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INTERNATIONAL JOURNAL ON ORANGE TECHNOLOGIES

www.journalsresearchparks.org/index.php/IJOT e-ISSN: 2615-8140|p-ISSN: 2615-7071

Volume: 03 Issue: 03 | March 2021

Detoxification of cadmium from the Human Blood plasma using Dried Allium Cepa Biomass: An Equilibruim and Kinetic Study

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Abstract: *This study investigates the efficiency of Allium cepa biomass in removal Cadmium ions from aqueous solution of human blood plasma. The biosorbent was prepared and identified using FTIR which revealed the presence of carbonyl group, amide group, sulphoxide group, ether and aromatic groups. The optimum sorption was investigated and the experimental data revealed equilibrium pH 4, Cd2+ concentration 70 mgL-1 and biosorbent dose 0.80 g were obtained and used to study the equilibrium sorption rate which occurred at 80 mins with 99.98% removal at ambient temperature. The experimental data fitted Pseudo Second order kinetic as indicated by the correlation coefficient value (R2) = 0.9961 with a rate constant K2= 0.3730 g.mg-1.min-1. The experimental data conforms to Freundlich isotherm and Jovanovis isotherm, however Freundlich isotherm showed best fit with correlation coefficient (R2) = 0.632, sorption capacity (KF) = 3.3113 and sorption intensive (n) = 1.870. The separation factor of the Langmuir isotherm (RL) = 0.0141, suggests that the overall adsorption process was favourable.*

Key words: *Allium cepa; Biosorption; Flory-Huggins Isotherms; Freundlich Isotherms; Jovanovic Isotherms; Langmuir Isotherms; Kinetic models; Toxic metal.*

I. INTRODUCTION

Health challenges often arise due to the presence of toxic metals present in industrial chemicals which adversely affect animals and human lives. Toxic metals (Cadmium) are harmful been adduced to their ability to bio-accumulate in various plants and body parts due to their non-biodegradable nature [1]. These metals have a wide application in agriculture as fungicides, pesticide and herbicide to control pest and improve agricultural yield. Exposure to these metals even at low concentration often causes a wide range of illness such as nausea, vomiting, destruction of the blood cell, damage liver and kidney failure to mention but a few. The metals enter the human body through inhalation, drinking of contaminated water and consumption of contaminated plant and animal. These metal are often transported to various body part through the human blood plasma and tend to bind to protein cite by displacing the essential metals from their natural binding cite in the body thereby causing health challenges [2]. Techniques such as adsorption, coagulation, biosorption, solvent extraction, oxidation, reverse osmosis and phytoremediation have being employed in the removal of these metals. However, increase in the amount of hazardous chemicals makes these conventional techniques insufficient.

Biosorption technology exploits biomaterials in the elimination of toxic metals from aqueous solution via physiochemical and/or metabolically mediated pathways. This practice has being employed for a while as it provides an eco-friendly, effective and low cost material option. Amongst these biomaterials are Allium cepa, which is vegetable plant widely consumed for it therapeutic important. They have being reported to contain health promoting phytochemicals (quercetin, disulphides, trisulphides and vinly dithiins), acrid and strong antioxidants [3]. They are important in disease prevention, tracking free radicals in the body and preventing blood platelets from sticking together and forming clots and reduce blood pressure [4].

The human blood plasma is a component of the human blood. It makes up 55 per cent of total blood volume. It helps in suspension of the blood cells and also in the transportation of essential nutrients, antibodies, unwanted materials and toxic substances around the body. Several studies have being carried out utilizing plants and animal remaining in heavy metal removal. For instance, Chromium (IV) adsorption from aqueous solution by Leucaena leucocephala seed shell [5]; Biosorption of heavy metals from aqueous solution using Streptomyces rimosus biomass [1]; Lead biosorption from aquesous solution by waste biosorbent from derived from biotrickling filter: Kinetics and, isotherm and thermodynamics [2]; Multicomponent isotherm for biosorption of Zn (II), Co (II) and Cd(II) from temary mixture onto pretreated dried Aspergillus niger biomass [6]; Cadmium biosorption from aqueous using Aspergillus cristatus [7]; Evaluation of Ulva Fasciata and Sargassum sp for the biosorption of Cu2+ from aqueous solution [8]; amongst others. This study seeks to investigate the kinetics and equilibrium of the decontamination of cadmium from human blood fluid utilizing dehydrated Allium cepa biomass. The equilibrium pH, initial Cd2+ concentration and biosorbent dose will be established and employed to study the rate of Cd2+ removal from human blood fluid. The experimental date obtained will be fitted into Freundlich Isotherm, Freundlich isotherm, Jovanovic Isotherm and Langmuir Isotherm. The kinetic study was investigated using pseudo first and second order kinetic model.

II. MATERIALS AND METHODS

A Collection and preparation of sample materials and chemicals

All chemicals used were of annular grade. The stock solution of Cd2+ was prepared in 1.0 gL-1 concentration using 3CdSO4.8H2O then diluted to the required concentration prior to analysis (Abdel-Aty et. al. 2013). 0.1 molL-1 HNO3 and 0.1 molL-1 NaOH were employed to adjust the pH Value of the aqueous solution. The human blood sample from which the plasma was extracted and used for the study was collected from the Department of Hematology, Ahmadu Bello University, Zaria. Allium cepa sample was collected from samaru market and taken to the Department of Chemistry Multi User Research Science Laboratory (MURSL) prior to analysis. Preparation and characterization of samples (Allium cepa and Human Blood plasma) has being reported by [9].

B. Biosorption Experiment

i. Study of equilibrium pH

The equilibrium pH was studied at varying pH range (0.5 – 10) by introducing 0.80 g of biosorbent into 100 cm3 conical flask containing 50 cm3 aqueous solution composed of human blood plasma and 70 mgL-1 Cd2+

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concentration. The mixture was adjusted to the desired pH using 0.1 HNO_3 and 0.1 NaOH then agitated for 120 mins at 150 rpm using a rotary shaker [10]. The filtrate separated from the mixture using Whatman No 11 filter paper, digested and analyzed for residual Cd^{2+} concentration using Atomic Adsorption Spectrophotometer (AAS).

ii. Study of equilibrium Concentration

The equilibrium concentration was studied at varying metal ion concentration (20 – 100) mgL^{-1} by introducing 0.80 g of biosorbent into 100 cm^3 conical flask contain 50 cm^3 aqueous solution composed of human blood plasma and 20 mgL^{-1} Cd^{2+} concentration. The mixture was adjusted to the equilibrium pH, then agitated for 120 mins at 150 rpm using a rotary shaker [9]. After the preset contact time, the filtrate separated from the mixture using Whatman No 11 filter paper, digested and analyzed for residual Cd^{2+} concentration using Atomic Adsorption Spectrophotometer (AAS).

Study of equilibrium biosorbent dosage

The equilibrium biosorbent dosage was investigated at varying biosorbent dosage (0.20 – 1.00) g by introducing 0.20 g of biosorbent into 100 cm^3 conical flask containing 50 cm^3 aqueous solution composed of human blood plasma and equilibrium metal ion concentration. The mixture adjusted to equilibrium pH, then agitated for 120 mins at 150 rmp using a rotary shaker [11]. After the preset contact time, the filtrate separated from the mixture using Whatman No 11 filter paper, digested and analyzed for residual Cd^{2+} concentration using Atomic Adsorption Spectrophotometer (AAS).

iv. Study of equilibrium contact time

The rate of biosorption was studied at varying contact time (10 – 120) mins, by the introduction of equilibrium biosorbent dose into 100 cm^3 conical flask, containing a solution composed of 50 cm^3 human blood plasma solution and equilibrium metal ion concentration. The mixture adjusted to equilibrium pH using 0.1 HNO_3 and 0.1 NaOH, then agitated for various contact time (10 - 120) mins respectively [12]. After the preset contact time, the filtrate separated from the mixture using Whatman No 11 filter paper, digested and analyzed for residual Cd^{2+} concentration using Atomic Adsorption Spectrophotometer (AAS).

V. Data Analysis

The percentage removal of Cd^{2+} was calculated using equation 1

$$\%R = (C_o - C_e)/C_o \times 100 \quad (1)$$

Where Co and Ce represent the initial and final metal ion concentration (mg/L^{-1}), present in the human blood plasma solution respectively [10].

The amount of metal ion absorbed per unit mass (qe) is calculated using equation 2.

$$q_e = (C_o - C_e)V/M \quad (2)$$

where Ci and Ce represents the initial and final (Equilibrium) metal ion concentration after time t min., V represents the volume of human blood plasma in Cm^3 and M is the mass of adsorbent in gram [10].

vi. Adsorption Kinetics

The adsorption kinetics was investigated by employing the pseudo first and second order kinetic models to analyze metal ion uptake from the aqueous solution at different time intervals. When plotted, the linearity indicates if the models suitably describe the adsorption process [13].

The pseudo first order kinetic model is expressed in equation 3

$$\text{Log}(q_e - q_t) = \text{Log}(q_e) ¬– K_1/2.303 \quad (3)$$

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Where, qe and qt represents the sorption capacity at equilibrium and at time t, respectively (mgm-1) and K1 is the rate constant of pseudo first order sorption (L.min-1) [14]. A plot of Log (qe -qt) against t give a straight line with log (qe) as slope and K1 as intercept.

The Pseudo second order kinetic is expressed in equation 4.

$$t/qt = (1/(K_2 q_e^2))+(t/q_e) \quad (4)$$

Where qe and qt represents the sorption capacity at equilibrium and at time t, (mgg-1) respectively, while K2 is the pseudo second order kinetic rate constant (g.mg-1.min-1) [15].

vii. Adsorption Isotherms

The adsorption isotherm describes the interaction between the adsorbate in the solution and the adsorbent to establish equilibrium between the metal ions absorbed and the residual metal ions [16]. However, the potential of two parameter isotherms (Flory-Huggins Model, Freundlich model, Jovanovic model and Langmuir model) were tested to identify the model that best describe the interaction between the metal ions in the solution and the adsorbent.

The linear form of Flory-Huggins is expressed in equation 5

$$\text{Log } \theta/Co = \text{Log } K_{FG} + n\text{Log } (1-\theta) \quad (5)$$

Where K_{FG} is Flory-Huggins equilibrium constant (Lmg-1), θ = (1 – Ce/Co) represents fractional coverage, and n is the interaction energy between the absorbed molecules [17]. A plot of Log θ/Co against Log (1- θ) is used to ascertain the value of n and KFG as the slope and intercept respectively.

The Gibbs free energy is calculated using equation 6.

$$\Delta G = -RT \text{ InKFHB} \quad (6)$$

The linear form of Freundlich isotherm is expressed in equation 7.

$$\text{Log } qe = \text{Log } KF + 1/n \text{ Log } Ce \quad (7)$$

where KF is the Freundlich adsorption capacity (L/mg) and 1/n represent the adsorption intensity, which also is an indication of the relative distribution of the energy level of heterogeneity of the active cite on the adsorbent. A plot of Log qe against Log Ce will produce a straight line with slope 1/n and intercept KF [18].

The linear form of Jovanovic isotherm is expressed in equation 8

$$\text{In } qe = \text{In } qmax – KfCe \quad (8)$$

where qe (mgg-1) = represent the amount of Cd2+ on the biosorbent at equilibrium, qmax represents the maximum metal ions absorbed obtained from a plot of In qe against Ce, Kj represents the Jonanovic isotherm constant [19].

The linear form of Langmuir isotherm is expressed in equation 9.

$$Ce/Qe = 1/Qm \text{ } Ce + 1/(Kl.Qm) \quad (9)$$

Where, qe represents equilibrium conc. of metal Cd2+ in solid phase, Ce represents equilibrium conc. of metal Cd2+ in liquid, Qm represents Langmuir constan while KL represents Langmuir sorption equilibrium constant [20]. A plot of Ce/Qe against Ce gives straight line from which Qm and KL can be calculated from the slope and intercept respectively. The isotherm further predicts the affinity between the metal ions in aqueous solution and the biosorbent as expressed in equation 10.

$$RL = 1/(1 + KLCo) \quad (10)$$

Where RL represents the separation factor and Co represents the initial metal ion concentration in the aqueous solution. A favorable adsorption is recorded when value of RLis inbetween 0 and1. Thus RL>1 is an unfavourable adsorption.

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However were RL = 1 suggests linear adsorption and RL = 0 suggests irreversible adsorption [21].

FTIR Spectroscopy

FTIR spectra of adsorbent before and after Cd2+ binding were recorded to identify the active cite believed to be responsible for the metal ion uptake as reported by [22].

II *RESULT AND DISCUSSION*

FTIR Spectroscopy

The FTIR spectra of the adsorbent before and after biosorption are presented in Fig. 1 and Fig. 2 respectively. The result revealed a general shift in the peaks from 3272.6 cm-1 – 3268.9 cm-1, 1636.3 – 1625.1 cm-1, 1364.2 cm-1 – 1319.5 cm-1, 1252.4 cm-1 – 1237.5 cm-1, 920.7 cm-1 – 890.8 cm-1. The general shift in the peak revealed presence of O-H stretch of carbonyl group, C=O stretch of amide group, S=O of sulphoxide group, =C-O-O asymmetric stretch of ether group and =C-H bend of aromatic group were involved in the overall adsorption process. These functional groups are believed to have participated in the process of adsorption[23].

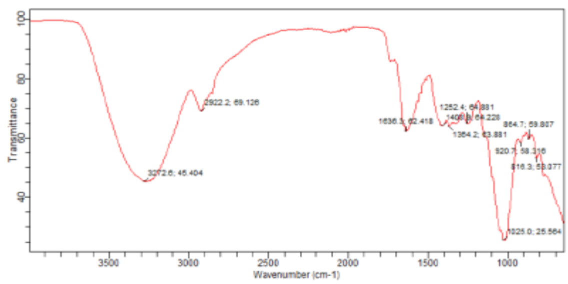

Fig. 1: FTIR of Allium Cepa biomass

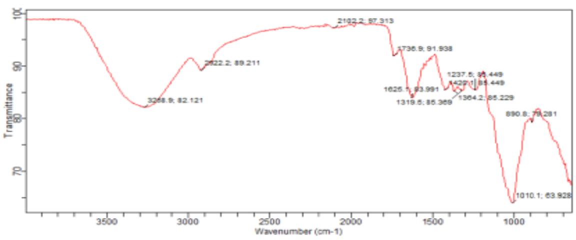

Fig. 2: FTIR of Cd2+ loaded Allium cepa biomass

B. Equilibrium pH

The pH of the adsorption process is significant as it directly affect the chemistry of the active cites on the adsorbent with an attendant effect on the adsorption capacity [24]. Fig. 3. Represent a plot of percentage removal against varying pH. The result showed that there was an increase in percentage removal with increase in the pH of the solution. Equilibrium sorption was attained at pH 6 with 98.446 % removal. Further increased in the pH of the solution resulted to a decrease in percentage removal. This suggests a low adsorption capacity of the Allium cepa biomass in alkaline medium which is an indication that the solubility of the metal ions in the aqueous solution is affected by the availability of hydrogen ions however, at high pH, these ions are precipitated to hydroxides [25].

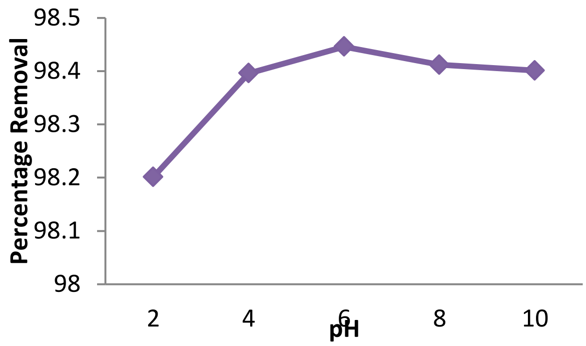

Fig. 3: Percentage removal of Cd2+ as a function of pH

C. Equilibrium metal ion concentration.

Fig. 4 represents the plot of percentage removal against varying metal ion concentration. The result revealed a steady increase in percentage removal with an increase in the metal ion concentration. Equilibrium concentration was attained at 70 mgL-1 with 98.89% removal. Further increase in the concentration of metal ions in the solution, resulted to a reduction in the percentage removal. This suggest unavailability of active sites for metal ion

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uptake due to high saturation of the biding sites by metal ions [26].

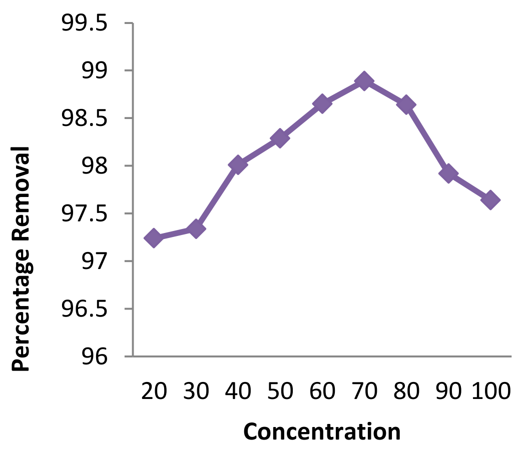

Fig. 4: Percentage removal as a function of metal ion concentration

D. Equilibrium biosorbent dosage

Fig. 5 represents a plot of percentage removal against biosorbent dosage. The result revealed an increase in percentage removal with an increase in biosorbent dosage. Maximum sorption was attained at 0.80 g with 99.92 % removal. Further increase in biosorbent dosage yield a decrease in percentage removal. This is been adduced to high competition for the available metal ions in the solution by the active sites.

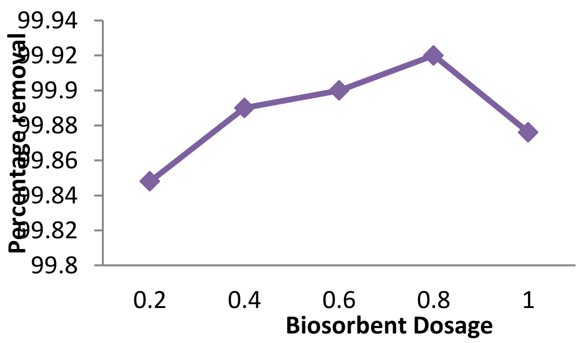

Fig. 5: Percentage removal as a function of Biosorbent dosage

E. Equilibrium contact time

Fig. 6 represents a plot of % removal against contact time. The curve revealed an increase in % removal with contact time. This increase in % removal is been adduce to the availability of free biding cites on the adsorbent. Equilibrium sorption was attained at 80 mins with 98.98 % removal. Thereafter, increases in the contact time yield a decrease in the percentage removal. This is an indication of unavailability of free binding cites on the adsorbent [9].

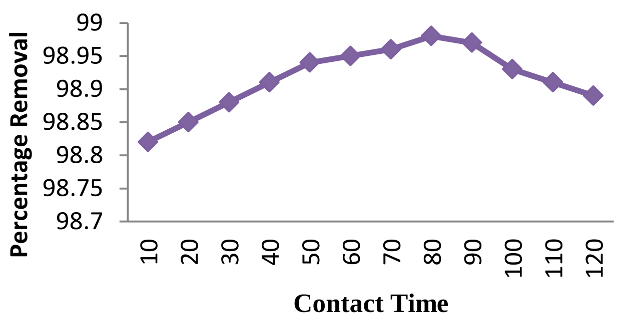

Fig. 6: Rate of removal of Cadmium

F. Adsorption Kinetics

i. Pseudo first order kinetic model

Fig. 7 represents the pseudo first order kinetic model for Cd2+ sorption. The correlation parameters are presented in Table. 1. The qe value (4.37 mgg-1) is an indication that significant amount of Cd2+ was adsorbed at equilibrium [14]. The correlation coefficient (R2) = 0.869 suggest that the experimental data fits pseudo first order kinetic model.

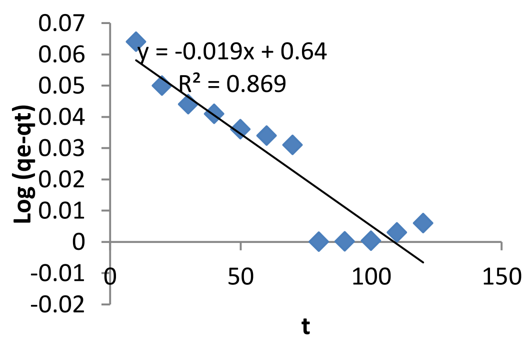

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Fig. 7: The pseudo first order kinetic model for Cd2+ sorption.

ii. Pseudo second order kinetic

Fig.8 represents the pseudo second order kinetic for Cd2+ sorption, while the correlation parameters are presented in Table. 1. The qe value (3.48 mgg-1) indicates that significant amount of Cd2+ was absorbed by the biosorbent. The correlation coefficient R2 = 1 indicates that the experimental data fits pseudo second order kinetic model.

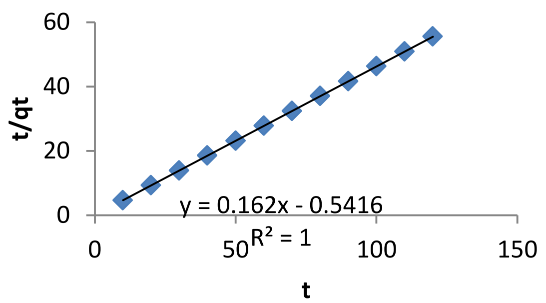

Fig.8: The pseudo second order kinetic for Cd2+ sorption

Table. 1: Adsorption parameters for Pseudo First and Second order kinetic models

	Pseudo First Order			Pseudo Second Order		
Metal ion	q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 (g/mg/min)	R^2
Cd^{2+}	4.37	0.0438	0.869	3.48	0.3730	1

G. Adsorption Isotherm

i. Flory-Huggins Isotherm

The Flory-Huggins adsorption isotherm for Cd2+ sorption is presented in Fig. 9. The isotherm parameters are presented in Table 2. The result reveals that the experimental data obtained fits the Flory-Huggins adsorption isotherm as indicated by a correlation coefficient value R2 = 0.245 while the Flory-Huggins constant (KFG) = -2.0941 and the energy of interaction between the absorbed molecules n = 0.817. This indicates there is a low energy of interaction between the adsorbates [27]. The Gibbs free energy = 55.05 KJmol-1 suggests an enthalpy change in the overall physiochemical process.

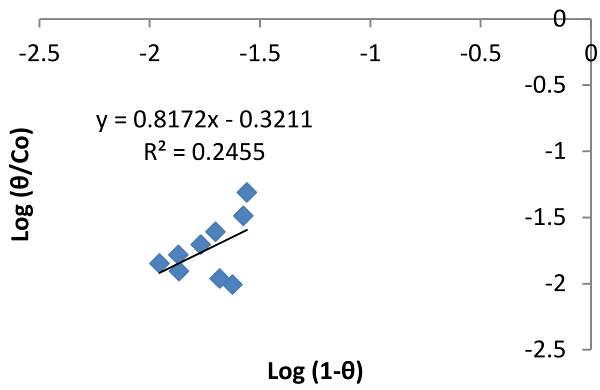

Fig. 9: The Flory-Huggins adsorption isotherm for Cd2+ sorption

ii. The Freundlich isotherm

The Freundlich isotherm for Cd2+ sorption is presented in Fig. 10. The Freundlich isotherm parameters for Cd2+ sorption are presented in Table 2. The result reveals that the experimental data fits Freundlich isotherm as indicated by the correlation coefficient value R2 = 0.632. The Freundlich adsorption capacity KF = 3.3113 indicates that a significant amount of Cd2+was absorbed per site. The adsorption intensity (n) = 1.870 Lmg-1 suggests a favorable adsorption of Cd2+ by Allium cepa biomass [28].

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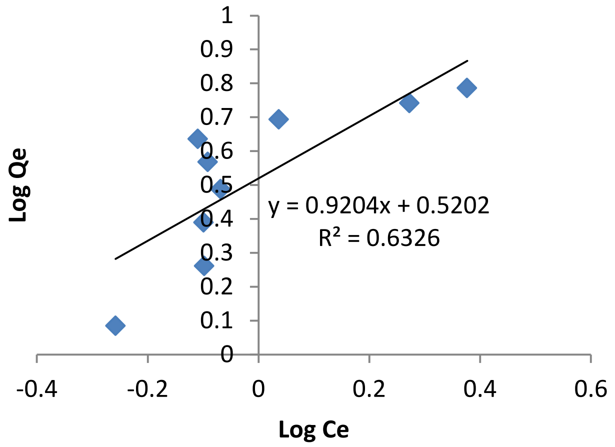

Fig. 10: Freundlich Adsorption isotherm for Cd2+ sorption

iii. The Jovanovic isotherm

The Jovanovic isotherm for Cd2+ sorption is presented in Fig. 11. The isotherm parameters are presented in Table. 2. The result reveals that experimental data obtained fits Jovanovic adsorption isotherm as indicated by a correlation coefficient (R2) = 0.517. The maximum uptake qmax = 1.6242 mgg-1 suggests that a significant amount of Cd2+ was absorbed by the biosorbent. The experimental data also suggests that the biosorbent has a poor retention capacity as indicated by Jovanovic constant (KJ) = 0.637 [19]

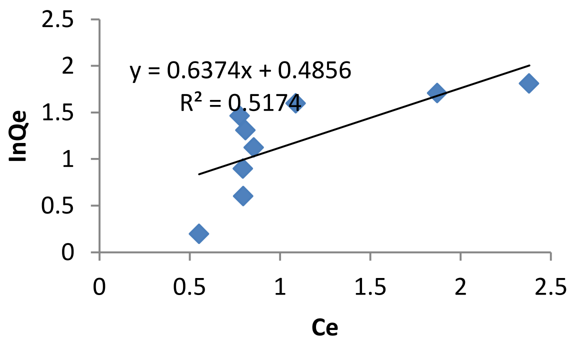

Fig. 11: The Jovannovic isotherm for Cd2+ sorption

iv. The Langmuir isotherm

The Langmuir isotherm for Cd2+ sorption is present in Fig. 12. The isotherm's parameters as presented in Table 2. The result revealed that the experimental data did not conform to Langmuir isotherm as indicated by a correlation coefficient (R2) = 0.063. The Qmax = 2.0739 mgg-1 suggests a significant amount of Cd2+ was absorbed by Allium cepa biomass, However KL = 0.1203 suggest a low biosorption capacity of the Allium cepa biomass in removal of Cd2+ from the aqueous solution of human blood plasma. The value of RL= 0.0141 suggests that adsorption process was favourable [29].

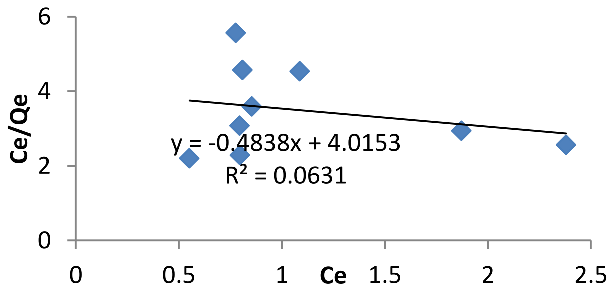

Fig. 11: The Langmuir isotherm for Cd2+ sorption.

Table. 2: Isotherm Parameters for Cd2+ sorption using Allium cepa biomass

Fowler Geggenheim	Freundlich
$K_{FG} = 2.0941$	$K_F = 3.3113$
$R^2 = 0.245$	$R^2 = 0.632$
N = 0.817	n = 1.870
Jovanovic	**Langmuir**
$K_J = 0.637$	$K_L = 0.1203$
$R^2 = 0.517$	$Q_m = 2.0739$
$q_{max} = 1.6242$	$R^2 = 0.063$
	$R_L = 0.0141$

IV. CONCLUSION

The study revealed that the efficacy of Allium cepa for the decontamination of aqueous solution of human blood plasma was dependant on pH, metal ion concentration and biosorbent dosage. The experimental data was well interpreted by the Freundlich isotherm. Though the experimental data did not conform to Langmuir isotherm, however the Langmuir separation factor suggests that the overall adsorption process was favourable. The study further revealed adsorption process followed a pseudo second order reaction path way. The Flory-Huggins isotherm revealed a low energy interaction between the adsorbates in the aqueous solution of human blood plasma. Allium cepa has proven to be an economically available and effective biosorbent for detoxification of Cd2+ from the aqueous solution of human blood plasma invitro. However further study can be done on chemically modified Allium cepa extract for removal of toxic metals from the human body in-vivo.

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