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Cadmium (II) Sorption Using Unmodified and Thioglycol Acid-Modified Plantain (*Musa Paradisiaca*) Stalk

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Abstract

The presence of cadmium in industrial effluents and agricultural runoff has become a significant environmental concern, requiring green methods to reduce cadmium level in the environment, such as sorption using plant and animal wastes. Thioglycolic acid-modified plantain stalk (TGPS) and unmodified plantain stalk (UPS) were tested for their applicability in the sorption of cadmium (II) ions from aqueous systems by batch method. The adsorption process revealed a strong pH and temperature-dependent process with maximum adsorption obtained at 318 K for both the UPS and TGPS and at a pH of 7. The kinetics of both adsorption processes were conformed to the pseudo-second order model with an uptake of 16.95 mg g^{-1} and 15.68 mg g^{-1} and a rate constant of 0.00761 g mg^{-1} min^{-1} and 0.02407 g mg^{-1} min^{-1} for TGPS and UPS respectively. The Freundlich adsorption isotherm best fitted the adsorption isotherm for both UPS and TGPS. Studies on the thermodynamic characteristics revealed an endothermic process with $\Delta H°$ values of approximately 75 $kJmol^{-1}$ and 106 $kJmol^{-1}$ for UPS and TGPS, respectively. Negative ΔG values at the studied temperatures suggest that the process was feasible and spontaneous. Also, there was a noticeable increase in the reaction's spontaneity as the temperature increased. The results generally showed that the TGPS exhibited greater sorption efficiency than the UPS as far as cadmium (II) ions were concerned. However, both UPS and TGPS have the efficacy to take up Cd(II) from aqueous solutions.

Keywords: Thermodynamics, Thioglycol, Kinetics, Pseudo-second order, Freundlich isotherm

INTRODUCTION

The presence of heavy metals in water bodies poses a significant environmental challenge, necessitating effective and sustainable remediation strategies. Among these heavy metals, cadmium (Cd) attracts significant concern because it is naturally toxic and persistent in the environment. Cadmium pollution arises from various industrial activities, mining, and agricultural practices, making it crucial to develop innovative and eco-friendly methods to remove unwanted elements from contaminated water sources (Babalola *et al.*, 2011)

Adsorption has emerged as a promising and cost-effective option for reducing the concentration of heavy metal ions in aqueous solutions. In recent years, researchers have

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explored using various adsorbents derived from natural sources to tackle water pollution. Due to their abundant availability, biodegradability, and low cost, plant-based materials have gained substantial attention in this context.

Among these plant-based adsorbents, the plantain tree (*Musa paradisiaca*) stalk stands out as a potential candidate due to its unique physicochemical properties. The plantain stalk, often considered agricultural waste, possesses a porous structure and contains functional groups that could facilitate the adsorption of these ions (Eyenubo and Overah, 2018).

To enhance the adsorption efficiency of the plantain stalk, modifying it with thioglycolic acid was proposed. Thioglycolic acid modification can introduce additional active sites and alter the surface chemistry, thus potentially improving the affinity for Cd(II) ions. However, the comparative adsorption performance of thioglycolic acid-modified and unmodified plantain stalks for Cd(II) ions remains relatively unexplored.

This study aims to investigate and compare Cd(II) adsorption tendency using thioglycolic acid-modified and unmodified plantain stalks. The research will explore the influence of various experimental factors on the adsorption efficiency such as pH, contact duration, initial Cd(II) concentration, and adsorbent dose. The equilibrium adsorption isotherms and kinetics will also be analyzed to gain insights into the adsorption mechanisms and reaction kinetics.
The findings from this research hold significant implications for developing sustainable and environmentally friendly techniques for heavy metal removal. The utilization of waste plantain stalks as effective adsorbents could contribute to the remediation of Cd(II)-contaminated water bodies and offer a viable approach to valorize agricultural by-products.. Therefore, this investigation using thioglycolic acid-modified and unmodified plantain stalks marks a vital step towards sustainable resource management and greener water remediation technology.

MATERIALS AND METHOD

Materials or reagents applied in this study include Cadmium (II) trioxonitrate (V) (99 % LabChem), thioglycolic acid (95%, S.G 1.32 Qualikems), Trioxonitrate (V) acid (96-70.5 %, S.G 1.42 LOBA Chemie Lab Reagent and fine chemicals), and sodium hydroxide (99% Fisher Scientific). A laboratory test sieve (mesh no. 63 µm Pascal Eng. Co. Ltd Sussex England, Serial No: 42729) was used to sieve the adsorbent. An AAS (Bulk Scientific Model 210 VGP) was employed to determine metal ion concentration. Fourier Transform Infra-Red Spectrophotometer (Bruker FTIR laser class 1 spectrophotometer absorption band range of 4000-400 cm^{-1}) was used for functional group analysis. Whatman (No. 1) Filter Paper was applied to separate the adsorbent from the suspension. An electric blender (QASA QBL-1861A) was used to pulverize the adsorbent into fine particles.

Sample collection

The method used by Aderigbe *et al.*, (2017) was employed with slight modification. The plantain stalks were collected from farms at Usiefrun in Ughelli-South Local Government Area, Delta State. The plant stalks were thoroughly washed with deionized water and dried under sunlight for three weeks. After complete drying, they were ground with an electric blender and homogenized using a size 63 µm sieve, stored in air-tight containers and used for the study.

Modification of biosorbent

To form a slurry, 900 mL of HNO_3 (0.5 M) was mixed with 98 g of ground plantain stalk, stirred for 30 minutes with a magnetic stirrer at 200 rpm and left for 24 hours. The essence of

treatment with HNO_3 was to remove any impurities or molecules that may interact with the cadmium ions during the process. The mixture was filtered to separate the adsorbent which was then washed repeatedly with deionized water to a neutral pH and then oven-dried at 85 °C for 2 hours. A 900 mL of NaOH (0.5 M) was added to the acid-treated GPS and stirred for 30 minutes with a magnetic stirrer at 200 rpm. The suspension was soaked for 24 hours, suction-filtered, and rinsed with deionized water to obtain a neutral pH. After treatment with acid and base, the ground plantain stalk was referred to as unmodified plantain stalk (UPS).
A 360 mL of 1.0 M thioglycolic acid (mercaptoacetic acid, $HSCH_2COOH$) was added to 26 g of UPS and stirred for 30 minutes with a magnetic stirrer, heated in a water bath at 80 °C, and refluxed for 2 hours. The suspension was left to cool and filtered. The residue was washed copiously with deionized water and oven-dried at 85 °C. The residue was called thioglycolic acid-modified ground plantain stalk (TGPS). The thioglycolic acid treatment caused the thiolation of the adsorbent by the following reaction (Horsfall *et al.*, 2004):
Biomass + $HSCH_2COOH \rightarrow$ Biomass-SH + $H_3CCOO^- + H^+$ ………………………… (1)

Functional groups investigation
Fourier Transform Infrared (FTIR) Spectroscopy (IRXross model Shimadzu scientific instruments. Inc, USA), was employed to characterize the UPS and TGPS. This technique was employed to determine the chemical groups in the adsorbent that are responsible for the adsorption of the selected heavy metal. For this analysis, 0.20 g of both adsorbents was, in each case, encapsulated in 200 mg of KBr in making the dry pellets. The FTIR was performed on the pellets/discs in the range of 4000-400 cm^{-1} with a 4 cm^{-1} resolution.

Determination of Cd(II) concentration.
1000 mgL^{-1} stock solution was prepared by dissolving 2.7542 g of $Cd(NO_3)_2.4H_2O$ in deionized water, made up to the 1-litre mark, and analyzed with AAS to get the actual concentration. From this, dilution was done to obtain 50 mgL^{-1} working aqueous solutions. A fresh dilution of the stock solution was prepared for each adsorption study.

Adsorption procedure
The Cd(II) ion adsorption rate by the UPS and TGPS was studied while varying the pH, contact duration, adsorbent dosage, temperature, and adsorbate concentration, following standard adsorption procedures reported by Overah *et al.*, (2011).
Estimation of adsorption capacity and adsorption efficiency.
The uptake, q_e (mg g^{-1}) and adsorption efficiency of the UPS and TGPS adsorbents were calculated using equations 2 and 3 respectively expressed as (Asiagwu *et al.*, 2017):

$$q_e = \frac{(Co-Ce)V}{m} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$\text{Removal efficiency (\%)} = \frac{(Co-Ce)}{Co} * 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where, Co is the initial Cd(II) concentration in mg L^{-1}, Ce the final concentration in mgL^{-1}, V is the adsorbate volume in litres, m is the mass of adsorbate (g) and qe, the amount of metal ion adsorbed in mg g^{-1}.

Kinetic, isotherm and thermodynamic studies
To define the kinetic mechanism and the degree of the adsorption pathways, the data acquired from the time and concentration experiments were fitted into two kinetic models and two adsorption isotherm models respectively. Thermodynamic analysis was performed using the temperature-dependent study to estimate the values of important thermodynamic factors which can give good description of the process' feasibility and characteristics.
The linear Pseudo-first and Pseudo-second order models are shown in equations 4 and 5 respectively (Asuquo *et al.*, 2017; Overah, 2011,).

$log\ (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$ -- (4)

Where, k_1 is the rate constant for pseudo-first-order relation, and q_e represents the adsorption amount in milligrams per gram. A graph of $(\ln q_e - q_t)$ vs t should be linear of which K_1 is the slope and $ln q_e$ is the vertical intercept.

The pseudo-second order equation as adopted from Ho and Mckay, 1998a; Asiagwu *et al.*, 2017; Aderigbe *et al.*, 2017 is given below:

$\frac{t}{qt} = \frac{1}{K_2 {q_e}^2} + \frac{t}{qe}$ --- (5)

Where, K_2 is the rate constant ($gmg^{-1}\ min^{-1}$) for the pseudo-second order relation

The adsorbate concentration data generated were applied to the Langmuir and Freundlich isotherms. The values of the constants were obtained from experimental data for the UPS and TGPS when put to Langmuir and Freundlich isotherm. The Langmuir isotherm is founded on the postulation that the adsorption process is restricted to a monolayer adsorption and reversible process, indicating that no interaction occurs between the adsorbed entities on the active sites and those on the neighboring sites (Febrianto *et al.*, 2009; Asuquo *et al.*, 2017). The Langmuir isotherm indicates a chemisorption process in distinct localized adsorption sites. The Langmuir adsorption isotherm as described by Weber and Morris (1914); Overah (2011) is defined as;

$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m}$ --- (6)

A graph of C_e/q_e against C_e is linear with a slope equal to $1/q_m$ and intercept of $1/K_Lq_m$ where K_L is the Langmuir constant and q_m the monolayer adsorption capacity.

The Freundlich isotherm assumes that adsorption takes place on heterogeneous sites which may be mono-layered or multi-layered but with interactions between the adsorbed molecules. (Foo and Hameed, 2010; Febrianto *et al.*, 2009). The experimental data were tested with the Freundlich model to ascertain the adsorption mechanism. The modified linear form of this isotherm is:

$log\ q_e = \frac{1}{n}\ logC_e + \log K_f$ -- (7)

From the plot of log q_e against log C_e, $1/n$, which processes the surface's heterogeneity is the slope while Log K_f is the intercept. The 'n' indicates the favorability of the adsorbent-adsorbate system, which is the enormousness of the adsorption efficacy with temperature (Igwe *et al.*, 2007; Atkins, 1999; Uchimiya *et al.*, 2011; Asuquo *et al.*, 2017).

Thermodynamic studies were done to define the process' spontaneity. The ΔH°, ΔS°, and ΔG° are factors that need to be investigated before a conclusion can be drawn on the nature, spontaneity, and feasibility of the process. The relationship between the change in Gibbs free energy, temperature, and equilibrium constant is:

$\varDelta G = -RTInK$ -- (8)

The changes in enthalpy and entropy on the adsorption process are calculated from the graph of equilibrium constant against Kelvin temperature using the Van't Hoff equation stated below:

$InK = \frac{\varDelta s}{R} - \frac{\varDelta H}{RT}$ -- (9)

A straight line with $-\frac{\Delta H}{R}$ as the slope and $\frac{\Delta s}{R}$ as the vertical intercept is obtained from which ΔS and ΔH can be calculated. The variation in Gibb's free energy at all the investigated temperatures was calculated using the relationship below:

$$\Delta G = \Delta H - T\Delta S \qquad (10)$$

Results and Discussion

FTIR study of the adsorbents

The FT-IR bands of UPS and TGPS are shown in Figures 1a and b, respectively. The thioglycolic acid modification was done to make additional binding sites available in the form of the thio-group on the surface of the UPS. Prominent among the peaks in Figure 1a are those at 3333, 2917, 1611, 1315, 1029, and 778 cm^{-1}, while in Figure 1b are those at 3324, 2917, 1614, 1313, 1029, 778, and 2338 cm^{-1}. In the spectra, a broad peak appears at 3333 cm^{-1} (Figure 1a) and 3324 cm^{-1} (Fig 1b), which could be attributed to –OH stretch. This assignment is confirmed by the presence of a peak at 2917 cm^{-1} and signifies the presence of a C-H stretch. The appearance of a strong peak at 1611 cm^{-1} (Figure 1a) and 1614 cm^{-1} (Figure 1b) could be attributed to C=O stretch. Peaks at 1315 cm^{-1} (Figure 1a) and 1313 cm^{-1} (Figure 1b) were also observed, which could be ascribed to S=O stretch.

A new peak appeared at 2338 cm^{-1} (Figure 1b), which could be attributed to -SH, confirmation of the fact that the ground plantain stalk was indeed modified with thioglycolic acid.

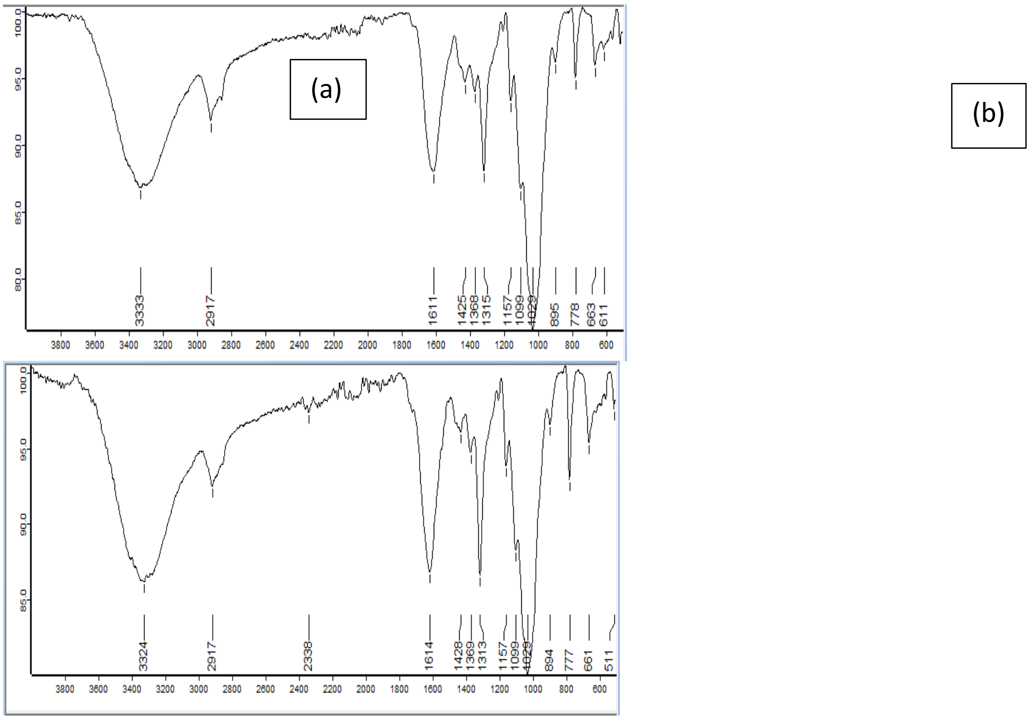

Fig. 1: FTIR spectra for (a) UPS (b) TGPS

Effect of pH:

Solution pH, a vital factor of the adsorption, was examined over a range of 2 to 9. Figures 2a and b represent the % adsorption and uptake or adsorption capacity respectively, of Cd(II) ion onto UPS and TGPS adsorbents at varied pH. The percentage removal and adsorption capacity or uptake (q_e) increased at a steady rate for UPS and TGPS adsorbent with increasing pH up to pH 7, attaining a maximum of 81 % equivalent to an adsorption capacity of 19.33 mg g^{-1} for unmodified adsorbent and 85 % with an absorption capacity of 20.02 mg g^{-1} for TGPS. After this, there was a decline in the adsorption of Cd (II) ions. This trend may result from a rise in the overall negative charge on the adsorbent surface between pH 2 and 7. Also, as the pH is increased, there is a decrease in the H^+ concentration, thereby resulting in a reduction in the struggle for adsorption sites between the metal ions and protons on the exterior of the plantain adsorbent (Asiagwu *et al.*, 2017; Cimbolakova *et al.*, 2019).

Also, increasing the pH likely encouraged Cd(II) precipitation from solution, leading to the development of soluble hydroxides, which caused a fall in the adsorption observed after pH 7 (Asuquo *et al.*, 2017). Eyenubo and Overah (2018), demonstrated using a speciation diagram that cadmium ions begin to precipitate significantly as from pH 8. Hence pH 7 was taken as the optimum pH in this experiment and used for further studies.

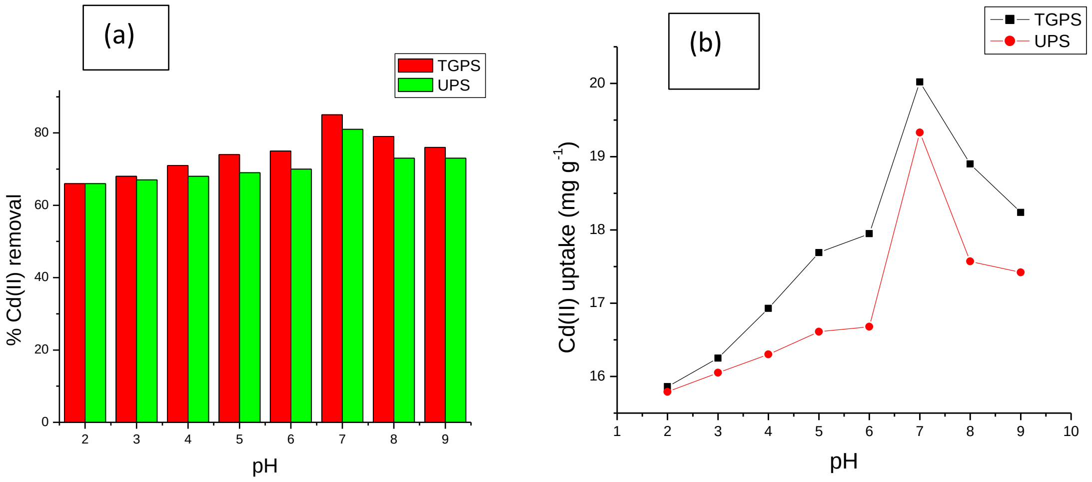

Fig. 2: Impact of pH on (a) percentage Cd(II) adsorbed (b) Cd(II) uptake from aqueous solution onto UPS and TGPS. (Temp. 298 K, Time: 30 mins, adsorbent dose 0.1 g, concentration of adsorbate 50 mg L^{-1}, agitation speed: 200 rpm).

Effect of contact time

To maintain equilibrium and to ensure that the process of adsorption is complete, a specific time is required for the interactions between the solute of the solution and the adsorbent. The impact of contact duration on the uptake of Cd (II) onto the UPS and TGPS is shown in Figure 3. Maximum Cd(II) adsorption was noticed at 30 minutes for both the UPS and TGPS. At first, the adsorption process was quick and gradually became slower (Asuquo *et al.*, 2017). This trend can be attributable to the early stage's powerful attraction or interaction between the ionic species and the adsorbent. The adsorption rate later began to slow down because the binding sites were gradually saturated. Several researchers have recorded similar adsorption time tendencies. Gupta *et al* (2004), obtained a maximum time of 80 minutes for lead adsorption onto bagasse fly ash adsorbent. Ho *et al.* (2006) obtained an equilibrium time of 60 minutes using palm kernel fiber as an adsorbent for Cu (II) ion. Eyenubo and Overah, (2018), obtained an optimum time of 10 minutes using ordinary plantain stalk for Cd(II) sorption. It was concluded in this study, that the metal solution and the adsorbent should be in contact for at least 30 minutes to get maximum percentage removal for cadmium for the unmodified and modified forms.

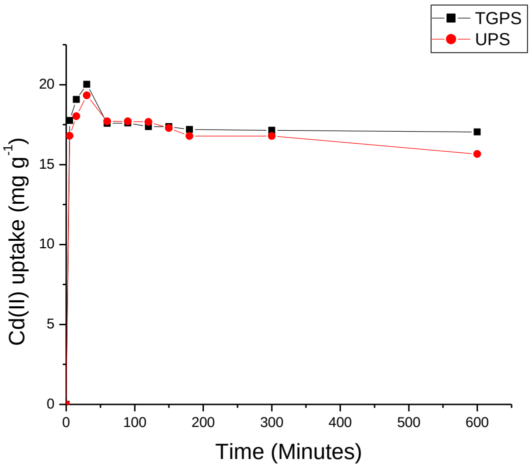

Fig.3: Impact of contact time on Cd(II) uptake onto UPS and TGPS. (Temp. 298 K, pH: 7, adsorbent dose 0.1 g, concentration of adsorbate 50 mg $L^{-1,}$ agitation speed: 200 rpm)

Effect of dose of UPS and TGPS

The dosage of the UPS and TGPS is another factor that helps in determining the ability of the UPS and TGPS at a given concentration.

The influence of dosage of the adsorbent on the Cd(II) sorption amount and efficiency of the UPS and TGPS are displayed in Figures 4a and 4b

It was noticed that rise in the dosage of adsorbent led to a matching increase in the degree of adsorption of Cd(II)· For Cd(II) a maximum adsorption efficiency of 94.90 % and 96.23 % was detected for the UPS and TGPS respectively as the dosage was increased up to 0.7 g for the UPS and 0.5 g for the TGPS. Increasing the dosage might have provided a larger surface area for adsorption and increased active sites on the surface of UPS and TGPS. It appears that the TGPS had extra sites for adsorption and linkages for bonding leading to the upturn in the adsorption (Asuquo *et al.*, 2017).

At a point, it was perceived that further rise in the dosage of the UPS and TGPS does not actually increase the percentage of Cd(II) adsorbed rather, there is a gradual downfall in the percentage adsorption. This could be that the already available sites for adsorption are sufficient enough for the sorption and thus, a further increase in dosage lead to an increase in the adsorption density which causes inadequacy of the Cd(II) in solution compared with the available active centers.

Also, the uptake of Cd(II) decreases with a raise in the dosage of the adsorbent. Gilbert *et al.*, (2011) investigated the effect of adsorbent dose on *defatted Carica papaya* seeds as adsorbent for Pb(II) ions. He reported an optimum dosage of 0.5 g with an adsorption efficacy of 1666.67 mg g^{-1}. Aderigbe *et al.*, (2017) reported a maximum dosage of 0.4 g using plantain peels for Pb(II) ions uptake (Asuquo et al., 2017).

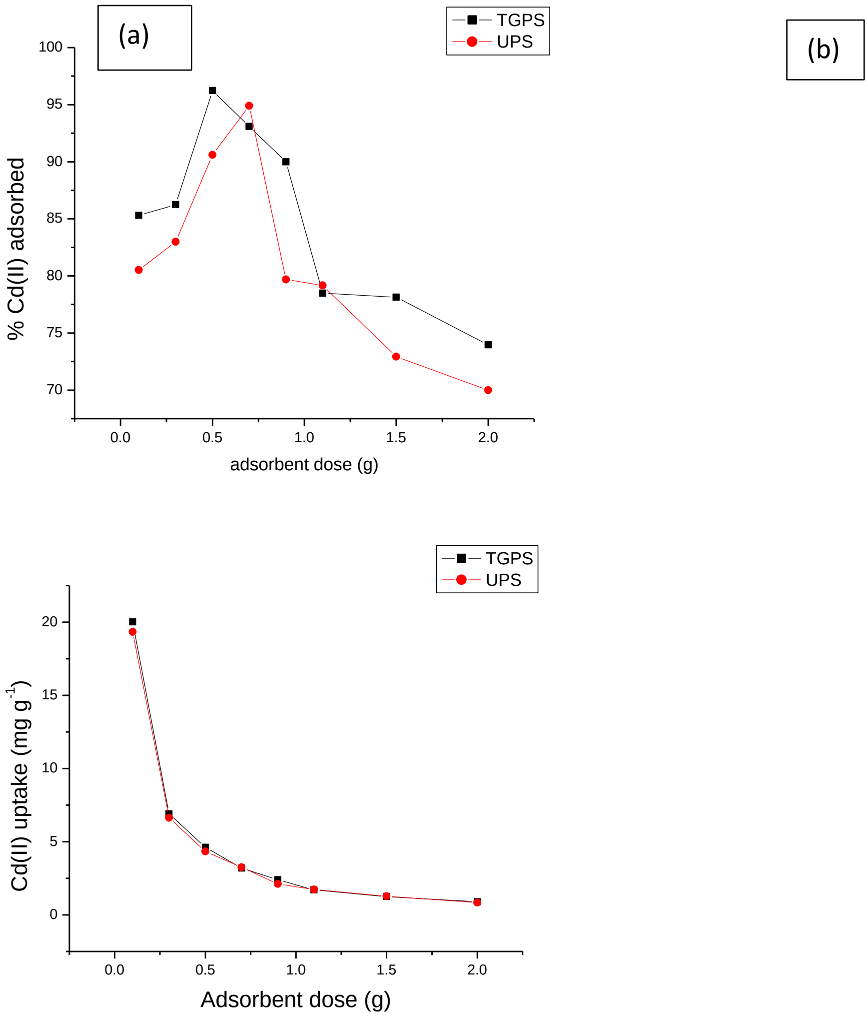

Fig 4: Impact of dosage on the (a) percentage Cd(II) adsorbed (b) uptake, q_e, of Cd(II) from aqueous solution onto UPS and TGPS. (Temp. 298 K, pH:7,Time: 30 mins, concentration of adsorbate 50 mg L^{-1} , adsorbate volume:50 mL, agitation speed: 200 rpm)

Effect of Cd (II) concentration:

The preliminary concentration of Cd(II) solution is another factor that can alter the metal removal efficiency through a blend of factors, such as the availability of a particular surface functional groups and its capacity to bind to metal (Malkoc *and* Nuhoglu., 2005; Asuquo *et al.*, 2017).

Figure 5 shows the effect of Cd(II) ion concentration for both modified and unmodified GPS. Maximum Cd(II) removal occurred at a preliminary concentration of 100 mg L^{-1} for both the UPS and the TGPS. The UPS has a maximum percentage adsorption of 95.29 %, while the TGPS has a maximum percentage adsorption of 96.70 % with an adsorbate concentration of 100 mgL^{-1} for the TGPS. The outcome showed that the percentage adsorption attained for the TGPS for Cd(II) was higher than that of the UPS. This outcome could be due to acid sites on the modified adsorbent or a rise in pore size/volume. As the adsorbate concentration increased, a corresponding increase in the percentage adsorption of Cd(II) resulted. The increase in the adsorption became insignificant, above 100 mgL^{-1}, probably because of the saturation at the active places of the TGPS and UPS adsorbent.

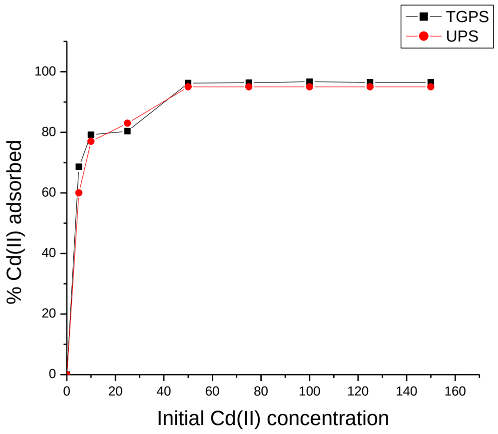

Fig. 5: Impact of initial concentration on % Cd(II) adsorbed from aqueous solution onto UPS and TGPS. (Temp. 298 K, pH: 7 Time: 30 mins, adsorbent dose: UPS 0.7 g, TGPS 0.5 g, volume of adsorbate 50 mL, agitation speed: 200 rpm)

Temperature studies;

Temperature is another factor that can affect the adsorption efficiency subject to the nature of the adsorbent applied. Temperature has impact on the equilibrium of adsorption depending on the endothermic or exothermic character of the adsorption course.

The impact of temperature on the process for the modified and unmodified GPS adsorbent is visualized in Figures 6a and b.

Similar to the work of Umukoro *et al.,* (2014), it was spotted that as temperature rose from 15 to 45 °C, the adsorption of the Cd(II) from aqueous media also increased (Asuquo *et al*., 2017) which implies that there was an increase in the frequency of collision between the Cd(II) and the surface of the plantain stalks. Maximum adsorption was observed at 45 °C for both the modified and unmodified GPS for cadmium. Additional raise in the temperature led to a sharp decline in the metal uptake from the aqueous solution. High temperatures tend to decrease the boundary level thickness. This may lead to an increase in the likelihood of the already adsorbed metal ions to discharge from the UPS and TGPS surface back into the solution phase. The decreased adsorption due to increase in temperature may also be due to weak interaction between the surface of the UPS and TGPS and the cadmium ions or even a thermal breakdown of active sites (Asuquo *et al*., 2017; Horsfall *et al*., 2004).

Maximum percentage Cd(II) adsorption of 98.72 % and 99.61 % was observed at 45 °C corresponding to an uptake of 5.26 and 9.96 mg g^{-1} (Figure 6b) for the UPS and TGPS adsorbents respectively.

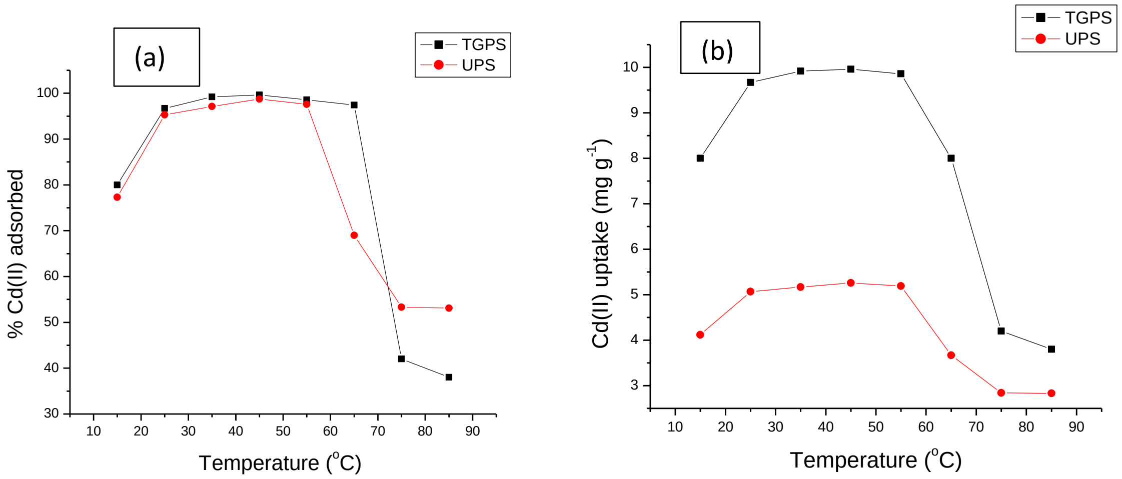

Fig 6: Impact of temperature on the (a) percentage Cd(II) adsorbed (b) uptake, q_e of Cd(II) adsorbed onto UPS and TGPS. [pH:7, Time: 30 mins, adsorbent dose (UPS 0.7 g, TGPS-0.5g), concentration of adsorbate(UPS- 75 mg L^{-1} ,TGPS-100 mgL^{-1}), adsorbate volume- 50 mL, agitation speed: 200rpm].

Adsorption Kinetics

When compared, the tested experimental data matched the Pseudo-second order (Figure 7b) more than the Pseudo-first order Kinetics (Figure 7a), with correlation values (R^2) = 0.99931 and 0.99998 for the UPS and TGPS respectively.

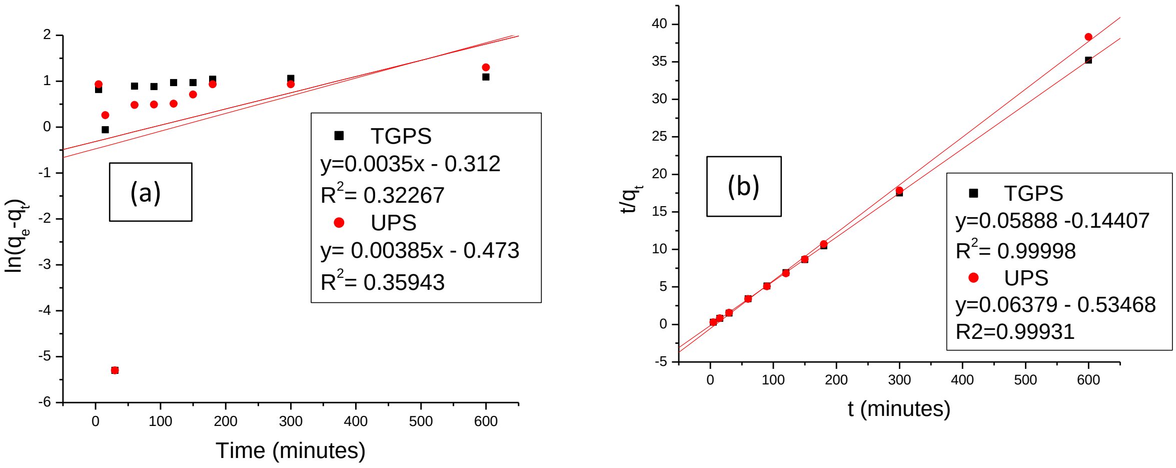

Fig. 7: (a) Pseudo-first-order kinetics and (b) Pseudo-second order kinetics for Cd(II) ion adsorption onto UPS and TGPS adsorbent.

Table 1: Pseudo-second order model parameters for Cd(II) ion adsorption onto UPS and TGPS

Cd(II)	K_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	h(mg g^{-1} min^{-1})	R^2
UPS	0.00761	15.67	-1.87	0.99931
TGPS	0.02407	16.97	-6.94	0.99998

The pseudo-second order model suggests a second-order mechanism for Cd(II) removal onto both UPS and TGPS. Thus, the rate-determining step is a chemical reaction between the adsorbent and the adsorbate, also known as the chemisorption mechanism (Ho and Mckay, 1999). This order of kinetics is in agreement with the works of Aderigbe *et al.*, (2017); Umukoro *et al.*, (2014); Abia *et al.*, (2006); Babalola *et al.*, (2011); Eyenubo *et al.*, (2018).

Table 2: Pseudo-second order adsorption capacities for Cd(II) ion

	(qe) experimental	(qe) calculated
UPS	19.33	15.67
TGPS	20.02	16.97

Adsorption isotherm

The Langmuir plots of C_e/q_e versus C_e for Cd(II) adsorption onto UPS and TGPS are shown in Figure 8 below:

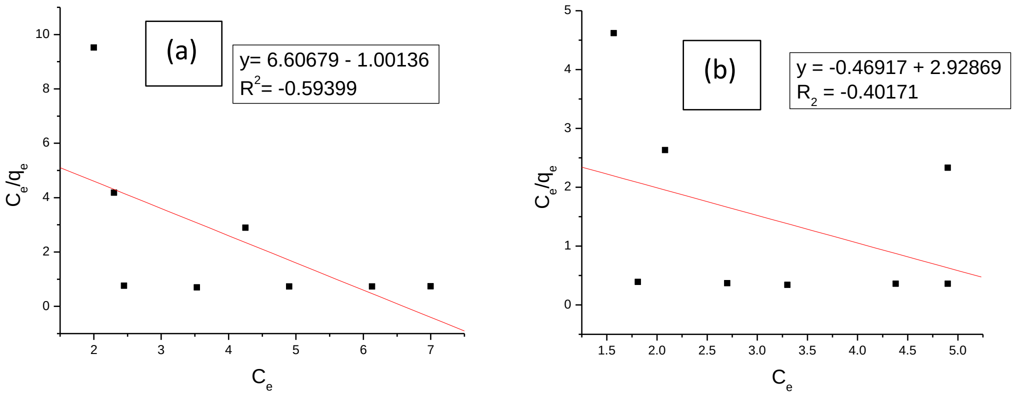

Fig. 8: Langmuir isotherm for Cd(II) adsorption onto (a) UPS and (b) TGPS adsorbent

The correlation coefficient value being far less than unity in both cases depicts the Langmuir isotherm, as being unfit for the experimental data, and so cannot be used to describe and predict the adsorption of cadmium (II) ions unto UPS and TGPS adsorbent. It indicates that the adsorption processes are not monolayer in nature. Hence, it was needless to consider the model any further.

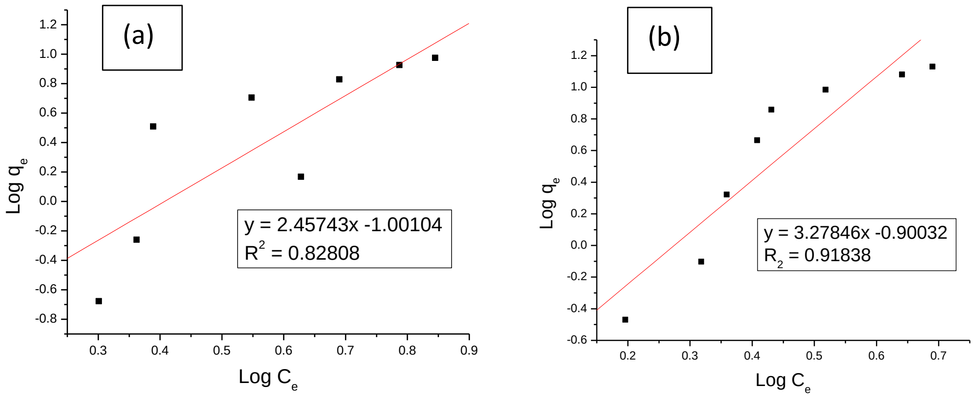

Fig. 9: Freundlich Isotherms for Cd(II) adsorption on (a) UPS (b) TGPS

Table 3: Freundlich Isotherm parameters for Cd(II) ion UPS and TGPS

Freundlich isotherm	n	K_f	R^2
UPS	0.4070	10.02	0.8281
TGPS	0.3050	7.949	0.9184

The correlation coefficient values in Table 3 above show that Freundlich isotherm model (Fig. 9) gave a closer fit compared to the Langmuir Isotherm for Cd(II) adsorption onto the UPS and TGPS adsorbent. This model gave a good fitting for the experimental data, and by implication, the adsorption path-way for Cd(II) ion was a multilayer and heterogeneous surface process. The values of '1/n' from the slopes for Cd(II) on UPS and TGPS are more significant than one, indicating a cooperative adsorption process (Haghseresht *et al.*, 1998). Also, the value of the constant, n, for both adsorbents for the Cd(II) ion is less than one ($n<1$), which confirms that the process is a chemical process and validates the pseudo-second-order kinetics for this work. Chong *et al.,* (2013), Hussain *et al.*, (2013), Overah (2020), Bamgbose *et al.*, (2010), Syed *et al.,* (2015), and Umukoro *et al.,* (2014) reported similar results.

Adsorption thermodynamics:
Thermodynamics studies were done to define the spontaneity or randomness of the process. Changes in entropy, enthalpy, and Gibbs free energy are factors that need to be investigated before a conclusion can be drawn on the spontaneity and nature of the process. The relationship between the change in Gibbs free energy, temperature, and equilibrium constant is:

$\Delta G = -RTInK$ -- (7)

Where $\ln K = C_a/C_e$. From equation (7) the ΔG at the investigated temperatures were estimated and recorded on Table 4. The change in enthalpy and entropy change were projected from the graph of InK versus 1/T (equation 8) which is a straight line with $-\frac{\Delta H}{R}$ as the slope and $\frac{\Delta s}{R}$ as the vertical intercept.

$InK = \frac{\Delta s}{R} - \frac{\Delta H}{RT}$ -- (8)

The ΔS and ΔH were calculated from the graph's intercept and grad in the Figure below. The variation in Gibb's free energy was calculated using the relationship below;

$\Delta G = \Delta H - T\Delta S$ ………………………………………………………….. (9)

The numerical values of the thermodynamic factors are displayed in Table 4.
The occurrence of positive ΔH confirms the process as being endothermic. The increase in disorderliness throughout the process at the solid/liquid boundary is indicated by a positive ΔS. During adsorption, the number of free active sites at the solid-liquid interface increased. The Cd(II) removal process was likely spontaneous, and the spontaneity increased noticeably with rising temperature, according to the negative values of ΔG. This trend demonstrates the viability of the adsorption procedure and the system's lack of reliance on external energy (Achmad *et al.*, 2012). This finding is consistent with reports of researchers such as Overah (2011) and Umukoro *et al.* (2014), where different adsorbents were used to treat wastewater.

The plots obtained for the thermodynamic parameters for both UPS and TGPS are shown in Figure 10 below:

A comparison of the mechanism of adsorption of cadmium ions by various adsorbents
The mechanism of cadmium adsorption onto UPS and TGPS and other adsorbents is presented in Table 5. Like most adsorbates, the cadmium adsorption kinetics is known to especially follow the pseudo-second order model. This indicates that the process likely depends on both the amount of active sites on adsorbent and the concentration of the adsorbate solution. However, depending on the nature of the adsorbent and the different

reaction conditions, the adsorption of cadmium may be exothermic or endothermic and may be mono-layered or multi-layered.

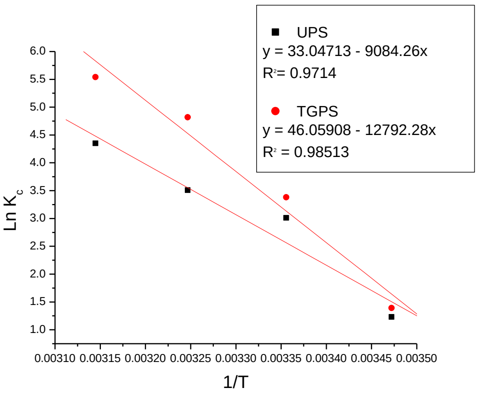

Figure 10. Van't Hoff plot for Cd(II) ion UPS and TGPS adsorbent

Table 4: Extrapolated values for thermodynamic parameters for Cd(II) using Van't Hoff equation.

				ΔG (KJ mol^{-1})			
Cd(II)	**ΔS(kJmol^{-1}K^{-1})**	**ΔH(kJmol^{-1})**	**R^2**	**288K**	**298K**	**308K**	**318K**
UPS	+0.2748	+75.53	0.9714	-3.6124	-6.3604	-9.1084	-11.8594
TGPS	+0.3829	+106.36	0.9851	-3.9152	-7.7442	-11.5732	-15.4022

Table 5. A comparison of the mechanism of adsorption of cadmium ions by various adsorbents.

adsorbent	Thermodynamics (type of reaction)	Kinetics	Isotherm type	Reference
UPS (untreated *Musa Paradisiacae*)	Endothermic	Pseudo-second-order	Freundlich	This work
TGPS Thioglycol-treated *Musa Paradisiacae*)	endothermic	Pseudo-second-order	Freundlich	This work
Untreated *Musa Paradisiacae*	Not reported	Pseudo-second-order	Langmuir	Eyenubo and Overah, 2018
Calotropis procera	endothermic	Pseudo-second-order	Langmuir	Babalola *et al*., 2011
Bamboo Charcoal	Not reported	Pseudo-second-order	Langmuir, Freundlich & Tempkin but mostly Langmuir	Wang *et al*., 2010
Defatted *Carica papaya* seeds	Exothermic	Not reported	Freundlich	Gilbert *et al*., 2011
dopamine-modified magnetic nano-adsorbent	Endothermic	Pseudo-second-order	Freundlich	Ting *et al*., 2019
MNO-modified red mud	Exothermic	Pseudo-second-order	Langmuir	Yin *et al*., 2022

Conclusion: From this study, it can be seen that ground plantain stalk can be chemically reformed using thioglycolic acid. The removal of Cd(II) using the modified and unmodified ground plantain stalk adsorbent was found to depend on pH, contact time, adsorbent dosage, initial concentration and temperature. The adsorption efficiency decreased with increase in dosage of the adsorbent. The removal of Cd(II) by both adsorbents was observed to be a pseudo-second order process on the postulation that the rate determining step may be a chemical sorption process. From the values obtained for free energy change, change in enthalpy and change in entropy, the adsorption of Cd(II) by both adsorbents was a physisorption process and the process was spontaneous, endothermic and feasible and therefore could be applied industrially. The values of the constants obtained when experimental data were built-in to the Langmuir and Freundlich isotherm showed that the adsorption of Cd(II) ion unto UPS and TGPS can be best described with the Freundlich isotherm.

Conflict of interest: The authors affirm the nonexistence of conflicting interests.

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