

Biosorption of Cr (VI) ion from Aqueous Solution by Maize Husk: Isothermal, Kinetics and Thermodynamic Study

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Summary: The kinetics, equilibrium and thermodynamic of the biosorption of Cr (VI) ion onto maize husk biomass from aqueous solution were investigated. The effects of contact time, initial metal concentration, pH, temperature as well as modification with oxalic acid on biosorption capacity were studied. The maximum biosorption capacity of the untreated corn shaft biomass (UTCS) was found to be 28.49 mg g⁻¹ which slightly increased to 29.33 mg g⁻¹ when treated with oxalic acid treated corn shaft biomass (ATCS). The kinetics studies showed that the biosorption process of the metal ion fitted well with second order model. The calculated thermodynamic parameters (ΔG° , ΔH° and ΔS°) showed that the biosorption of Cr (VI) ion onto the biomass maize husk is feasible, spontaneous and exothermic in nature.

Key words: Biosorption, Kinetics, Maize husk, Thermodynamics, Equilibrium.

Introduction

Environmental contamination by toxic metals is a serious problem worldwide due to their incremental accumulation in the food chain and continued persistence in the ecosystem. Conventional technologies, such as ion exchange, chemical precipitation, oxidation reduction, filtration, electrochemical techniques and other sophisticated separation processes using membranes, are often ineffective and/or expensive, particularly for the removal of heavy metal ions at low concentrations (below 50 mg L⁻¹). Furthermore, most of these techniques are based on physical displacement or chemical replacement, generating yet another problem in the form of toxic sludge, the disposal of which adds further burden on the techno-economic feasibility of the treatment process.

Chromium (VI) ion is a major toxic pollutant which entered the water streams through various industrial operations. The potential sources of chromium (VI) ion are effluents from metallurgy, electroplating, leather tanning, textile dyeing, paint, ink, and aluminium manufacturing industries. Cr(VI) ion is carcinogenic to both human and animals [1]. Strong exposure of chromium ion causes cancer in the digestive tract and lungs. It may also cause gastric pain, nausea, and vomiting, severe diarrhea and haemorrhage [2]. According to the United States Environmental Protection Agency (USEPA) the maximum permissible limits of total chromium in

wastewater and potable water is below 1.0 mg L⁻¹ and 0.05 mg L⁻¹ respectively [3].

Biosorption is regarded as an innovative technology to remove metals from aqueous solution because it has some obvious advantages [4] such as; high efficiency and selectivity for absorbing metals in low concentrations, energy-saving, broad operational range of pH and temperature, easy reclamation of metals, and easy recycling of the biosorbent. In the recent years, many biosorbent materials of agricultural based have been utilized for heavy metal biosorption [5, 6, 7]. These include: coconut husk and shell [8, 9], sea weeds [10], and bagasse ash [11]. In this study, we used maize husk for the preparation of biosorbent for the removal of chromium (VI) ion. The effect of solution pH, biosorbent dose, initial chromium (VI) ion concentrations and contact time were investigated in a batch system.

Results and discussion

Characterization of the Biosorbent

Fig. 1 shows the FTIR vibrational spectra of maize husk. The sharp band at 3893 and 3796 cm⁻¹ is assigned to C=C of phenyl group. The wide band with maxima at 3421 cm⁻¹ was assigned to the stretching of O-H group of macromolecular association, the band at 2822 cm⁻¹ was assigned to –

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CH- bond of methyne group present in the maize huk structure. The sharp band observed at 1716 cm^{-1} was assigned to a C=O bond of carboxylic acid that is usually present in fiber materials containing pectin. The strong peak that appears at 1647 cm^{-1} is C-O stretching vibration of a carboxylic acid that exists in with intermolecular hydrogen bond. The sharp peak

observed at 1541 cm^{-1} is assigned to C - C ring stretch of aromatic rings. In addition the band of 1419 cm^{-1} confirms the presence of C=C of aromatic rings. Several bands ranging from 1314 to 1041 cm^{-1} refer to C O bonding of phenols. The FTIR data corroborated by the proximate analysis confirms the functional groups in the biosorbent [12].

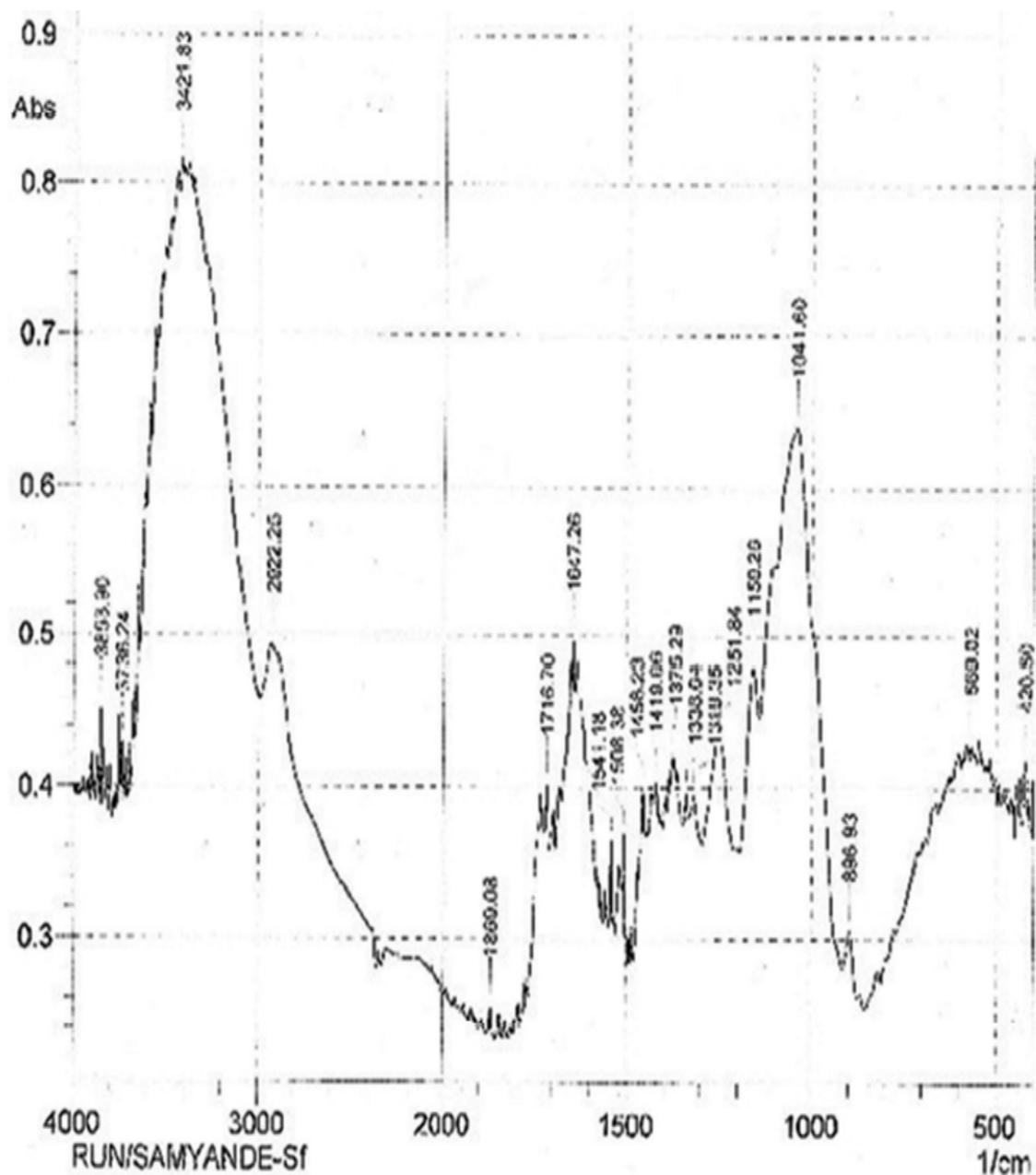


Fig. 1: FTIR spectra of maize husk before adsorption.

Effect of Hydrogen ion Concentration

The results show that maize husk biosorbed substantial quantity of Cr (VI) at lower pH, however, it was observed that the extent of sorption of chromium ion by the biosorbent decreases with increase in pH. Fig. 2 shows that maximum sorption was observed at the pH 2.0 with the percentage sorption of 91.7 % for raw biosorbent (UTCS) and 94.6 % for oxalic acid modified biosorbent (ATCB). Minimum sorption of 60.4 % was observed for UTCS while that of ATCS was 65.4 % at pH of 11. Cr (VI) occurs in the form of oxy anion as $HCrO_4^-$, $Cr_2O_7^{2-}$, CrO_4^{2-} , $Cr_4O_{13}^{2-}$ and $Cr_3O_{10}^{2-}$; the lowering of pH causes the surface of the sorbent to be protonated to a large extent. This results in a stronger attraction for negatively charged Cr complex ion in the solution. Hence, the sorption increases with the decrease pH of the solution. But as the pH rises, the concentration of OH^- ion increases and overall charge on the sorbent surface becomes negative which causes hindrance in the sorption of negatively charged Cr complex ion, resulting in the decreased sorption of Cr (VI) at higher pH [13].

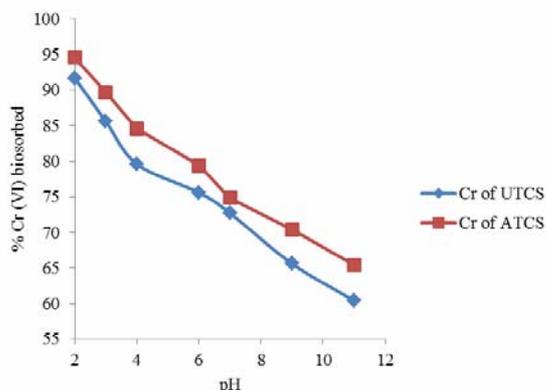


Fig. 2: pH dependence of sorption of Cr (VI) ion onto raw and oxalic acid treated maize husk.

Effect of Biosorbent Dosage

The study of the effect of biosorbent dosages on the removal of Cr (VI) ion from aqueous solution was carried-out at different adsorbent doses ranging between 0.20 – 3.0 g using 100.0mg L^{-1} of the metallic ion solution. It was observed that highest quantitative removal of the metallic ion was attained at biosorbent dosages of about 0.8 g (Fig. 3). The initial increases in the percentage of metallic ion removal with biosorbent dosages could be attributed to increases in the adsorbent surface areas, augmenting the number of adsorption sites available

for adsorption. For biosorbent dosages higher than the optimum dosage values for the metal ion stated above, decrease in the percentage of metallic ion removal may be due to the concentration gradient between adsorbate and biosorbent with increasing biomass concentration causing a decrease in the amount of metallic ion adsorbed per gram of biomass [14].

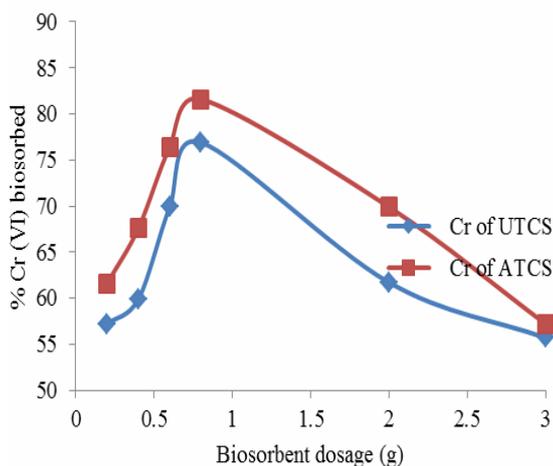


Fig. 3: Dependence of sorption of Cr (VI) ion on the amount of raw and oxalic acid treated maize husk.

Effect of Contact Time and Initial Metal Concentration

Experimental studies for investigating the effect of contact time were carried out at constant temperature (298 K) with varying initial metal ion concentrations of Cr(VI) ($50, 100, 150, 200, 250$ and 300 mg L^{-1}) using 1.0 g L^{-1} adsorbent dosage at pH 2.0. Fig. 4 and 5 illustrate the effect of contact time on Cr(VI) biosorption. The equilibrium time of Cr(VI) biosorption onto maize husk (UTCS) seems to be independent of the initial metal ion concentration due to the fact that in all cases, equilibrium is reached within 80 min (Fig. 4). This result is important because equilibrium time is one of the parameters for economical wastewater treatment plant application [15]. This behavior suggests that at the initial stage adsorption takes place rapidly on the external surface of the adsorbent followed by a slower internal diffusion process, which may be the rate-determining step. From Fig. 5, (i.e. on ATCS) it is evident that when the initial concentration increases, the equilibrium time is longer. While at low initial concentrations the equilibrium time is around 80 min, at higher concentrations the equilibrium time seems to be prolonged to 150 min.

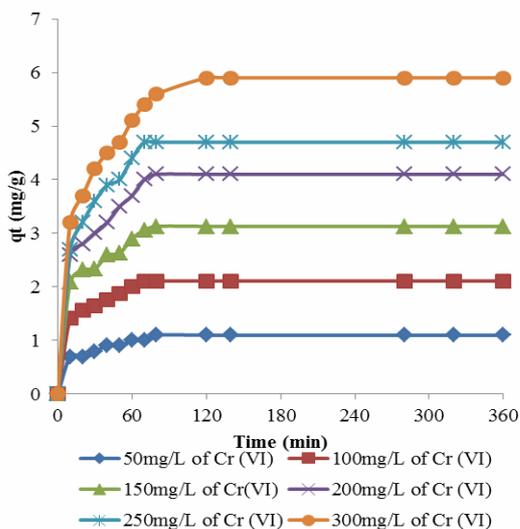


Fig. 4: Effect of contact time and initial Cr(VI) ion concentration on biosorption process for acid treated maize husk (ATCS).

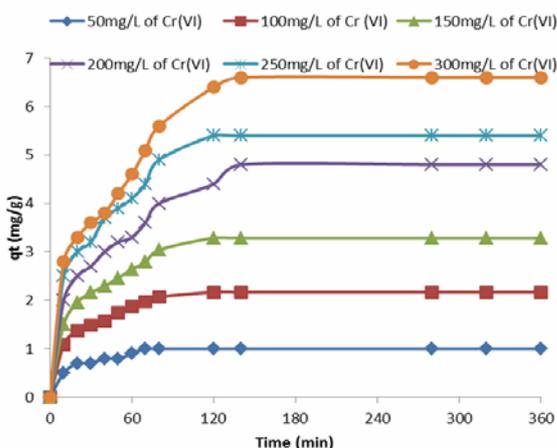


Fig. 5: Effect of contact time and initial Cr(VI) concentration on biosorption process for raw maize husk (UTCS).

Biosorption Kinetics

Adsorption kinetic study is important in treatment of aqueous effluents as it provides valuable information on the reaction pathways and the mechanism of adsorption process. Many kinetic models had been developed in order to determine the intrinsic kinetic adsorption constants, traditionally, the kinetics of metal ion adsorption is described following the expression originally given as equation

3 [16]. A simple kinetic analysis of adsorption under the pseudo-first-order assumption is given by equation 3 below:

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{3}$$

where q_e and q_t are the amounts of Cr (VI) ion biosorbed (mg g^{-1}) at equilibrium and at time t (min), respectively, and k_1 the rate constant adsorption (min^{-1}), and t is the contact time (min). The integration of Eq. (3) with initial condition, $q_t = 0$ at $t = 0$, and $q_t = q_t$ at $t = t$, yields equation 4 below:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

Values of k_1 were calculated from the plots of $\ln(q_e - q_t)$ versus t (Fig. 6) for different concentration of Cr (VI) ion. The correlation coefficient values ranged between 0.88 and 0.97. It is obvious from Table-2 that, the experimental q_e values are not in agreement with the calculated ones. This shows that, although, the biosorption process fitted somehow well with pseudo first-order kinetics, but unacceptable due to the disparity in the values of experimental q_e and calculated q_e .

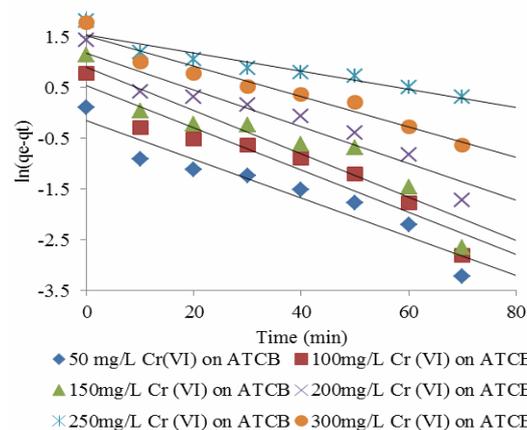


Fig. 6: Pseudo first order kinetic model for the biosorption of Cr(VI) ion on acid treated biomass.

Table-1: Proximate Analysis of maize husk.

Parameters	% composition
Moisture	5.2
Crude protein	4.8
Ash contents	10.1
Crude fibre	1.05
Carbohydrate	56.47
Fat contents	22.38

Table-2: Kinetic parameters of Biosorption of Cr (VI) on maize husk biomass.

Cr(VI) Biosorption on raw maize husk							Cr(VI) Biosorption on acid treated maize husk					
Conc (mg/L)	50	100	150	200	250	300	50	100	150	200	250	300
Pseudo first order kinetic model												
$q_{e(Exp)}$ (mg/g)	1.000	2.070	3.040	4.000	4.900	5.600	1.100	2.170	3.130	4.100	6.100	5.900
$q_{e(Calc)}$ (mg/g)	0.777	1.780	2.432	3.115	3.866	4.708	0.776	1.709	2.487	3.511	4.691	4.565
k_1	0.033	0.038	0.031	0.028	0.028	0.029	0.031	0.042	0.043	0.042	0.018	0.030
R^2	0.920	0.960	0.970	0.950	0.960	0.940	0.920	0.910	0.880	0.880	0.910	0.950
% SSE	0.037	0.048	0.101	0.148	0.172	0.149	0.054	0.077	0.107	0.098	0.235	0.223
Pseudo second order kinetic model												
$q_{e(Calc)}$ (mg/g)	1.060	2.164	3.125	4.049	4.983	5.708	1.113	2.232	3.211	4.243	5.718	6.002
k_2	0.099	0.051	0.034	0.025	0.020	0.015	0.122	0.069	0.049	0.031	0.014	0.018
R^2	0.962	0.969	0.966	0.960	0.957	0.936	0.974	0.981	0.980	0.973	0.901	0.966
% SSE	0.010	0.016	0.014	0.008	0.014	0.018	0.002	0.010	0.014	0.024	0.064	0.017

A second-order kinetic model is based on equilibrium adsorption [17] and it is expressed as shown equation 5:

$$t/q_t = 1/k_2 q_e^2 + (1/q_e)t \tag{5}$$

where k_2 ($g\ mg^{-1}\ min^{-1}$) is the rates constant of second-order adsorption. If second-order kinetics is applicable, the plot of t/q versus t should show a linear relationship (Equation 5). There is no need to know any parameter beforehand and q_e and k_2 can be determined from the slope and intercept of the plot. The linear plots of t/q versus t (Fig. 7) show a good agreement between experimental and calculated q_e values (Table-2). The correlation coefficients for the second-order kinetic model ranged between 0.90 and 0.98 indicating the suitability of the pseudo second order kinetic equation model. Therefore, the biosorption process of Cr (VI) ion on maize husk is second-order in nature.

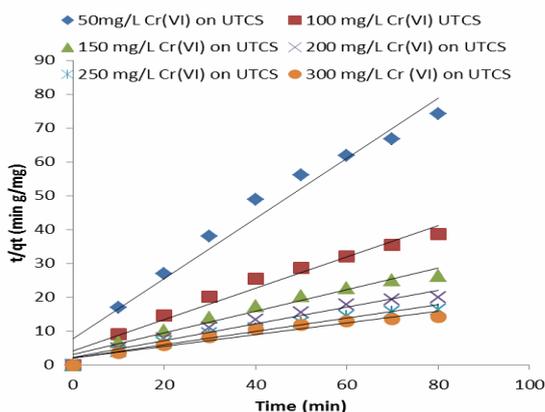


Fig. 7: Pseudo second order kinetic model for the biosorption of Cr(VI) ion on raw biomass. Statistical Test for the Kinetic Data

Although, the R^2 i.e. the correlation coefficients were used to compare the data, the models were also evaluated further by the percentage

error function which measures the differences (% SSE) in the amount of the metallic metal ion up taken by the adsorbent predicted by the models, (q_{cal}) and the actual, i.e. q_{exp} measured experimentally [1, 14]. The validity of each model was determined by the sum of error squares (SSE, %) given by:

$$\% SSE = \sqrt{\frac{(q_{(exp)} - q_{(cal)})^2}{N}} \tag{6}$$

where, N is the number of data points. The higher is the value of R^2 and the lower is the value of SSE; the better will be the goodness of fit. From Table-2, the lower values of % SSE further confirm the acceptability of the pseudo second order kinetic model.

Adsorption Isotherms:

An adsorption isotherm represents the equilibrium relationship between the adsorbate concentration in the liquid phase and that on the adsorbents surface at a given condition. A number of isotherms have been developed to describe equilibrium relationships. In the present study, Langmuir, Freundlich, and Temkin models were used to describe the equilibrium data. The results are shown in Table-3 and the modeled isotherms are shown in Fig. 8-10.

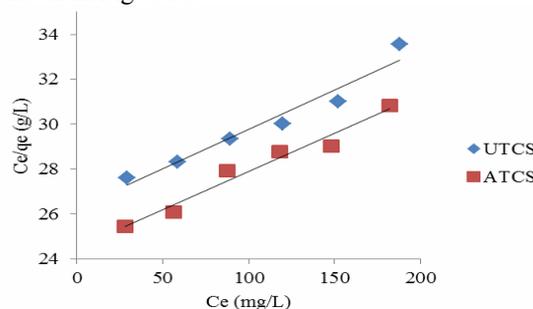


Fig. 8: Langmuir adsorption isotherm for the biosorption of Cr(VI) ion on raw and acid treated biomass.

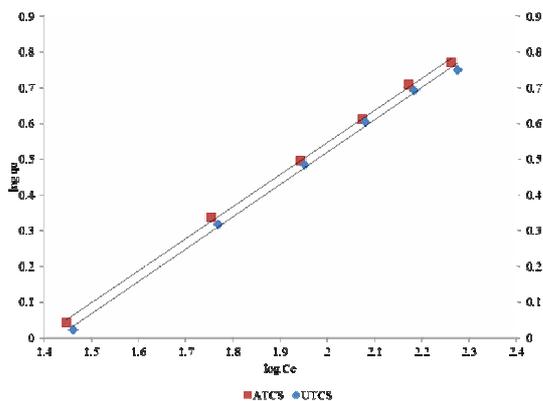


Fig. 9: Freundlich adsorption isotherm for the biosorption of Cr(VI) ion on raw and acid treated biomass.

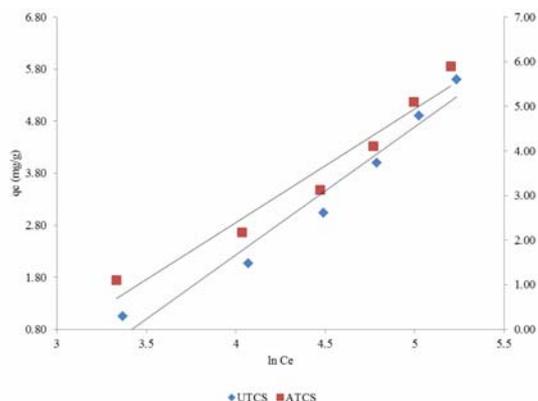


Fig. 10: Temkin adsorption isotherm for the biosorption of Cr(VI) ion on raw and acid treated biomass.

The Langmuir Isotherm Model

Langmuir, in 1918 [18] observed sorption phenomena and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. He proposed the sorption isotherm based on the assumption that (i) adsorbates are chemically adsorbed at a fixed number of well defined sites, (ii) each site can only hold one adsorbate specie; (iii) all sites are energetically equivalent and (iv) that there are no interactions between the adsorbate species.

The Langmuir isotherm equation is written as:

$$q_e = \frac{Q_{max} b C_e}{1 + b C_e} \tag{10}$$

where C_e is the supernatant concentration after the equilibrium of the system (mg L^{-1}), b the Langmuir affinity constant (L mg^{-1}), and Q_{max} is the maximum

adsorption capacity of the material (mg g^{-1}) assuming a monolayer of adsorbate uptaken by the adsorbent. The linear form of the equation can be written as in equation 11 below.

$$\frac{C_e}{q_e} = \frac{1}{Q_{max} b} + \left(\frac{1}{Q_{max}}\right) C_e \tag{11}$$

The shape of the Langmuir isotherm can be used to predict whether a sorption system is favorable or unfavorable in a batch adsorption process (Fig. 8).. The values of R^2 in Table-3 show that Cr(VI) biosorption has a better fitting for Langmuir Isotherm and the biosorption capacities obtained compared favourably with other biosorbent [8, 11, 13, 22 - 26] (Table-5).

The essential features of the isotherm can also be expressed in terms of a dimensionless constant separation factor (R_L) that can be defined by the relationship in equation 12 [14].

$$R_L = \frac{1}{(1 + b C_i)} \tag{12}$$

where C_i is the initial concentration (mg L^{-1}). The value of separation parameter R_L provides important information about the nature of adsorption. The value of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$). It can be explained apparently that when $b > 0$, sorption system is favorable [19, 27, 28]. The values of R_L in this study are presented in Table-3 and it implied that the process is favourable.

The Freundlich Isotherm Model

The Freundlich isotherm is based on the assumption of non-ideal adsorption on heterogeneous surfaces and the linear form of the isotherm can be represented as in equation 13 [20]:

$$\log q_e = \log K_F + \log C_e \tag{13}$$

where, K_F is the Freundlich constant related to sorption capacity ($(\text{mg g}^{-1}) (\text{L g}^{-1})^{1/n}$) and n is related to the adsorption intensity of the adsorbent. Where, K_F and $1/n$ can be determined from the linear plot of $\log q_{eq}$ versus $\log C_e$. The value of K_F from this study showed that Cr (VI) have high affinity for the biosorbent and has a better fitting. The values of $1/n$ indicate that the surface is heterogeneous (Table-3, Fig. 9).

Table-3: Isotherm parameters.

	Raw maize husk	Acid treated maize husk
Langmuir Isotherm		
q_{max} (mg/g)	28.49	29.33
b	0.0013	0.0014
R_L (L mg ⁻¹)	0.714	0.705
R^2	0.948	0.966
Freudlunch Isotherm		
$1/n$	0.998	0.999
K_F (mg g ⁻¹)	0.0507	0.055757
R^2	0.9074	0.901
Temkin Isotherms		
a_T (L mg ⁻¹)	0.045	0.047
b_T (kJ mol ⁻¹)	1.01	0.97
R^2	0.9617	0.953

The Temkin Isotherm Model

Temkin isotherm model was also used to fit the experimental data. Unlike the Langmuir and Freundlich equation, the Temkin isotherm takes into account the interaction between adsorbents and metal ion to be adsorbed and is based on the assumption that the free energy of sorption is a function of the surface coverage [19]. The linear form of the Temkin isotherm is represented as in equation 14:

$$q_e = \frac{RT}{b_T} \ln a_T C_e \quad (14)$$

Upon linearization, the equation becomes:

$$q_e = B \ln a_T + B \ln C_e \quad (15)$$

where C_e is concentration of the adsorbate at equilibrium (mg L⁻¹), q_e is the amount of adsorbate sorbed at equilibrium (mg g⁻¹), $RT/b_T = B$ where T is the temperature (K), and R is the ideal gas constant (8.314 J mol⁻¹ K⁻¹) and ‘ a ’ and b_T are constants. A plot of q_e versus $\ln C_e$ (Fig. 10), enables the determination of constants ‘ a ’ and b_T . The constant b_T is related to the heat of adsorption and also related to bonding energy. The parameter “ a ” is the equilibrium binding constant (L min⁻¹) corresponding to the maximum bonding energy. The typical binding energy reported for ion exchange mechanism is between 8 and 16 kJ mol⁻¹. Bonding energy of up to -20 kJ mol⁻¹ indicates physiosorption due to electrostatic interaction between the charged particle, whereas more negative than -40 kJ mol⁻¹ indicates chemisorption process [20,21]. The values b_T in this study (see Table-3) show that the process is not purely chemisorption [14].

Biosorption Thermodynamics

Equilibrium distribution of the metal ion between the solution and the biosorbent, the equilibrium constant K_D could easily be written as:

$K_D = \frac{M^{n+}_{solution}}{M^{n+}_{Biosorbed}}$, in other word, the equilibrium constant, $K_D = \frac{C_e}{q_e}$.

This constant can be used to estimate the thermodynamic parameters owing to its temperature dependence. The thermodynamic parameters i.e. ΔG° , ΔH° and ΔS° were estimated from the following relation:

$$\Delta G^\circ = -RT \ln K_D \quad (18)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S \quad (19)$$

A plot of ΔG° against the temperature, (Fig. 11) gives a straight line graph with intercept as ΔH° and slope as ΔS° . The thermodynamic parameters are presented in Table-4. The negative ΔG° values indicated thermodynamically feasible and spontaneous nature of the biosorption. The decrease in ΔG° values show a decline in feasibility of biosorption as temperature is increased. The ΔH° parameter was also found to be negative indicating exothermic nature of the biosorption processes. The negative ΔS° value means a decrease in the randomness at the solid/solution interface during the biosorption process.

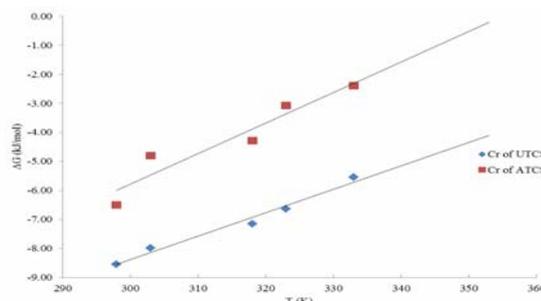


Fig. 11: Temperature dependent of the free energy (ΔG) for the biosorption of Cr(VI) ion on raw and acid treated biomass.

Table-4: Thermodynamic parameters.

Temperature (K)	$\ln K_D$	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (kJ mol ⁻¹ K ⁻¹)	R^2
Cr(VI) Biosorption on raw maize husk					
298	3.451	-8.55			
303	3.17	-7.99			
318	2.71	-7.15	-32.59	-0.0807	0.9788
323	2.47	-6.64			
333	2.00	-5.54			
353	0.378	-1.11			
Cr(VI) Biosorption on acid treated maize husk					
298	2.62	-6.50			
303	1.91	-4.81			
318	1.62	-4.29	-37.47	-0.106	0.907
323	1.15	-3.08			
333	0.86	-2.39			
353	1.37	-4.01			

Table-5: Comparison of Adsorption capacity of various adsorbents for Cr (VI) ion.

Adsorbent	Maximum adsorption Capacity (mg g ⁻¹)	Reference
Bagasse fly-ash	260	[8]
Coconut husk fibers	29	[5]
M. hiemalis	47.4	[10]
R. Nigerican	47	[19]
Red mud	1.6	[20]
Sawdust	3.3	[21]
Sugar cane bagasse	34	[22]
Groundnut Husk	7	[23]
Maize husk	28.49	Present study
Oxalic acid Maize husk	29.33	Present study

Experimental

Biosorbent Preparation

Maize husk was collected from the University of Agriculture's Farm, in Abeokuta Nigeria. It was washed with distilled water and cut into small pieces. The pieces was blended and extracted with hot water several times until the supernatant was colourless. It was then dried at 105 °C. The biomaterial was sieved to obtain particle sizes in the range of 150 - 500 µm. The material was divided into two parts. One part was used raw, while the other was treated with oxalic acid as earlier described [14]. The concentration of Cr (VI) ion in the biosorbent were determined by placing 1g of the adsorbent in 10 ml de-ionized water for two hours with continuous agitation, after which it was centrifuged at 2000 rpm. The supernatant was analysed using a flame Atomic Absorption Spectrophotometer (FAAS) Buck Scientific 310 VGP. The proximate analyses of the maize husk used for this study is presented in Table-1. The sorbent was further characterized with FTIR analysis before and after the experiment.

Preparation of Aqueous Solution of Metal Ion

The aqueous solution of Cr (VI) ion was prepared from analytical grade of K₂CrO₇. 1000 mg L⁻¹ aqueous solution (stock solution) of the salts was prepared with de-ionized water in 1 % HNO₃ solution, the stock solution were diluted with de-ionized water to obtain the working standard solution. The pH of the solutions were adjusted with aliquots of 1.0 mol L⁻¹ of HCl and NaOH and checked on a Radiometer PHM 85 Research pH meter, which had earlier been standardized with standard buffer solution pH 4.00 and 7.00.

Equilibrium Studies

Equilibrium adsorption isotherms were performed in a batch process as earlier described [14]. The amount of metal ion sorbed by the

biosorbent at equilibrium, q_e (mg g⁻¹), was calculated using equation 1 below:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

where C_o and C_e (mg L⁻¹) are the liquid-phase concentration of the metal ion at initial and equilibrium, respectively. V is the volume of the solution (L), and W is the mass of dry adsorbent used (g).

Batch Kinetic Studies

The procedures of kinetic experiments were basically identical to those of equilibrium tests [14]. The aqueous samples were taken at preset time intervals, and the concentration of the metal ion was measured. The amount of metal ion sorbed at time t , q_t (mg g⁻¹), was calculated with equation 2:

$$q_t = \frac{(C_o - C_t)V}{W} \quad (2)$$

where C_o and C_t (mg L⁻¹) are the liquid-phase concentration of the metal ion at initial and at time t , respectively. V is the volume of the solution (L), and W is the mass of dry adsorbent used (g).

Conclusion

The results of this study added maize husk to the list of agricultural waste that can be used for heavy metal remediation of the aqueous environment even at low concentration contamination. Its use as biosorbent can be of commercial benefit because of its low preparation cost and besides, it is highly available in all parts of Nigeria. Modification with oxalic acid also enhanced the capacity for the removal of the metal ion. Its use in environmentally friend manner will be a value added rather than being a nuisance to the environment especially during the harvesting period.

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