

Potential of Oxalic Acid Treated *Saccharum officinarum* Bagasse as Adsorbent to Remove Cd (II) from Aqueous Solution.

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ABSTRACT

The adsorption potential of *Saccharum officinarum* bagasse towards Cd (II) ions in dilute aqueous solution has been investigated in a batch process. The adsorption characteristics of Cd (II) by *S. officinarum* bagasse depended on the metal-ion substrate contact time, initial concentration of metal ion, pH and temperature. The adsorption capacity of the *S. officinarum* bagasse was enhanced by treatment with 0.1M oxalic acid. Under the optimum conditions, the adsorption capacities of the untreated (USOB) and treated (TSOB) *S. officinarum* bagasse were found to be 0.564 and 1.972 mgg⁻¹ respectively.

The equilibrium data obtained from this study fitted well with both Langmuir and Freundlich isotherms which were used for the quantitative analyses while the adsorption kinetics followed Ho's pseudo-second-order kinetic model adequately. Thermodynamic parameters obtained revealed that the adsorption of Cd (II) ion onto USOB or TSOB was feasible, spontaneous and endothermic under studied conditions. The adsorbents could be regenerated with up to 73.78 and 65.90 % recovery from USOB and TSOB respectively.

(Keywords: cadmium, adsorbent, *S. officinarum* bagasse, isotherm, kinetics, thermodynamics)

INTRODUCTION

The presence of heavy metals in the environment poses a serious pollution problem to surface and ground water and it has been a major concern all over the world because these heavy metals are non-biodegradable and therefore, persistent with tendency to bioaccumulate (Marques et al., 2000, Osasona et al., 2013). Growing concerns with environmental protection in recent years is in

either decreasing the influx of pollutants to the environment or by their removal from contaminated media.

Cadmium is one of the heavy metals which is highly toxic to humans and their biotic environment. It is listed by the US-EPA as one of the priority contaminants and as a known carcinogen by the International Agency for Research on Cancer (IARC, 1994; Hamzah et al., 2009). Chronic exposure to cadmium even at very low doses leads to kidney damage, bone lesions, renal disorder or itai-itai disease. It may even induce anemia through hemolysis (Hutton et al., 1987; David et al., 2003, Hamzah et al., 2009, Hyogo et al., 2011).

Cadmium may enter surface and ground water systems indirectly via run off from solid waste disposal sites and agriculture fields or directly through effluent from mines, fertilizer production or electroplating (David et al., 2003, Izanloo et al., 2005). Several natural water sources contain high concentration of Cd (II) ions exceeding the World Health Organization's permitted level of 3 ppb in drinking water (WHO, 2011). This makes it essential to remove this metal from contaminated water to protect human health.

Various methods including membrane separations, reverse osmosis, chemical precipitation, ion-exchange, ultra-filtration and electro dialysis have been in use for the removal of heavy metals from contaminated water (Feng et al., 2000, Matlock et al., 2002, Mohammadi et al., 2005). These methods require high capital due to high chemical or energy requirements. They are therefore not economically feasible most especially in developing countries; besides, generation of secondary wastes and low metal uptake at low metal concentrations are part of demerits of these methods (Kuyucak and

Volesky, 1988, Ibrahim et al., 2006, Khan et al., 2008).

The search for new, effective and economical know-hows towards the removal of toxic metals from wastewaters has directed attention to adsorption technology based on metal binding capacities of various agricultural waste materials at little or no cost. Recent studies have shown the use of various adsorption materials derived from plants in metal ions sorption (Ho et al., 2004, Shin et al., 2008, Mataka et al., 2010, Zheng et al., 2010, Adeogun et al., 2011, 2013). The interest in this study is to evaluate the use of *S. officinarum* (sugar cane) bagasse treated with oxalic acid as adsorbent for removal of Cd (II) ions from aqueous solutions and to compare the result to the use of untreated *S. officinarum*.

Oxalic acid occurs widely in nature, it is present in the tissues of many plants and algae. In water, its negative ion forms complexes with a number of metal ions; and both aerobic and anaerobic conditions biodegrade oxalic acid in less than one day (USEPA, 1992), which makes it a good reason for its use in the modification of the *S. officinarum* bagasse.

The uptake of Cd (II) by untreated (USOB) and treated (TSOB) *S. officinarum* bagasse under different sorption conditions is studied. Experimental data were fitted with Langmuir and Freundlich isotherms whilst the Lagergren pseudo-first-order and Ho's pseudo-second-order models were used to study the kinetic data. The thermodynamic parameters are also reported.

MATERIALS AND METHODS

The chemicals used in this study were analar grade of $\text{H}_2\text{C}_2\text{O}_4$, NaOH and CdCO_3 purchased from Sigma-Aldrich. The adsorbent used for the studies were both untreated and treated *S. officinarum* bagasse. The *S. officinarum* obtained from Lafenwa local market, Abeokuta, Nigeria was washed thoroughly with de-ionized water, peeled, juiced and air dried for 10 days to obtain *S. officinarum* bagasse. The dried *S. officinarum* bagasse was then pulverized with an electric blender and sieved through a 100 μm mesh copper sieve and kept in air tight container. To obtain the TSOB, 5 g of USOB was stirred in 200 mL of 1 M oxalic acid in a 500 mL conical flask for 24h according to Park et al., 2005. This was kept

in an air tight container after treatment until time of usage.

Adsorption Measurements

The stock solution was prepared with de-ionized water at an initial concentration of 1000 mgL^{-1} of Cd(II) from CdCO_3 . The solutions used for the study were obtained by dilution of the stock solution to the required concentrations. The initial pH of each of the solutions was adjusted to the optimum pH value by addition of 0.1M $\text{H}_2\text{C}_2\text{O}_4$ and/or 0.1M NaOH solutions in drops except for the experiment of the effect of pH where the study was carried out at different pH values. Fresh dilution of the stock solution was done for each adsorption study. The pH of the solution was monitored on a Radiometer PHM 85 Research pH meter. The concentration of Cd (II) ions in the raw adsorbent was determined by placing 1 g of the adsorbent in 50 mL de-ionized water for 24h with continuous agitation, after which it was centrifuged at 200 rpm. The supernatant was analyzed using a flame atomic absorption spectrophotometer (FAAS) Buck Scientific 310 VGP.

Batch Equilibrium Studies

Equilibrium studies were performed in a batch process similar to what was described earlier (Adeogun et al. 2010, 2011). Briefly, the studies were carried out in a set of 100 mL Erlenmeyer flasks wherein a working volume of 20 mL of the solutions of Cd (II) ions with different initial concentrations (100 to 500 mg dm^{-3}) were placed. Equal mass of the adsorbent USOB or TSOB (0.2 g) were added to the solutions of Cd (II) ions and agitated on an isothermal orbital shaker at 150 rpm at room temperature for 24h to reach equilibrium of the solid-solution mixture.

Samples were then centrifuged and the supernatant analyzed for the final concentration of the Cd (II) ions in the solutions using FAAS. All experiments were conducted in triplicate under identical conditions and the mean value was calculated. A control experiment was also set up under similar conditions and procedure but without the adsorbent. The amount of metal ion adsorbed by the adsorbent at equilibrium, Q_e (mg g^{-1}), was calculated by difference using Equation 1a:

$$Q_e = \frac{(C_0 - C_e)V}{W} \quad (1a)$$

The percentage of heavy metal removed R (%) was also estimated with the Equation 1b.

$$R = \frac{(C_0 - C_e)100}{C_e} \quad (1b)$$

where, C_0 and C_e (mg dm^{-3}) are the liquid-phase concentrations of the metal ion at initial and equilibrium concentration, respectively. V is the volume of the solution (L), and W is the mass of dry adsorbent used (g). The effect of initial solution pH, contact time, initial metal ion concentration and temperature on the adsorption of Cd(II) ions were studied.

Batch Kinetic Studies

The procedures of kinetic experiments were basically identical to those of equilibrium tests. The aqueous samples were taken at pre-set time intervals and the concentrations of the metal ions were similarly determined. The experiment was carried out in three replicate and the mean value was used. The amount of metal ion adsorbed at time t , Q_t (mg g^{-1}), was calculated using Equation 2:

$$Q_t = \frac{(C_0 - C_t)V}{W} \quad (2)$$

where, C_0 and C_t (mg dm^{-3}) are the liquid-phase concentrations of the metal ion at initial and at time t , respectively. V is the volume of the solution in liters and W is the mass of dry adsorbent used (g).

Isotherm studies were by varying the initial concentration of Cd (II) ions from 100 mg/L to 500 mg/L at a pH of 2. From the experimental data, the applicability of Langmuir and Freundlich isotherm models were determined. Kinetics of adsorption were also analyzed from the experimental data obtained where Lagergren pseudo-first-order and Ho's pseudo-second-order were used to examine the experimental data.

RESULTS AND DISCUSSION

The adsorption of cadmium ions in aqueous solution onto USOB and TSOB were examined by optimizing various physiochemical parameters such as pH, contact time, initial concentration of metal ions and temperature.

Effect of pH on Adsorption

The effect of pH on the adsorption of metal ions was carried out within the range that would not be influenced by the metal precipitated (Pavasant et al., 2006). Reports have shown that the suitable pH ranges for the sorption of different metal ions are slightly different with pH of 1.0-8.0 working well for Cd^{2+} . The batch adsorption studies at different pH values were examined in the range of pH 2.0-10.0. The percentage removal of the metal ions was pH dependent as shown in Figure 1.

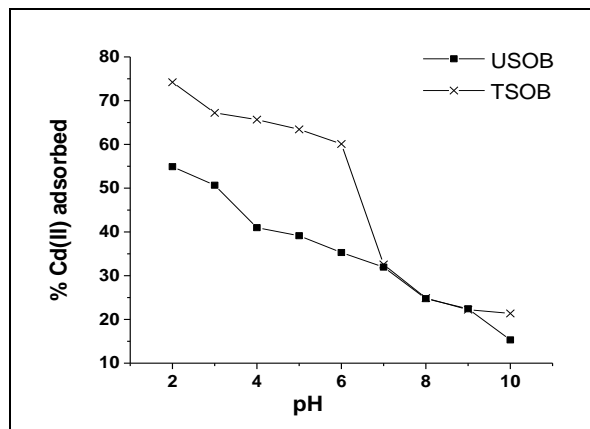


Figure 1: Effect of pH on the amount of Cd(II) ions adsorbed by USOB and TSOB. (Initial $[\text{Cd}^{2+}] = 100 \text{ mg dm}^{-3}$, Adsorbent dosage=0.2 g / 20 mL, Contact time=100 min., Agitation speed=150 rpm).

The removal efficiency decreased steadily with increasing pH. The sorption of the Cd(II) ions by both USOB and TSOB was preferred in the acidic range with maximum adsorption capacity observed at pH 2.0., though adsorption capacity was higher for TSOB. At low pH, cadmium would be present predominantly as M^{2+} ions.

The *Saccharum officinarum* bagasse is composed of cellulose and hemicellulose, so its cell wall will carry functional groups such as alcoholic, carbonylic, carboxylic or phenolic groups which are assumed to be the active sites for attachment of the metal ions (Marshall et al., 1995). Mechanism of adsorption of metal ions onto adsorbent surface involves a surface complexation mechanism which may involve the synergic effect of the nature of the surface and presence of acid and base used to adjust the pH of the solution. Earlier reports by Adeogun et al., 2011 also shows that the pH of the medium affects the solubility of the metal ions and concentration of the counter ions on the functional groups of the adsorbent cell walls.

Effect of Contact Time

The efficiency of adsorption of Cd (II) ions onto USOB and TSOB as a function of contact time at different time intervals of 10 to 120 minutes were studied. A constant concentration of 100 mg dm^{-3} was used at an optimum pH of 2. Figure 2 showed that the efficiency of adsorption increased with increase in contact time.

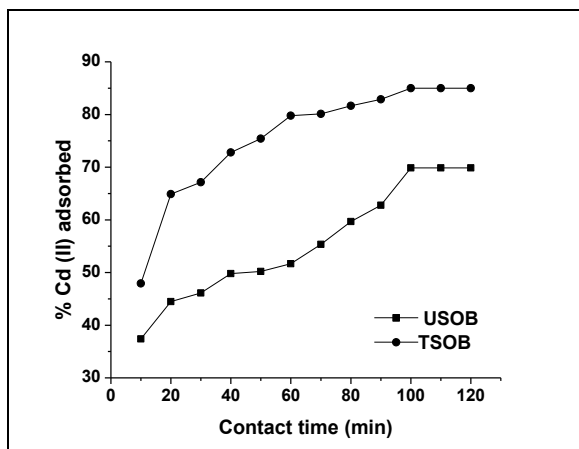


Figure 2: Variation of the amount of Cd(II) ions adsorbed by USOB and TSOB with contact time (Initial $[\text{Cd}^{2+}] = 100 \text{ mg dm}^{-3}$, Adsorbent dosage = $0.2 \text{ g} / 20 \text{ mL}$, pH 2, Agitation speed = 150 rpm).

The adsorption of Cd (II) onto USOB and TSOB was rapid for the first 40 minutes and the maximum adsorption was observed at 100 minutes, after which there was saturation. Erol et al., 2008 attributed such rapid initial adsorption

phenomenon to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface. The period of 100 min was considered as the optimum since at equilibrium the rate of uptake is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles.

Effect of initial concentration of adsorbate

The initial concentration of Cd (II) ions led to the reduction in adsorption capacity of both USOB and TSOB (Figure 3). The percentage sorption decreased from 70.8 to 57.3 % for USOB and 84.9 to 69.8 % for TSOB as the initial concentration of Cd (II) ions increased from 100 to 500 mg dm^{-3} .

At lower concentration, the likelihood of competition for the available binding site is low, thus percentage adsorption was higher at lower concentration than at higher concentration, where saturation of the binding sites and competition between the ions for the binding sites was obvious. Similar report was shown in the adsorption of Cd (II) ions from aqueous solutions by hazelnut shell, where lack of available active sites at high concentration, resulted in increased competition for the adsorption sites and the adsorption process increasingly slowed down (Hamzah et al., 2009).

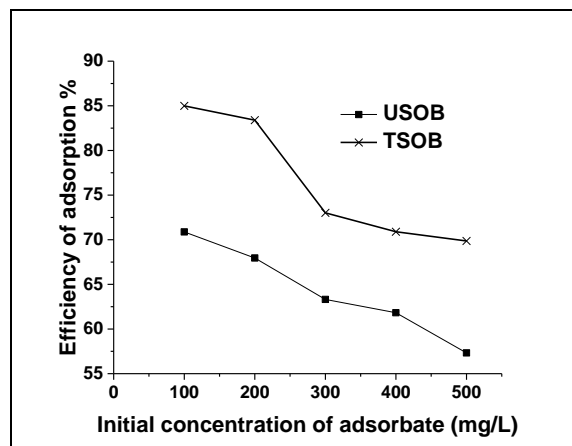


Figure 3: Effect of initial concentration on adsorption of Cd(II) ions onto USOB and TSOB. (Adsorbent dosage = $0.2 \text{ g} / 20 \text{ mL}$, pH 2, Contact time = 100 min ., Agitation speed = 150 rpm).

THERMODYNAMIC STUDIES

Temperature dependence of Cd (II) ions adsorption onto USOB and TSOB was carried out within the temperature range of 25 °C to 45 °C as shown in Figure 4. A gradual increase in the efficiency of adsorption was observed. The adsorption capacity increased with about 7 or 20% for TSOB or USOB respectively with an increase in the temperature from 25 to 45 °C for an initial concentration of 100 mg/L and adsorbent dosage of 0.2 g/20 mL with a more effective adsorption observed in TSOB. Increased sorption with temperature increase may be due to increase in the number of active surface sites available for sorption on the adsorbent as temperature increases due to bond rupture and it signifies endothermic nature of the adsorption process. This may be indicative of a chemisorption process (Kara et al., 2003).

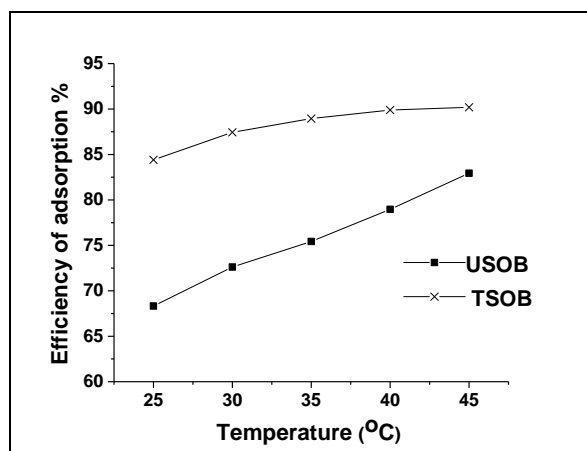


Figure 4: Effect of Temperature on adsorption of Cd(II) ions onto USOB and TSOB. (Initial $[Cd^{2+}] = 100 \text{ mg dm}^{-3}$, Adsorbent dosage = 0.2 g / 20 mL, pH 2, Contact time = 100 min., Agitation speed = 150 rpm).

Thermodynamic Parameters

Thermodynamic parameters such as change in free energy (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were determined using the equations below to interpret the data obtained from the experiment.

$$\Delta G = -RT \ln k_c \quad (3)$$

and

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (4)$$

where, ΔG^0 is the standard free energy change (in Joules), R is universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature, k_c , the apparent equilibrium constant of the adsorption is C/C_e where, C is the concentration of the adsorbate adsorbed on the adsorbent, C_e is the concentration of unadsorbed adsorbate.

The values of ΔH and ΔS for the adsorption of Cd (II) ions onto USOB and TSOB were calculated from the intercept and slope, respectively of the plot of ΔG against T shown in Figure 5 (Ertugay and Bayhan, 2008).

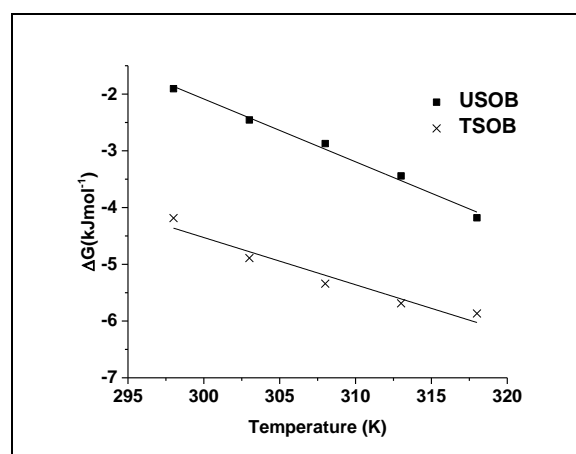


Figure 5: Free energy change versus temperature for the sorption of Cd (II) ions onto USOB and TSOB.

The values of thermodynamic parameters obtained from the plot are presented in Table 1.

The negative values of Gibbs free energy from values generated from experimental data confirm the thermodynamic feasibility and spontaneity of the adsorption process.

Positive values were obtained for ΔH for both USOB and TSOB which indicates that the process is endothermic due to increase in efficiency of adsorption with increase in temperature, however ΔH value for TSOB was lower than for USOB, implying that higher temperature will be required for sorption in USOB to be able to attain comparable results as TSOB. The obtained positive ΔS values shows increase in randomness at solid solution interface (Gupta et al., 2009). The degree of randomness is greater in USOB compared to TSOB during the adsorption process, hence, decreased adsorption in the former.

Table 1: Thermodynamic Studies Parameters for the Adsorption of Cd (II) Ions onto USOB and TSOB.

T (K)	USOB				TSOB			
	k_c (mg/g)	ΔG (kJmol ⁻¹)	ΔS (kJK ⁻¹ mol ⁻¹)	ΔH (kJmol ⁻¹)	k_c (mg/g)	ΔG (kJmol ⁻¹)	ΔS (kJK ⁻¹ mol ⁻¹)	ΔH (kJmol ⁻¹)
298	2.158	-1.906	0.110	31.13	5.414	-4.185	0.083	20.43
303	2.652	-2.457			6.962	-4.889		
308	3.070	-2.873			8.050	-5.341		
313	3.755	-3.443			8.891	-5.687		
318	4.862	-4.181			9.194	-5.866		

Table 2: Adsorption Isotherms Data for Adsorption of Cd (II) Ions.

Adsorbents	Langmuir parameters				Freundlich parameters		
	q_m (mgg ⁻¹)	b (Lmg ⁻¹)	R_L	R^2	n	K_f (mgg ⁻¹)	R^2
USOB	62.50	0.0041	0.71	0.992	1.768	0.564	0.995
TSOB	45.45	0.0156	0.39	0.984	1.348	1.972	0.969

ADSORPTION ISOTHERMS

Analysis of equilibrium data by means of different isotherm models is important in finding a suitable model that can be used for design purposes (Haghsereht and Lu, 1998). The results obtained from the adsorption process of Cd (II) ions onto USOB and TSOB were analyzed with Langmuir and Freundlich models (Figures 6 and 7). The isotherm shows how the adsorbed molecules are distributed between the liquid and solid phases when the adsorption process reaches the equilibrium state.

The Langmuir model represents one of the first theoretical treatments of non-linear adsorption and assumes monolayer coverage of adsorbent surface and no interaction of adsorbate in the plane of the adsorbent surface (Fytianos et al., 2003). The linear form of Langmuir isotherm is given by:

$$\frac{1}{q_e} = \frac{1}{q_m b C_e} + \frac{1}{q_m} \quad (5)$$

where, q_e is the amount of adsorbate adsorbed per unit amount of adsorbent (mgg⁻¹), C_e the equilibrium concentration (mgL⁻¹), b , Langmuir equilibrium or adsorption constant (Lmg⁻¹) and q_m Langmuir monolayer saturation capacity (mgg⁻¹).

In the Langmuir model for the adsorption of Cd (II) ions onto USOB and TSOB, figure 6, the plot of $1/q_e$ against $1/C_e$ gave straight lines with R^2 values

of 0.992 and 0.984 for USOB and TSOB respectively, indicating that the adsorption followed Langmuir isotherm. The values of q_m and b deduced from the slope $1/q_m b$ and intercept $1/q_m$ are shown in Table 2.

The constant, b is related with the affinity of the active binding sites. Its values were 0.0041 and 0.0156 for USOB and TSOB respectively. The higher value of b for TSOB indicates the increased adsorption with this material.

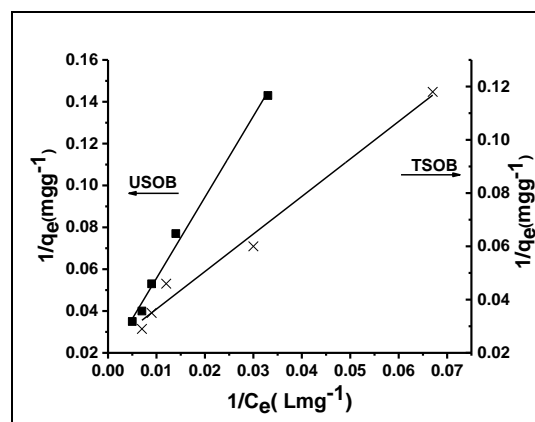


Figure 6: Langmuir Isotherm Model for adsorption of Cd (II) ions onto USOB and TSOB.

The essential feature of the Langmuir isotherm can be expressed by means of R_L , a dimensionless constant referred to as a

separation factor or equilibrium parameter (Webi and Chakarvort, 1974). R_L is calculated by:

$$R_L = \frac{1}{1 + bC_0} \quad (6)$$

where, C_0 is the initial concentration of Cd (II) ions (mgL^{-1}) and b is obtained from slope of Langmuir plot. The value of R_L indicates the isotherm type to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$).

The favorable uptake of cadmium adsorption onto USOB and TSOB is confirmed by the value of R_L in the range of 0 to 1 (Table 2) at all initial Cd (II) ions concentration within the conditions of this study.

The Freundlich isotherm model assumes heterogeneous surface energies in which the energy term in Langmuir equation varies as a function of the surface coverage (Fytianos et al., 2003). The Freundlich linearized logarithmic equation can be described by;

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

where, K_f is the constant that describes the adsorption capacity of the adsorbent (mgg^{-1}), representing the quantity of Cd (II) ions adsorbed onto USOB or TSOB for a unit equilibrium concentration; n is an empirical parameter that dictates the intensity of the adsorption. A value of $1/n < 1$ suggests a normal Langmuir isotherm while $1/n$ above one is suggestive of a cooperative sorption (Fytianos et al., 2003).

The value of K_f and n were determined from the intercept and slope of the plot of $\log q_e$ against $\log C_e$ respectively, which gave straight lines (Figure 7) with R^2 values of 0.995 and 0.969 for USOB and TSOB respectively, indicating that the adsorption also followed Freundlich isotherm.

Table 2 shows the values of K_f and n deduced from the intercept and slope respectively. The values of $1/n$; 0.566 for USOB and 0.742 for TSOB is an indication of favorable adsorption (Adeogun et al., 2011, Fytianos et al., 2003).

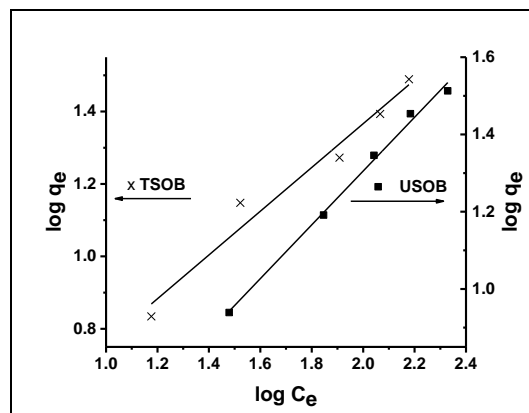


Figure 7: Freundlich isotherm model for adsorption of Cd (II) ions onto USOB and TSOB.

The equilibrium data obtained from this study fitted well with both isotherms considered, however, in comparison, for USOB, the correlation coefficient, R^2 , is higher in Freundlich model ($R^2 = 0.995$) compared to Langmuir model ($R^2 = 0.992$) while with TSOB, it is higher in Langmuir model ($R^2 = 0.984$) compared to Freundlich model ($R^2 = 0.969$). It can therefore be suggestive that using TSOB as adsorbent, the adsorption process is more of monolayer coverage. This is likely from the higher porosity of TSOB due to acid treatment.

KINETIC MODELS

Kinetic studies of the obtained experimental data which describes the mechanism and potential rate determining step of the adsorption of Cd (II) ions onto USOB and TSOB is an important characteristic in evaluating the efficiency of adsorption.

Kinetic rate of Cd (II) ions adsorption by USOB and TSOB were analyzed by Lagergren pseudo-first-order and Ho's pseudo-second-order models.

The rate of adsorption onto an adsorbent surface depends upon a number of parameters such as structural properties of the adsorbent, initial concentration of the adsorbate and the interaction between the adsorbate and the active sites of the adsorbent (Elangovan et al., 2008).

Lagergren pseudo-first-order model explains that the rate of occupation of adsorption sites is proportional to the number of unoccupied sites (Cruz et al., 2004) and can be expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \cdot t \quad (8)$$

where, q_t is the amount of Cd(II) ions adsorbed on USOB and TSOB at time t , q_e is the experimental adsorption capacity, k_1 is the equilibrium rate constant of pseudo-first-order adsorption (min^{-1}).

The plot of $\log(q_e - q_t)$ against t should give a straight line with a slope of $k_1/2.303$ and the intercept, $\log q_e$. The correlation coefficient, R^2 , value and the calculated adsorption capacity at equilibrium concentration, $q_{e, \text{exp}(eq)}$, are important to evaluate how the data fit the kinetic model (Vijayaraghavan et al., 2004).

As shown in Table 3, USOB and TSOB show strong correlation coefficient, with a stronger R^2 in TSOB, however, $q_{e, \text{exp}(eq)}$ does not agree with q_e , indicating the inadequacy of the pseudo-first-order model for this experiment.

The Ho pseudo-second-order model is expressed as (Adeogun et al., 2011):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e t} \quad (9)$$

where, k_2 is the equilibrium rate constant of pseudo-second-order adsorption ($\text{mg}^{-1} \text{min}^{-1}$).

A plot of t/q_t against t as shown in Figure 8 gives a straight line with a slope of $1/q_e$ and an intercept of $t/k_2 q_e^2$ indicating that the Ho's pseudo-second-order model is a better model suitable to describe the kinetic studies of the adsorption of Cd (II) ions onto USOB and TSOB.

The values of R^2 from the plots as shown in Table 3 present good agreement. Also, q_e , was quite comparable to $q_{e, \text{exp}(eq)}$ confirming the fit of the second-order model rather than the first-order model. The good fits shows that the adsorption processes support the assumption of this model that adsorption is based on chemical sorption between the metal and the adsorbents and it follows the second order mechanism (Ibrahim et al., 2006). This confirms the suggestive chemisorption process from the thermodynamic data.

DESORPTION STUDIES

Desorption of the adsorbed adsorbate is one of the advantages of adsorption process which is the possibility of recovering the adsorbate adsorbed from the adsorbent. Desorption process should yield the adsorbate in a concentrated form and restore the adsorbent to close to the original condition for effective reuse.

In this experiment, desorption was carried out using 0.1M NaOH. The used USOB which had adsorbed 69.88 mg/L Cd (II) ions and used TSOB which had adsorbed 84.99 mg/L Cd (II) ions were selected and treated with 0.1M NaOH for 24 hours.

Table 3: Constants in Kinetic Models for the Adsorption of Cd (II) ions onto USOB and TSOB.

Adsorbents	Lagergren pseudo-first-order model			Ho's pseudo-second-order model			$q_{e, \text{exp}(eq)}$ (mgg^{-1})
	k_1 (min^{-1})	q_e (mgg^{-1})	R^2	k_2 ($\text{mg}^{-1} \text{min}^{-1}$)	q_e (mgg^{-1})	R^2	
USOB	0.058	14.32	0.764	0.054	7.81	0.967	7.01
TSOB	0.069	14.96	0.883	0.109	9.17	0.999	8.50

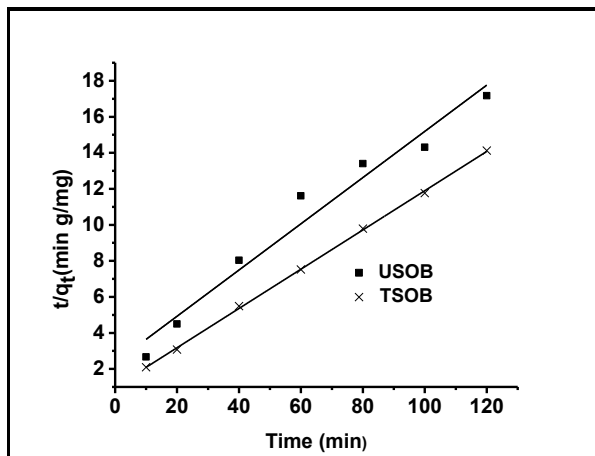


Figure 8: Ho's pseudo-second-order model for adsorption of Cd (II) ions onto USOB and TSOB.

The results from AAS showed that 73.78% of Cd (II) ions were desorbed from used USOB and 65.90% of Cd (II) ions were desorbed from used TSOB. The adsorbate desorbed from used USOB is more than that of TSOB because the adsorbate occupied more space in TSOB and not all can be desorbed easily because of high bond between the adsorbate and adsorbent.

CONCLUSION

The results from the experiment explained that the untreated and treated *S. officinarum* bagasse is a viable option for the effective removal of Cd (II) ions from aqueous solution, with the treated *S. officinarum* bagasse proving to be a better adsorbent.

The adsorption capacity of both USOB and TSOB was optimum at pH 2.0. Variation of efficiency of adsorption with time showed that the efficiency of adsorption increased with time and the equilibrium time was determined to be 100 minutes while the efficiency of adsorption decreased with increase in the initial concentration of the Cd (II) ions. Langmuir and Freundlich adsorption isotherm models gave good fit to the equilibrium experimental data.

The adsorption isotherm studies showed that the adsorption capacity is higher using TSOB compared to USOB. It was observed from the determined thermodynamic parameters that the

process of adsorption of Cd (II) ions onto the adsorbents is endothermic, spontaneous and feasible. Ho's pseudo second-order kinetic model gave a better description of the adsorption process with an assumption that the rate-limiting step may be a chemical adsorption process. This study shows that it is possible to enhance the capacity of *S. officinarum* by modification with oxalic acid.

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