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Kinetic, thermodynamic and isothermal parameters of biosorption of Cr (VI) and Pb (II) ions from aqueous solution by biosorbent prepared from corncob biomass

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ABSTRACT

The kinetics, equilibrium and thermodynamic of the biosorption of Cr (VI) and Pb (II) ions onto corncob from aqueous solution were investigated. Optimum experimental parameters were determined to be pH 5.8 for Pb (II) and pH 2.0 for Cr (VI), contact time of 80 min, and temperature 25 °C. The maximum biosorption capacity of the biomass was found to be 8.07 mg g^{-1} for Cr (VI) and 9.05 mg g^{-1} for Pb (II). Upon treatment with oxalic acid, the values of maximum biosorption capacity for Cr (VI) and Pb (II) were found to be 10.74 and 10.27 mg g^{-1} respectively. The kinetic studies showed that the biosorption process of the metal ions fitted well with second order model. The calculated thermodynamic parameters ($\Delta G°$, $\Delta H°$ and $\Delta S°$) showed that the biosorption of Cr (VI) and Pb (II) ions onto corncob biomass is feasible, spontaneous and exothermic in nature.

KEYWORDS

Biosorption;
Kinetics;
Corncob;
Thermodynamics;
Equilibrium.

INTRODUCTION

Heavy metals presence in the environment is of major concern due to their extreme toxicity. Their accumulations in the food chain, even at relatively low concentrations pose threats to human, plants and animals. According to the United States Environmental Protection Agency (USEPA) list of organic and inorganic pollutants of 1978, antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium and zinc constitute serious health hazards, when found in wastewater.

Various industrial processes had been identified as sources of lead contamination in wastewater which include: battery manufacturing, printing and pigment, metal plating and finishing, ammunition, soldering material, ceramic and glass industries, iron and steel manufacturing units[18]. Exposure to lead causes severe damage to kidney, nervous system, reproductive system, liver and brain in man[4]. Similarly, chromium is a toxic metal with many in-dustrial applications. Although, it exist in two oxidation states – Cr (III) and Cr (VI) – the hexavalent form is considered to be dangerous to human owing to its mutagenic and car-cinogenic properties[7]. Also Cr (VI) has been indicated to cause severe diarrhea, ulcers, eye and skin irritation, kidney dysfunction and probably lung carcinoma[32]. Its uses include: electroplating, tan-ning, textile dyeing and as a biocide in cooling water of power plants, all these culminated to the discharge of chro-mium containing effluents.

Since most heavy metal ions are toxic to living organisms and are non-degradable, they are persistent in the environment. Therefore, their elimination from wastewater is important to protect public health. Various treatment techniques and processes have been used to remove the pollutants especially metal ions from contaminated water[34] some of which include; reverse osmosis, ion exchange, reduction precipitation and lime coagulation. These methods are ineffective at lower concentrations of metal ions and also generate large quantity of toxic sludge, which is to be disposed in further steps[1,2].

Among all the proposed alternatives, sorption is one of the most popular methods and is currently considered as an effective, efficient and economical method of wastewater purification. Biosorption is a relatively new process that has proven very promising in the removal of contaminants from aqueous effluents using low-cost adsorbents derived from agricultural materials[26]. Compared with conventional treatment methods, biosorption is characterized by low-cost, high efficiency, minimization of chemical and/or biological sludge, regeneration of biosorbent, no additional nutrient requirement, and possibility of metal recovery. Agricultural residues are lignocellulosic substances, containing three main structural components: hemicelluloses, cellulose and lignin[34]. [17](2008) investigated the sorption of Pb (II), Cu (II), Zn (II) and Ni (II) on a lignin isolated from black liquor, a waste product of the paper industry, and found that lignin had affinity to the metal ions in the following order: Pb (II) > Cu (II)> Cd (II) >Zn (II) >Ni (II). The sorption of Cd (II) from aqueous solution by rice husk, a surplus agricultural byproduct was also investigated by Kumar and Bandyopadhyay[19]. They reported an increase in the sorption capacity of rice husk upon simple and low-cost chemical modifications.

Recently, we have reported the biosorption of Mn (II) from aqueous solution using corncob biomass, in this study, corncob biomass was used as a biosorbent for the removal of Cr (VI) and Pb (II) ions in aqueous solution in batch processes. In order to understand the nature of the sorption process, kinetic data, equilibrium isotherms and thermodynamic parameters have been evaluated, the effect of parameters such as pH, biosorbent dosage and desorption study were also reported.

MATERIALS AND METHODS

Biosorbent preparation

Corncob 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 extracted with hot water several times until the supernatant was colourless, and dried at 105 °C. The biomaterial was sieved to obtain a particle size range of 150 - 500 μm, this was stored in clean air-tight containers. The material was divided into two parts. One part was used raw, while the other was treated with oxalic acid as earlier described[2]. The concentrations of Cr (VI) and Pb (II) in the adsorbent 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 corncob 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 ions

The aqueous solutions of Cr (VI) and Pb (II) metal ions were prepared from analytical grades of K_2CrO_7 and $Pb(NO_3)_2$ respectively. 1000 mg L^{-1} aqueous solutions (stock solutions) of these salts were prepared with de-ionized water in 1 % HNO_3 solution and these stock solutions were diluted with de-ionized water to

TABLE 1 : Proximate analysis of the corncob

Parameter	% composition
Moisture contents	5.9
Crude protein	18.43
Ash contents	2.8
Crude fibre	0.86
Carbohydrate	68.71
Fat contents	3.3

obtain the working standard solutions. The pH adjustments of the solutions were made with aliquots of 1.0 mol L^{-1} of HCl and NaOH, The pH of the solution was checked on a Radiometer PHM 85 Research pH meter, which had earlier been standardized with standard buffer solutions pH 4.00 and 7.00.

Equilibrium studies

Equilibrium adsorption isotherms were performed in a batch process as earlier described[2]. The amount of metal ion adsorbed by the biosorbent at equilibrium, qe (mg g-1), was calculated using equation 1 below:

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

where Co and Ce (mg L^{-1}) are the liquid-phase concentrations 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. The aqueous samples were taken at preset time intervals, and the concentrations of the metal ions were similarly measured. The amount of metal ion adsorbed at time t, qt (mg g-1), was calculated with equation 2:

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

where Co and Ct (mg L^{-1}) are the liquid-phase concentrations 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).

Desorption studies

In order to know if the adsorption process is less economical, regeneration of the exhausted biosorbents is necessary. After the attainment of equilibrium, the supernatants were decanted and desorption experiments were carried out. The used biosorbents was washed with 40 mL of distilled-deionized water for 5 minutes followed by drying in an oven at 80 oC and cooled at room temperature. Thereafter, 20 mL of 0.5 M of HCl was added as a desorbing agent to each of the biosorbent contained in a conical flask. The mixture was place on a rotator shaker at a speed of 150 rpm with a contact time of 60 minutes. After removing the conical flask from the shaker, solutions were decanted and diluted prior to analysis by AAS. To regenerate, the sample procedure was followed for three cycles. After each adsorption and desorptions, the biosorbent was washed with distilled-deionized water and reconditioned for adsorption in the succeeding cycle.

RESULTS AND DISCUSSION

Characterization of the biosorbent

Figure 1 shows the FTIR vibrational spectra of corncob. The wide band with maxima at 3416 and 3405 cm^{-1} were assigned to the stretching of O-H and N-H groups of macromolecular association, the band at 2864 cm^{-1} was assigned to –CH– bond of methyne group presented in the corncob structure. The sharp band observed at 1734 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 1653 cm^{-1} is C-O stretching vibration of a carboxylic acid that exists in with intermolecular hydrogen bond. The sharp peak observed at 1516 cm^{-1} is assigned to C – C ring stretch of aromatic rings. In addition the band of 1429 cm^{-1} confirms the presence of C=C of aromatic rings. Several bands ranging from 1314 to 1041cm^{-1} refer to C O bonding of phenols. The FTIR data corroborated the proximate analysis and confirm the functional groups in the biosorbent[17].

Effect of hydrogen ion concentration

The results show that corncob biosorbed substantial quantity of Cr (VI) at lower pH, however, it was

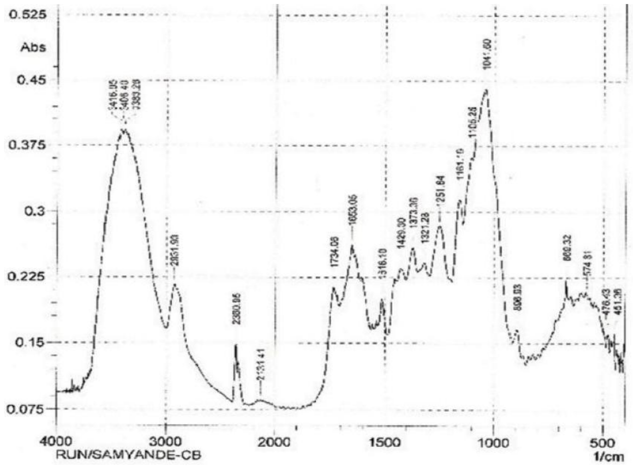

Figure 1 : FTIR spectra of corncob before adsorption

observed that the extent of sorption of chromium ions by the biosorbent decreases with increase in pH. Figure 2a shows that maximum sorption was observed at the pH 2.0 with the percentage sorption of 72.6 for raw biosorbent (UTCB) and 75.6 for oxalic acid modified biosorbent (ATCB). Minimum sorption of 11.8 % was observed for UTCB at pH of 7.0 while that ATCB was 13 % at pH of 9. 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 ions in the solution. Hence, the sorption increases with the decrease pH of the solution. But as the pH rises, the concentration of OH- ions increases and overall charge on the sorbent surface becomes negative which causes hindrance in the sorption of negatively charged Cr complex ions, resulting in the decreased sorption of Cr (VI) at higher pH [32].

Figure 2b shows the pH dependence biosorption of Pb (II) ion by UTCB and ATCB, the maximum absorption was obtained at pH of around 6 for the two biosorbents. However, oxalic acid modification improves the biosorption of Pb (II) on to the corncob. While the maximum sorption of 68 % was recorded for the raw biosorbent, 76 % was recorded for the oxalic acid modified sorbent. The sorption capacity increases with increase pH with minimum at pH of 2, as the pH approaches 7, sorption capacity begins to fall. This has been attributed to the formation of hydroxide of lead at alkaline pH[4].

Effect of biosorbent dosage

The study of effect of biosorbent dosages for removal of Cr (VI) and Pb (II) 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 solutions. It was observed that quantitative removals of the metallic ions were attained for biosorbent dosages of at least 0.8 g for Cr (VI) and 0.7 g for Pb (II) (see Figure 2c). The initial increases in the percentage of metallic ions 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 ions stated above, decrease in the percentage of metallic ions 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[33].

Biosorption kinetics

Adsorption kinetic study is important in treatment of aqueous effluents as it provides valuable information

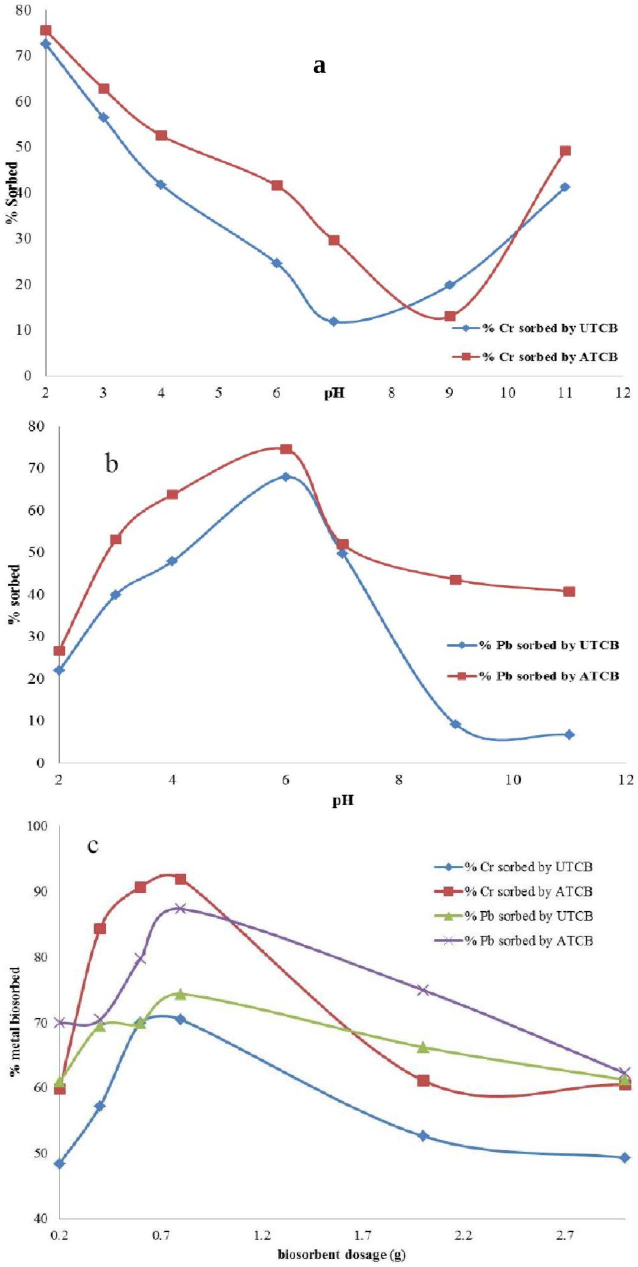

Figure 2: pH (a and b) and Dosage (c) dependence of sorption of Cr (VI) and Pb (II) ion onto raw and oxalic acid treated corncob.

on the reaction pathways and in the mechanism of adsorption process. Many kinetic models had been developed in order to find intrinsic kinetic adsorption constants, traditionally, the kinetics of metal ions adsorption is described following the expressions originally given by [22](1898). A simple kinetic analysis of adsorption under the pseudo-first-order assumption is given by equation 3 below:

$$\frac{dq}{dt} = k1(q_e - q_t) \qquad (3)$$

where qe and qt are the amounts of Cr (VI) and Pb (II) ions biosorbed (mg g-1) at equilibrium and at time t (min), respectively, and k1 the rate constant adsorption (min-1), and t is the contact time (min). The integration of Eq. (3) with initial conditions, qt = 0 at t = 0, and qt = qt at t = t, yields equation 4:

$$In(q_e - q_t) = Inq_e - k_1t \qquad (4)$$

Values of k1 were calculated from the plots of ln (qe - qt) versus t (Figure 3) for different concentrations of Cr (VI) and Pb (II) ions. The correlation coefficient values ranged between 0.81 and 0.97. It is obvious from TABLE 2 that, the experimental qe values are not totally 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 qe and calculated qe.

A second-order kinetic model is based on equilibrium adsorption[23] and it is expressed as shown equation 5:

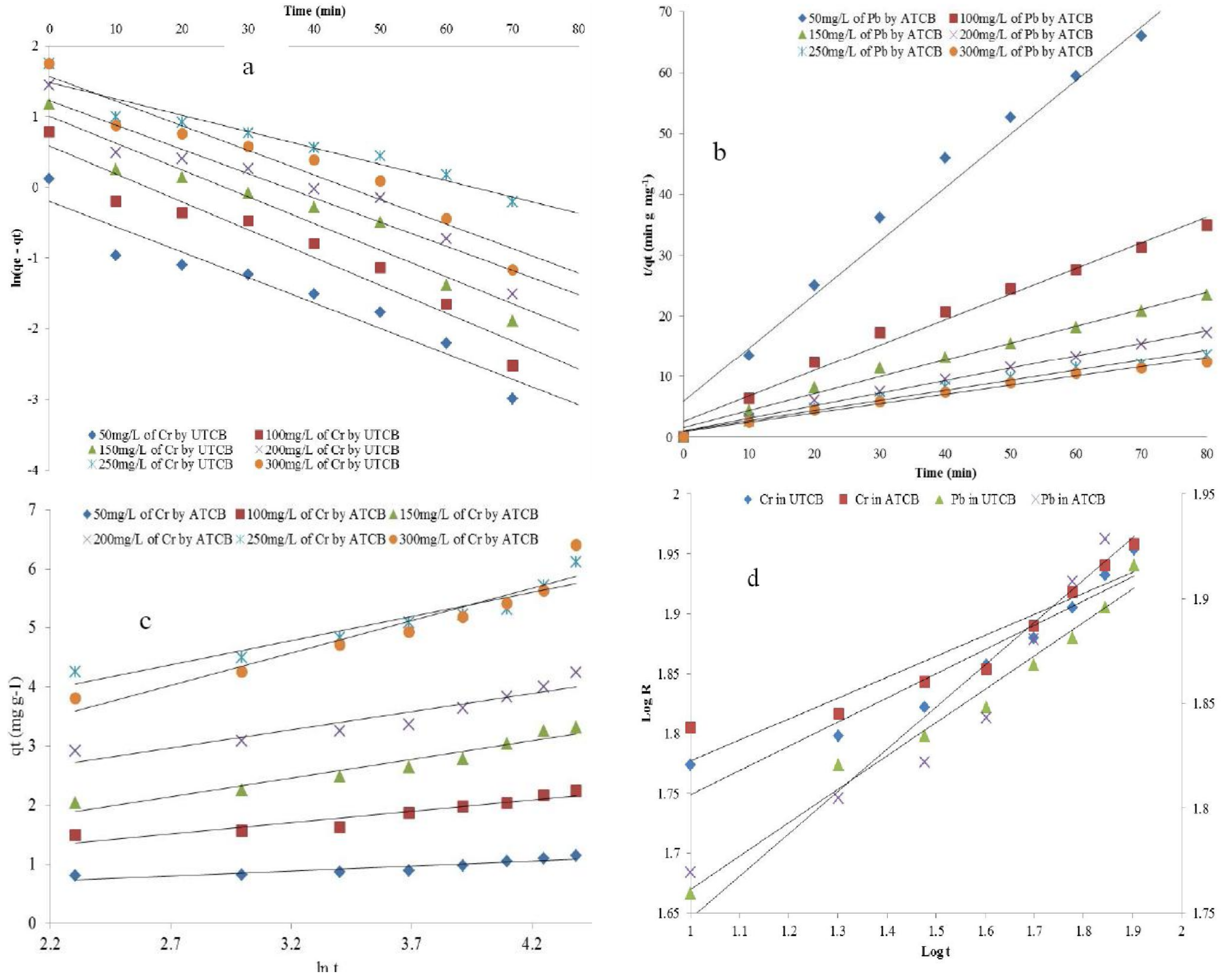

Figure 3 : Kinetic isotherms for the biosorption of Cr (VI) and Pb (II) ions (a) pseudo first order (b) pseudo second order (c) Elovich Model (d) Intraparticulate diffusion model.

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

where k2 (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 qe and k2 can be determined from the slope and intercept of the plot. The linear plots of t/q versus t (Figure 3b) show a good agreement between experimental and calculated qe values (TABLE 2). The correlation coefficients for the second-order kinetic model ranged between 0.929 and 0.992 indicating the suitability of the pseudo second order kinetic equation model. Therefore, the biosorption process of Cr (VI) ion and Pb (II) on corncob is second-order in nature.

Statistical test for the kinetic data

Although, the R2 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, (qcal) and the actual, i.e. qexp measured experimentally[2]. The validity of each model was determined by the sum of error squares (SSE, %) given by:

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

where, N is the number of data points. The higher is the value of R2 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 ofthe pseudo second order kinetic model.

TABLE 2: Kinetic parameters of Biosorption of Cr (VI) and Pb (II) using corncob biomass

	Cr (VI) Biosorption with raw corncob						Cr (VI) Biosorption with treated corncob						Pb (II) Biosorption with raw corncob						Pb (II) Biosorption with treated corncob					
Conc (mg/L)	**50**	**100**	**150**	**200**	**250**	**300**	**50**	**100**	**150**	**200**	**250**	**300**	**50**	**100**	**150**	**200**	**250**	**300**	**50**	**100**	**150**	**200**	**250**	**300**
Pseudo first order kinetic model																								
q_e (exp)	1.10	2.19	3.24	4.20	5.70	5.70	1.10	2.24	3.31	4.20	6.10	6.40	1.00	2.24	3.80	4.57	5.60	6.14	1.10	2.20	3.40	4.60	5.88	6.40
q_e (calc)	0.78	1.79	2.72	3.48	4.43	4.78	0.68	1.74	3.02	2.91	3.70	4.26	0.82	1.71	2.89	3.81	3.87	4.96	0.75	1.64	2.81	3.41	4.87	4.48
k_1	0.031	0.040	0.038	0.035	0.023	0.034	0.028	0.041	0.045	0.035	0.030	0.025	0.038	0.034	0.026	0.051	0.040	0.039	0.030	0.045	0.051	0.053	0.045	0.036
R^2	0.920	0.930	0.930	0.900	0.930	0.920	0.810	0.930	0.880	0.910	0.870	0.900	0.950	0.940	0.930	0.970	0.940	0.900	0.880	0.950	0.970	0.960	0.830	0.930
%SEE	0.054	0.066	0.087	0.121	0.212	0.153	0.070	0.083	0.048	0.216	0.400	0.357	0.031	0.089	0.152	0.127	0.289	0.196	0.059	0.093	0.099	0.198	0.169	0.321
Second order kinetic model																								
q_e (calc)	1.113	2.268	3.361	4.312	5.618	5.882	1.088	2.311	3.446	4.252	6.042	6.270	1.074	2.289	3.810	4.771	5.724	6.309	1.099	2.304	3.574	4.780	5.949	6.515
k_2	0.122	0.057	0.035	0.026	0.016	0.018	0.145	0.064	0.038	0.038	0.031	0.022	0.100	0.057	0.026	0.036	0.032	0.022	0.130	0.073	0.045	0.045	0.027	0.025
R^2	0.974	0.974	0.966	0.960	0.929	0.959	0.967	0.980	0.975	0.979	0.983	0.970	0.969	0.974	0.948	0.988	0.988	0.978	0.967	0.986	0.986	0.992	0.982	0.985
%SEE	0.002	0.013	0.020	0.019	0.014	0.030	0.002	0.012	0.023	0.009	0.010	0.022	0.012	0.008	0.002	0.033	0.021	0.028	0.000	0.017	0.029	0.030	0.011	0.019
Elovich Model																								
A	0.495	0.875	1.007	1.259	1.041	1.459	2.678	1.361	1.248	4.405	10.14	2.807	0.187	0.862	0.931	2.669	6.389	2.254	0.749	1.578	1.646	4.572	3.869	3.789
B	5.141	2.449	1.571	1.227	0.857	0.865	7.342	2.618	1.581	1.593	1.202	0.911	4.155	2.412	1.345	1.221	1.176	0.851	5.731	2.666	1.564	1.334	1.011	0.909
R^2	0.881	0.916	0.898	0.876	0.816	0.890	0.642	0.898	0.943	0.863	0.895	0.894	0.961	0.924	0.840	0.971	0.942	0.961	0.819	0.937	0.948	0.938	0.940	0.956
Intraparticulate diffusion																								
K^{id}	35.205	29.444	26.878	26.971	24.166	22.387	40.031	33.978	29.282	36.358	37.316	30.627	35.441	40.579	32.085	24.194	29.499	26.897	40.607	37.008	35.826	34.332	43.082	27.756
A	0.202	0.239	0.255	0.245	0.267	0.267	0.175	0.212	0.245	0.180	0.163	0.211	0.216	0.178	0.225	0.282	0.241	0.248	0.193	0.203	0.216	0.206	0.181	0.241
R^2	0.923	0.944	0.928	0.914	0.936	0.932	0.872	0.913	0.963	0.910	0.945	0.986	0.979	0.953	0.942	0.977	0.957	0.984	0.936	0.927	0.948	0.925	0.972	0.904

Conditions: Temperature was fixed at 25 °C, pH 5.8 for Pb (II) and pH 2 for Cr (VI) biosorbent dosage 1.0 g.

The Elovich equation

The Elovich equation is based on equilibrium adsorption and it is generally expressed as shown by equation 7[27]:

$$q_t = 1/\beta\, \text{In}(\alpha\beta) + 1/\beta\, \text{In}(t) \qquad (7)$$

where α is the initial adsorption rate (mg g-1 min-1), β is the desorption constant (g mg-1) during any experiment. If the adsorption fits the Elovich model, a plot of qt vs ln (t) should yield a linear relationship with a slope of (1/β) and an intercept of (1/β)ln (αβ). The graph of the Elovich model for the biosorption of the Cr (VI) acid treated corncob biomass at 25 oC is shown in Figure 3c. The values of R2 for the parameters of the Elovich model show that the data does not fit well for Cr (VI) ion biosorption thereby suggesting that the process is not purely chemisorption. However, the Pb (II) biosorption on to the biomass could be said to involve chemisorption process.

The intraparticle diffusion model

The intraparticle diffusion model is expressed as in equation 8:

$$R = K_{id} t^{a} \qquad (8)$$

The linearised form of equation 8 is written as follow:

$$\log R = \log K_{id} + a \log t \qquad (9)$$

where R is the percentage metal ion biosorbed, t is the contact time (min), "a" is the gradient of linear plots, Kid is the intraparticle diffusion rate constant (min-1), "a" depicts the adsorption mechanism. Kid is taken as a rate factor, i.e. percentage metal ion biosorbed per unit time. If the mechanism of adsorption fits the intraparticle diffusion model, then a plot of 1og R against 1og t will yield a straight line (Figure 3d) with a slope "a" and an intercept of 1og Kid. The intraparticle diffusion model for the adsorption of the Cr (VI) and Pb (II) ions by the raw and treated corncob biomass at 25 oC is shown in Figure 8 below. The curves show a kind multi-linearity for the two metal ions, which implies that the adsorption process involves more than one kinetic stage (or sorption rates)[13]. The values of Kid were calculated from the slope of such plots and the R2 values led to the conclusion that the intraparticle diffusion process is the rate-limiting step. Higher values of Kid illustrate an enhancement in the rate of biosorption; such high Kid values illustrate a better adsorption mechanism, which is related to an improved bounding between the metal ions and the biosorbent particles (TABLE 2).

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, Temkin, Dubinin-Radushkevich (D-R) models were used to describe the equilibrium data. The results are shown in TABLE 3 and the modeled isotherms are shown in Figure 4 (a – c).

The langmuir isotherm model

Langmuir, in 1918 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 assumptions 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:

$$q_e = \frac{Q_{max} b c_e}{1 + b c_e} \qquad (10)$$

where Ce is the supernatant concentration after the equilibrium of the system (mg L^{-1}), b the Langmuir affinity constant (L mg-1), and Qmax 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.

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

The shape of the Langmuir isotherm can be used to predict whether a sorption system is favorable or unfavorable in a batch adsorption process. The values of R2 in TABLE 3 for Langmuir Isotherm show that Cr (VI) have a better fitting than the Pb (II) ion.

The essential features of the isotherm can also be expressed in terms of a dimensionless constant separation factor (RL) that can be defined by the relationship in equation 12[5].

$$R_L = \frac{1}{(1 + b c_i)} \qquad (12)$$

where Ci is the initial concentration (mg/L). The value of separation parameter RL provides important information about the nature of adsorption. The value of RL indicated the type of Langmuir isotherm to be irreversible (RL = 0), favourable (0 < RL <1), linear (RL = 1) or unfavourable (RL > 1). It can be explained apparently that when b > 0, sorption system is favorable[8]. The values of RL in this study are presented in TABLE 3 and it implied that the process is favourable, however, Cr (VI) data fitted well than those of the Pb (II) ion (Figure 4a).

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[11]:

$$\log q_e = \log K_F + 1/n \log C_e \qquad (13)$$

where, KF is the Freundlich constant related to sorption capacity ((mg g-1) (L g-1))1/n and n is related to

TABLE 3 : The Adsorption isotherms of biosorption of Cr (VI) and Pb (II) on corncob biomass

	Cr (VI)		Pb (II)	
	Raw Biomass	Acid Treated Biomass	Raw Biomass	Acid Treated Biomass
Langmuir Isotherm				
qmax (mg/g)	8.636	10.741	9.0498	10.267
b (L/mg)	0.0282	0.0238	0.0440	0.0437
R^2	0.995	0.969	0.840	0.721
R_L	0.415	0.457	0.312	0.314
Freudlinch Isotherm				
KF (mg/g)(l/mg)1/n	1.565	1.497	0.588	0.528
1/n	0.010	0.012	0.050	0.050
R^2	0.753	0.834	0.947	0.937
Temkin Isotherm				
a	1.808	2.096	2.598	2.673
b_T (kJ/mol)	0.313	0.302	0.260	0.881
R^2	0.983	0.962	0.884	0.960
Dubinin - Radushkevich Isotherm				
qmax (mg/g)	249.46	246.88	6637.56	1933.53
B	6 x10^{-07}	6 x10^{-07}	1 x10^{-06}	9 x10^{-07}
R^2	0.926	0.915	0.982	0.937
Ea (kJmol)	2.582	2.582	2.000	2.108

the adsorption intensity of the adsorbent. Where, KF and 1/n can be determined from the linear plot of log qeq versus log Ce. The value of KF from this study showed that Cr (VI) have higher affinity than the Pb (II) ion, although the latter has a better fitting than the former, and the value of 1/n showed that the surface is heterogeneous (TABLE 3; Figure 4b).

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 interactions between adsorbents and metal ions to be adsorbed and is based on the assumption that the free energy of sorption is a function of the surface coverage[8]. The linear form of the Temkin isotherm is represented as in equation 14:

$$qe = \frac{RT}{b_T} Ina_T C_e \qquad (14)$$

Upon linearization, the equation becomes:

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

where Ce is concentration of the adsorbate at equilibrium (mg/L), qe is the amount of adsorbate sorbed at equi-

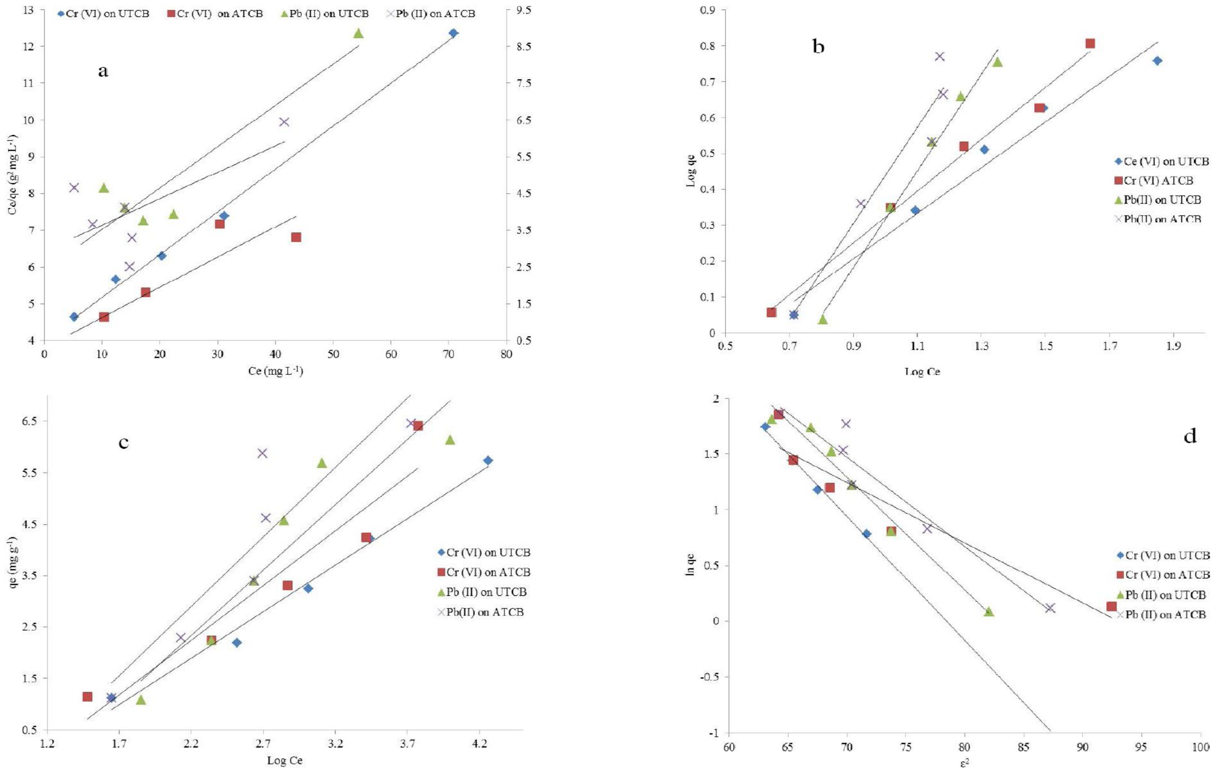

Figure 4: Biosorption isotherms for the biosorption of Cr (VI) and Pb (II) ions (a) Langmuir Isotherm (b Freudlinch Isotherm (c) Temkin Isotherm (d) Dubinin - Radushkevich Isotherm.

librium (mg/g), RT/bT = B where T is the temperature (K), and R is the ideal gas constant (8.314 J mol^{-1} K^{-1}) and 'a' and bT are constants. A plot of qe versus lnCe (Figure 4c), enables the determination of constants 'a' and bT. The constant bT is related to the heat of adsorption and a is the equilibrium binding constant (L/min) corresponding to the maximum binding energy. The values bT in this study (see TABLE 3) show that the process is not purely chemisorption[2].

The Dubinin - Radushkevich isotherm

The Dubinin-Radushkevich model[10] was chosen to estimate the heterogeneity of the surface energies and also to determine the nature of biosorption processes as physical or chemical. The D–R sorption isotherm is more general than the Langmuir isotherm as its derivation is not based on ideal assumptions such as equipotent of the sorption sites, absence of stoic hindrance between sorbed and incoming particles and surface homogeneity on microscopic level[4]. The linear presentation of D-R isotherm is represented by equation 16:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \qquad (16)$$

where qm is the theoretical saturation capacity (mol g^{-1}), β is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol2 J-2), and ε is the polanyi potential given by the relation $\varepsilon = RT\,\mathrm{In}(1 + {}^{1}\!/_{C_e})$. Ce is the equilibrium concentration of adsorbate in solution (mol L^{-1}), R (J mol^{-1} K^{-1}) is the gas constant and T (K) is the absolute temperature. The D-R constants qm and β were calculated from the linear plots of lnqe versus ε2 (Figure 4d) and are given in TABLE 2.

The constant β gives an idea about the mean free energy E (kJ/mol) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated from the relationship[20]

$$E = {}^{1}\!/\!\sqrt{-2\beta} \qquad (17)$$

If the magnitude of E is between 8 and 16 kJ mol^{-1}, the sorption process is supposed to proceed via chemisorption, while for values of E < 8 kJ mol^{-1}, the sorption process is of physical in nature[20]. Since the values obtained in this study are outside the ranges specify by the model, the process therefore, cannot be purely chemisorption or physisorption.

Biosorption thermodynamics

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

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

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 relations:

$$\Delta G° = -RT \ln K_D \qquad (18)$$

$$\Delta G° = \Delta H° - T\Delta S \qquad (19)$$

A plot of ΔG° against the temperature, (Figure 5) 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.

Desorption and recycling efficiency

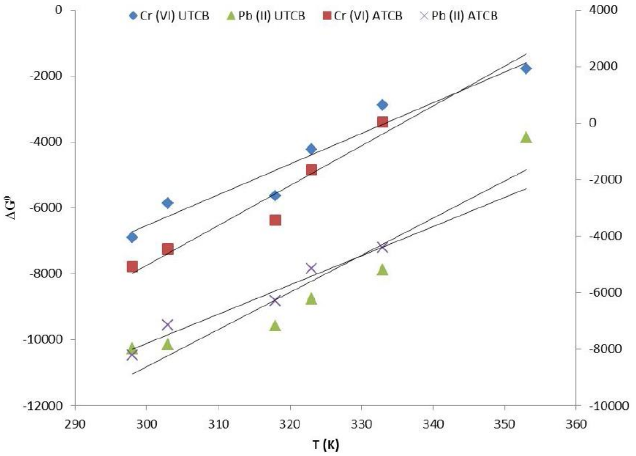

Figure 5: The plot of free energy change versus temperature

TABLE 4: Thermodynamic parameters of biosorption of Cr (VI) and Pb (II) using corncob biomass

	Cr (VI) Biosorption with raw corncob						Cr (VI) Biosorption with treated corncob						Pb (II) Biosorption with raw corncob						Pb (II) Biosorption with treated corncob					
T	298	303	318	323	333	353	298	303	318	323	333	353	298	303	318	323	333	353	298	303	318	323	333	353
(Ce/qe)	16.18	10.25	8.43	4.84	2.83	1.84	7.73	5.87	3.67	1.84	0.98	0.57	63.09	56.08	37.54	26.01	17.20	3.73	27.57	17.03	10.80	6.817043	4.907407	7.34
ΔG (kJ/mol)	-6.90	-5.86	-5.63	-4.24	-2.88	-1.79	-5.07	-4.46	-3.44	-1.64	45.76	1.66	-1.03	-1.01	-9.56	-8.75	-7.88	-3.86	-8.22	-7.14	-6.29	-5.15	-4.40	-5.85
ΔH (kJ/mol)	-34.55						-43.53						-44.57						-38.88					
ΔS (J/mol)	-93.40						-128.77						-112.53						-103.62					
R^2	0.937						0.961						0.8896						0.961					

TABLE 5 : Comparison of adsorption capacity of various adsorbents for Pb (II) ion and Cr (VI) ion

Adsorbent	Maximum adsorption Capaxity (mg g^{-1})		Reference
	Pb (II) ion	Cr (VI) ion	
Activated carbon	6.68	-	Mishra and Patel, 2009
Bagasse fly ash	2.5	-	Gupta and Ali, 2004
Bagasse fly-ash	-	260	Gupta et al., 1999
Coconut husk fibers	-	29	Tan et al., 1993
Kaolin	4.5	-	Mishra and Patel, 2009
M. hiemalis	-	47.4	Tewari et al.,2006
Periwinkle shell carbon	0.0558	-	Badmus et al., 2007
R. Nigerican	-	47	Bai and Abraham, 2001
Red mud	-	1.6	Pradhan et al., 1999
Rolling mill scale	2.74	-	Martin et al., 2005
Saraca indica leaf powder	1.19	-	Goyal et al., 2008
Sawdust	-	3.3	Srivastav et al., 1986
Sugar cane bagasse	-	34	Sharma and Forster, 1994
Groundnut Husk		7.0	Dubey, and Gopal, 2007
Corncob	9.05	8.64	Present study
Oxalic acid modified corncob	10.27	10.74	Present study

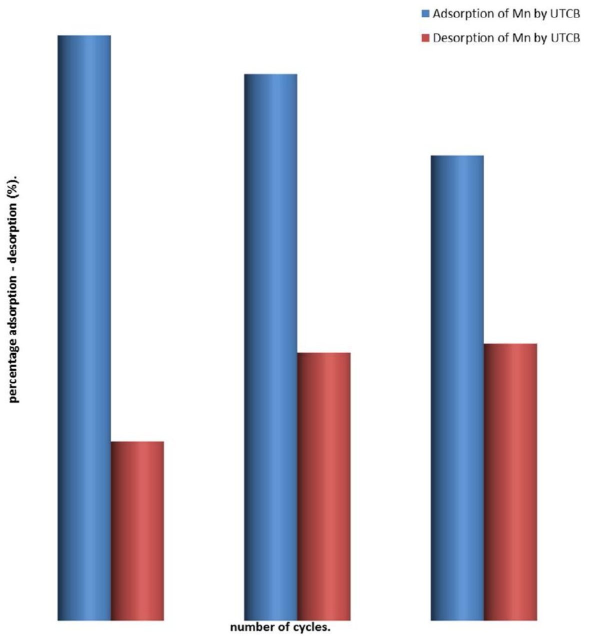

Figure 6: Desorption studies of the Cr (VI) raw corncob biomass

0.5 M HCl (20 mL) was used to recover the Cr (VI) and Pb (II) ions from the biosorbent. More than 95 % of the adsorbed metal ions were desorbed from the biosorbent. HCl was selected as desorption agent for the metal ions from the biosorbent due to the attainment of the best regeneration using this solution. On the other hand, the reusability of the biosorbent was also tested during three consecutive biosorption-desorption cycles (Figure 6). The lost in the biosorption capacity of the biomass for both metal ions was determined to be 5 %. These results indicated that the corncob biomass offers potential to be used repeatedly with only a minute loss in the total biosorption capacity.

CONCLUSION

The results of this study reinforced the fact that corncob could be a good alternative for the removal of Cr (VI) and Pb (II) ions from the aqueous solution even at low concentrations. 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 ions. Its use environment friendly manner will be a value added rather than its being a nuisance to the environment.

REFERENCES

[1] A.I.Adeogun, O.S.Bello, M.D.Adeboye; Pakistan Journal of Scientific and Industrial Research, **53(5)**, 246-251 **(2010)**.
[2] A.I.Adeogun, A.E.Ofudje, M.Idowu; S.O.Kareem; BioResources, **6(4)**, 4117-4134 **(2011)**.
[3] S.S.Ahluwalia, D.Goyal; Engineering and Life Science, **5(2)**, 158-162 **(2005)**.
[4] R.A.Anayurt, A.Sari, M.Tuzen; Chemical Engineer-

ing Journal, **151**, 255-261 **(2009)**.

[5] T.S.Anirudhan, P.G.Radhakrishnan; Journal of Chemical Thermodynamics; **40(4)**, 702-709 **(2008)**.

[6] M.A.O.Badmus, T.O.K.Audu, B.U.Anyata; Turkish Journal Engineering and Environmental Science, **31(4)**, 251-263 **(2007)**

[7] R.S.Bai, T.E.Abraham; Bioresources Technology, **79**, 73-81 **(2001)**.

[8] Z.Chen, W.Ma, M.Han; Journal of Hazardous Materials, **155(1-2)**, 327-333 **(2008)**.

[9] S.P.Dubey, K.Gopal; A Comparative Study Journal of Hazardous Materials, **145**, 465-470 **(2007)**.

[10] M.M.Dubinin, E.D.Zaverina, L.V.Radushkevich; Journal of Physical Chemistry, **21,** 1351-1362 **(1947)**.

[11] H.M.F.Freundlich; Journal of Physical Chemistry, **57**, 385-471 **(1906)**.

[12] M.Ghaedi, F.Ahmadi, Z.Tavakoli, M.Montazerozohori, A.Khanmohammadi, M.Soylak; Journal of Hazardous Materials, **152**, 1248-1255 **(2008)**.

[13] B.Guo, L.Hong, H.X.Jiang; Industrial Engineering Chemical Research, **42**, 5559-5567 **(2003)**.

[14] X.Guo, S.Zhang; X.Q.Shan; Journal of Hazardous Materials, **151**, 134-142 **(2008)**.

[15] V.K.Gupta, I.Ali; Journal of Colloid and Interface Science; **271(2),** 321-328 **(2004)**.

[16] V.K.Gupta, M.Gupta, S.Sharma; Water Resources, **35(5),** 1125-1134 **(2001)**.

[17] G.F.Huang, Q.T.Wu, J.W.C.Wong, B.B.Nagar; Bioresource Technology, **35**, 132-137 **(2005)**.

[18] M.K.Jamali, T.G.Kazi, M.B.Arain, H.I.Afridi, N.Jalbani, A.R.Menon; Journal of Agronomy Crop Science, **193(3),** 218-228 **(2007)**.

[19] U.Kumar, M.Bandyopadhyay, Bioresource Technology, **97**, 104-109 **(2006)**.

[20] S.Kundu, A.K.Gupta; Chemical Engineering Journal, **122(1-2)**, 93-106 **(2006)**.

[21] I.Langmuir; Journal of American Chemical Society, **40**, 1361-1403 **(1918)**.

[22] S.Largegren; Kungliga Suensk Vetenskapsakademiens Handlingar, **241,** 1-39 **(1898)**.

[23] P.K.Malik; Journal of Hazardous Materials, **B113,** 81-88 **(2004)**.

[24] M.I.Martın, F.A.Lopez, C.Perez, A.Lopez-Delgado, F.J.Alguacil; Journal of Chemical Technology and Biotechnology, **80(11)**, 1223-1229 **(2005)**.

[25] P.C.Mishra, R.K.Patel; Journal of Hazardous Materials; **168(1)**, 319-325 **(2009)**.

[26] F.Pagnanelli, S.Mainelli, F.Vegli, L.Toro; Chemical Engineering Science, **58**, 4709-4717 **(2003)**.

[27] A.B.Perez-Marin, V.Meseguer-Zapata, J.Ortuno, F.M.Aguilar, J.Sa´es, M.Llore´ns; Journal of HazardousMaterials, **139**, 122-131 **(2007)**.

[28] J.Pradhan, S.N.Das, R.S.Thakur; Journal of Colloid and Interface Science, **217**, 137-141 **(1999)**.

[29] A.Sari, D.Cıtak, M.Tuzen; Chemical Engineering Journal, **162(2)**, 521-527 **(2010)**.

[30] D.C.Sharma, C.F.Forster; Bioresources Technology, **47,** 257-264 **(1994)**.

[31] H.C.P.Srivastava, R..P.Mathur, I.Mehrotra; Environmental Technology Letter, **7,** 55-63 **(1986)**.

[32] N.Tewari, P.Vasudevan, B.K.Guha; Biochemical Engineering Journal, **23,** 185-192 **(2005)**.

[33] J.C.P.Vaghetti, E.C.Lima, B.Royer, B.M.da Cunha, N.F.Cardoso, J.L.Brasil, S.L.P.Dias; Journal of Hazardous Materials, **162,** 270-280 **(2009)**.

[34] G.Zhao, X.Wu, X.Tan, X.Wang; The Open Colloid Science Journal, **4**, 19-31 **(2011)**.