

REMOVAL OF SOME HEAVY METAL IONS (Cd^{2+} , Cr^{3+} , Pb^{2+} , Hg^{2+} , and Ni^{2+}) FROM AQUEOUS SOLUTIONS USING SOURSOP FRUIT BARK (SSB)

E.C. ANAETO¹, M.O. EKEOMA², V.I.E. AJIWE¹, AND U.C EKPUNOBI¹

1. Department of Pure and Industrial Chemistry, Nnamdi Azikiwe University, Awka

2. Department of Chemistry, Michael Okpara University of Agriculture, Umudike.

Received 15th February, 2020, Accepted 10th September, 2020

Corresponding Author: E.C. Anaeto

ABSTRACT

The adsorption capacity of soursop fruit bark (SSB) (*Annona Muricata L.*) towards metal ions such as Cd^{2+} , Pb^{2+} , Hg^{2+} , Cr^{3+} , and Ni^{2+} were studied. The adsorption capacity was investigated by batch experiments using different experimental conditions such as pH, contact time, adsorbent dosage, adsorbent temperature and metal ion concentration to identify the optimum conditions. The effects of these parameters on the adsorption capacity were studied. The adsorption data were modeled using both the Langmuir and Freundlich classical adsorption isotherms. The results showed that the removal percentages increased as the sorbent temperature increased (298^oK-343^oK). The effect of metal ion concentration was studied at six different concentrations (40 -140 ppm) and the results showed that the removal percentages increased as pH increased (pH 4-14). The fitness of experimental data to equilibrium isotherm models was tested and thermodynamic parameters were calculated. The values of the separation factor (R_L) for soursop fruit barks are in the range of 0.362-0.472 which indicated favourable biosorption. The biosorption process of the metal ions onto SSB was favoured by both Langmuir and Freundlich models. Results showed that the Pseudo-Second order equation provided the best model for the biosorption process of the metal ions onto SSB. Thermodynamics parameters evaluation for all the metal ions gave a positive value of ΔH^o . ΔH^o for SSB were 22.38KJ/mol, 42.38KJ/mol, 30.27KJ/mol, 42.19KJ/mol, 10.69KJ/mol for Cd^{2+} , Pb^{2+} , Hg^{2+} , Cr^{3+} , and Ni^{2+} respectively. The negative values of the Gibbs free energy at all the temperatures showed that the adsorption process was spontaneous and the positive values of ΔS^o for the SSB reflected good affinity of the metal ions towards the soursop fruit barks. The results confirmed that SSB had a good potential to be used as biosorbent for the removal of cadmium, chromium, nickel, mercury and lead from waste water.

Keywords: Adsorption, Soursop Fruit Barks, heavy metal ions, Kinetics.

INTRODUCTION

Although "heavy metal" lacks a consistent definition in medical and scientific literature, the term is commonly used to describe the group of dense metals or their related compounds, usually associated with environmental pollution or toxicity¹. Heavy metal² is a term used to denote a metal that is toxic to human and aquatic life. The rather broad definition of heavy metals may also be applied to toxic metalloids like arsenic, as well as nutritionally-essential trace minerals with potential toxicities at elevated intake or exposure (eg, iron, zinc, or copper)¹.

These metals include arsenic, beryllium, bismuth, cadmium, chromium, cobalt, copper, lead, mercury, nickel, selenium, strontium, thallium, tin, titanium and zinc. Heavy metals such as cadmium, lead, zinc, copper and mercury, are used in several industries and constitute pollutants often found in the industrial aqueous effluents. Unlike organic pollutant, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products³. In the last few decades, industrialization in many regions has increased the discharge of heavy metals into the environment and aquatic ecosystems.

Toxic metal can seriously affect plants and animals and have been involved in causing a large number of afflictions⁴.

Cadmium (Cd) is a toxic heavy metal of significant environmental and occupational concern⁵. It is one of the toxic heavy metals with the greatest potential hazard to humans and the environment.

Lead toxicity is one of the most frequently reported unintentional toxic heavy metal exposures and the leading cause of single metal toxicity in children⁶. Inhalation of lead particulates is a primary route of occupational lead exposure, while oral ingestion is a primary form of exposure in the general population⁷.

Hg can cause mental and emotional derangement in many cases. Its sources include dental amalgams, large fish, shellfish, medications, air pollution, manufacture of paper, chlorine, adhesives, fabric softeners and waxes⁸. Nickel dissolves slowly in dilute acids but, like iron, becomes passive when treated with nitric acid. Finely divided nickel adsorbs hydrogen¹⁰.

Soursop belongs to the family of *Annonaceae*, (*A. muricata L.*). The flesh of the fruit consists of a white edible pulp that is high in carbohydrates and considerable amounts of Vitamin C, Vitamin B1, Vitamin B2, potassium and dietary fiber. Soursop is low in cholesterol, saturated fat and sodium. Not only is soursop a good health food, it also tastes delicious. The tree and fruit are known by various names: Guyabano in Filipino, Soursop in English, Graviola in Brazil, and Guanabana in Spanish. The heart shaped / oblong soursop fruit has a dark green, leathery and spike-like skin that measures from 27-33 cm long and can weigh up to 2.5 kg. The creamy and delectable flesh contains from 60 to 100 black-brown seeds that are indigestible and non-edible¹¹. The green leathery spike bark is a waste.

The aim of this study is to know how the heavy metal ions such as Cd²⁺, Cr³⁺, Pb²⁺, Hg²⁺ and Ni²⁺ can be removed from aqueous solutions using soursop fruit bark (SSB).

EXPERIMENTAL

Adsorbent Materials

The Soursop fruit bark (SSB) used in this research was collected from Amansea in Awka North Local government of Anambra State. The ripped soursop fruit was peeled to separate the seeds from the shell bark and the bark was oven dried for 48 hours at 300°C and was ground severally into powdered form and sieved into six different sizes ranging from 0.075µm, 0.10µm, 0.25µm, 0.5µm, 0.71µm and 1µm.

Chemical Activation of the Adsorbents

The adsorbent was boiled with 0.04M HNO₃ for 1 hour to activate it. It was then washed several times with distilled water, dried, ground again and sieved into six different particle sizes.

Adsorbate Solutions

Stock solutions of the following metal ions were prepared in deionised water:

- i. 1000 ppm solution of Pb(II) ion was prepared by dissolving 1.5999g of Pb (NO₃)₂ in deionised water and the volume was made up to the mark in a 1000 ml volumetric flask.
- ii. 1000 ppm solution of Cd(II) ion solution was prepared by dissolving 2.774g of Cd (NO₃)₂.4H₂O in deionised water and the volume was made up to the mark in a 1000 ml volumetric flask.
- iii. 1000 ppm solution of Ni(II) ion was prepared by dissolving 4.951g of Ni (NO₃)₂.6H₂O in deionised water and the volume was made up to mark in a 1000 ml volumetric flask.
- iv. 1000 ppm solution of Cr(III) ion was prepared by dissolving 3.73g of K₂CrO₄ in deionized water and the volume was made up to mark in a 1000 ml volumetric flask.
- v. 1000 ppm solution of Hg(II) ion was prepared by dissolving 1.59g of (CH₃COO)₂Hg in deionized water and the volume was made up to mark in a 1000 ml volumetric flask.

All solutions used in this study were prepared by the serial dilution of the standard solutions using deionized water. All the salts used were of analytical grade.

Characterization of the Adsorbent

The soursop fruit bark was characterized for moisture contents, ash contents, pH, surface area, specific gravity and bulk density.

The batch adsorption process of the metal ions was carried out to determine the effect of adsorbent dosage, effect of pH of the solution, initial concentrations and contact time on the adsorption of metal ions on the SSB.

The metal ions uptake (Adsorption capacity) at a particular time q_t and the uptake percentage (% removal of metal ion) was determined by mass balance, as follows: $q_t = \frac{(C_o - C_t)V}{W}$ (1)

$$\text{Uptake percentage} = \frac{(C_o - C_t)}{C_o} \times \frac{100}{1} \quad (2)$$

Where q_t = the amount of metal ion adsorbed (mg per g of sorbent) at time "t", "V" was the volume of the sample solution, "W" denoted the weight of sorbent (g), "C_o" and "C_t" are the initial metal concentration in the aqueous solution (mg/l) and metal concentration at time t, respectively. Metal ion uptake (adsorption capacity) at equilibrium q_e was determined by mass balance using Equation 3:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (3)$$

Where:

q_e is the equilibrium adsorption capacity (mg/g), c_o and c_e are the initial and equilibrium metal concentrations in the water (mg/l), respectively V is the Volume of used (solution) (l) W is the weight of used (adsorbent) (g).

These equations were used to obtain the percentage removal or percentage adsorption of the metal ions and the quantity of metal ions adsorbed at a time t and at equilibrium.

All studies were carried out in triplicate, and the mean values are reported.

Determination of Effects of Adsorbent Dosage on the Adsorbent

The amount of Cd²⁺, Cr³⁺, Hg²⁺, Ni²⁺ and Pb²⁺ ions adsorbed by soursop fruit barks was studied at different adsorbent doses at a fixed concentration (150mgL⁻¹) of the metal ions. To aliquots (20mL) of the metal ions in separate conical flasks, the required amount (0.2g, 0.4g, 0.6g, 0.8g, 1g and 2g) of the adsorbent was added. Each flask was corked and shaken on a rotator electrical shaker for 30 mins with a constant agitation speed of 500 rpm and then filtered. The metal ion content of these filtrates were determined using Atomic Absorption Spectrometer (AA 240 FS). The amount of metal ion sorbed at equilibrium q_e (mg/g) and percentage adsorbed was calculated.

Determination of the Effect of contact time on Adsorption of Metal Ions by SSB

By keeping all other variable constant, the effect of contact time on the amount of removal of metal ions from the solution were obtained by contacting 20mL of 150mg/L of the metal solutions with 2g of the adsorbents at the optimum pH and room temperature. The sample was agitated for the time of 20 to 120 mins respectively in plastic tube at 200rpm and at room temperature. Then the sample was filtered with Whatmann filter paper no. 1 and the concentrations of the filtrate solutions at each time were analyzed using Atomic Absorption Spectrometer (AA 240 FS). The amount of metal sorbed at equilibrium q_e (mg/g) and percentage adsorbed was calculated with equations 1-3.

Determination of the Effect of pH on the Adsorption of Metal Ions by SSB

The effect of pH on the amount of metal ions removal was analyzed over the pH range of 4 to 14. 20mL of the metal solutions of 150mg/L was taken in plastic tube and was agitated with 2g of SSB at 200rpm for 2hrs at room temperature. The sample was filtered using Whatmann filter paper no 1 and the concentrations of the metal ion solutions were analyzed using Atomic Absorption Spectrophotometer (AA 240 FS). The amount of metal sorbed at equilibrium q_e (mg/g) and percentage adsorbed was calculated with equations 1-3.

Determination of the Effect of metal ion concentration on the Adsorbent

Different metal ion concentrations were used ranging from (40-140ppm). The soursop fruit bark (2g) was dispersed into 20 mL of the separate metal ion solutions. Each mixture was shaken mechanically on a shaker for 90 mins at room temperature (30°C) and filtered. The residual concentration of metal ions in the filtrate was determined using AAS (AA 240 FS). The amount of metal sorbed at equilibrium q_e (mg/g) and percentage adsorbed was calculated with equations 1-3.

Determination of the Effects of Temperatures on the Adsorbent

The sorption experiments for the adsorption of metal ion system were carried out using 20mL of 150mg/L of metal ion concentration on the adsorbent (SSB). The metal solutions were adjusted to

pH 8.0 and agitated manually on a magnetic stirrer for 60 mins. This was carried out at different temperatures of 25°C to 70°C. At the end of the time, the suspension was filtered through what man No.41 filter paper. The filtrates were analyzed using Atomic Absorption spectrophotometer (AA 240 FS). The amount of metal sorbed at equilibrium q_e (mg/g) and percentage adsorbed was calculated with equations 1-3.

Determination of the Effect of particle size on the Adsorbent

2g of 0.075 μ m adsorbent was introduced into a beaker containing 20mL of 150mg/L of metal ion solutions with the pH and temperature (pH14 and 70°C) respectively. The mixture of the solution was shaken manually on the magnetic stirrer for 1 hr and was filtered. The filtrate was used to determine the metal ions using AAS. The same procedure was used for other adsorbent particle sizes. The amount of metal sorbed at equilibrium q_e (mg/g) and percentage adsorbed was calculated with equations 1-3.

RESULTS AND DISCUSSION

Physico-Chemical Characterization of the adsorbent

The physico-chemical characteristics of SSB are shown in Table 1. From the analysis it can be observed that the SSB has low moisture content, ash content, pH, specific gravity, bulk density and high surface area.

Table 1 Physical Characteristics of SSB

Parameter	SSB
Moisture content (%)	6.50
Ash content (%)	2.00
pH	5.95
Surface Area (m ² /g)	1255
Specific Gravity	0.47
Density (g/cm ³)	0.47

Effect of Adsorbent Dosage

The biosorbent dosage is an important parameter because it determines the capacity of a biosorbent for a given initial concentration.

Fig 1 showed the adsorption capacity of Cd (II) as a function of adsorbent dosage.

It is clear from fig 1 that cadmium adsorption was found to increase with increasing adsorbent dose. The other ions followed similar trend.

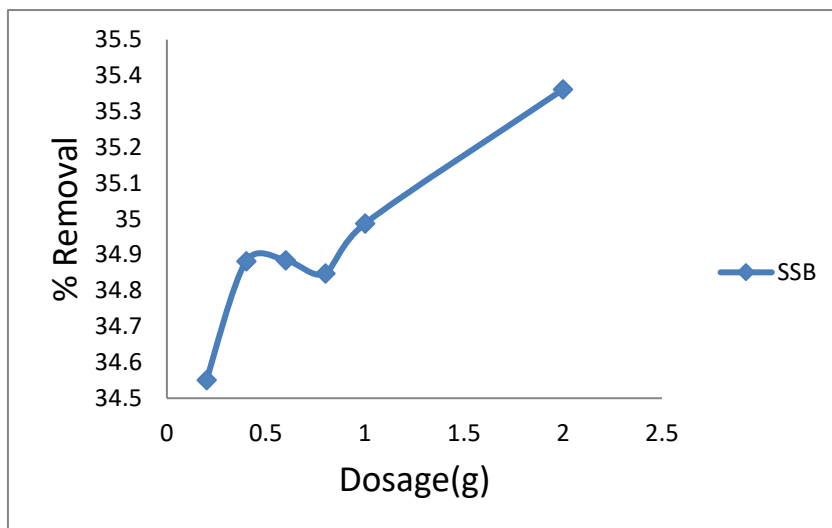


Fig. 1: Effect of Adsorbent Dosage on SSB for Cd (II)

EFFECT OF pH ON THE ADSORPTION OF Lead ION FOR SSB

pH is one of the most important controlling parameters in all adsorption processes. The pH of the solution affects the extent of adsorption because the distribution of surface charge of the adsorbent can change (because of the composition of raw materials and the technique of activation) thus varying the extent of adsorption

according to the adsorbate functional groups¹².

Fig 2 showed the adsorption capacity of Pb(II) a function of the adsorbate at fixed adsorbent dose, fixed agitation time, fixed adsorbate concentration at room temperature. It was clear that the metals adsorption was found to increase with increasing pH of the solution within the range studied. Other ions followed the same trend.

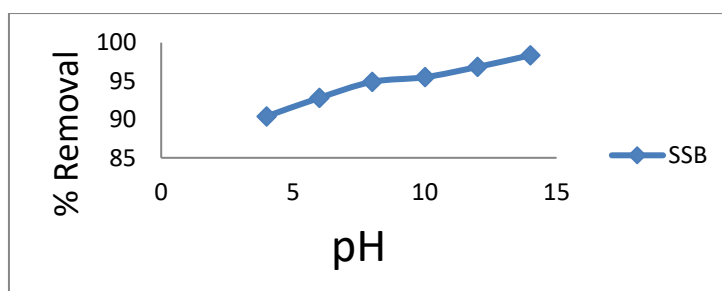


Fig. 2. Effect of pH on SSB for Pb (II)

EFFECT OF CONTACT TIME ON THE ADSORPTION OF MERCURY ION FOR SSB

The rate of biosorption is important for designing batch biosorption experiments. The required agitation time for sorption to be completed is important to give insight into a sorption process. This also provides information on the minimum time required for considerable adsorption to take place, and also the possible diffusion controlled mechanism between the adsorbate¹⁵.

The effect of agitation time on Hg (II) Removal (%) at fixed adsorbent dosage,

fixed pH and fixed adsorbate concentration at room temperature is presented in Fig. 3. From the figure the minimum amount of time required for considerable adsorption to take place is 20 min; further increase resulted in slight increase in percentage of Mercury removed.

Based on the result obtained from this study the agitation for further experiment were maintained at 120min to ensure that equilibrium was attained.

From figure 3, it could be seen that as the time increases, the % removal also increases.

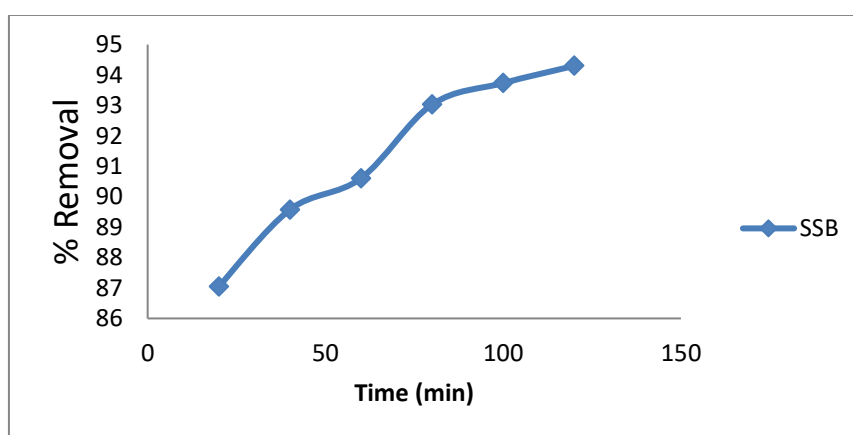


Fig. 3. Effect of contact time on SSB for Hg (II)

EFFECT OF METAL ION CONCENTRATION ON THE ADSORPTION OF CHROMIUM ION FOR SSB

The effect of metal ions concentration on amount of Chromium adsorbed (mg/g) are presented in figure 4. As the concentration of the metal ions was increased the percentage removal of the metal ions decreased as shown in the Fig 4. This according to¹² is due to the fact that at high-level concentrations, the available sites of adsorption become fewer and

therefore the rate of adsorption decreases. The amount of adsorbate in the solid phase with lower initial concentration of adsorbate was smaller than the amount when higher concentrations were used, although not in a linear relationship. The metal uptake mechanism is particularly dependent on the initial heavy metal concentration: at low concentrations, metals are adsorbed by specific active sites, while at higher concentrations; lower adsorption yield is due to the saturation of adsorption sites¹³.

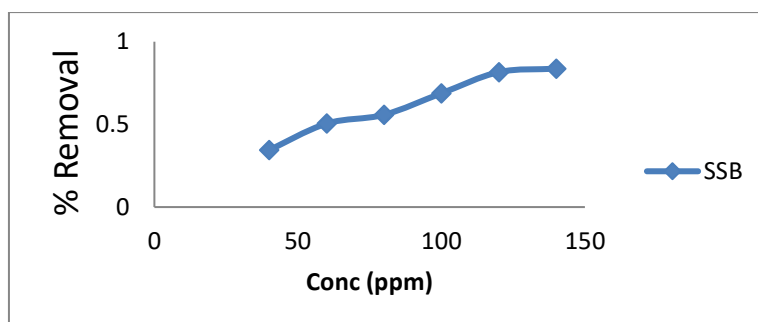


Fig. 4. Effect of metal ion concentration on SSB for Cr (III)

Biosorption Isotherms

Adsorption isotherms or capacity studies are of fundamental importance in the design of adsorption systems since they indicate how the metal ions are partitioned between the adsorbent and liquid phases at equilibrium as a function of increasing metal concentration. When an adsorbent and metal ion solution is placed in contact, the concentration of metal ions on the adsorbent will increase until a dynamic equilibrium is reached; at this point, there is a defined distribution of metal ions between the solid and liquid phases. In order to optimize the design of a sorption system to remove Cd (II), Pb (II), Hg (II), Ni (II) and Cr (III) from waste water, it is important to establish the most appropriate correlation for the equilibrium curve. Two isotherm equations were tested in this work namely; Langmuir and Freundlich.

Langmuir Adsorption Isotherm

The values of Langmuir parameters q_{\max} and K_L for Ni(II) ion were calculated from

the slope and intercept of the linear plot of C_e/q_e versus C_e as shown in the figure 5. Values of q_{\max} , K_L and regression coefficient R^2 for SSB are listed in Table 2. The other ions followed similar trend.

The essential characteristics of the Langmuir Isotherm parameters could be used to predict the affinity between the sorbate and sorbent using separation factor or dimensionless equilibrium parameter, R_L expressed as in the following equation:

$$R_L = \frac{1}{(1 + K_L C_i)} \quad (4)$$

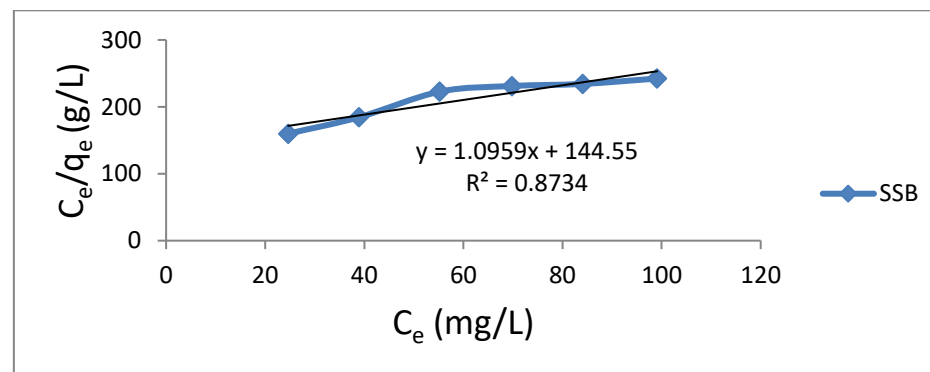
Where C_i is the initial concentration and K_L is the Langmuir constant.

The value of separation factor 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 ($R_L > 1$). The values of R_L for SSB are less than 1 which indicated favourable biosorption, in this study.

Table 2 Langmuir Isotherm Constant for the adsorption of the metal ions onto SSB

Adsorbent	Metal ions	Isotherm model	Parameters				
			R^2	$q_{\max}(\text{mg/l})$	N	K_F	K_L
SSB	Cd(II)	Langmuir	0.981	1.115			0.044
		Freundlich	0.920		1.942	0.106	
	Pb(II)	Langmuir	0.984	1.721			0.019
		Freundlich	0.998		1.486	0.061	
	Hg(II)	Langmuir	0.974	1.346			0.027
		Freundlich	0.975		1.667	0.076	
	Cr(III)	Langmuir	0.958	1.003			0.082
		Freundlich	0.926		2.725	0.195	
	Ni(II)	Langmuir	0.873	0.913			0.008
		Freundlich	0.989		1.451	0.017	

1983

**Fig 5.** Langmuir isotherms for adsorption on Ni (II)

Freundlich Isotherm

Freundlich equilibrium constant were determined from the plot of $\log q_e$ versus $\log C_e$, Figure 6 on the basis of the linear of Freundlich equation:

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (5)$$

The values of Freundlich parameters n and K_F were calculated from the slope and intercept of $\log q_e$ versus $\log C_e$ as shown in fig 6 for Ni(II) ion. Values of n , K_F and regression coefficient R^2 for SSB are listed in Table 3. The other ions followed similar trend.

Table 3 Freundlich Isotherm Constant for the adsorption of the metal ions onto SSB

Adsorbents	Metal ions	Kinetic model	Parameters				
			R^2	K_1	K_2	$q_e(\text{exp})$	$q_e(\text{cal})$
SSB	Cd(II)	First Order	0.902	0.051		0.534	0.321
		Second Order	0.999		0.543	0.534	0.548
	Pb(II)	First Order	0.852	0.041		1.486	0.543
		Second Order	0.999		0.200	1.486	1.522
	Hg(II)	First Order	0.889	0.044		1.415	0.617
		Second Order	0.996		0.064	1.415	1.610
	Cr(III)	First Order	0.889	0.044		1.000	0.617
		Second Order	0.997		0.069	1.000	1.111
	Ni(II)	First Order	0.797	0.035		1.036	0.447
		Second Order	0.998		0.254	1.036	1.059

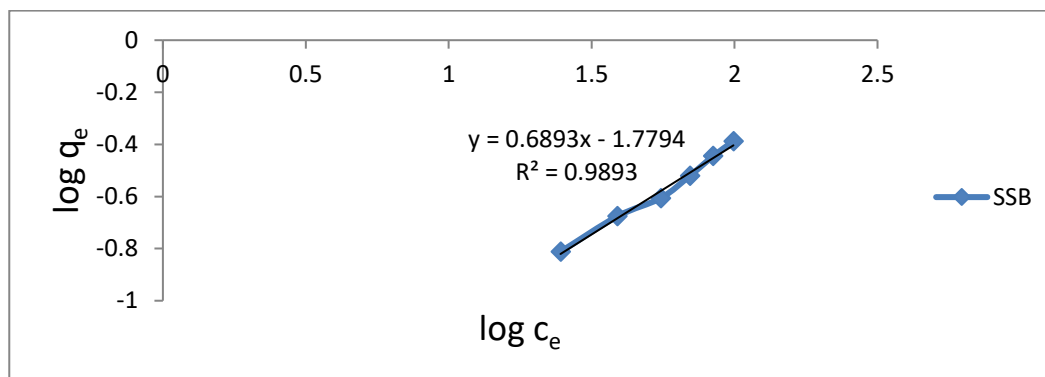


Fig 6: The Freundlich isotherms for adsorption on Ni (II)

SORPTION REACTION MODELS

In order to investigate the biosorption process of Cd (II), Pb (II), Hg (II), Cr (III) and Ni (II) on SSB, Pseudo-first order of Lagergren rate equation and Pseudo-second order model were used to find the best fit kinetic model for the adsorption of Cd (II), Pb (II), Hg (II), Cr (III) and Ni (II) onto SSB.

The Lagergren rate equation is the most widely used rate equation for sorption of a solute from a liquid solution¹⁴. The Pseudo first order rate constant of Lagergren rate equation is obtained from the slope of plot between $\log (q_e - q_t)$ against time t . Figure 7 showed the Lagergren pseudo-first order

kinetic plot for the adsorption of Cd^{2+} onto SSB powder. The calculated values and their corresponding linear regression correlation coefficient values are shown in Table 4. This showed that this model cannot be applied to predict the adsorption kinetic model¹⁵⁻¹⁶. Also the values of calculated adsorption capacities (q_e), calculated were far much lower than experimental ones suggesting that the adsorption process did not fit the pseudo-first order model but fit into second order. Similar result was obtained by HO and McKay¹⁷. The other ions followed similar trend.

Table 4. Kinetic Parameters for Adsorption of Metal Ions on SSB

Adsorbents	Metal ions	Kinetic model	Parameters				
			R ²	K ₁	K ₂	q _e (exp)	q _e (cal)
SSB	Cd(II)	First Order	0.902	0.051		0.534	0.321
		Second Order	0.999		0.543	0.534	0.548
	Pb(II)	First Order	0.852	0.041		1.486	0.543
		Second Order	0.999		0.200	1.486	1.522
	Hg(II)	First Order	0.889	0.044		1.415	0.617
		Second Order	0.996		0.064	1.415	1.610
	Cr(III)	First Order	0.889	0.044		1.000	0.617
		Second Order	0.997		0.069	1.000	1.111
	Ni(II)	First Order	0.797	0.035		1.036	0.447
		Second Order	0.998		0.254	1.036	1.059

1986

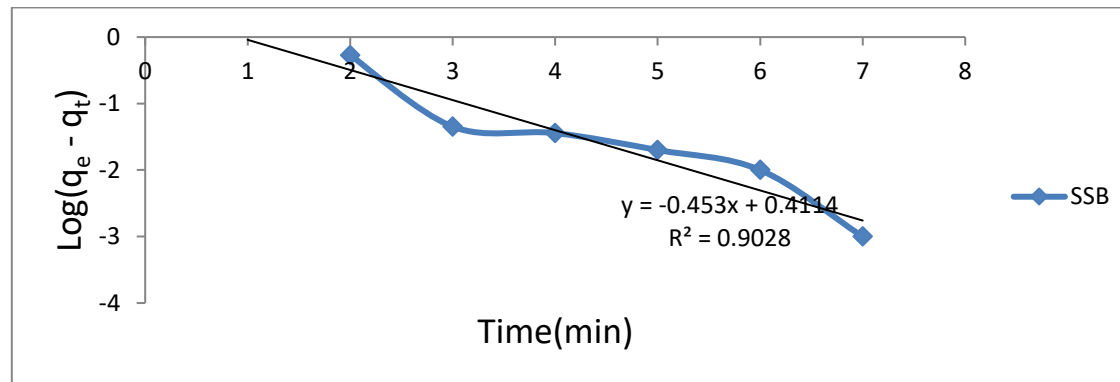


Fig 7: Pseudo first order for adsorption on Cd (II)

Figure 8 showed the pseudo-second order kinetic plot for the adsorption of Cd (II) onto SSB powder, from which q_e and rate constant were determined from the slope and intercept. From Table 4, the results for the linear regression correlation coefficient R^2 values for SSB are higher than the pseudo first order kinetics. The higher values confirmed that the adsorption data are well represented by Pseudo-second order

kinetics¹⁶. The calculated maximum adsorption capacity values of q_e , are quite close to the experimental values, q_e , for adsorption of Cd (II), Pb (II), Hg (II), Cr (III) and Ni (II) onto SSB (Table 4). This indicated that the pseudo second order model fitted the kinetic data very well. Similar results were obtained by Aki and Ahlam¹⁹. The other ions followed similar trend.

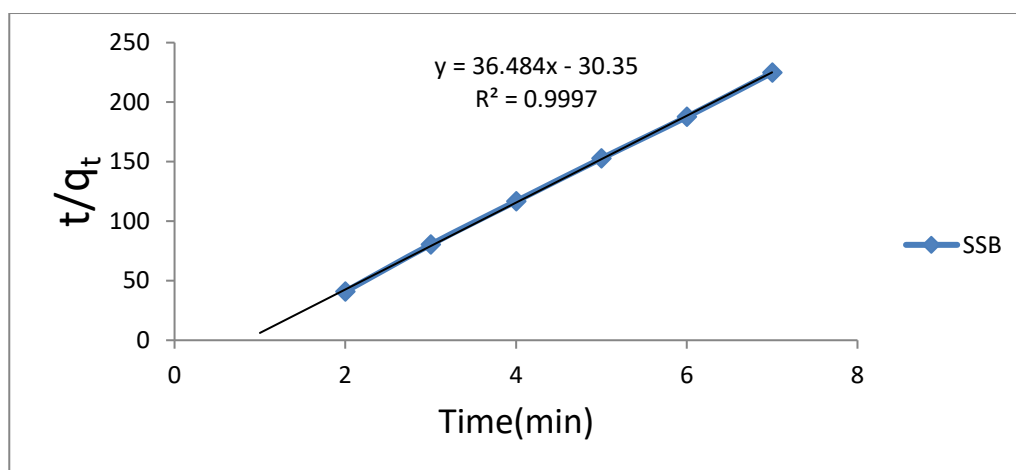


Fig 8 Pseudo second order for adsorption on Cd (II)

Van't Hoff Plots

From the van't Hoff plot shown in Figure 9, it could be observed that as the temperature increases, $\ln K_C$ decreased for the adsorbents. Thermodynamic parameters associated with the adsorption, viz standard free energy change (ΔG^0), standard enthalpy change (ΔH^0), and standard entropy change (ΔS^0) were calculated and the results are shown in Table 5. The free energy of adsorption process considering the adsorption equilibrium constant K_C is given by the equation⁶:

$$K_c = \frac{C_{ae}}{C_e} \quad (6)$$

The values of enthalpy change (ΔH^0), and entropy change (ΔS^0) were calculated

from the slope and intercept of the plot of $\ln K_C$ vs. $1/T$, (Figure 9). The calculated values of thermodynamic parameters, ΔG^0 , ΔH^0 and ΔS^0 for the biosorption of Cd^{2+} , Pb^{2+} , Hg^{2+} , Cr^{3+} , and Ni^{2+} onto SSB powder are reported in Table 5. Positive values of ΔH^0 for SSB were 22.38KJ/mol, 42.38KJ/mol, 30.27KJ/mol, 42.19KJ/mol, 10.69KJ/mol for Cd^{2+} , Pb^{2+} , Hg^{2+} , Cr^{3+} , and Ni^{2+} respectively indicated the endothermic nature of the process. Negative values of the free energy ΔG^0 for SSB at all temperatures indicated the process to be feasible and the spontaneous nature of the biosorption process. Similar results were got by some workers^{16,17}.

TABLE 5. Thermodynamic Parameters of Adsorption of Cd (II) on SSB

T(K)	ΔG^0 (KJ/MOL)	ΔH^0 (KJ/MOL)	ΔS^0 (KJ/MOL)
298	-42.12		
303	-259.47		
313	-1069.54	22.38	0.076
323	-1847.57		
333	-4127.93		
343	-5047.51		

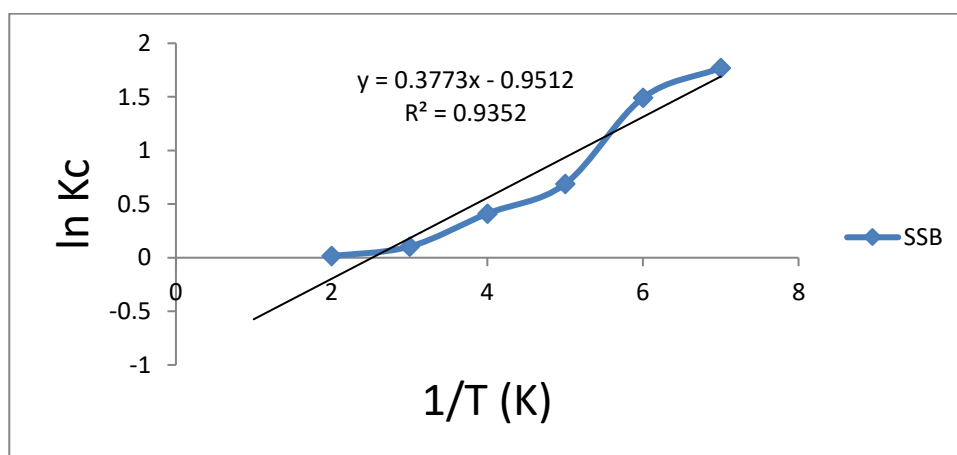


Fig 9. Van't Hoff plot for Adsorption of Cd (II) on SSB

CONCLUSION

From the Tables, graphs and discussions, the following conclusions have been drawn:

Adsorption of (Cd²⁺, Cr³⁺, Hg²⁺, Ni²⁺ and Pb²⁺) onto SSB are found to be dependent on pH of the solution, agitation time, initial metal concentration and temperature of adsorption.

On the basis of Correlation factor R² the equilibrium data showed that Freundlich models described the biosorption process of Cd²⁺, Cr³⁺, Hg²⁺, Ni²⁺ and Pb²⁺ onto SSB. The value of separation factor (R_L) for SSB is less than 1 which indicated favourable biosorption.

The n values for SSB is greater than 1, indicating that the biosorption of Cr³⁺, Hg²⁺, Ni²⁺ and Pb²⁺ onto SSB is a physical process. The pseudo second order kinetic model fitted the adsorption of Cd²⁺, Cr³⁺, Hg²⁺, Ni²⁺ and Pb²⁺ onto SSB favourably.

The thermodynamic study indicates that the adsorption procedure was spontaneous having negative Gibbs free energy values at all the temperatures. ΔS^0 values for SSB were 0.076KJ/mol, 0.197KJ/mol, 0.141 KJ/mol, 0.147 KJ/mol, and 0.051 KJ/mol for Cd²⁺, Pb²⁺, Hg²⁺, Cr³⁺, and Ni²⁺ respectively. ΔH^0 values for SSB were 22.38KJ/mol, 42.38KJ/mol, 30.27KJ/mol, 42.19KJ/mol, and 10.69KJ/mol respectively. This work has confirmed that Soursop fruit bark (SSB) is an effective biosorbent for the removal of heavy metal ions (Cd²⁺, Cr³⁺, Hg²⁺, Ni²⁺ and Pb²⁺) from aqueous solutions. The advantages of their uses are that the materials are cheap and readily available hence they are very suitable for water purification. SSB can therefore be used in the treatment of effluents from industries, thereby reducing the level of water pollution.

REFERENCES

- Duffus, J. H., (2002). "Heavy metals"—A Meaningless Term? Pure Applied Chemistry, 74(5): 793–807.
- Ademoroti, C.M.A., (1996). Environmental Chemistry and Toxicology. Foludex press Ltd, Ibadan. pp 121-183.
- Galanis, A., Karapetsas, A., and Sandaltzopoulos, R., (2009). Metal-Induced carcinogenesis, oxidative stress and hypoxia signalling. Mutat Resource, 674(1-2): 5-31.
- Hinwood, A.L, Callan, A.C., Ramalingam M., (2013). Cadmium, lead and mercury exposure in non smoking pregnant women Environment, 126:118-124.
- Waalkes, M.P., (2000): Cadmium Carcinogenesis in review, Journal of Inorganic Biochemistry.79: 241-244.
- Bronstein, A. C., Spyker, D. A., Cantilena, L. R., Jr, Rumack, B. H., and Dart, R. C., (2011). Annual Report of the American Association of Poison Control Centers' National Poison Data System (NPDS): Clinical Toxicology, Philadelphia. pp. 911–1164.
- ATSDR. (2008) ToxGuide for Lead. 2008a:1–2. Available online at <http://www.atsdr.cdc.gov/toxguides/toxguide-13.pdf> Retrieved September 18, 2012.
- Abelsohn, A.R., Sanborn, M., (2010). Lead and children: clinical management for family physicians. Can Fam Physician, 56(6): 5-53.
- Salem, H.M., Eweida, A.E., and Farag, A., (2000). Heavy metals in drinking water and their environmental Impact on human health. ICEHM2000, Cairo university, Egypt, pp 542-556.
- Golimowski, J., Valenta, P., and Nurnberg I., (1985). Trace Determination of chromium in various water types by adsorption differential pulse voltametry. Institute of Applied Physical chemistry, Nuclear Research centre (KFA) Juelich, Federal Republic of Germany. Fresenius Analytical Chemistry, 315 -322.
- Mertz, W., (1993). Chromium Human Nutrition; A review: Journal of Nutrition, 123: 626-635 and Anderson, R.A., (1998) Effects of chromium on body composition and weight loss. Nutritional Paris, 52(20): 66-77.
- Lawrence, W. (2012): Toxic Metals and Human Health. The Center for Development <http://drlwilson.com/articles/Toxic%20METALS.htm>
- Chang, F.R., and WU Y.C., (2001). Novel cytotoxic annonaceous acetogenins from Annona muricata. Journal Natural Product, 64 (7): 925-931.
- Gao, J and Pederson, J.A., (2005): Adsorption of sulfonamide Antimicrobial Agents to Clay Minerals. Environmental Science Technology, 39: 9509-9516.
- Al-Anber, M. (2010), Removal of High-level Fe³⁺ from aqueous solution using Jordanian Inorganic materials: Bentonite and Quartz, Desalination, 250:885-891.
- El-Sayed, G.O., Dessouki, H.A and Ibrahim, S.S., (2010): Biosorption of Ni (II) and Cd (II) ions from Aqueous Solutions onto Rice Straw. Chemical Sciences Journal, 9, 1-11.
- Ho, Y.S., and McKay, G., (2000). The kinetics of sorption of divalent metal ions onto *Sphagnum* peat moss. *Water Resources*, 34:735-742.
- Al-Dujaili, A.H., Awwad, A.M. and Salem, N.M., (2012): Biosorption of cadmium (II) onto loquat leaves (*Eriobotrya Japonica*) and their ash from aqueous solution, equilibrium, kinetics and thermodynamics studies. International Journal of Industrial chemistry, 3: 12-22.
- Aki, M.A and Ahlam, M.F., (2012): Equilibrium, Kinetic and Thermodynamic of Biosorption of Lead (II) Copper (II) and Cadmium (II) ions from aqueous solution onto olive leaves powder, American Journal of Chemistry, 2(4): 238-244.

