Assessment of Langmuir, Freundlich and Dubinin-Radushkevich Adsorption Isotherms for the Biosorption of Mn (ii) Ions from Aqueous Solution by Untreated and Acid-Treated Corn Shaft

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Abstract – Manganese is widely known to be an essential element but not too many are aware of its toxicity in living organisms once it exceeds the ceiling value in the body. The application of agricultural waste prepared from untreated and acid-treated corn shaft were used for the removal of Mn(II) ions from aqueous solutions in a batch experiments on a temperature controlled orbital shaker at a speed of 150 rpm. The equilibrium studies involved the investigations of effect of contact time, initial metal concentrations, biosorbent dosage, pH and temperature on the adsorption capacity of the biosorbents. The uptake of Mn (II) ions by untreated and acid-treated corn shaft were found varies with all the factors mentioned above. Optimum uptake of Mn (II) ions was attained at a contact time of 80 minutes, initial metal concentration of 300 mg/L, biosorbent dosage of 1g, temperature of 80°C and pH of 3.0. The equilibrium data fitted well with the Langmuir isotherm followed by Freudlich isotherm and least in Dubinin-Radushkavich isotherm. Also, kinetic modeling revealed that the biosorption process is governed by Largergren first-order model. Desorption studies showed the reusability of corn shaft for subsequent biosorption studies. It was deduced that corn shaft is an effective biosorbent for the removal of Mn (II) ions from aqueous solutions.

Index Terms – Biosorption, Pollution, Corn shaft, Adsorption isotherms, Kinetic modeling and Manganese **Nomenclature** -UTCS = Untreated corn shaft, ATCS = Acid-treated corn shaft

1 INTRODUCTION

TNCREASE industrialization and advancement in technolog-Lical developments in this 21st century has been a thing of major concern as a result of its role in the environmental pollution. Many of their by-products contained toxic substances such as heavy metals. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metals are non-biodegradable. They tend to accumulate in the body system of living organisms which can eventually leads to death. Several industries such as mining, pigments, lather industries, electroplating and metallurgical processes often release metal ions such as copper, manganese, cadmium, chromium, lead, zinc and iron into the environment with the aquatic system been the most recipient [1]. The cost of removing these pollutants from contaminated environment using chemical precipitation, reverse osmosis, ion-exchange resins and electro-flotation is so exorbitant and in some cases, not efficient [3]. Thus, the use of biological origin as a biosorbent for the removal of heavy metals from aqueous solution is one of the most promising alternatives to conventional methods. Biosorption is a physicochemical process that occurs naturally in certain biomass which allows it to passively concentrate and bind contaminants onto its cellular structure [3]. Several bio-

logical biomasses have been demonstrated for effective removal of pollutants from the environment like hazelnut husks [4], cocoa shell [5], peanut hull [6], maize husk [7], kaolinite [8], magna [9], palm kernel fibre [10], agaricusbisporus [11] and natural zeolitic tuff [12].

Manganese is an essential chemical element that has daily dose requirements between 1.0 mg to 5.0 mg. It is necessary for born formation and metabolism of lipids, glicids and amino acids [13]. However, exposure to manganese above the ceiling value is harmful and has been linked to motor skill impairment and cognitive disorders [14]. Increased ferroportin protein expression in human embryonic kidney (HEK293) cells is associated with decreased intracellular manganese concentration and attenuated cytotoxicity, characterized by reversal of manganese-reduced glutamate uptake and diminished lactate dehydrogenase leakage [15]. Maize is an economical crop which is widely crown and well consumed locally in Nigeria. The shaft (which covers the cob) is left unused, thereby constituting environmental pollution.

The aim of this study is to examined the efficiency of raw and acid-treated corn shaft (a cellulosic agricultural waste) as sorbents for the removal of Mn(II) ions from aqueous solu-

tions. Biosorptionbehaviour was determined on the effect of contact time, initial metal concentrations, temperature, biosorbent dosage and pH. Kinetic parameters were also evaluated from the biosorption data. The suitability of Freundlich, Langmuir and Dubinin-Raduishkevich isotherms in the study of the biosorption of Mn (II) ions were also verified.

2 MATERIALS AND METHODS

2.1. Preparation of biosorbent

Fresh corn was obtained from Eruku village in Ewekoro Local government area of Ogun State, Nigeria and was used in this investigation as biosorbent. The shaft was removed from the cob and it was cut into smaller pieces and sun dried for 21 days. The biomass was then grounded using a mechanical grinder to very fine powder and sieved through a 150 mesh copper size. For the pre-treatment, about 100 g of the finely divided biosorbent was dissolved in 250 ml solution of 0.1M HCl acid in a 500 ml conical flask for 48 hours. It was then filtered and dried at 80°C for 12 hours.

2.2. Preparation of Mn (II) ion solution.

All chemicals were of analytical reagent grade. Mn (II) ion solutions were prepared by using MnCl₂ (Merck, Germany). Stock solution (1000 mg/L) of Mn (II) ions was prepared by dissolving 2.3g of MnCl₂ in 1dm³ distilled-deionized water. Several concentrations of Mn (II) ions ranging from 50 – 300 mg/L were prepared from this stock solution. The pH of the solution was adjusted with 0.1M HCl and NaOH solutions before the addition of the biosorbent.

2.3. Batch biosorption experiments

The batch biosorption experiments were carried out in 250 ml Erlenmeyer flasks containing 25 ml of Mn (II) ion solution on a temperature control shaker (SI-600R, Japan) at a temperature of 25°C. For the equilibrium experiment, 1g of the biosorbent was equilibrated with 25ml of Mn (II) solution at speed of 150 rpm for 80 minutes to attained equilibrium. The contents were filtered through whatman No1 filter paper and analysed for residual of Mn (II) ions. For the kinetic studies, the samples were taken at definite time intervals of 10, 20, 30, 40, 50, 60, 70 and 80 minutes and were filtered immediately to remove the biosorbent and Mn(II) ions in the remaining solution was analysed using a Unicam model 929 Atomic Absorption Spectroscopy. A Hanna 8521 model pH was used to determine the pH of the solution. The experiments were carried out in triplicate and the mean values calculated. The amount of metal ion adsorbed per unit mass of the biosorbent was estimated by using the equations below:

Where C_v is the initial metal ion concentration, and C_v is the metal ion concentration at equilibrium and v is the volume of metal ion solution in milliliters, w is the weight of the adsorbent in grams. The percentage of metal ion removed was estimated from the equation below:

Sorption percentage = $C_o - C_e \times v/m \times 100 \dots \dots \dots (2)$

3 RESULTS AND DISCUSSION

3.1. Effect of contact time and initial metal concentration on the biosorption of Mn (II) ions

The biosorption data for the sorption of Mn (II) ions on raw and acid-treated corn shaft showed that a contact time of 80 minutes was enough to attain equilibrium. Fig.1 shows the graph of the effects of contact time and initial metal concentrations on the uptake of Mn (II) ions by corn shaft. As can be seen from the graph, the uptake of Mn (II) ions increases with an increase in the contact time. The uptake of Mn (II) ion by raw corn shaft increases from 0.5 to 1.0 mg/g at initial metal concentration of 50 mg/L and then from 2.8 to 5.2 mg/g when the initial metal concentration was raised to 300 mg/L. Upon treatment with HCl acid, the uptake of Mn (II) ions increases from 0.7 to 1.3 mg/g at initial metal concentration of 50 mg/L and from 2.9 to 5.6 mg/g when the initial metal concentration was raised to 300 mg/L. From the experimental data, it is obvious that the biosorption process is high at initial stages and it becomes slower while approaching the equilibrium stage.

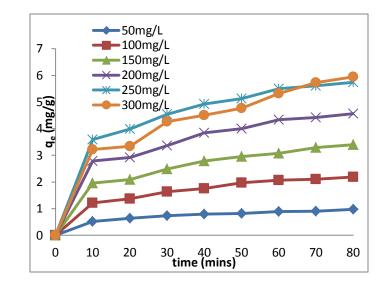


Fig. 1: Effect of contact time and initial metal concentration on the biosorption of Mn (II) ions by corn shaft.

At the beginning of the reaction, the number of the vacant negatively charged sites are much at the biosorbent surface to absorb the adsorbate and these sites gradually filled up as the process approaches the equilibrium stage and finally there were no more vacant sites to absorb the adsorbate at a contact time of above 80 minutes. This observation has been extensively reported in literature [16, 17].

3.2. Effect of biosorbent dosage on the biosorption of Mn (II) ions.

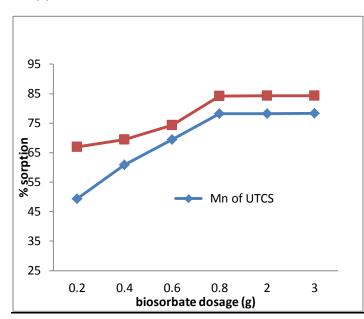


Fig.2: Percentage sorption of Mn (II) ions against biosorbent concentration by untreated and acid-treated corn shaft at a temperature of 80°C, pH of 3.0 for a contact time of 80mins and initial metal concentration of 300 mg/L.

The effect of biosorbent dosage on the biosorption of Mn (II) ion by corn shaft is presented in figure 2. As can be seen from the graph, the biosorption of Mn(II) ions increases with an increase in the biosorbent dosage and almost constant at dosage higher than 1g. Optimum uptake of Mn(II) ion by raw and acid-treated biosorbent prepared from corn shaft was 78.2% and 84.2% respectively at a biosorbent dosage of 1g. Above this dose, there was a decrease in sorption percentage. This could be as a result of partial aggregation of biosorbent at higher biosorbent dosage; which leads to a decrease in effective surface area for the biosorption [18].

3.3. Effect of temperature on the biosorption of Mn (II) ions.

Biosorption studies of Mn (II) with ordinary and acid-treated biomass was performed in a temperature controlled orbital shaker with a metal ion working capacity of 25 ml at a pH of 3.0 with initial metal concentration of 50 mg/L. The selected temperature for the biosorption of Mn (II) ions are: 25, 30, 45, 50, 60 and 80°C, while the graphical representation is shown in figure 3. The increase in the temperature of the system greatly enhanced the biosorption process. The uptake yield increased from 66.4 to 88.4% when raw biosorbent of corn shaft was used and upon treatment, the sorption capacity increase from 76.8 to 94.6% when the temperature of the system was raised from 25 to 80°C. The increase in Mn (II) ion uptake with temperature may be due to the desolvation of the sorbing species [13].

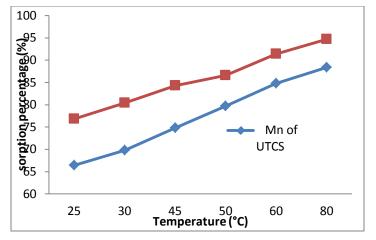


Fig.3: Percentage sorption of Mn (II) ions against temperature by untreated and acid-treated corn shaft at a pH of 3.0 for a contact time of 80mins and initial metal concentration of 300 mg/L.

3.4. Effect of pH on the biosorption of Mn (II) ions.

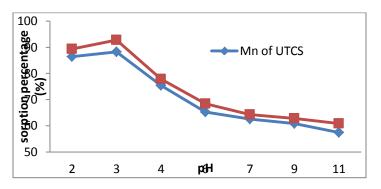


Fig.4: Percentage sorption of Mn (II) ions against pH by untreated and acid-treated corn shaft at a temperature of 80°C, biosorbents concentration of 1g, for a contact time of 80min and initial metal concentration of 300 mg/L.

The batch biosorption studies at different pH values were carried out in the range of 2.0, 3.0, 4.0, 6.0, 7.0, 9.0 and 11.0 on a temperature controlled orbital shaker at 25°C, initial metal concentration of 50 mg/L and a biosorbent dosage of 1g in a conical flask. Figure 4 shows that maximum uptake of Mn (II) by raw and acid-treated corn shaft were observed at a pH of 3.0. The sorption capacity of raw biosorbent increases from 86.4 to 88.3% when the pH was adjusted from 2.0 to 3.0 and then showed a gradual decrease from 88.3 to 57.4% when the pH was raised to 11.0. Upon treatment with acid, the efficiency of the corn shaft increased from 89.4 to 92.8% when the pH was raised from 2.0 to 3.0 and latter showed a decrease from 92.8 to 60.9% on adjusting the pH from 3.0 to 11.0. Earlier work on biosorption of metal ions showed that pH is an important parameter which is responsible for the protonation of metal binding sites, calcium carbonates solubility and metal specification in the solution [2]. Maximum metal sorption at lower pH seems to be due to a net positive charge on the sur-

face of corn shaft. On the other hand, increase in metal ions uptake with pH in acidic medium should be due to the electrostatic attraction between positively charged groups on the biosorbent surface and ions (CO_{3^2} , NO, OH) in the bulk for the biosorption of the active sites of the sorbate [13]. The possible formation of metal hydroxide at a pH of 7.0 and above may be responsible for the low biosorption capacity of the biosorbent.

3.5. Adsorption Isotherms Studies.

Where q_e is the amount adsorbed at equilibrium in mg/g, C_e is the concentration of the metal solution at equilibrium in mg/L, and n is the adsorption intensity.

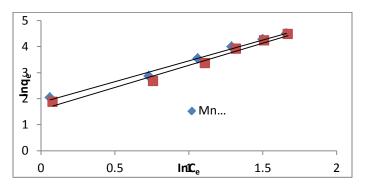


Fig.5: Freundlich adsorption isotherm plots for the biosorption of Mn(II) at pH 3.0. by untreated and treated corn shaft while the concentrations were varied.

The values of *n* indicate adsorption patterns while that of K_f estimates the bond strengths. The values of K_f and *n* were calculated from the intercept ($logK_f$) and slope (1/n) of the linear plots of lnq_e versus lnC_e which is shown in figure 5 and the tabulation of the results is shown in Table 1 and 2. The Freundlich isotherm gives a good fits to the biosorption process as evidence from the value of the correlation coefficient (R^2) for both biosorbents. The comparatively higher values of K_f obtained for acid-treated corn shaft shows that the metal ions bond strongly onto the surface of the biosorbents. The Langmuir model assumes a monolayer adsorption in a homogeneous surface. The linear form of the Langmuir equation is given as:

$$C_e/q_e = C_e/q_{max} + 1/bq_{max} \dots \dots (4)$$

Where C_e and q_e stand for the concentration at equilibrium and amount of sorbate adsorbed at equilibrium, b stands for adsorption or constant of affinity which is related to the heat of adsorption (dm³/g) and q_{max} stands for the biosorbentsorbing capacity. The values of q_{max} and b were calculated from the intercept (1/b q_{max}) and slope (1/ q_{max}) of the plot of C_e/q_e against C_e which is shown in figure 6 and the physical parameters are tabulated in Table 1 and 2. As can be seen from the table, high values of correlation coefficient for both biosorbents indicate that the sorption of Mn (II) ions fit into the Langmuir model. The values of q_{max} which are higher for the acid-treated corn shaft confirms that the sorption capacity of the raw biomass was higher than that of the raw. In the Langmuir isotherm, the adsorption intensity (R_L) is given as:

Where *b* is a constant of affinity and C_o is the initial concentration in mg/L. when the values of R_L at different concentrations is between 0 and 1, the biosorption process is favourable, if it is greater than unity, it is unfavourable and if it is unity, it is linear and if it is equal to zero, it is irreversible. For this study, the values of R_L obtained are presented in table 1 and 2. Since the values of R_L for raw and treated corn shaft are less than unity i.e. $0 < R_L < 1$, the biosorption process is favourable.

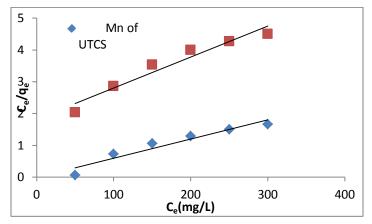


Fig.6: Langmuir adsorption isotherm plots for the biosorption of Mn(II) at pH 3.0. by untreated and treated corn shaft while the concentrations were varied.

The linear form of the Dubinin-Radushkevich isotherm is given is as:

Where *R* is the molar gas constant in Jmol⁻¹K⁻¹, *T* is the absolute temperature in Kelvin and *C*^{*e*} is the concentration of the sorbate at equilibrium. The values of q_m and β represent the intercept and slope of the plot of Inq^e against ϵ^2 as shown in figure 7 and the tabulations are presented in table 1 and 2.

The relationship: $\epsilon = 1/\sqrt{\beta}$, defines the free mean energy (kJmol⁻¹) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution. If the values of ϵ is less than 8kJmol⁻¹, the adsorption process is physical in nature, if it between 8 and 16kJmol⁻¹, it follows ion-exchange and higher values of 24.7±3.2kJmol⁻¹ indicates strong chemisorptions formation between the bio-

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sorbent and the adsorbate. The results showed that the value of ε is -2.69kJmol⁻¹ for raw corn shaft and -2.73kJmol⁻¹ for acid-treated corn shaft which suggeste that the biosorption process is physical in nature for both biosorbents. High values of q_m for both biosorbents implies high adsorption capacities. Throughout the adsorption process, acid-treated biomass shows high values of adsorption capacity for the three tested isotherms.

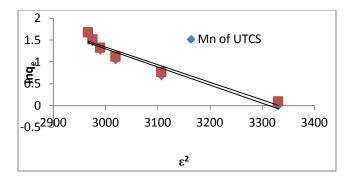


Fig.7: Dubinin-Raduishkavich adsorption isotherm plots for the biosorption of Mn(II) at pH 3.0. by untreated and treated corn shaft while the concentrations were varied.

On comparing the values of the correlation coefficient (R²) for the three tested isotherms, it can be observed that the biosorption data of the raw corn shaft fitted well with the Langmuir isotherm followed by Freundlich isotherm and least in Dubinin-Radushkevich isotherm. Upon treatment of the biosorbent with acid, the sorption data fitted well with Freundlich isotherm followed by Langmuir isotherm and least in Rubini-Radushkevich isotherm.

It is obvious from Table 3 that by comparing the maximum adsorption capacities (q_{max}) of UTCS and ATCS wastes with other adsorbents from literature, UTCS and ATCS have great potentials for the removal of Mn (II) ions from aqueous solutions.

 Table 1: Langmuir, Freundlich and Dubinin-Radushkevich

 Isotherms parameters for the adsorption of Mn (II) in single

 solute solution by untreated corn shaft

	Langmuir			Freundlich			Dubinin- Radushkevich			
Co	q _{max}	b	\mathbf{R}^2	R _L	n	K _f	\mathbf{R}^2	$\mathbf{q}_{\mathbf{m}}$	β	\mathbf{R}^2
50	1.0	0.2	0.9	0.6	2.2	1.5	0.8	0.7	10.4	0.7
100 150 300	1.1 2.5 5.2	0.2 0.1 1.7	0.9	0.2 0.2 2.1	2.9	1.7 1.9 2.2	0.9 0.8 0.9	0.8 0.9 1.1	10.8 11.1 13.2	0.8 0.8 0.9

 Table 2: Langmuir, Freundlich and Dubinin-Radushkevich

 Isotherms parameters for the adsorption of Mn(II) in single

solute solution by acid-treated corn shaft.

Langmuir			Freundlich			Dubinin- Radushkevich				
Co	q _{max}	b	\mathbf{R}^2	$\mathbf{R}_{\mathbf{L}}$	n	$\mathbf{K}_{\mathbf{f}}$	\mathbf{R}^2	каu q _m	-	R ²
50	1.3	0.2	0.9	0.8	4.3	3.6	0.8	0.7	12.4	0.8
100	1.6	0.3	0.9	0.8	4.4	3.7	0.9	0.9	13.1	0.9
150	2.9	1.2	0.9	1.2	6.3	4.2	0.8	1.2	13.4	0.8
300	5.6	2.4	0.9	2.7	8.1	5.5	0.9	2.6	13.4	0.7

Table 3: Maximum adsorption capacities for manganese adsorption by different adsorbents.

Adsorbents	q _{max} (mg/g)	References
Kaolinite	0.446	Yavuz, et al. 2003
Natural Zeolite tuff	10.0	Rajic, et al. 2009
Magna	175.2	Mohamed, 2001
Pseudomonas	22.4	Silva, et al. 2009
aeruginosa		
Aspergillus niger	19.34	Parvathi, et al.
		2007
Saccharomyces	18.95	Parvathi, et al.
cerevisiae		2007
UTCS	5.2	Present study
ATCS	5.6	Present study

3.6. Kinetic Modelling.

In order to examine the biosorption kinetics, the Lagergren firstorder model and Ho's pseudo-second-order model were applied. The linearized integrated form of the Largergren is given as:

$$\log(q_e - q_t) = \log q_e - tk_1/2.303 \dots \dots \dots \dots (8)$$

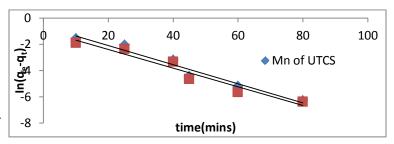


Fig.8:Largergren-speudo-first-order model of untreated and acd-treated corn shaft.

Where q_e is the amount of metal adsorbed at equilibrium (mg/g), q_t is the amount of metal adsorbed (mg/g) at time t and k_1 is the Largergren rate constant for adsorption (min⁻¹). The plot of $\log(q_e - q_t)$ versus *t* gives a straight line with a slope of $k_1/2.303$ and an intercept of $\log q_e$ as shown in figure 8 and the physical parameters are presented in Table 4.

Table 4: Kinetic Model parameters for the adsorption of Mn

 (II) ion untreated and acid treated corn shaft at different initial

First-o	rder kinetic mode	l				
Co	q _e exp.(mg/g)	k ₁	qecal.(mg/g)	\mathbf{R}^2		
		(min ⁻¹)				
50	1.01	0.07	1.41	0.97		
100	1.11	0.02	1.52	0.87		
150	2.12	0.13	3.52	0.95		
200	2.31	0.01	2.53	0.94		
Second-order kinetic model						
Second	-order kinetic mo	del				
Second C _o	-order kinetic mo q _e exp.(mg/g)	k ₂	q _e cal.(mg/g)	R ²		
		_	q _e cal.(mg/g)	R ²		
		k ₂	q_ecal.(mg/g) 6.67	R ² 0.94		
Co	q _e exp.(mg/g)	k ₂ (min ⁻¹)				
C _o 50	q e exp.(mg/g) 1.01	k ₂ (min ⁻¹) 0.44	6.67	0.94		

Kinetic Model parameters for the adsorption of Mn (II) ion acid-treated corn shaft

First-order kinetic model

metal ion concentrations.

Co	qeexp.(mg/g)	k ₁ (min ⁻¹)	qecal.(mg/g)	\mathbf{R}^2			
50	1.21	0.16	1.31	0.99			
100	1.61	0.026	1.82	0.96			
150	2.42	0.132	3.52	0.85			
200	4.31	0.51	6.53	0.93			
Second	Second-order kinetic model						
Co	q _e exp.(mg/g)	k ₂	qecal.(mg/g)	\mathbf{R}^2			
		(min ⁻¹)					
50	1.21	0.24	4.17	0.96			
100	1.61	0.58	5.22	0.94			
150	2.42	0.64	10.73	0.98			
200	4.31	0.77	1481	0.89			

The linearized intergrated form of the Ho's pseudo secondorder-model is expressed as: $t/q_t = 1/k_2q_e^2 + t/q_e \dots \dots \dots \dots \dots \dots (9)$

The plot of t/q_t against t should give a straight line with a slope of $1/q_e$ and intercept of $1/k_2q_e^2$. Figure 9 shows the graphical representation of the Ho's pseudo-second-order model and the fitting parameters are presented in Table 4. Although, the values of the correlation coefficient (R²) for both biosorbents were high enough for both first and second-order models, it is deduced from the plots that the data fitted very well with the Largergren pseudo-first-order. Also, the values of the calculated adsorption capacity (q_{ecal} .) for the first-order model are more close to the experimental adsorption capacity (q_{exp}) when compared with values of second-order model. It can therefore be concluded that the sorption process of Mn (II) ions by raw and acid-treated corn shaft in this study followed Largergren pseudo-first-order model.

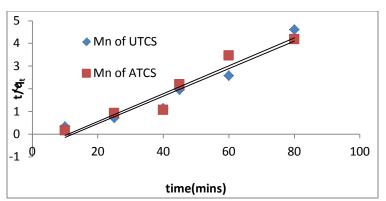


Fig 9: Ho's second-order model of untreated and acid-treated corn shaft.

3.7. Desorption study.

The ability of raw and acid-treated corn shaft to undergo regeneration and reusability were examined using 0.5M HCl as desorbing agent. Manganese-exhausted of raw and acidtreated corn shaft were subjected to desorbing using 20 ml of the eluent. The adsorption-desorption data are shown in figure 10, while the parameters are not shown in this studies. It can be observed from the plots that the percentage of adsorption of the untreated corn shaft decrease from 76.4 to 64.7%, while the percentage desorption increases from 20.46 to 36.78%. Upon treatment of the biosorbent with acid, the percentage adsorption decrease from 80.3 to 66.6%, while desorption percentage increases from 30.9 to 48.2%. The results revealed that the capabilities of reusability of both biosorbents in the sorption of Mn(II) ions from aqueous solution decreases with an increase in the number of cycles, mean while, the desorption capacities of both biosorbents increases with the number of cycles. The Langmuir parameters also showed that the adsorption capacity (q_{max}) decreases as the number of cycles (reusability) increases. This further confirms the weakness or reduction in the sorption potential of both biosorbents with an increase in the number of cycles. Desorption affinity values obtained from this study is less than one, which suggested that desorption is favourable.

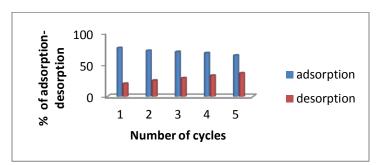


Fig. 10 : sorpetion percentage against number of cycles for untreated corn shaft.

4 CONCLUSIONS

The present study shows that untreated and acid-treated corn shaft were effective biosorbents for the sorption of manganese ions from aqueous solution. The uptake of Mn (II) ions by the biosorbents were found vary with initial metal concentration, biosorbent dosage, contact time, temperature and the pH of the system. The biosorption equilibrium data were found to fit Langmuir, Freundlich and Rubinin-Radushkevich isotherms; although, better fitting was observed with Langmuir isotherm followed by Freudlich isotherm and least with Rubinin-Radushkevich isotherm. However, acid-treated corn shaft exhibited the better biosorption potency for Mn (II) ions between the two biosorbents assessed.

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