:

$$\chi^2 = \sum_{n=1}^n \left(\frac{(qe_{exp.n} - qe_{model.n})^2}{(qe_{exp.n})} \right) \quad (17)$$

$$RMSE = \sqrt{\frac{1}{m-p} \sum_{i=1}^m (qm - qe)^2} \quad (18)$$

Where: qe_{model} is the equilibrium capacity obtained from the isotherm model

qe_{exp} is the equilibrium capacity obtained from experiment

qe_{av} is the average qe_{exp} .

qe and qm are the measured and model amount of cadmium(II) ion adsorbed at time t respectively

m is the number of data points evaluated

p is the number of parameters in the regression model

Whereby smaller the RMSE and χ^2 values and the higher the r^2 value indicates better fitting of model with the experimental data (Basha *et al.*, 2009).

Kinetic modelling of Cd(II) sorption using the PFO and PSO equations were carried out using the solver add-in optimization procedure in Microsoft excel 2010. The plots of the PFO and PSO models are presented in Figures 11. From these models, the kinetic parameters and their respective error functions obtained are presented in Table 4.

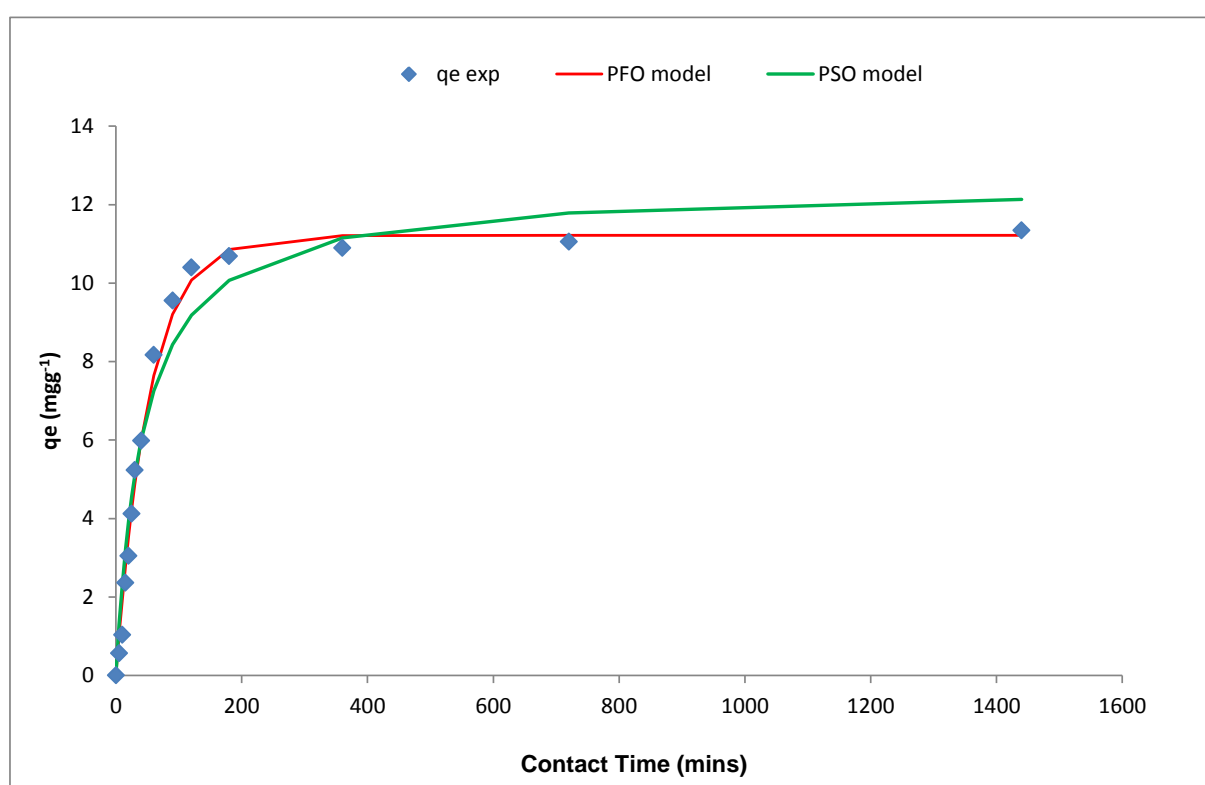


Figure 11: Pseudo-first order (PFO) & pseudo-second order (PSO) kinetic plot for PTPS adsorbent

The results presented in figure 11 and Table 4 indicates that the two models (PFO& PSO) could be used to characterise the kinetics of Cd(II) ion sorption and their prediction of the parameter ($q_{e,model}$) is close to the result obtained from the experimental analysis of Cd(II) ion sorption. For the PFO model the $q_{e,model}$ obtained was 11.2 mgg^{-1} and the rate constant of the pseudo first order reaction was $1.91 \times 10^{-2} \text{ min}^{-1}$, while for the PSO model the $q_{e,model}$ from the non-linear optimization was 12.5 mgg^{-1} and the rate constant of the pseudo second order reaction was $1.85 \times 10^{-3} \text{ gm}^{-1} \text{ min}^{-1}$.

These two models have different fundamental assumptions that premise their existence and this is used to interpret the significance of the rate constants. For the PFO model, the rate constant K_1 is based on the relationship between the sorption rate and equilibrium, whereby the assumption is that the kinetic rate is dependent on the concentration of ions in solution (Miyake *et al.*, 2013; De Haro-Del Rio *et al.*, 2015; Qiu *et al.*, 2009). On the other hand for the PSO model, the rate constant K_2 is based on the assumption that the chemisorption based interactions between the ions and the sorbent are the rate limiting step, whereby sorption is dependent on the adsorptive solid capacity in the form of available fraction of active sites on adsorbent (Ho and McKay, 1999; Ho and McKay, 2004; De Haro-Del Rio *et al.*, 2015; Qiu *et al.*, 2009; Ho and McKay, 1998).

Table 4: Kinetic models parameters for Cd(II) sorption on PTPS adsorbent

Kinetic Models	Parameters	Values
Pseudo-first order	$q_{e,cal} (mgg^{-1})$	11.2
	$K_1 (min^{-1})$	1.91E-02
	r^2	0.99
	χ^2	0.02
	RMSE	8.84E-02
Pseudo-second order	$q_{e,cal} (mgg^{-1})$	12.5
	$K_2 (gmg^{-1}min^{-1})$	1.85E-03
	$h (mgg^{-1}min^{-1})$	0.29
	r^2	0.96
	RMSE	3.52E-01
Intraparticle Diffusion	$K_{id}(mgg^{-1}min^{-0.5})$	1.119
	C	8.96E-01
	r^2	0.98

The assumption of the pseudo-second order model is that one cadmium ion is adsorbed onto two sorption sites on the surface of the PTPS adsorbent which can be represented as eqn(19) according to Boparai *et al.*, (2011).



Where A is an unoccupied sorption site on the adsorbent and K_2 is the pseudo second order rate constant($gmg^{-1}h^{-1}$). From the plot in Figure 11 and Table 4, it is observed that the $q_{e,model}$ of the PSO is after 72h sorption is $12.5mgg^{-1}$, while that of the PFO model is $11.2 mgg^{-1}$, whereas and the $q_{e,exp}$ was $11.34mgg^{-1}$, therefore it can be deduced that the value of q_e from

1 the PFO model is in closer agreement to the value obtained experimentally. Thus, it can be
2 said that the PFO model gave a better approximation of the kinetics of Cd(II) sorption than
3 the PSO order model and this can also be seen in the error parameters and correlation
4 coefficient values. This suggests that the kinetics supports the assumption that the rate limiting
5 step of Cd(II) ion sorption onto the PTPS adsorbent is dependent on the concentration of the
6 Cd(II) ions in solution (Kumar *et al.*, 2014). However, the closeness of the parameters
7 obtained from the PSO indicate that chemical interactions between the ions in the adsorbate
8 solution and the adsorbent may still influence sorption kinetics but this may depend on the
9 rate of diffusion. This implies that pore diffusivity of the ions onto the active sites may also
10 influence the kinetics as previously discussed in the analysis of the two stage metal uptake
11 (fast and slow) kinetics of Cd(II) ion sorption. To evaluate the diffusion effect on the
12 kinetics of Cd(II) ion sorption the intraparticle diffusion model was used to discriminate the
13 kinetics of Cd(II) ion sorption.

22 *Intraparticle Diffusion Model*

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26 Diffusion mass transport models have been applied to sorption systems and their role in
27 pollutant sorption is extremely important. Generally, the adsorption process description using
28 these diffusion models are usually based on one or more of the following, mechanistic steps:
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- 31 (i) Diffusion of the solute from the solution to the film surrounding the particle.
- 32 (ii) Diffusion from the film to the particle surface (external diffusion),
- 33 (iii) Diffusion from the film to the internal sites (surface or pore diffusion)
- 34 (iv) Metal ion uptake which can involve several mechanisms

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41 The Weber and Morris intraparticle diffusion model is based on the assumption that the
42 adsorption process may be controlled either by one of the following steps such as; film
43 diffusion, pore diffusion, surface diffusion and adsorption onto the adsorbent pore surface or a
44 combination of more than one step (Weber and Morris, 1963; Fierro *et al.*, 2008). These
45 regimes can be obtained in a stirred batch system, wherein the diffusive mass transfer can be
46 related by an apparent diffusion coefficient, which fits into an experimental sorption rate data
47 (Fierro *et al.*, 2008). The intraparticle diffusion model assumes that in batch adsorption
48 process, the adsorbate diffuses into the interior of the adsorbent and this process is dependent
49 on the square root of time ($t^{1/2}$) rather than time (t), where the intercept (C) is related to the
50 boundary layer (Azarudeen *et al.*, 2015; Qiu *et al.*, 2009; Gurses *et al.*, 2014; Alkan *et al.*,
51 2007). The relationship for the model is given as follows:
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$$q_t = K_{id}t^{1/2} + C \quad (20)$$

Where q_t is the amount of Cd (II) adsorbed at time t (mg g^{-1}), K_{id} is the intraparticle diffusion constant ($\text{mg g}^{-1} \text{min}^{-1/2}$) and C is the constant related to the thickness of the boundary layer (Ahmadi *et al.*, 2015). A plot of q_t vs $t^{1/2}$ gives a straight line if intraparticle diffusion is the rate limiting step in the adsorption. However, this is not always the case as other processes such as film diffusion and equilibrium adsorption may also be rate limiting for different stages of the kinetic profile and this will result in multi-linearity in the intraparticle diffusion plot (Fierro *et al.*, 2008; Basha *et al.*, 2009; Qiu *et al.*, 2009). The plot of the Weber and Morris intraparticle diffusion model for the adsorption of Cd(II) ion onto the PTPS adsorbent is shown in Figures 12 and 13 and Table 4 presents the model constants obtained from the plot.

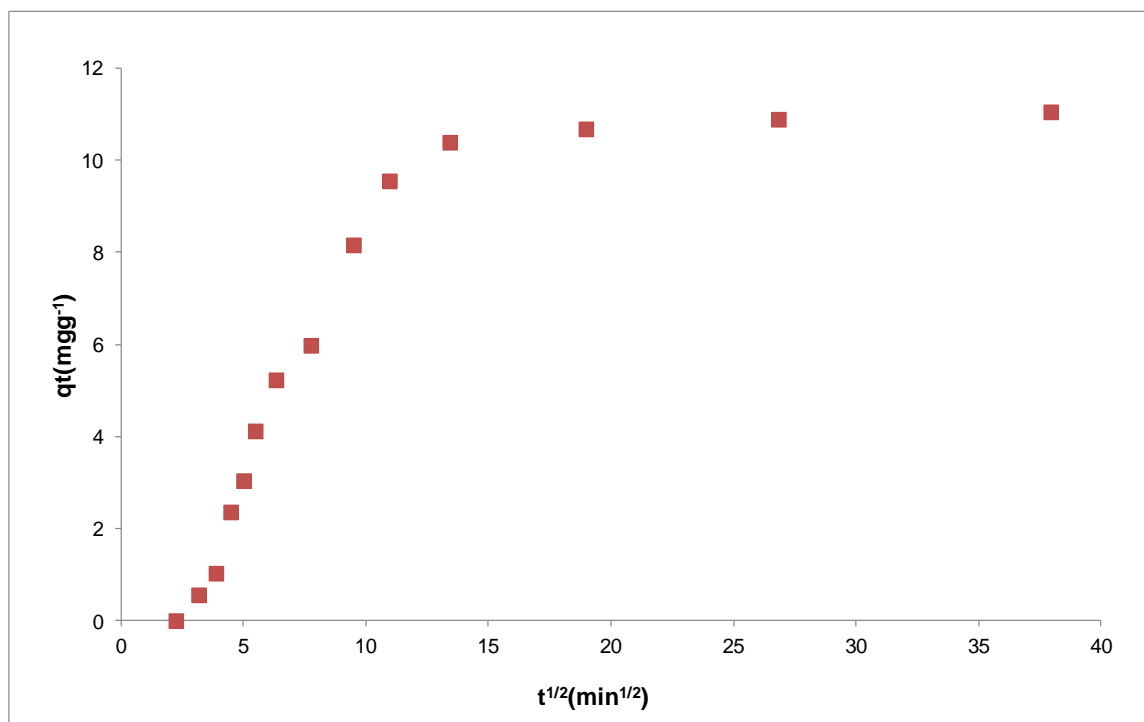


Figure 12: Intraparticle diffusion plot of Cd(II) ion sorption on PTPS residue adsorbent

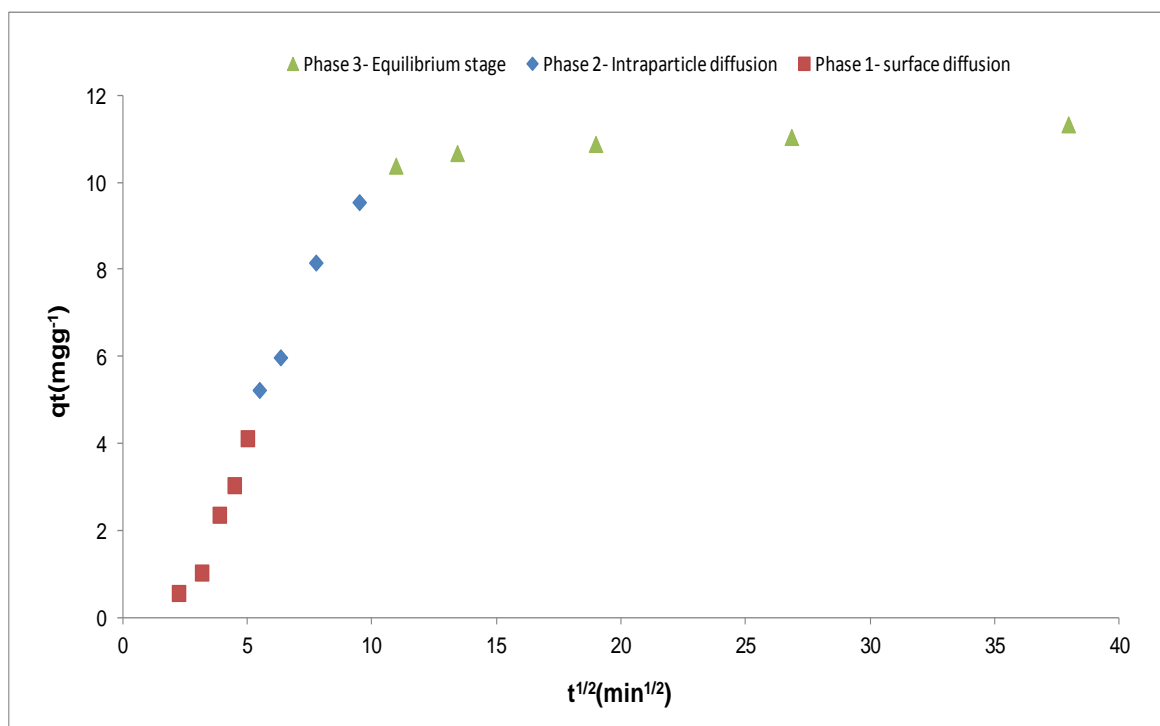


Figure 13: Kinetic stages in intraparticle diffusion plot of Cd(II) ion sorption on PTPS residue

From Figures 12 and 13, it is observed that the intraparticle diffusion plot is made up of 3 linear regions. Hence it is proposed that the sorption of Cd(II) ions onto the PTPS adsorbent occurred via 3 phases wherein:

- The initial first phase represents the region of external surface diffusion in which film diffusion pre-dominates the kinetics of Cd(II) uptake and is characterised by the diffusion of the Cd(II) ions across the boundary layer
- The second phase represents a gradual sorption of the Cd(II) ions onto the PTPS adsorbent where it is suggested that the intraparticle diffusion of the metal ions within the pores of the adsorbent is rate limiting (Sengil *et al.*, 2009) and
- The third phase is the process associated with the attainment of equilibrium during the sorption process seen as the plateau region wherein the uptake is slowed due to the low Cd(II) ion concentration in the adsorbate as well as the lower availability of active sites on the PTPS adsorbent for Cd(II) ion uptake and the repulsive interactions existing on the surface of the adsorbent (Basha *et al.*, 2009; Sengil *et al.*, 2009).

From the intraparticle plot and the above observation, phase 2 of the kinetic profile was taken as the region where intraparticle diffusion kinetics dominates and the intraparticle diffusion rate constant for the model (K_{id}) is $1.119 \text{ mg g}^{-1} \text{ min}^{-0.5}$. It should be noted that due to the existence of these multiple steps in the rate of Cd(II) ion uptake and since the intraparticle

diffusion plot for Cd(II) ion sorption did not go through the origin, then the diffusion controlled sorption process can be said to have been controlled by the three process described above and not just the intraparticle diffusion step. This also can be associated to the differences in the rate of mass transfer between the initial and final stages of adsorption. However, at each phase of the kinetic profile, it is assumed that only one mechanism was dominant (Fierro *et al.*, 2008; Diagboya *et al.*, 2014; Olu-Owolabi *et al.*, 2014). Furthermore, the boundary layer parameter (C) obtained from the intraparticle diffusion plot is 0.895 and this gives an indication of the effect of the boundary layer thickness on the Cd (II) ion diffusion. A higher value for C indicates that there is a greater effect of the boundary layer on metal ion diffusion across the adsorbent surface (Li *et al.*, 2012; Olu-Owolabi *et al.*, 2014). However, the multiple steps that are observed to operate based on the different kinetic models during the kinetics of Cd(II) ion sorption suggest that there are a number of other factors that have to be taken into consideration in the evaluation of metal ion sorption in an aqueous system. These include the implications of the dilute aqueous system that adsorption is being carried out, the rate of change of adsorbate concentration with time as sorption progresses and the type of mass transport that might occur based on the nature of the adsorbent. All these parameters may in one way or the other influence the transport of the adsorbate ions through the concentration barrier onto the adsorbent surface or active sites and have to be taken into consideration when evaluating the kinetics of sorption.

3.2.4 Equilibrium Isotherm Modelling

The interaction in an adsorption system between the adsorbent and the adsorbate is a dynamic process and the quantification of the impact of the adsorbent on the adsorbate is described by the amount of adsorbate that is removed by the adsorbent. This also depends on the loading of the adsorbent. The loading of an adsorbent can be described by an equilibrium isotherm which is characterised by certain constants whose values express the surface properties and affinity of the adsorbent to the adsorbate (Sari *et al.*, 2008). Hence, equilibrium modelling or adsorption isotherms are studied to characterize the equilibrium. In order to represent the equilibrium adsorptive behaviour of the adsorbent-adsorbate interaction, it is important to have a satisfactory description of the equilibrium relationship between the two phases comprising the adsorption system. These equations represent the relationship between the amount of substance adsorbed on the adsorbent and the amount of adsorbate remaining in solution (Athar *et al.*, 2013; El-Ashtoukhy *et al.*, 2008). The adsorption equilibrium data

1 indicates the relationship between the mass of the adsorbate sorbed per unit mass of adsorbent
2 (q_e) and the adsorbate concentration for the solution at equilibrium C_e (Sarada *et al.*, 2014).
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4 Two equilibrium isotherm models were used to characterize the removal of Cd(II) and ion
5 from aqueous solution using the PTPS adsorbent. These were the Langmuir, Freundlich and
6 isotherms. The Langmuir isotherm model has been successfully applied to pollutant
7 biosorption processes and is one of the most widely used isotherm. A basic assumption of the
8 Langmuir isotherm is that sorption takes place at specific sites, which are uniformly
9 distributed across the surface of the adsorbent (Langmuir, 1918; Basha *et al.*, 2009). The
10 model can be written in its non-linear format as:
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$$16 \quad q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (21)$$

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22 Where q_e is the equilibrium metal ion concentration on the adsorbent (mgg^{-1}),

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24 C_e is the equilibrium metal ion concentration in the solution (mgL^{-1}),

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26 q_m is the monolayer adsorption capacity of the adsorbent (mgg^{-1}) also known as q_{max}

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28 K_L is the Langmuir adsorption constant (Lmg^{-1}) related with the free energy of adsorption (Sari
29 *et al.*, 2008).
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33 The second isotherm model considered in this study was the Freundlich isotherm. The
34 Freundlich isotherm assumes a heterogeneous adsorption surface and active sites with
35 different energy based on multilayer adsorption. The model estimates the adsorption intensity
36 of the adsorbate on an adsorbent (Freundlich, 1906; Athar *et al.*, 2013). The model in its non-
37 linear form is given as:
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$$42 \quad q_e = K_F (C_e)^{1/n} \quad (22)$$

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46 Where K_F is a constant relating to the adsorption capacity (mgg^{-1})

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48 C_e is the concentration of metal ions at equilibrium (mgL^{-1})

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51 $1/n$ is an empirical parameter relating to the adsorption intensity which varies with the
52 heterogeneity of the material (Sari *et al.*, 2008).
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56 To determine the goodness of fit of the isotherm models to the experimental data using non-
57 linear regression, the optimization procedure requires that error functions be defined to enable
58 the fitting of the model parameters with the experimental values. In this study, the coefficient
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of determination (r^2), the chi-square test (χ^2) and the root mean square error (RMSE) for each model were determined based on eqns. 16, 17 and 18 respectively. In this study, the non-linear form of the Langmuir isotherm was applied using the Excel solver add-in optimization procedure in Microsoft Excel 2010. This process uses the co-efficient of determination as the normalization parameter to optimize the model and correlate it with the experimental isotherm data. This is done by the software by minimizing the distance between the experimental data points and the theoretical isotherm model predictions with the solver add-in function of the Microsoft Excel (Wong *et al.*, 2004; Hossain *et al.*, 2013). The utilization of the non-linear isotherms in this study was done to eliminate the tendency of error bias often observed in the use of the linearized isotherms for analysis of adsorption isotherm data. This is based on the value of the r^2 obtained using the linearization of isotherm models. Wong *et al.*, (2004) observed that since the r^2 factor is based on the square of the difference between the theoretical and experimental data points in an isotherm plot, it will result in higher weighting to the higher C_e value data points. Therefore, due to the inherent bias resulting from linearization, isotherm parameters should be determined by using the non-linear forms of the isotherm model with the aid of the solver add-in facility in Microsoft Excel.

The plot of the experimental and isotherm plots for Cd(II) ion removal using the PTPS adsorbent is shown in Figure 14 and this figure indicates that the adsorption of the Cd(II) metal ion was concentration dependent increasing with increase in initial metal ion concentration (C_e). From these experimental values, equilibrium isotherm models (Langmuir and Freundlich) were used to further characterize the sorption process. Adsorption isotherm modelling carried out for Cd(II) ion removal from aqueous solution. The non-linear isotherm plots obtained for the Langmuir and Freundlich isotherms are shown in Figure 15 for Cd(II) ion sorption onto the PTPS adsorbent. From this plot, the Langmuir and Freundlich isotherm constants and the value of the coefficient of determination (r^2) for the PTPS adsorbent were obtained and these are presented in Table 5.

Langmuir Isotherm

For the Langmuir isotherm model, it can be seen that the experimental data were quite in agreement with the isotherm model values with coefficient of determination values of 0.97 for the PTPS adsorbent. This model assumes that there exist a monolayer coverage of the surface of the adsorbent with Cd(II) ions (Athar *et al.*, 2013). From this model, the value of Langmuir constant K_L obtained was $5.21 \times 10^{-3} \text{ lmg}^{-1}$ for the PTPS adsorbent as seen in Table 5. The value of the Langmuir isotherm constant q_{max} from the Langmuir isotherm plot is also seen in

Table 5. This value indicates the maximum monolayer capacity of the adsorbent based on the Langmuir isotherm assumption of a saturated monolayer. It should be noted that the value of the q_{max} for the PTPS adsorbent is higher than the experimental loading of the adsorbent at the initial concentration of 500mg l^{-1} , which was the maximum initial concentration used in this study. Hence, the isotherm constant q_{max} models that maximum adsorption loading (capacity) of the surface of the adsorbent assuming the Langmuir monolayer coverage. This q_{max} value is an important parameter that is used to aid the design of adsorption systems when scaling up an adsorption process as it provides information on the maximum saturation capacity of the adsorbent (Rao *et al.*, 2006). From Table 5, it is observed that PTPS had a q_{max} value of 18.9mg g^{-1} implying the amount of the Cd(II) ion that the adsorbent would be have the capacity to remove from the adsorbate per gram of adsorbent.

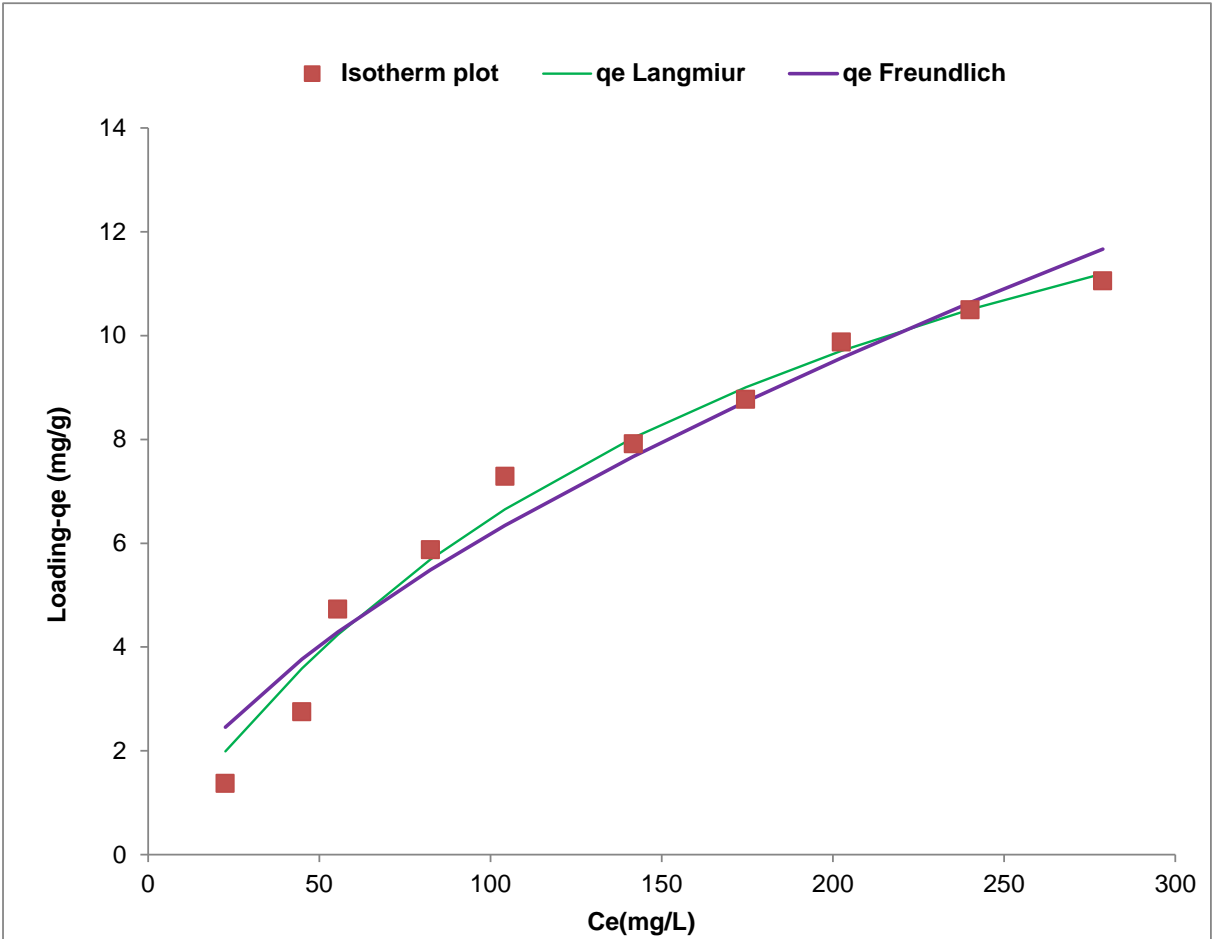


Figure 14: Langmuir and Freundlich equilibrium isotherm modelling for Cd(II) sorption on PTPS residue.

Table 5: Isotherm model parameters for sorption of Cd(II) onto PTPS adsorbent

Isotherm Models	Parameters	Values
Langmuir	$q_{\max}(\text{mgg}^{-1})$	18.9
	$K_L(\text{lmg}^{-1})$	5.21E-03
	r^2	0.97
	χ^2	0.03
	RMSE	1.17E-01
	$K_F(\text{mgg}^{-1})$	0.35
Freundlich	N	1.61
	r^2	0.96
	χ^2	0.06
	RMSE	2.49E-01

A characteristic of the Langmuir isotherm can be expressed using a dimensionless constant called "the separation factor" R_L which is defined as:

$$R_L = \frac{1}{1 + K_L C_o} \quad (23)$$

where K_L is the Langmuir constant and C_o is the initial concentration of cadmium ion in the solution. The value R_L indicates the shape of the plot as follows:

- $R_L > 1$ Unfavourable
- $R_L = 1$ Linear
- $0 < R_L < 1$ Favourable
- $R_L = 0$ Irreversible (Siswoyo *et al.*, 2014)

The plot of the separation factor for the Langmuir isotherm for the PTPS adsorbent is shown in Figure 15. From the plot it is observed that the value of the separation factor (R_L) for initial cadmium ion concentration ranged from 0.79(50mgL⁻¹) to 0.27(500mgL⁻¹) thereby indicating that the adsorption of Cd(II) ions by the PTPS adsorbent was favourable.

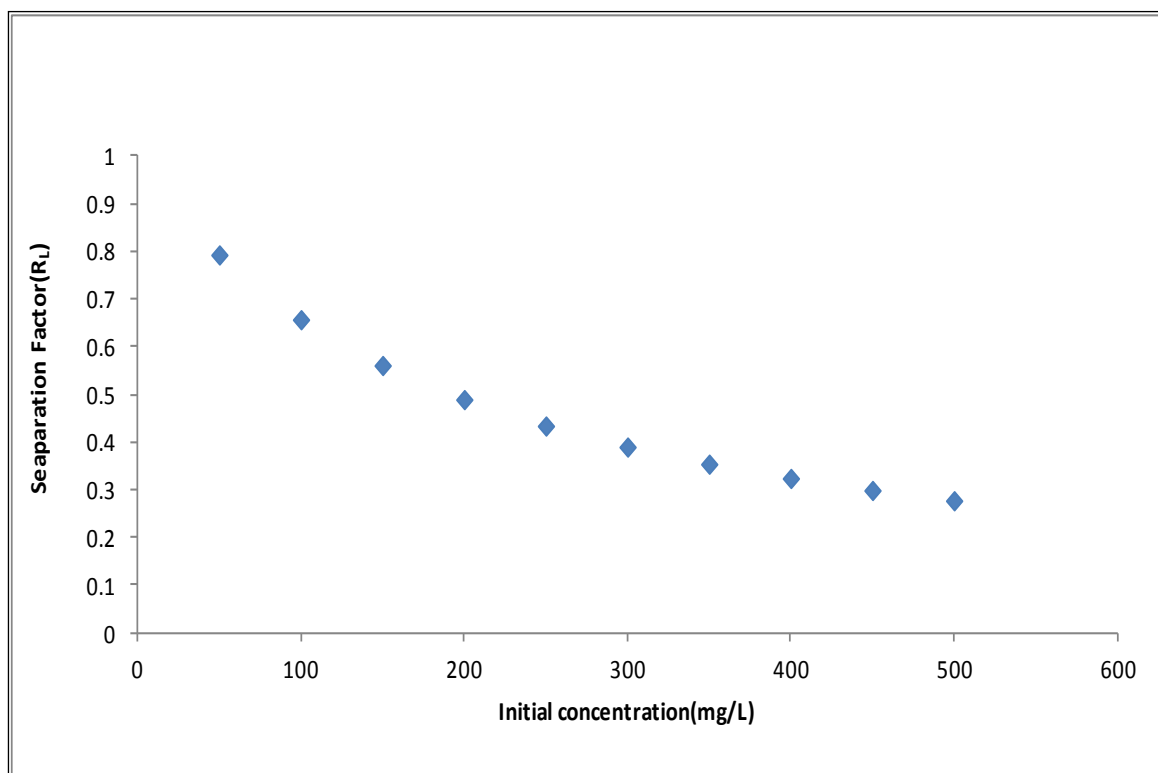


Figure 15: Langmuir Isotherm Separation factor plot for PTPS adsorbent

The value obtained for the Cd(II) ion maximum monolayer loading capacity q_{\max} for the PTPS adsorbent was compared to those of some adsorbents reported in literature as seen in Table 6. It is important to be noted that the shape of the isotherm can be used for the interpretation of the adsorption process. According to classification of Giles *et al.*, (1960), the adsorption isotherms are classified into four groups: L, S, H, and C. In this research paper, according to the aforementioned classification, the adsorption of Cd(II) onto the adsorbent (sweet peel) followed the L curve pattern which indicates that there is no strong competition between solvent and the adsorbate to occupy the adsorbent surface sites (Foroughi-dahr *et al.*, 2015). From the Table 6, it is observed that the adsorbents in this study had q_{\max} values that were higher and comparable to the reported in literature indicating that it capacity that is better than some already reported biomass residue adsorbents, hence there is potential for the exploitation of the PTPS adsorbent for metal ion remediation of polluted aqueous systems.

Table 6: Cd(II) Langmuir constant q_{\max} of this study with those reported in literature

Adsorbent	q_{\max} (mgg ⁻¹)	Reference
Rice husk	16.7	Krishnani <i>et al.</i> , 2008
Rape straw	17.53	Gong, 2013
Sunflower (<i>Helianthus annuus</i>)	14.9	Feizi and Jalali, 2015
Canola (<i>Brassica napus</i>)	14.7	Feizi and Jalali, 2015
Walnut Shell(<i>Juglans regia</i>)	8.3	Feizi and Jalali, 2015
Potato (<i>Solanum tuberosum</i>)	14.3	Feizi and Jalali, 2015
<i>Caulerapa fastigiata</i>	16.48	Sarada <i>et al.</i> , 2014
Teak leaf powder	29.94	Rao <i>et al.</i> , 2010
Juniper fibre	9.2	Min <i>et al.</i> , 2004
Coconut copra meal	5.1	Ho and Ofomaja, 2006
<i>Pinus sylvestris</i> sawdust	19.1	Taty-Costodes <i>et al.</i> , 2003
Kiwi cortex	15.9	Al-Qahtani, 2016
<i>Carica papaya wood</i>	17.4	Saeed <i>et al.</i> , 2005
<i>Glebionis Coronaria L.</i>	18.3	Tounsadi <i>et al.</i> , 2015
Sweet potato peels (PTPS)	18.9	This study

Freundlich Isotherm

The Freundlich isotherm model differs from the Langmuir model because it assumes a heterogeneous adsorption surface with active sites with different energy thereby implying a multilayer surface coverage whereas the Langmuir model assumes a homogenous surface with monolayer coverage. The Freundlich isotherm plots for the PTPS adsorbent is also shown in Figure 14. From this plot, the isotherm constants and coefficient of determination (r^2) for Cd(II) sorption was obtained and presented in Table 5. The values obtained for the r^2 indicate a close proximity of the model with the experimental data even though the data obtained for the Langmuir model were better. However, the r^2 values were still an indication of a good fit with experimental values with a value of 0.96. The value of the Freundlich isotherm constant “n” which describes the adsorption intensity of the adsorbents also shown in Table 5 and this was also obtained from the Freundlich isotherm. For the PTPS adsorbent this value was 1.61 and indicates that the adsorption of Cd(II) ions by the PTPS adsorbent was favourable. According to Sarada *et al.*, (2014) a Freundlich isotherm constant “n” value between 1 and 10 indicates that the adsorption intensity is favourable. This parameter has been reported to vary with the heterogeneity of the adsorbent material (Sari *et al.*, 2008). Furthermore, the value of the Freundlich constant “ K_F ” which relates to the adsorption

1 capacity for a multilayer system is also presented in Table 5. The value of K_F obtained for the
2 PTPS adsorbent was 0.35 mgg^{-1} , thus indicating that the multilayer loading capacity of the
3 PTPS adsorbent was low.
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5 From Table 5, it is observed that the high r^2 values and low χ^2 and RMSE values for the two
6 isotherm models implies that both can be used to described the sorption of Cd(II)ions onto the
7 PTPS adsorbent. However, the Langmuir model was a better fit as its r^2 value was higher than
8 that of the Freundlich, while the χ^2 and RMSE values were lower than that of the Freundlich
9 model.
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14 3.2.5 Mechanism of Cd(II) ion sorption 15

16 The application of adsorbents for the removal of metal ions from aqueous systems is carried
17 out using a wide range of materials however the process by which these adsorbents remove
18 metal ions from aqueous systems is still not fully understood. This is due to the complex
19 nature of adsorbent surfaces and the different interactions that exist between an adsorbent and
20 an adsorbate during sorption. A number of possible mechanisms have been proposed in
21 literature and these involve an integrative effect of different interactions such as; electrostatic
22 attraction-hydrogen bonding, ion-exchange, physical adsorption, chemisorption, surface
23 complexation and/or precipitation (Tan *et al.*, 2015; Nguyen *et al.*, 2013). According to
24 Krishnan and Anirudhan (2003), during the sorption of the metal ions, the ability of sorption
25 to proceed will depend on the pH and the type of species that exist at this condition. In the
26 present study the dominant species of the Cd(II) ions in solution at $\text{pH} > 8.0$ is the hydroxide
27 $\{\text{Cd}(\text{OH})_2\}$. At $\text{pH} < 8.0$ the dominant metal species are of the type Cd^{2+} and $\text{Cd}(\text{OH})^+$. The
28 interaction of these metal ion species with the species in solution and the adsorbent surface
29 will therefore affect the amount that is preferentially adsorbed onto the surface of the
30 adsorbents. The highest loading on the PTPS residue was observed to occur at pH 7 and this
31 pH was close to that chosen based on the zeta potential analysis of the residue (6.5). Thus, the
32 adsorption of the Cd(II) ions at this optimum pH may be due to the interaction of the species
33 that are dominant at $\text{pH} < 8$, such as Cd^{2+} and $\text{Cd}(\text{OH})^+$ and with the functional groups on the
34 adsorbents surface.
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54 Infra-red spectra evidence of adsorbents after metal ion sorption has been used in a number of
55 studies to confirm the participation of hydroxyl, carbonyl, phenolic functional groups found
56 on the surface or carbon adsorbents in metal ion sorption (Barkar *et al.*, 2013; Ding *et al.*,
57 2014). According to Bailey *et al.*, (1999), phenolic groups are believed to be accountable for
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1 the formation of complexes with heavy metal ions during sorption and evidence from infra-
2 red spectroscopy has been used to confirm this mechanism of sorption. Barkar *et al.*, (2013)
3 in their study on the sorption of Cd(II) ions using dried cactus observed a decrease in the
4 wave number of asymmetric stretching of the carboxylic double bond in the unloaded dried
5 cactus when compared to those of the metal ion loaded cactus. This shift in band was used to
6 conclude that the carboxylic acid groups were likely responsible for the binding of Cd(II) by
7 the dried cactus biosorbent. This inference can also be applied in the present study from the
8 evidence the infra-red spectra observed in the sorption of Cd(II) onto the residue adsorbent
9 shown in Figures 7 and 8 in this study. Thus it can be proposed that there was a complexation
10 reaction between the functional groups on the PTPS adsorbent and the Cd(II) ions leading to
11 proton (H^+) elimination into the adsorbate. This proton (H^+) effect was observed in the studies
12 on the effect of pH on Cd(II) ion studies with an increase in the final pH of the adsorbate after
13 metal ion sorption. Such a decrease in pH after sorption indicates the displacement of the
14 protons (H^+) from the adsorbent matrix by the Cd(II) ion which leads to a reduction in the
15 adsorbate pH.
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27 A further mechanism that can be used to describe the uptake of Cd(II) ions is that of ion-
28 exchange from the evidence obtained from the EDAX analysis (Figs.4 & 5). The EDAX
29 analysis of the residue adsorbent used in this study when compared to those of the fresh
30 adsorbent showed a decrease in the percentages of some elements such as molybdenum,
31 aluminium and calcium in the matrix of the used adsorbent with corresponding increase in the
32 percentage of Cd(II) ions, thus implying that the loading of the Cd(II) ion may also proceed
33 via an ion-exchange mechanism. This mechanism has also been observed by Swiatkowski *et*
34 *al.*, (2004) for the removal of Pb(II) on activated carbon surfaces. In their study they reported
35 that the approach of using ion-exchange and acid-based properties of a carbon surface alone
36 to explain the interactions leading to metal ion uptake in an adsorption system is insufficient
37 as there are different interactions that operate in this aqueous system. Hence the mechanism
38 by which the PTPS adsorbent interacts with metal ion adsorbate can be inferred from the
39 infra-red, EDAX and pH studies to be combinations of ion-exchange, surface complexation,
40 chemisorption and electrostatic interactions.
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4. Conclusion

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3 In this work, an experimental study on the utilisation of sweet potato peels (PTPS), an
4 abundantly available agricultural residue for the removal of Cd(II) ions from aqueous solution
5 was carried out. The effect of a number of parameters such as pH, contact time and initial
6 metal ion concentration on the loading of the metal ion onto the adsorbent were determined.
7
8 The results showed that the loading of Cd(II) ions (mgg^{-1}) increased with increase in initial
9 metal ion concentration, time and pH and the optimised pH range for adsorption was from 6.5
10 to 7. The kinetics of Cd(II) ion removal indicated an optimum contact time of 180 minutes via
11 a two stage kinetic uptake profile (initial fast and subsequent slow equilibrium). Kinetic
12 modelling of Cd(II) ion adsorption was carried out using the pseudo first order (PFO),
13 pseudo-second order (PSO) and intraparticle diffusion models. The PFO and PSO were
14 evaluated using a non-linear optimization procedure and the PFO described the kinetics better
15 than the PSO order model. The results from the intraparticle modelling suggest that
16 intraparticle diffusion mechanism was not the only rate controlling step for the sorption Cd(II)
17 ions by the PTPS adsorbent. The physico-chemical, elemental and spectroscopic properties of
18 the PTPS residue adsorbent were determined and the results obtained from the spectroscopic
19 analysis using (FTIR analysis and EDAX) indicates that ion-exchange and adsorption-
20 complexation mechanism may be involved in the loading of the Cd(II) ions onto the PTPS
21 adsorbent. The equilibrium sorption studies of Cd(II) ions were modelled using the Langmuir
22 and Freundlich isotherms using a non-linear optimization approach and the experimental data
23 was described better by the Langmuir model. This indicates that the monolayer adsorption
24 capacity of the PTPS adsorbent was 18.9 mgg^{-1} and a Langmuir constant of $5.21 \times 10^{-3} \text{ lmg}^{-1}$
25 at 25°C implying that the adsorbent was effective for Cd(II) ion removal from an aqueous
26 system as well as natural water bodies and effluents. The results of this study highlights the
27 potential of using an agricultural waste residue as an adsorbent for Cd(II) ion adsorption and
28 has also enabled comparisons to be made with similar adsorbents based on waste biomass.
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Figures Captions

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2 **Figure 1:** N₂ adsorption-desorption isotherm and pore size plot of PTPS residue adsorbent

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5 **Figure 2:** Photograph of sweet potato (a) dried sweet potato peel (b) and pulverised sweet
6 potato residue adsorbent-PTPS (c)

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10 **Figure 3:** Electron micrograph of PTPS adsorbent (a), PTPS after Cd(II) sorption (b)
11 Scale bar: 300/200μm

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13 **Figure 4:** EDAX spectrum of PTPS residue adsorbent

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17 **Figure 5:** EDAX spectrum of PTPS residue after Cd(II) adsorption

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21 **Figure 6:** Thermogravimetric & derivative thermogravimetric plot of PTPS in N₂ (20-500 °C)
22 & air (500-600 °C)

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26 **Figure 7:** ATR-FTIR spectrum of Sweet potato adsorbent PTPS

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30 **Figure 8:** ATR-FTIR spectrum of PTPS adsorbent after Cd(II) adsorption

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33 **Figure 9:** Effect of pH on the sorption of Cd(II) ion onto PTPS adsorbent

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36 **Figure 10:** Effect of contact time on Cd(II) ion sorption on PTPS adsorbent

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39 **Figure 11:** Pseudo-first order (PFO) & pseudo-second order (PSO) kinetic plot for PTPS
40 adsorbent

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43 **Figure 12:** Kinetic stages in intraparticle diffusion plot of Cd(II) ion sorption on PTPS
44 residue

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47 **Figure 13:** Kinetic stages in intraparticle diffusion plot of Cd(II) ion sorption on PTPS
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51 **Figure 14:** Langmuir and Freundlich equilibrium isotherm modelling for Cd(II) sorption on
52 PTPS residue.

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55 **Figure 15:** Langmuir Isotherm Separation factor plot for PTPS adsorbent

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2 **Tables Captions**
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5 **Table 1:** Physical and chemical characteristics of PTPS adsorbent
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8 **Table 2:** XRF of PTPS residue adsorbent
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11 **Table 3:** Initial and final pH of adsorbate solution for PTPS sorption of Cd(II)
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14 **Table 4:** Kinetic models parameters for Cd(II) sorption on PTPS adsorbent
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17 **Table 5:** Isotherm model parameters for sorption of Cd(II) onto PTPS adsorbent
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21 **Table 6:** Cd(II) Langmuir constant q_{\max} of this study with those reported in literature
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