The Effectiveness of Low Cost Adsorbents (Onion and Garlic Skins) In The Removal of Cd(II) from Aqueous Solution

Evbuomwan, B.O and Opute, C

Department of Chemical Engineering, University of Port Harcourt, Port Harcourt, Nigeria.

Abstract: **- In this study, the effectiveness of onion and garlic skins for the removal of Cd(ii) from aqueous solution was investigated. The physical characterization, equilibrium and batch studies were undertaken to examine the kinetic and thermodynamic aspect of Cd(ii) adsorption by these biosorbents. The results showed that pH, surface area, specific gravity, specific gravity, ash content and moisture contents were 7.02 and 6.87, 1021.4m^2/g and 874.2m^2/g, 2.25% and 1.25%, 42.5% and 27% for onion and garlic respectively. The macro elements contained in onion and garlic skins were Ca, Mg, K, Na, P, and Fe. The FTIR analysis showed that the major functional groups on the biosorbent surface took part in the metal ion uptake process.The Langmuir isotherm model was found to be suitable for the adsorption of Cd(ii) for both biosorbents. The kinetic study of the adsorption process follows the pseudo second-order. The thermodynamic process was feasible, spontaneous and endothermic. In general, onion and garlic skins exhibit effective sorption potentials for the removal of Cd(ii) from aqueous solution.**

Keywords: **Adsorption, Onion, Garlic, Cadmium, Isotherm, Kinetic, aqueous solution**

I. INTRODUCTION

In recent years, the increasing awareness of the environmental impact of heavy metals has prompted a demand for the purification of industrial waste water prior to discharge into waters bodies by regulating authorities. Also, the potential health hazard posed by the influx of these heavy metals in the environment has stimulated research into various means of removing them from the environment [1]

At present, there are number of different conventional ways for the removal of these heavy metal pollutants from waste waters when they are present in high concentrations. These include methods like precipitation, ion exchange, ultrafiltration, evaporation, electrodialysis and solvent extraction [2].

However, these technologies are ineffective for removing these heavy metals present in low concentrations and costly. Other drawbacks are incomplete removal of metals, limited tolerance to pH change, moderate or no metal selectivity, and production of toxic waste products that also need disposal [2].

As a result of the above challenges, of conventional metal separation methods, there has been need for researchers to look into alternatives for removing heavy metals from waste waters, which are cost effective. As a result, by-products of agriculture are receiving much attention due to their low cost, availability and environmental friendliness. Also, using agricultural waste for purifying water, provides means of reducing solid waste disposal. Onion and garlic are better alternative for the treatment of effluent polluted with heavy metals. The biosorbent are available locally and is cost effective. Both adsorbents will not pose any environmental problem because they are biodegradable. Therefore, instead of employing imported chemicals and technologies which are expensive and sometimes poses some environmental challenges, onion and garlic are better alternative.

The major cadmium compounds found in air are cadmium oxide, chloride, and sulfate e.t.c, and these compounds are usually expected to undergo transformation in the atmosphere. The main source of cadmium in air is through transportation and deposition. Cadmium can also travel through long distances in the atmosphere and then finally settle (wet or dry) onto soil surface and water, which will eventually result in elevated cadmium levels even in remote locations. It can be shown from the 2006 final report of EPA's Urban Air Toxic Monitoring program that the average daily cadmium levels of <0.01 µg/m^3 at several monitoring sites throughout the United States [3[. These sites include: Bountiful, Utah; Northbrook, Illinois; Austin, Texas; St. Louis, Missouri; Indianapolis, e.t.c[3]. Atmospheric concentration of cadmium is generally highest in the environment of cadmium-emitting industries [4]. Due to the advancement in pollution control technologies, cadmium emissions to air are not expected to increase, even though the industries emitting cadmium are expected to grow [5]. Apart from those who live near cadmium-emitting industries, inhalation of cadmium from the ambient air is not the main source of exposure.

However, immobilized cadmium is available to plant life and can easily be introduced into the food supply. Cadmium in soil tends to be more available when the soil pH is low (acidic) [6].

In this study, the effectiveness of onion and garlic skins for removal of Cd(ii) from aqueous solutions is studied. The skin of the onion and garlic is the dried up outer parchment of bulbs and are kitchen and agricultural waste products.

Literature survey has shown that there has been no previous study for removal of cadmium ion using onion and garlic skins.

II. MATERIALS AND METHODS

Sampling and sample preparation

Onion and garlic bulbs bought from market were cut into small pieces, dried, crushed, and washed thoroughly twice with distilled water to remove the adhering dirt. They were finally dried in an air oven at 200^{o}C for 24hours. After drying, the adsorbent were sieved.

Preparation of metal ion standard solution

1000mg/l cadmium was prepared by dissolving 1g of cadmium nitrate in 1 litre of distilled water. The pH of the solution was adjusted by using 0.1N of HCl and NaOH.

Characterization of biosorbent

The moisture content was determined by weighing exactly 2g of the sample into the petridish. Then the petridish and sample were put in the oven and heated at 100^{o}C for 1 hour and the result noted. This was repeated for another 1 hour until a steady result is obtained and the final weight noted.

$$\% Moisture = \frac{w_1 - w_2}{w_3} \times \frac{100}{1} \qquad (1)$$

Where w_1=Weight of petridish and sample before drying

W_2 =Weight of petridish and sample after drying

W_3=Weight of sample

pH was measured by electrometric method using Laboratory pH meter (pH meter Hanna model H1991300) [7].The functional group present in the adsorbents (Onion and Garlic) were determined using the Fourier Transform Infra Red Spectroscopy (FTIR). The surface area was determined by preparing 1.5g of the sample in 100ml of dilute hydrochloric acid (HCl) at pH of 3. Thereafter, sodium chloride (NaCl) of mass 30g was added to it and the volume made up to 150ml using deionized water. Finally, the solution was titrated with 0.IN NaOH until the pH is raised to the range of 4 to 9. The volume V is recorded.

$$S = 32V - 25 \qquad (2)$$

Where S is the specific surface area

V is the final volume of solution at pH 4 to 9.

Adsorption experiment

Four different sets of batch experiments were carried out to investigate separation of Cd(II) using onion and garlic bulb. The experiments were repeated at pH from 2-10, concentration of metal from 10ppm to 50ppm, time intervals of 20mins-100mins, dose of adsorbent ranging from 0.1g – 0.5g, temperature range of 50^{o}C to 90^{o}C to investigate the bestparameterfor the removal of Cd(II) from aqueous solution.

The batch experiments were done using a 250ml volumetric flask. For pH adjustments, concentrated hydrochloric acid or sodium hydroxide solutions were added to adjust the pH of the solution.At equilibrium, the mixtures were filtered using Whatman No 42 and analyzed for free metal concentrations using Atomic Adsorption Spectrophotometry.

The percentage of the metals adsorbed at equilibrium, %M is given in the equation below.

$$\% M = \frac{C_0 - C_e}{C_0} \times \frac{100}{1} \qquad (3)$$

The adsorption capacity of the adsorbents. q_t is given as:

$$q_t = \frac{C_0 - C_e}{C_0} \times V \qquad (4)$$

Where C_o is the initial concentration of the metal ions (mol), Ce is the concentration of the metal ions at equilibrium (mol), v is the volume of the metal ions in contact with the adsorbent and m is the mass of the adsorbent in (g).

Determination of the effect of agitation time on biosorption of Cd(ii) by onion and garlic

20ml of water with 60mg/l of the cadmium solution were contacted with 0.4g of the adsorbents at the room temperature and optimum pH to determine the effect of contact time on the amount of Cd(ii) adsorbed by these adsorbents. The samples were shaken with 0.4g of the adsorbents (onion and garlic) at 200rpm for a duration of 20mins, 40mins, 60mins, 80mins,and 100mins respectively using a plastic tube and then filtered. Finally, the initial and final concentrations were determined using AAS.

Determination of the effect of particle size on biosorption of Cd (ii) by onion and garlic

The effect of particle sizes on the amount of Cd(ii) ion adsorbed was investigated by contacting the sample with varying sizes of the adsorbent to determine the adsorbent size for highest removal capacity. After agitation, the solution was filtered and the concentration of free cadmium ion in the filtrate was determined using AAS.

The percentage of the metals adsorbed at equilibrium, %M is given in the equation below.

$$\% M = \frac{C_0 - C_e}{C_0} \times \frac{100}{1} \qquad (6)$$

Determination of the effect of temperature on biosorption of Cd(ii) by onion and garlic

15ml of 50mg/l of the sample solution was agitated with 0.4g of the adsorbents (onion and garlic) respectively at temperatures of 20^0C, 40^0C, 60^0C, 80^0C and 100^0C to investigate the effect temperature on the amount of cadmium ion removed.The agitated solution was filtered and the equilibrium concentration of the free Cd(ii) ion in the sample was determined using AAS.

Determination of ash content of the biosorbent

The sample (2g) was weighed into a porcelain crucible. This was transferred into the muffle furnace set at 550^oc and left for about 4 hours. About this time it had turned to white ash. The crucible and its content were cabled to about 100^oc in air, then room temperature in a desiccator and weighed. The percentage ash was calculated from:

$$\% \text{ ash content} = \frac{\text{weight of ash} - \text{weight of dish}}{\text{Original weight of sample}} \times \frac{100}{1} \qquad (7)$$

III. RESULTS AND DISCUSSION

FTIR spectra analysis

Fourier Transform Infrared Spectroscopy was used to analyze the biosorbent samples loaded with Cadmium metal to identify the compounds and its functional group available for the uptake of heavy metal. FTIR spectra for onion and garlic loaded with heavy metal (Cadmium) are shown in Figures 4.1 and 4.2. From figure 4.1, the peak value at 876.8866cm^{-1} is assigned to C-Cl stretch while the peak values at 1021.937cm^{-1} and 1284.604cm^{-1} are assigned to C-N stretch (medium) and stretch of aliphatic and aromatic amines respectively.

Furthermore, FTIR spectra interpretation of garlic loaded with cadmium can be seen in figure 4.2. Alkyl halides functional group was present as indicated with a peak value of 827.3554 which can be assigned to C-Cl stretch. Peak values of 1113.406cm^{-1} and 1322.785 corresponds to C-N stretch of Aliphatic and Aromatic Amines respectively.

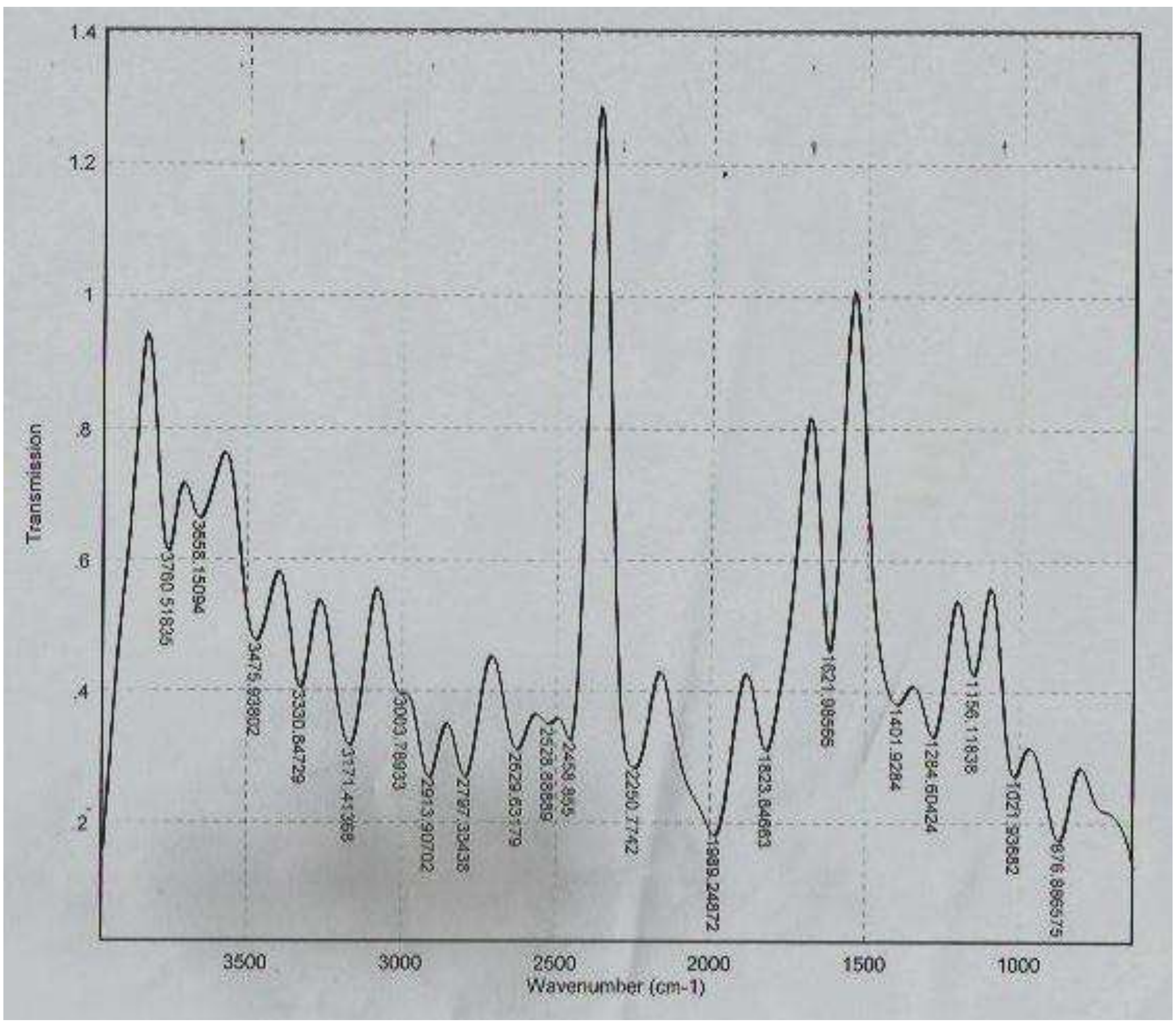

Fig. 4.1 FITR of onion loaded with cadmium

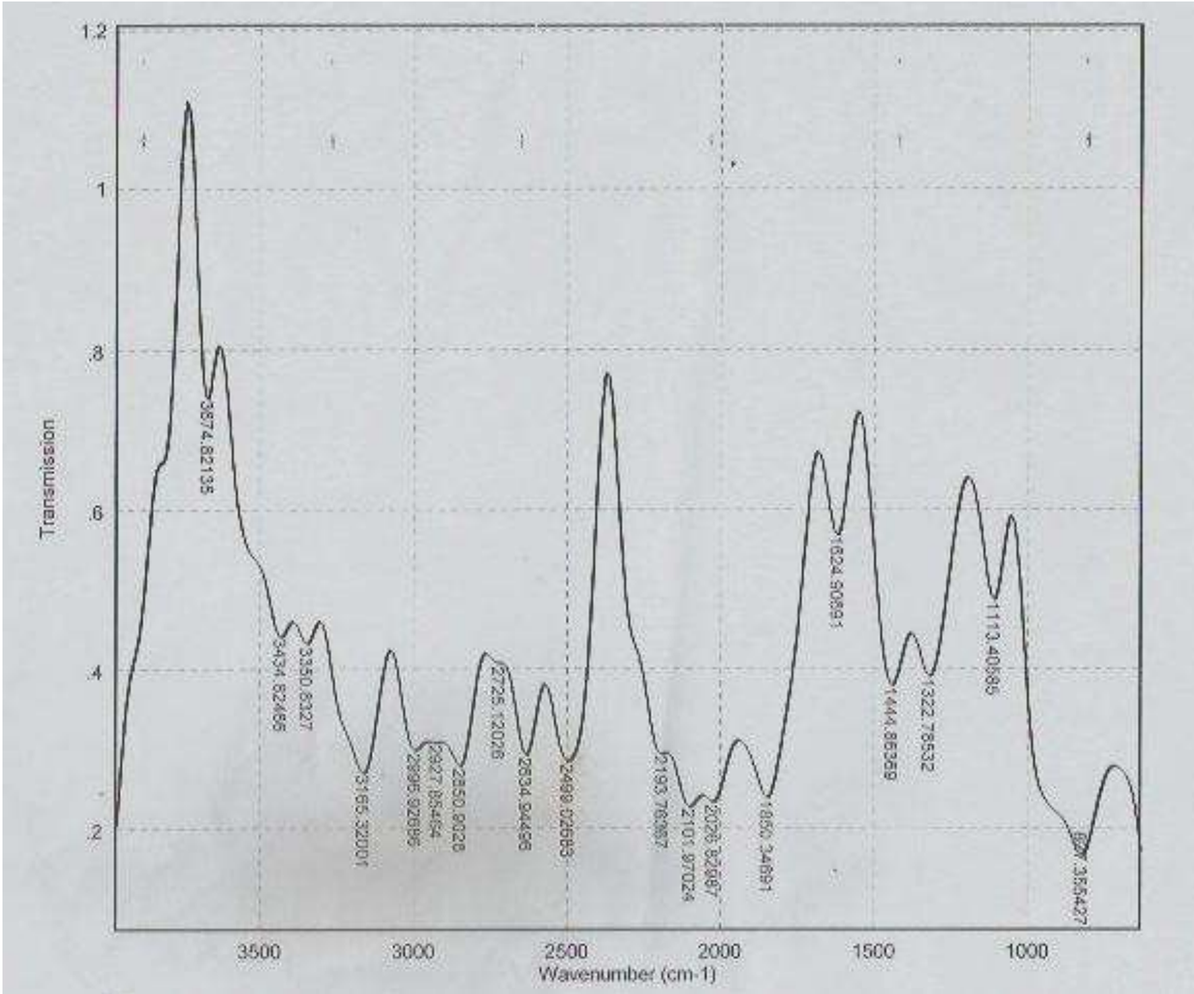

Figure 4.2 FITR of garlic loaded with cadmium

TABLE 1: Physical characterization of Onion and Garlic

Composition	Onion	Garlic
pH	7.02	6.87
Specific Gravity	0.24	0.3928
Moisture content %	42.5	27.0
Surface Area (m^2/g)	1021.4	874.2
Ash content (%)	2.25	1.25

TABLE2: Metal ion concentration of Onion and Garlic

Parameters ppm	Onion	Garlic
Calcium	19.409	21.315
Magnesium	18.347	18.815
Potassium	10.00	0.969
Sodium	10.249	0.00
Phosphorus	2.34	1.43
Iron	2.778	3.115

The pH, specific gravity, moisture content, bulk density, surface area, ash content and metal ion present in the samples was determined as shown in tables 1 and 2. The pH of onion and garlic skin were found to be 7.02 and 6.87 respectively. These pH levels result in more negative charges on the biosorbent surface that is likely to attract the positively charged Cd(ii) ions to bind to its surface. Also, the surface area of onion and garlic skin are 1021.4m^2/g and 874.2m^2/g respectively. The larger the surface area of an adsorbent, the greater its adsorptive capacity[8]. The specific gravity of garlic is higher than that of onion. The ash content of the biosorbents were also determined. The ash contents of the biosorbents were found to be 2.25% for onion and 1.25% for garlic. Ash content is the portion of any organic material that remains after it is burned at very high temperature. It represents the total mineral content in an organic material. Ash content plays an important role from a physicochemical, technological and nutritional point of view. Onionhas higher moisture content of 42.5% than garlic with moisture content of 27%. Finally, the macro elements contained in Onion and Garlic skin are Ca, Mg, K, Na, P and Fe.

TABLE 3: Effect of adsorbent dosage on Cd (ii) % removal and adsorptive capacity

S/N	Mass	q_t (Onion) mg/g	% Removal (Onion)	q_t (Garlic) mg/g	% Removal (Garlic)
1.	0.2	3.24	64.89	3.38	77.65
2.	0.4	1.736	69.44	2.096	83.87
3.	0.6	1.395	83.71	1.504	90.25
4.	0.8	1.04	82.85	1.108	82.85
5.	1.0	0.83	83.17	0.88	83.17

TABLE 4: Effect of contact time on Cd (ii) removal (%) and amount adsorbed.

S/N	Time (mins)	q_t (onion) (mg /g)	% Removal (Onion)	qt (Garlic) (mg /g)	% Removal (Garlic)
1.	20	1.562	62.49	2.414	96.56
2.	40	1.520	60.40	1.86	74.51
3.	60	1.564	62.57	1.84	73.61
4.	80	1.606	64.26	1.861	74.46
5.	100	1.583	63.32	2.484	99.34

TABLE 5: Effect of temperature on Cd (ii) removal (%) and amount adsorbed.

S/N	Temperature (^{o}C)	q_t (Onion) (mg/g)	% Removed (Onion)	q_t (Garlic) (mg/g)	% Removed (Garlic)
1.	20	1.611	64.45	1.91	76.43
2.	40	1.58	63.20	1.77	70.90
3.	60	1.623	64.90	1.97	78.61
4.	80	1.69	67.74	2.09	83.71
5.	100	1.428	57.11	1.97	78.69

Effect of adsorbent dosage

The effect of adsorbent dosage on the amount of cadmium adsorbed was carried out at fixed time, concentration, temperature and pH. The biosorbents adsorbed maximum cadmium at dosage level of 0.2g but decrease as the dosage is increase from 0.4g to 0.6g. This is as a result of more competition for available Cd(II) ion. However, the amount adsorbed increased slightly as dosage of the biosorbents was increased from 0.8g to 1.0g. Hence, smaller mass of adsorbent can effectively remove Cd(II) ion from aqueous solution

Effect of agitation time

The uptake of cadmium metal ions from aqueous solution occurred rapidly at a contact time of 20mins further increase of agitation time only result in slight changes in metal ion concentration until the equilibrium time of 100mins was achieved for garlic sample and 80mins for onion sample. From the figures below, it can be seen that the uptake of the metal ions by the biosorbent occurs in two stages: the initial rapid stage where the adsorption process is very fast and the second slower stage where the adsorption

Effect of temperature on the adsorption of Cd(ii)

The effect of temperature on the adsorption of cadmium onto onion and garlic skins was also determined. It can be shown from the results that the amount of cadmium uptake increased steadily as the temperature rises with the maximum cadmium uptake at a temperature level of 80^0C which is due to the increase in the number of available sites as the temperature is increasing.

Fitting experimental data to adsorption model

Langmuir model equation can be given as:

$$\frac{C_e}{q_e} = \frac{1}{KQ^0} + \frac{C_e}{Q^0} \qquad (8)$$

Plotting $\frac{C_e}{q_e}$ against C_e gives a straight line graph with slope: $\frac{1}{Q^0}$ and intercept $\frac{1}{KQ^0}$

The Langmuir, Freundlich, Temkin and D-R isotherms models were employed to describe the uptake of Cd (II) ions by onion and garlic.

Langmuir parameter K_L was calculated from the intercept of the linear plot of $^{Ce}/q_e$ against C_e as shown in Figures 4.3 and 4.4. This was used to calculate the separation parameter R_L which shows the nature of adsorption. The values of R_L ranges from 0.13 to 0.43 for Onion and 0.11 to 0.38 for garlic which confirms that the adsorption processes was favourable ($0<R_L<1$). Also, the value of R^2 for both onion and garlic shows that Langmuir isotherm model favours both adsorbent [9].

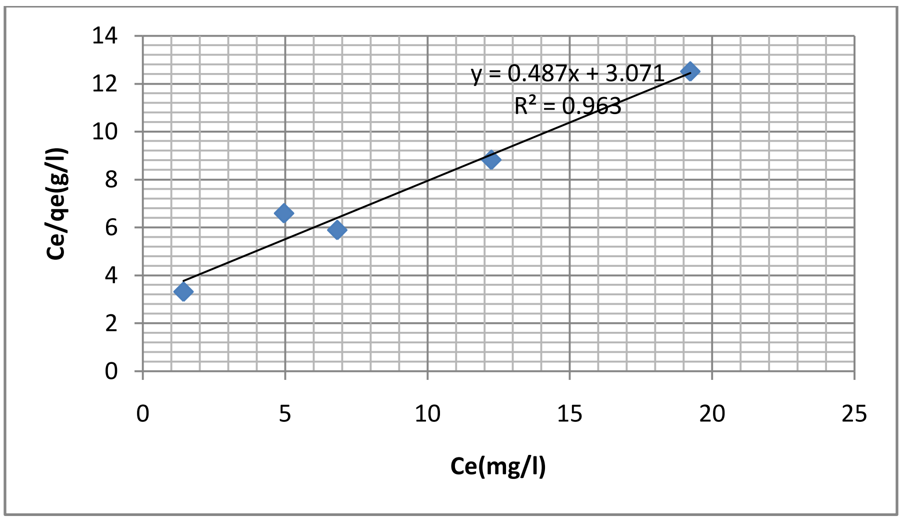

Fig. 4.3: Langmuir adsorption Isotherm for garlic

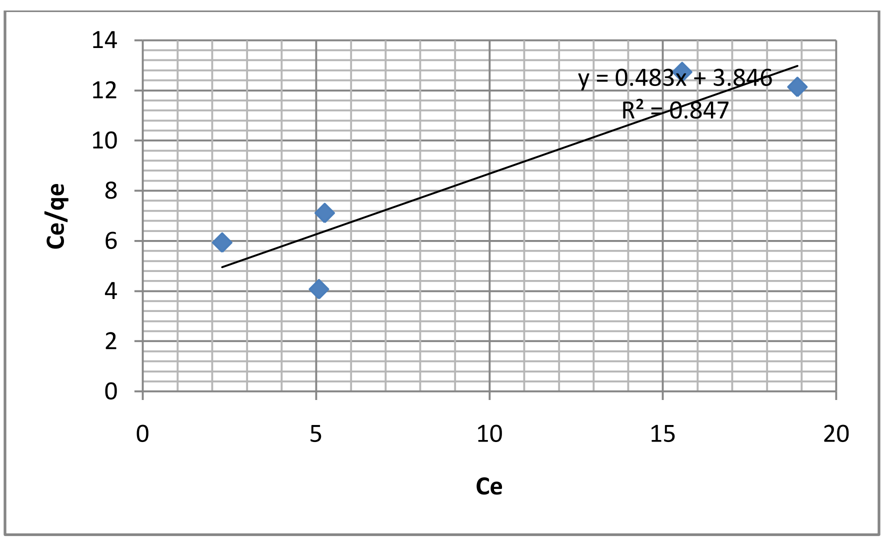

Fig.4.4: Langmuir adsorption Isotherm For onion

Further more, freundlich equilibrium constant n obtained for onion and garlic are 1.825 and 1.9305 respectively which means that both adsorption is a physical process. If n = 1, that adsorption is linear, if n < 1, the adsorption is a chemical process and if n > l, then adsorption is a physical process [10].Temkin isotherm was also employed where q_e was plotted against InCe to determine the isotherm constants K_T and B_I, where K_t is the equilibrium binding constant corresponding to the maximum binding energy while B_1, shows the heat of adsorption

The adsorption energy obtained for both onion and garlic are 0.5kJ/mol and 0.91kJ/mol respectively, which are in the energy range of physical adsorption reaction (0 – 1kJ/mol).

Table 6: Isotherm constants for the adsorption of Cd(ii) onto onion and garlic.

	ONION		GARLIC	
ISOTHERM MODEL	**PARAMETERS**	**VALUES**	**PARAMETERS**	**VALUES**
Langmuir	q_t (mg/g)	2.07	q_t (mg/g)	2.05
	K_L (l/mg)	0.13	K_L (l/mg)	0.16
	R^2	0.847	R^2	0.963
Freundlich	K_f (mg/g)	0.32	K_f (mg/g)	0.36
	n	1.825	N	1.9305
	R^2	0.741	R^2	0.958
Temkin	B_1 (kg/mol)	0.461	B1 (kJ/mol)	0.447
	K_T (l/mg)	1.31	K_T (l/mg)	1.62
	R^2	0.756	R^2	0.946
D-R				
	β (mol^2/kJ^2)	6E – 07	β (mol^2/kJ^2)	2E – 06
	R^2	0.817	R^2	0.855
	E (kJ/mol)	0.91kJ/mol	E (kJ/mol)	0.5kJ/mol

Kinetic models

Lagergren pseudo first order equation The lagergren rate equation is given as:

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_{ad}}{2.303}\right)t \qquad (9)$$

Pseudo Second Order

The Pseudo Second Order equation is given as:

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{t}{q_e} \qquad [11]$$

(10)

TABLE 7: Kinetic model parameters

KINETIC MODEL	PARAMETER	ONION	GARLIC
Lagergren pseudo first order equation	K_{ad}	0.04	0.002
	q_e (exp) (mg/g)	1.58	2.48
	q_e (cal) (mg/g)	0.32	0.59
	R^2	0.471	0.004
Nataraja and Khalas Pseudo first order kinetic	K_{ad} (min^{-1})	-	0.02
	R^2	0.35	0.099
Pseudo second order kinetic	K_2 (g/mg min^{-1})	0.47	0.08
	q_e (exp) (mg/g)	1.53	2.48
	q_e (cal) (mg/g)	1.61	2.17
	R^2	0.999	0.815

Intra particle diffusion	K_d (mg/g min$^{-1}/_2$)	0.008	0.120
	I	1.499	2.818
	R^2	0.35	0.691
Bangham's kinetic model	K_o	0.00059	0.0017
	A	0.017	-0.194
	R^2	0.267	0.779

Table 8: Thermodynamic parameters for the adsorption of Cd(ii) ontoonion and garlic

Onion				Garlic		
T (K)	△G° (KJ/mol)	△H° (KJ/mol)	△S° (KJ/mol)	△G° (KJ/mol)	△H° (KJ/mol)	△S° (KJ/mol)
293	-1.45			-2.87		
313	-1.41			-2.32		
333	-1.70			-3.60		
353	-2.18	2.11	0.012	-4.80	4.58	0.024
373	-0.89			-4.05		

Equation 9 shows the Lagergren first order rate equation which isa plot of Log(q_e-q_t) against time t. The linear correlation coefficientvalues obtained for the adsorion of cd(ii) onto Onion and Garlic Skins arefound to be 0.471 and 0.004 (Table 7) which indicates that Lagergren first order rateequation is not suitable for predicting adsorption kinetic model. Beside, the adsorption capacities calculated(q_e) values for both adsorptionis far less that those obtained from the experiment. Similar result was obtained by [12]. The linear regression correlation coefficient values obtain for both adsorption of Cd(ii) onto onion and garlic skins was found to be 0.35 and 0.099 which is an indication that Natarjan and Khalaf rateequation is not suitable for the prediction of adsorption kinetic model. Table 7 shows the Pseudo-second order rate plot. This is Plot of t/qversus time ,t. The linear regression correlation coefficient obtained for the adsorption of Cd(ii) onto onion and garlic skins were found to be 0.999 and 0.815 respectively which indicates that this modelfit the adsorption kinetic model. Also, the adsorptive capacitiescalculated for both adsorptions was found to be very close when compared with those obtained from the experiment which is a confirmation of the suitability of Pseudo-second order rate equation.Similar to this result are those obtained by [13] .

Furthermore, the thermodynamic parameters of the adsorption processes were also calculated such as Gibbs free energy (ΔG^0), Enthalpy change (ΔH^0) and the standard Entropy

change (ΔS^0). The enthalpy change for the adsorption of cadmium onto Onion and Garlic were both positive (2110.92kJ/mol and 4575kJ/mol respectively) which indicates that both adsorption processes are endothermic process. However, the values of Gibbs free energy at all temperature for both adsorbent were all negative which indicates that both adsorption process are feasible and spontaneous process [11].

IV. CONCLUSION

The results obtained from this study showed that:

- Onion and garlic are effective adsorbent for the removal of Cd (II) from aqueous solution.
- The value of the separation parameter (R_L) obtained for onion and garlic are both in the range of 0-1 which indicate favourable adsorption.
- From Langmuir isotherm model, the adsorptive capacity of onion and garlic are 2.07mg/g and 2.05mg/g respectively.
- Langmuir isotherm favoured the biosorption of Cd (II) onto onion and garlic on the basis of correlation factor R^2.
- Adsorption of Cd (II) onto onion and garlic depends on pH, initial metal concentration, adsorbent dosage, agitation time and temperature of adsorption.
- The value on n obtained from Freundlich isotherm model for the biosorbent are both greater than 1, which indicates that the adsorption of Cd (II) onto onion and garlic is a physical process.
- Among all the kinetic models used, the pseudo-second order kinetic model was proved as the best fit for the adsorption of Cd(II) onto onion and garlic skin.
- From the thermodynamic studies, it can be shown that the adsorption processes was endothermic, spontaneous and increased degree of randomness.

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