

# Kinetic and Equilibrium Studies on Lead (II) Ion Removal from Aqueous Solution Using Succinic Acid Modified Red Onion Skin Extract

Millicent U. Ibezim-Ezeani, Ikodiya Orji

**Abstract**— The removal of Pb (II) ions from synthetic waste water by red onion skin extract modified with succinic acid was studied as a function of experimental parameters: contact time, pH and initial metal ion concentration. Maximum metal removal was observed at pH 6.3, initial metal ion concentration of 20 mg/L, temperature of 28 °C and 50 mins contact time. Kinetic studies indicated that the adsorption of Pb (II) ions onto the modified extract followed a pseudo-second order kinetic model. The removal efficiency rate at the different temperatures is in the order: 28 > 40 > 50 > 60 > 70 °C. The adsorption process was investigated by fitting the data obtained into Freundlich, Langmuir, Temkin and Flory-Huggins isotherms; and the results obtained from the correlation coefficients of the plots indicated that Freundlich adsorption isotherm is the best fit for the experimental data. Calculations of thermodynamic parameters revealed that the sorption process was spontaneous ( $\Delta G$  values of -33.629, -27.176, -20.867, -17.218 and -5.402 kJ/mol at 28, 40, 50, 60 and 70 °C respectively); and exothermic with value of  $\Delta H$  as -224.220 kJ/mol, while that of  $\Delta S$  as -630.384 JK<sup>-1</sup>mol<sup>-1</sup>. Results obtained from plotting the Dubinin-Radushkevich (DR) isotherm at different temperatures showed that the dominant mechanism responsible for the removal of Pb (II) ions was particle diffusion, since the free energy values are in the range of 24.784 - 30.261 kJ/mol for 28 - 70 °C.

**Index Terms**— Dubinin-Radushkevich and Freundlich isotherms, Pb (II) ions, red onion skin extract, succinic acid.

## I. INTRODUCTION

The toxic and persistent nature of heavy metals in the aquatic ecosystem has made their contamination a major environmental and public health issue. Industrial effluents are the main source of direct and often continuous input of heavy metals into aquatic environment with long-term implications on ecosystem functioning [1]. Lead, because of

its prevalence and severe toxicity, is one heavy metal that has attracted a lot of attention from researchers. It is harmful to the health of many animals including humans because it can inhibit the action of many enzymes in the body [2]. It is a systemic poison causing anaemia, kidney malfunction, tissue damage of brain and even death in extreme poisoning situation [3]. Disposal of lead contaminated water from processing industries like acid battery manufacturing, metal plating and finishing, ammunition manufacturing, tetraethyl lead manufacturing, ceramic and glass industries and environmental clean-up services are the major sources of lead pollution in aquatic ecosystems [4], [5].

The techniques usually employed in remediation of Pb (II) ions contaminated water include coagulation, chemical precipitation, chemical oxidation and reduction, reverse osmosis, and ion exchange. The quest for reducing the cost associated with these techniques has stimulated researchers to investigate different agricultural wastes in their modified and unmodified forms for their ability to remove Pb (II) ions from aqueous solutions. The agricultural waste products that have been employed include coconut coir dust and resins synthesized from its extract [6], orange mesocarp [7], [8], sawdust [9], [10], rice husk [11], [12], peanut hull [13], [14], and corn cob [15]. These agricultural wastes are readily available in large quantities and their utilization as adsorbents in Pb (II) ions removal processes will not only reduce the cost incurred in their removal from lead contaminated water, but improve the aesthetic value of the environment while increasing the profit margin of these rural farmers as they convert these wastes to value added products.

In the first quarter of 2010, a deadly outbreak of acute lead poisoning among children was discovered in one of the states of Nigeria; Zamfara State [16]. The outbreak occurred as a result of artisanal mining and processing of lead-rich gold ores. These activities are widespread in many villages within the state because the state is blessed with abundant mineral resources, including gold and lead deposits [17]. In the study carried out by the United Nations Environment Programme / Office for the Coordination of Humanitarian Affairs, it was discovered that in some community wells in the state, concentrations of up to 10-15 times the world health organization (WHO) guideline for lead in drinking water were found [18]. In most cases, exceeding of the guideline was coupled with high concentrations of lead in the soil around the well. High concentrations of lead, up to more than 1,000 µg/l – 10 times higher than the exposure limit suggested by Food and Agricultural Organization (FAO) for livestock were often found in ponds, rivers and

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lakes sampled by the UNEP/OCHA mission. This is understandable because surface water sources most often are used for processing the ore.

Incidentally, the Northern states of Kano, Kaduna, Jigawa, Plateau, Bauchi, Sokoto, and Kebbi States in Nigeria are major producers of onion [19], [20]. Onion skin obtained as by-product from the processing of these abundant onion bulbs could be harnessed in the removal of Pb (II) ions from the water obtained from lead-contaminated rivers and ponds prior to domestic use such as bathing and washing clothes.

This research therefore, is designed to investigate the Pb (II) ions removal capacity of modified red onion skin extract from lead-contaminated aqueous solutions.

## II. MATERIALS AND METHODS

The collection and extraction of the red onion skin; the preparation of the succinic acid modified red onion skin resin (SROSE); and the spectroscopic analysis were described by Orji *et al.* [21].

### A. Sorption Studies

Standard solution (20 ml) of the Pb (II) ions of initial concentration of 20 mg/l and pH of  $7.0 \pm 0.2$  was transferred into various 150 cm<sup>3</sup> conical flasks with stopper. Thereafter, 0.3g of SROSE was transferred into the different flasks and agitated in a mechanical shaker at temperature of 28°C (301K) for different contact times (10, 20, 30, 40, 50, 60, and 70 minutes). At the end of each agitation period, the content of the flask was filtered using Whatman No.41 filter paper. The concentration of metal ions in the filtrate of each metal solution was determined using Atomic Adsorption Spectrophotometer (AAS) (GBC SCIENTIFIC AVANTA PM AAS A.C.N 005472686 manufactured by GBC Scientific equipment Pty Ltd. Dandenong Victoria Australia). The quantity of Pb (II) ions removed was calculated by difference.

The procedure was repeated at different initial ion concentrations (5 to 50 mg/L), temperatures (28 to 70 °C), pH values (~ 2 to 10) and contact times (10 to 70 mins). The percentage Pb (II) ions removed was deduced using equation 1 and plotted as a function of initial ion concentrations, contact time and pH in each case.

## III. RESULTS AND DISCUSSION

### A. Sorption Studies

The percentage metal ion removed was calculated using equation 1, while the sorption capacity was evaluated by the difference between the initial Pb (II) ions concentration and the equilibrium concentration in the liquid phase using equation 2.

$$\text{Percentage metal ion removal} = \left(1 - \frac{C_e}{C_o}\right) \times 100 \quad (1)$$

$$q_e = \frac{V}{m} (C_o - C_e) \quad (2)$$

$C_o$  = Initial concentration of metal ion in solution (mol/L)

$C_e$  = Equilibrium concentration of metal ion (mol/L)

$V$  = Volume of initial Pb ion solution used (L)

$m$  = Mass of SROSE (g).

### Effect of Initial Ion Concentration

The chemical potential gradient of a system determines how the removable ions in the system will move from the bulk of the solution towards the active site of the adsorbent. These removable metal ions usually migrate from a region of higher concentration in the metal ion solution to a region of lower metal ion concentration in the active sites of the adsorbent being employed for the metal removal process. At the active sites, the metal ions from the solution will replace equal amounts of positively charged ions. The variation of the initial Pb (II) ions concentration in the synthetic waste water and percentage removal is shown in Fig.1.

The plot shows that the highest percentage removal of 96.36% occurred at the initial concentration of 20 mg/L.

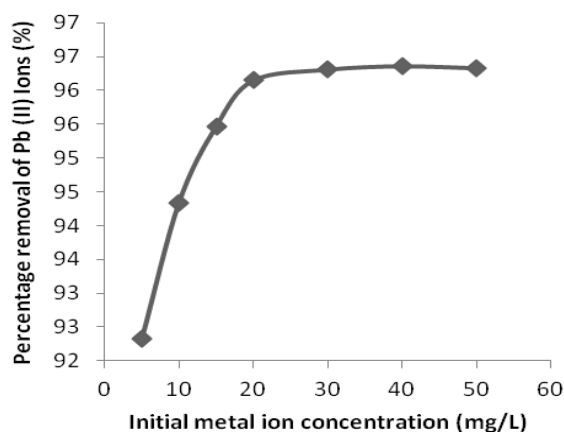


Fig. 1: Plot of Percentage Removal of Pb (II) Ions at Different Initial Ion Concentrations

As the initial concentration of the solution increased to 50 mg/L, there was a marginal decrease in the percentage of Pb (II) ions removed from 96.36% to 96.33%.

At high concentrations, the active sites available for interaction with the metal ions in solution are less numerous relative to those available at low concentrations. Therefore, at lower concentrations, the degree of competition between the metal ions in solution for the limited number of active binding sites in the modified extract is higher relative to the degree of competition at lower concentrations. Therefore, once the active sites of the SROSE are exhausted, the remaining metal ions will not be removed, so the ions will attain a steady state with the adsorbed ions, such that no matter the initial concentration of the metal ions, there will always be a residual concentration of the Pb (II) ions in solution. This explains the 96.36 percentage removal of the Pb (II) ions at the initial concentration of the ions of 20 mg/L and a reduction to 96.33% ions removed as the initial concentration increased to 50 mg/L.

### Effect of pH

The results obtained from investigating the effect of pH on the Pb (II) ions removal capacity of SROSE showed that the

process is highly pH dependent. The percentage of Pb (II) ions removed increased steadily from 87.94 % at pH of 2.2 to 92.62% at pH 4.1. The highest percentage removal of 96.15% was recorded at pH 6.3, thereafter; the percentage of Pb (II) ions removed exhibited a continuous decrease to 91.44% at pH 8.2 and 86.2% at pH 10.1. This information is represented in the plot of the percentage of Pb (II) ions removed against the pH of the solution shown in Fig. 2. The optimal solution pH for the removal of Pb (II) ions using SROSE is pH 6.3 under the experimental conditions of investigation.

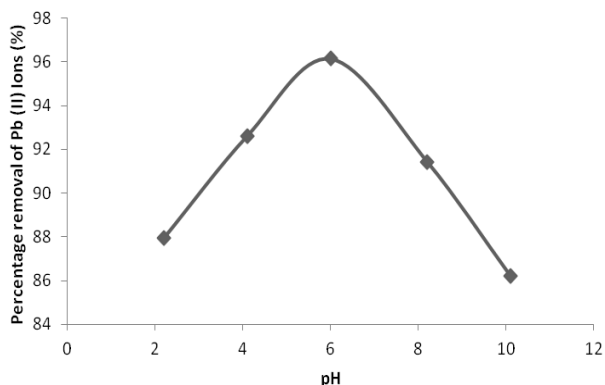


Fig. 2: Plot of Percentage Removal of Pb (II) Ions at Different pH

Previous work on the sorption of heavy metals from aqueous solutions indicates that sorption process is dependent on the pH of the solution [22] [23], this is because ionization of chemical species in any solution is dependent on the pH of the solution [24], The behavior of the active sites of adsorbents is also affected by the solution pH. At low pH, the active sites are protonated because of the high concentration of H<sup>+</sup> in solution. Thus, there will be a competition between Pb (II) ions and the H<sup>+</sup> ions. This competition will lead to the reduction of the percentage of metal ions removed. At higher pH, the concentration of the H<sup>+</sup> ions in solution is reduced; therefore, the active sites are less protonated, and consequently, the competition between the positively charged protons and metal ions is reduced and more metal ions are sorbed, leading to an increase in the percentage of Pb (II) ions removed.

#### Effect of Agitation Time

In order to determine the optimum agitation time for the removal of Pb (II) ions using SROSE, the relationship between the percentage of Pb (II) ions removed as a function of agitation time was investigated. The minimum time required for considerable adsorption to take place provides an insight into the metal removal process involved in the system, as well as the possible diffusion controlled mechanism between the metal ions as it moves from the bulk solution towards the active site of the SROSE. The plot of the percentage Pb (II) ions as a function of the agitation time is shown in Fig. 3. The plot showed a continuous increase in the percentage removal of Pb (II) ions from 10 mins (87.46%) to 20 mins (90.65%). The maximum percentage removal of Pb (II) ions occurred after the first 50 mins with a percentage removal of 96.62%, showing that

adsorption equilibrium was attained after 50 mins. The percentage removal of Pb (II) ions reduced after the fiftieth minute to 96.15% (60 mins) and 96.20% (70 mins).

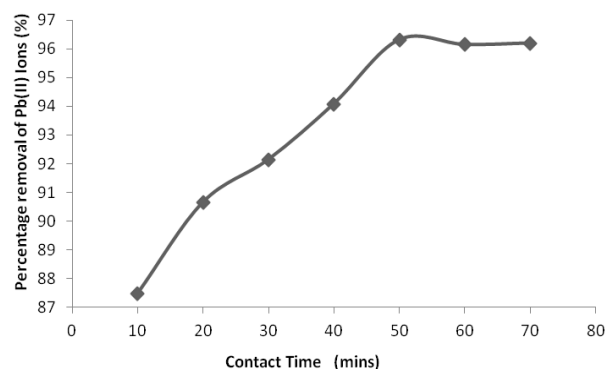


Fig.3: Plot of Percentage Removal of Pb (II) Ions at Different Contact Times

This could be attributed to the availability of the active sites of the SROSE for interaction with the Pb (II) ions at the beginning of the process. However, as more metal ions are adsorbed, metal – metal repulsion and the reduced availability of the active sites for attachment of the metal ions do not lead to a remarkable increase in the percentage of Pb (II) ions removed [25]. Therefore, it could be rightly inferred that the time for most of the active sites of the SROSE to be saturated with Pb (II) ions and thereby attain equilibrium is 50 mins.

#### B. Sorption Kinetic Studies

The sorption kinetics data for the metal removal process was determined by fitting the experimental data into two kinetic models: pseudo - first order model and pseudo – second order kinetic models, whose linear forms are represented in equations 3 and 4.

$$\ln(q_e - q_t) = \ln q_e - \frac{k_1}{2.303} t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

$q_e$  = amounts of the Pb (II) ions adsorbed (mol/g) at equilibrium

$q_t$  = amounts of the Pb (II) ions adsorbed (mol /g) at time, t

$k_1$  = pseudo-first order rate constant adsorption ( $\text{min}^{-1}$ ).

$k_2$  = pseudo-second order rate constant adsorption (g/mol/min).

A linear graph was obtained by plotting  $\log (q_e - q_t)$  against t (Fig. 4), from which slope and intercept,  $k_1$  and  $q_e$  were determined.  $k_2$  was also determined from the straight line graph obtained from the plot of  $t/q_t$  against t (Fig. 5).

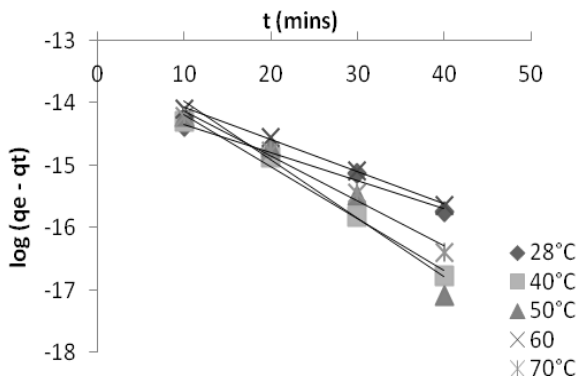


Fig. 4: First Order Plot of  $\log (q_e - q_t)$  against  $t$

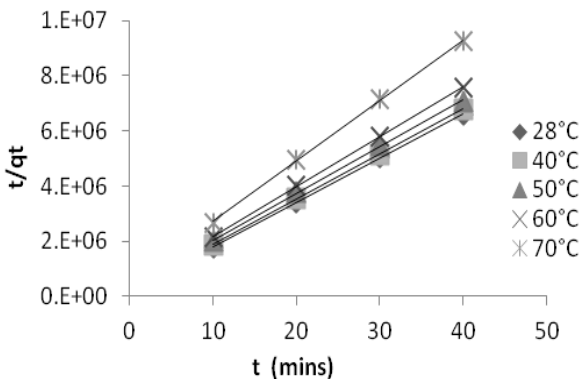


Fig. 10: Second Order Plot of  $t/q_t$  against  $t$

The comparison of the  $R^2$  values obtained from the two plots (Figs. 4 and 5); are presented in Table I.

Table I:  $R^2$  Values for the Models and Rate Constants of the Second Order Model

Temp (°C)	Pseudo-first order $R^2$	Pseudo-second order $R^2$	$k_2$ (g/mol/min)
28	0.9815	0.9998	138750.0294
40	0.9874	0.9998	99653.6616
50	0.9295	0.9994	83220.4535
60	0.9976	0.9997	92097.4957
70	0.9841	0.9996	87847.4665

Both kinetic models described the experimental data fairly well with  $R^2$  values greater than 0.9200. However, higher  $R^2$  values were obtained from fitting the experimental data into the pseudo-second order kinetic model; indicating that the pseudo-second order gives a better explanation for the kinetic behavior of SROSE in removing Pb (II) ions from aqueous solutions.

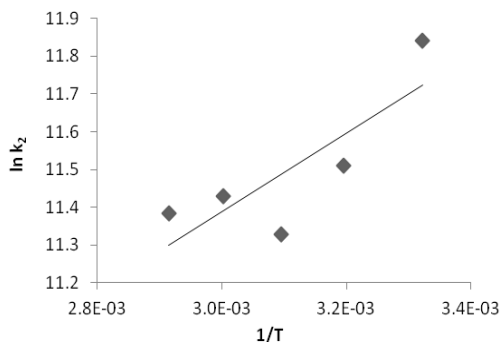


Fig. 6: Plot of  $\ln k_2$  against  $1/T$

Consequently, the natural logarithms of the second order rate constant  $k_2$  obtained at different temperatures was plotted against  $1/T$  (Fig. 6), in accordance with Arrhenius equation (equation 5) and the kinetic parameters determined from equation 6.

$$k_2 = A (\exp) -E_a/RT \quad (5)$$

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad (6)$$

The activation energy calculated from the slope of the plot has a value of  $-8.63 \text{ kJmol}^{-1}$ . The negative value of the activation energy indicates that the sorption process was an exothermic process. The pre-exponential factor was determined to be  $3.921 \times 10^4 \text{ g/mol/min}$ .

### C. Sorption Isotherm Studies

The sorption isotherms were simulated using four adsorption isotherms: Langmuir, Freundlich, Temkin, and Flory-Huggins [26], [27], [28], [29]. The linearized forms of these isotherms are presented in equations 7 through 10.

$$q_e = \frac{1}{x_m b} + \frac{C_e}{X_m} \quad (7)$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (8)$$

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \quad (9)$$

$$\ln \frac{\theta}{C_0} = \ln K_{FH} + n \ln (1 - \theta) \quad (10)$$

$b$  = Langmuir constant ( $\text{L mol}^{-1}$ )  
 $K_F$  = Freundlich constant ( $\text{mol}^{(1-n)} \text{L}^n \text{mol}^{-1}$ )  
 $K_T$  = Temkin constant  
 $K_{FH}$  = Flory-Huggins constant

$X_m$  = the maximum adsorption capacity upon complete coverage of the adsorption sites of the modified extract ( $\text{mol/g}$ )

$1/n$  = a measure of the surface heterogeneity, with values between 0 and 1

$R$  = gas constant

$T$  = temperature (K)

$b_T$  is related to the adsorption intensity

$$\theta = \left(1 - \frac{C_e}{C_0}\right)$$

The plots of the different adsorption isotherms are presented in Figs. 7 to 10.

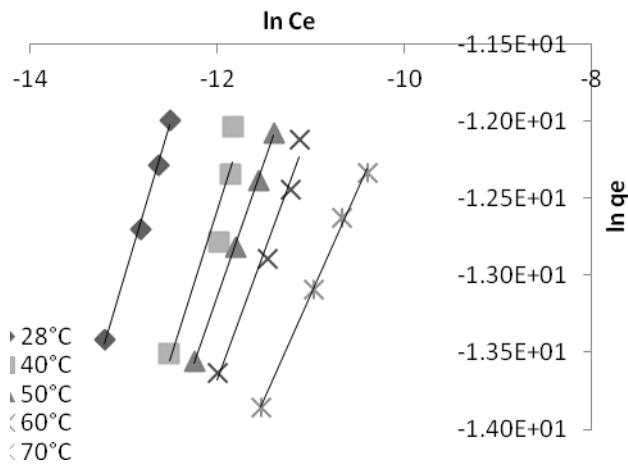


Fig. 7: Freundlich Isotherm at Different Temperatures

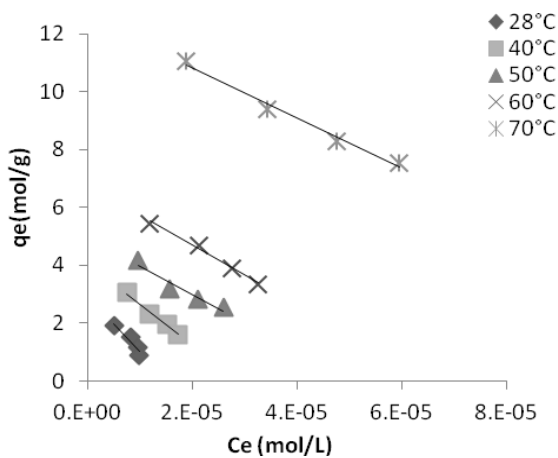


Fig. 8: Langmuir Isotherm at Different Temperatures

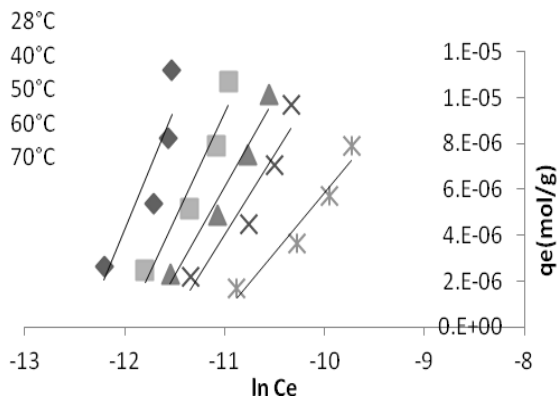


Fig. 9: Temkin Isotherm at Different Temperatures

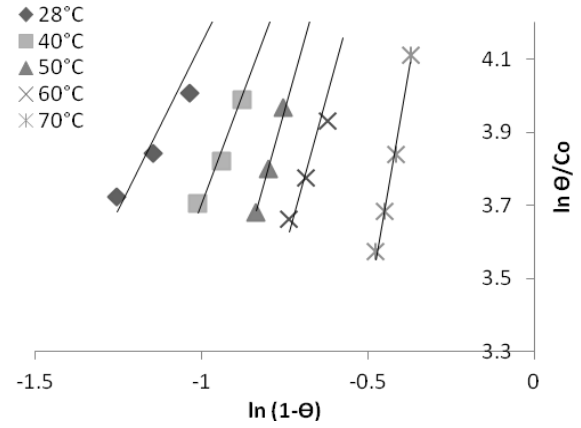


Fig. 10: Flory-Huggins Isotherm at Different Temperatures

The regression factors and the linear equations of the adsorption isotherms investigated are presented in Tables II and III respectively.

Table II: Comparison of Coefficient of Determination ( $R^2$ )

Temp. (°C)	Langmuir	Freundlich	Tempkin	Flory - Huggins
28	0.9086	0.9397	0.8061	0.9368
40	0.9875	0.9958	0.9284	0.9896
50	0.9301	0.9995	0.9628	0.9977
60	0.9881	0.9905	0.9074	0.9415
70	0.9868	0.9993	0.9408	0.9876

Table III: Linear Equations for the Isotherm Models

Temp (°C)	Langmuir	Freundlich	Tempkin	Flory - Huggins
28	$y = -1906x + 2.9121$	$y = 1.944x + 10.825$	$y = 1E-05x + 0.0001$	$y = 1.814x + 5.9598$
40	$y = -1415x + 4.0612$	$y = 1.718x + 7.3375$	$y = 9E-06x + 0.0001$	$y = 2.4121x + 6.1192$
50	$y = -9692x + 4.9421$	$y = 1.492x + 4.2597$	$y = 8E-06x + 9E-05$	$y = 3.2523x + 6.4065$
60	$y = -1024x + 6.7337$	$y = 1.459x + 3.4724$	$y = 7E-06x + 8E-05$	$y = 3.2589x + 6.0317$
70	$y = -8696x + 12.554$	$y = 1.330x + 1.1793$	$y = 5E-06x + 6E-05$	$y = 5.1978x + 6.0249$

A careful look at the coefficient of determination recorded on Table II shows that the Freundlich isotherm exhibited the highest  $R^2$  values, indicating that the model gave the best fit to the equilibrium data obtained and described the adsorption process better than the other isotherms. The Langmuir model assumes a monolayer adsorption of metals onto homogeneous adsorbent surface with no interactions between the adsorbed molecules, while the Freundlich model is an empirical equation commonly used for multilayer adsorption onto heterogeneous surfaces [13] [29]. This implies that the adsorbent surface is heterogeneous and sorption occurs through a multilayer of adsorbent. Thus, the Freundlich isotherm was employed in the determination of the best-fit isotherm model parameters which are displayed in Table IV.

Table IV: Freundlich Isotherm Constants and  $\Delta G$  Values

Temp (°C)	n	1/n	$K_F$ (mol/g)	$\Delta G$ (kJ/mol)
28	0.491	2.037	685566.0	-33.629
40	0.521	1.919	34303.41	-27.176
50	0.574	1.742	2369.656	-20.867
60	0.603	1.658	502.2008	-17.218
70	0.732	1.366	6.648558	-5.402

The Freundlich parameter,  $n$  is a measure of surface heterogeneity of the adsorbent and the value of  $1/n$  ranges between 0 and 1. A  $1/n$  value closer to zero implies a more heterogenous adsorbent surface. When the value of  $1/n$  is below unity, a chemisorption process is implied and cooperative sorption is indicated when  $1/n$  is above one [30]. The values of  $1/n$  obtained are above one at all temperatures investigated (Table 3), we therefore, conclude that cooperative sorption process is at play in the removal of Pb (II) ions using SROSE. Consequently,  $\ln K_F$  was plotted against  $1/T$  (Fig.8) and the thermodynamic parameters  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  were determined from the slope and intercept using equations 11, 12 and 13 [31].

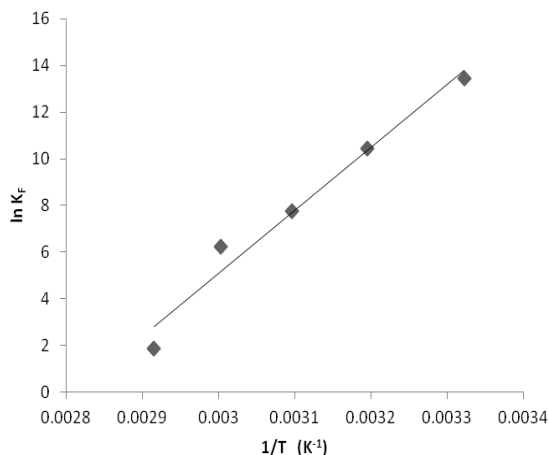


Fig. 11: Plot of  $\ln K_F$  against  $1/T$

$$\ln K_F = \Delta S/R - \Delta H/RT \quad (11)$$

$$\Delta G = -RT \ln K_F \quad (12)$$

$$\Delta G = \Delta H - T\Delta S \quad (13)$$

The  $\Delta G$  values calculated at the different temperatures are presented in Table 3. The negative values of  $\Delta G$  indicate that the metal removal process is spontaneous and feasible at the temperatures investigated. The  $\Delta S$  value determined from the slope of the graph is  $-630.384 \text{ JK}^{-1}\text{mol}^{-1}$ , while the  $\Delta H$  value is  $-224.220 \text{ kJ/mol}$ . The degree of randomness at the interface between the adsorbent and the solution during the adsorption of Pb (II) ions on the modified extract was reduced; hence the negative  $\Delta S$  value obtained. The negative  $\Delta H$  value is an indication that the adsorption process is exothermic and therefore the adsorption process is better performed at low temperatures.

#### D. Sorption Mechanism

The likely adsorption mechanism at work in the removal of Pb (II) ions from the aqueous solution was simulated by fitting the experimental data into the Dubinin-Radushkevich (DR) isotherm at different temperatures. The linearized form of this model is presented in equation 14.

$$\ln q_e = \ln q_D - B_D \epsilon^2 \quad (14)$$

$q_D$  = maximum ion exchange capacity

$B_D$  = DR model constant

$\epsilon$  = Polanyi potential which is represented by the equation given below.

$$\epsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (15)$$

$B_D$  is related to the mean free energy of sorption per mole of metal ion ( $E$ ), through equation 13:

$$E = \frac{1}{\sqrt{2B_D}} \quad (16)$$

A linear graph was obtained from the plot of  $\ln q_e$  against  $\epsilon^2$ . The values of  $B_D$  and  $q_D$  were deduced from the slope and intercept of the plots and  $E$  was calculated by substituting the values of  $B_D$  into equation 13. These values are presented in Table V.

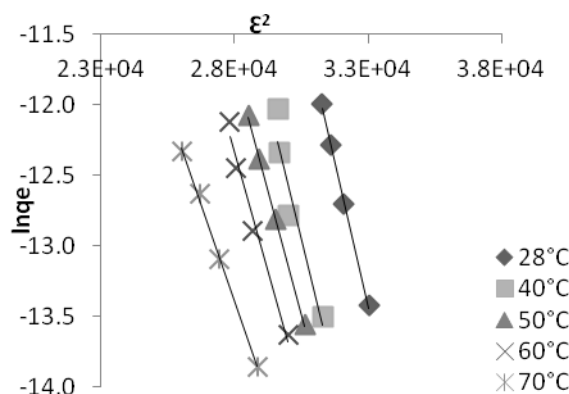


Fig. 12: Plot of  $\ln q_e$  against  $\epsilon^2$

It is observed that increase in temperature brings about a decrease in the values of  $B_D$  and  $q_D$ . Therefore, the maximum ion exchange capacity of the SROSE reduces as the temperature increases, supporting the negative  $\Delta H$  values obtained for the process.

Table VI: DR Parameters for the Removal of Pb (II) Ions

Temp (°C)	Linear equation	$B_D$ ( $\text{mol}^2/\text{J}^2$ )	$q_D$ (mol/g)	$E$ (kJ/mol)
28	$y = -8.14E-04x + 13.438$	$-8.14E-04$	685565.963	24.784
40	$y = -7.67E-04x + 10.443$	$-7.67E-04$	34303.409	25.532
50	$y = -6.96E-04x + 7.7706$	$-6.96E-04$	2369.893	26.803
60	$y = -6.63E-04x + 6.2192$	$-6.63E-04$	502.301	27.462
70	$y = -5.46E-04x + 1.8947$	$-5.46E-04$	6.6515	30.261

Information on the mechanism of sorption involved in the metal removal process is obtained from the value of  $E$ . An  $E$  value less than 8 kJ/mol implies physisorption as the major sorption mechanism, a value between 8 and 16 kJ/mol implies sorption mechanism involving ion exchange. If the value of  $E$  is above 16 kJ/mol, the major sorption mechanism is particle diffusion [24], [30]. The values of  $E$  obtained in this work are between 24.784 and 30.261 kJ/mol, indicating that within the temperature range studied, the main sorption mechanism is particle diffusion.

#### IV. CONCLUSION

This work has investigated the Pb (II) ions removal efficiency of succinic acid modified red onion skin extract. The result obtained showed that the initial concentration of the metal ions in solution, the contact time and pH of synthetic waste water affected the metal percentage of Pb (II) ions removed by SROSE. The adsorption kinetics was best described by the pseudo-second order kinetic model. Simulation of the adsorption isotherm using different isotherm models indicated that Freundlich isotherm gave the best fit for experimental data as deduced from the values of the regression factor. Results also showed that the adsorption process is exothermic following the negative  $\Delta H$  values obtained, and spontaneous with negative  $\Delta G$  values at all the temperatures investigated. There was decreased randomness at the solid-solution interface during the process as indicated by the negative  $\Delta S$  value. The result obtained from fitting the experimental data into the Dubinin-Raduskevich isotherm showed that the maximum ion exchange capacity of the SROSE reduced as the temperature increases; moreover, the major sorption mechanism for the sorption process was found to be particle diffusion controlled.

#### ACKNOWLEDGMENT

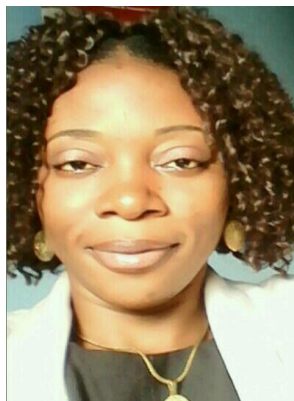
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