



## Thermodynamic feasibility of Mn (II), Fe (II) and Pb (II) ions exchange in aqueous medium by red onion (*Allium Cepa*) skin extract resin

M. U. Ibezim-Ezeani\* and O. Akaranta

Department of Pure and Industrial Chemistry, University of Port Harcourt, P.M.B. 5323, Choba, Port Harcourt, Nigeria.

**Abstract :** Feasibility studies on the thermodynamics of  $Mn^{2+}$ ,  $Fe^{2+}$  and  $Pb^{2+}$  ions exchange in aqueous medium by carboxylated-epichlorohydrin red onion skin extract resin (CERR) was undertaken. The acetone extract of red onion skin was used in the synthesis of CERR. Maximum ion exchange capacities of  $3.050 \times 10^{-5}$ ,  $2.804 \times 10^{-5}$  and  $6.404 \times 10^{-6}$  mol/g for  $Mn^{2+}$ ,  $Fe^{2+}$  and  $Pb^{2+}$  ions respectively were obtained with 0.04g/L metal ions concentration at 29°C. The trend ( $Mn^{2+} > Fe^{2+} > Pb^{2+}$ ) of the ion exchange capacity of CERR for the metal ions is in conformity with that of their ionic radii. The experimental exchange capacity of the ions was analyzed with Langmuir, Freundlich and Temkin isotherm models at different temperatures and concentrations. The regression analysis of the models was found to closely fit the experimental data in the order: Freundlich > Langmuir > Temkin. An assessment of the thermodynamics of the exchange reaction revealed values for the change in enthalpy,  $\Delta H$ , Gibbs free energy,  $\Delta G$ , and entropy,  $\Delta S$ ; which reflected the process spontaneity, exothermic nature and feasible affinity of the interacting metal ions at the exchange sites.

**Keywords :** Thermodynamics, Red onion skin, Ion exchange capacity, Metal ions, Resin, Isotherm models.

### Introduction

The percentage purity of water is related to its beneficial use and scope of application; and in turn, contributes positively or negatively to the quality of lives (animal and plant), goods, processes, products, services and ecosystem. The pollution of water and the environment by effluents laden with heavy metals is worrisome since they are biologically indestructible; and persist in the aquatic and terrestrial environments, which overtime accumulate to varied levels of toxicity in flora and fauna systems<sup>1-6</sup>. Thus, the sustenance of healthy living in a standard environment inevitably entails the proper treatment of effluents to acceptable limits, as a major precautionary measure before their discharge into waterways. The involvement of ion exchange mechanism in the removal and management of toxic ions from aqueous solutions has been demonstrated in some advances in separation science and technology<sup>7-10</sup>. The choice of exchangers for ion exchange technique in the area of cations and anions removal from solutions are made based on their biodegradability, applicability, reusability, affordability, insolubility, selectivity, manageability, stability, availability, eco-compatibility and regenerability<sup>11-14</sup>.

Isothermal studies on the thermodynamic feasibility of  $Mn^{2+}$ ,  $Fe^{2+}$  and  $Pb^{2+}$  ions exchange in aqueous medium by chemically modified red onion skin extract resin is presented in this paper. Indications from some research on agro materials have noted the use of onion skin aqueous extract as natural colorant for dyeing<sup>15-16</sup>,

acetone extract as antioxidants for the oxidative stability of vegetable oil<sup>17</sup>, acetone extract as corrosion inhibitor<sup>18-19</sup> and ethanol extract as acid-base indicator<sup>20</sup>. These authors hinted that the polyhydroxyphenolic composition of onion skin extract is utilized in bonding with compounds of choice to form moieties, which have improved exchange characteristics and functions.

Thermodynamics of ion exchange process provides insight into the characteristic equilibrium distribution of exchanging ions and any attendant effect on the surface properties of the exchanger, as well as the energy transformations associated with the system at a given condition. This information is valuable in:

1. Resolving the most favorable condition for a given exchange application
2. Evaluating the practicability of the process design with mathematical representation and analysis of the quantitative values of the exchanging and exchangeable ions
3. Elucidating the underlying principles of the process through critical examination of the energy transformation variables
4. Determining suitable amounts and ratios of exchanging species with exchanger in order to secure maximum operational efficiency
5. Adjusting the actual proportions of the constituents that produced the optimum result to required scale as represented on a model for specific application
6. The detection and elimination of any fault in the system during regeneration and maintenance operations.

The focus of this research therefore, is to identify conditions which are conducive to producing best possible results in the elimination of metal ions from aqueous solution with the formulated resin and the technical transfer of the process design to allied industries.

## Materials and methods

### Sample Collection and Preparation:

This study was carried out with red onion bulbs purchased from the fruit garden market in Port Harcourt, Nigeria. The papery outermost skin was carefully stripped, washed with deionised water and air dried for 3 days. Electric milling machine was used in grinding the dried red onion skin, sieved to 150  $\mu\text{m}$  particle size and preserved in tightly capped plastic bottle at 29 °C.

### Extraction Procedure:

Soxhlet extractor was used for the extraction of 2940 g of red onion skin (150  $\mu\text{m}$  size) with acetone as the extractant. The extracted sample was recovered by expelling acetone from the acetone-extract mixture using rotor evaporator.

### Synthesis of Carboxylated-Epichlorohydrin Red Onion Skin Extract Resin (CERR):

Epichlorohydrin (10 ml) was poured into a beaker containing 17.3 g of 4-hydroxy-benzoic acid (dissolved in 70 ml acetone) and stirred vigorously. 38 g sample of the extract (dispersed in 180 ml of acetone) was added to the mixture and the beaker with its content placed on a heating mantle. The beaker was gently heated at 60 °C, with the content constantly stirred until the mixture turned into a brown coloured slurry in about 3 hours. This slurry solidified after 15 minutes and was allowed to stand for 20 hours before use. The mass of the resin was then crushed, sieved with British standard sieve plates to obtain different particle sizes and preserved in corked bottles at ambient atmospheric condition.

### Preparation of standard solutions:

The metal ion stock solutions (1000 mg/l) were each prepared in 1litre volumetric flask by dissolving 3.0785 g of  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ , 4.973 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and 1.59 g of  $\text{Pb}(\text{NO}_3)_2$  in distilled deionised water. Working standard solutions of 50 mg/l  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Pb}^{2+}$  ions were obtained by dilution of the respective stock solutions. All the reagents used were of analytical grade.

### Ion exchange capacity studies:

The batch experiments were performed by shaking the tightly corked conical flask containing 1g of CERR with 50 cm<sup>3</sup> of metal ion solution (10 to 70 mg/l) at 120 oscillations / min. After the shaking period of 1hour at 29 °C, the mixture was centrifuged and filtered through glass wool. The quantity of metal ion in the liquid phase was determined by analysing the clear filtrate using the Atomic Absorption Spectrophotometer (Perkin Elmer, Analyst 200). Evaluation of ion exchange capacity ( $q_e$ ) of CERR was done by the mass balance from initial to equilibrium compositions of metal ions in the liquid phase using the relationship in equation (1) and the values plotted against those of initial metal ion concentration<sup>21-22</sup>.

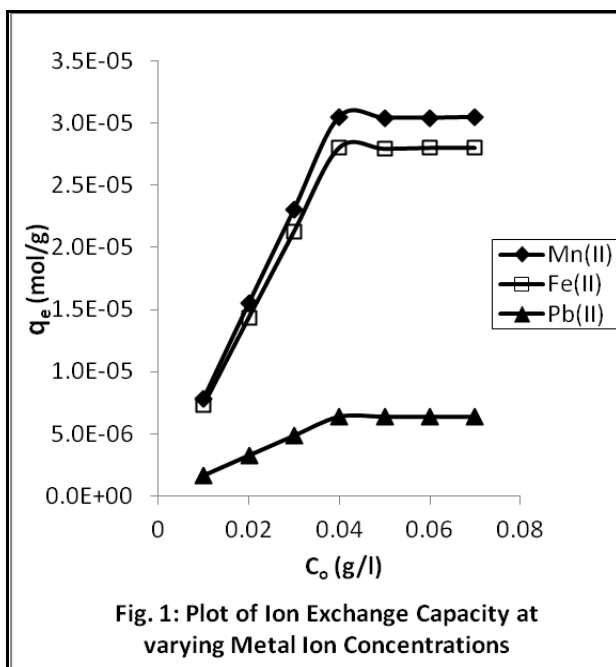
$$q_e = \frac{V}{m} (C_o - C_e) \quad (1)$$

where  $C_o$  is the initial metal ion concentration in solution (mg/l) and  $C_e$  is the metal ion concentration in solution (mg/l) at equilibrium,  $V$  is volume of initial metal ion solution used (l), and  $m$  is mass of CERR (g).

## Results and discussion

### Ion exchange capacity studies:

In the uptake of metal ions by ion exchanger, the mobility of metal ions to the active sites is controlled by the gradient in chemical potential of the system which eventually proceeds to an equilibrium state. These metal ions move randomly from the region of high concentration to that of zero metal ions (exchanger) where they displace equivalent amount of like charged ions. The dependence of the amount of metal ion exchanged at equilibrium with that in solution at the initial metal ion concentrations (0.01 to 0.07 g/l) for 1g CERR is presented in Figure 1.



At low metal ion concentration, the ion exchange capacity gains the advantage of surplus binding sites on CERR to metal ion ratio, thus enhancing a very high degree of exchange of the few metal ions present. As the concentration of metal ion is increased (from 0.01 to 0.03 g/l) and with the maintained number of specific positions of contact on the CERR, the exchange capacity increased from  $7.804 \times 10^{-6}$  to  $2.303 \times 10^{-5}$  mol/g for Mn(II),  $7.264 \times 10^{-6}$  to  $2.1261 \times 10^{-5}$  mol/g for Fe(II) and  $1.632 \times 10^{-6}$  to  $4.858 \times 10^{-6}$  mol/g for Pb(II); reaching a maximum at 0.04 g/l concentration of metal ions which is apparently the amount commensurate with that of the exchangeable hydrogen ions, signifying the attainment of equilibrium concentration. Beyond this level, an increase in concentration did not lead to a corresponding increase in the ion exchange capacity since the limited

exchange sites are occupied while leaving the excess metal ions in the system without being exchanged, confirming the attainment of equilibrium concentration. In all the experiments, there was high percentage metal uptake indicating that the metal ions which are of higher valence preferentially displaced the exchangeable hydrogen ( $H^+$ ) ions which are of lower valence. For the metal ions, the extent of exchange reaction is in the order:  $Mn^{2+} > Fe^{2+} > Pb^{2+}$ , which is similar to the order of their ionic radii (0.67, 0.78 and 1.21 Å for  $Mn^{2+}$ ,  $Fe^{2+}$  and  $Pb^{2+}$  ions respectively)<sup>23</sup>. This relationship suggests that smaller ionic radii could facilitate the metal ion uptake by the CERR. Previous research on the removal of heavy metals remarked that Pb(II) and Cd(II) having larger radii showed lower adsorption than Cu(II) and Zn(II) which have smaller ionic radii. Thus, the smaller the ionic radius, the easier it is for a metal ion to penetrate through the boundary layer and adsorb onto the multi-walled carbon nanotubes surface<sup>24</sup>.

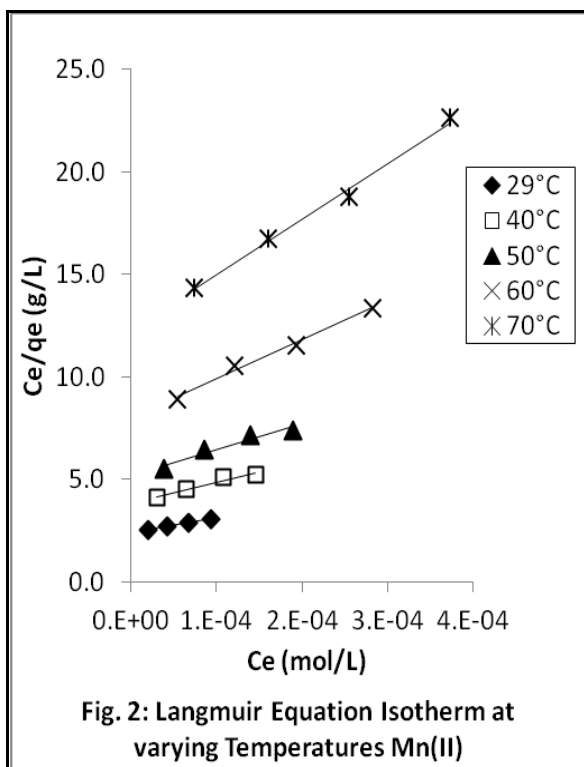
### Isotherm studies:

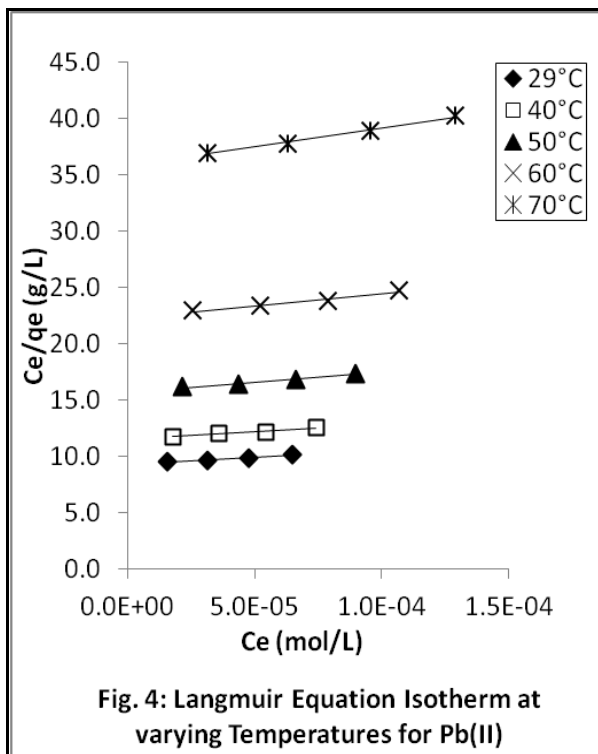
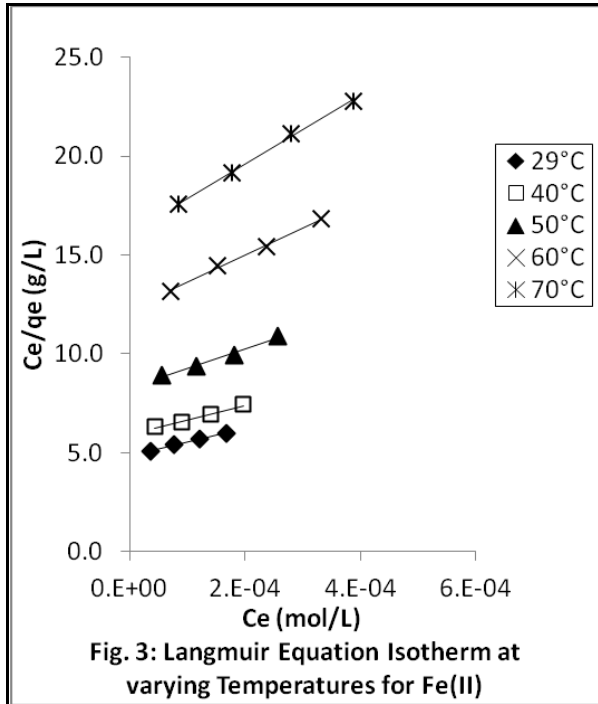
The potentiality of an ion exchanger in a given process is closely related to the properties of the surface and its readiness to chemically attract and intermingle with the exchanging ions in solution. Hence, the isotherm that best suited the ion exchange process was explored by applying the equilibrium data obtained at temperatures of 29, 40, 50, 60 and 70 °C to the Langmuir, Freundlich and Temkin models<sup>25-30</sup>.

The Langmuir equation assumes that the solid surface presents a finite number of identical sites which are energetically uniform and a monolayer is formed when the solid surface reaches saturation<sup>31</sup>. The linearized form of Langmuir equation<sup>32-33</sup> is:

$$\frac{C_e}{q_e} = \frac{1}{X_m b} + \frac{C_e}{X_m} \quad (2)$$

where  $X_m$  (mol/g) and  $b$  (l/mol) are the Langmuir constants, representing the maximum sorption capacity of the solid phase loading and the energy constant related to the heat of sorption, respectively. The plots of  $C_e/q_e$  against  $C_e$  are presented in Figures 2, 3, and 4 for  $Mn^{2+}$ ,  $Fe^{2+}$  and  $Pb^{2+}$  ions respectively.

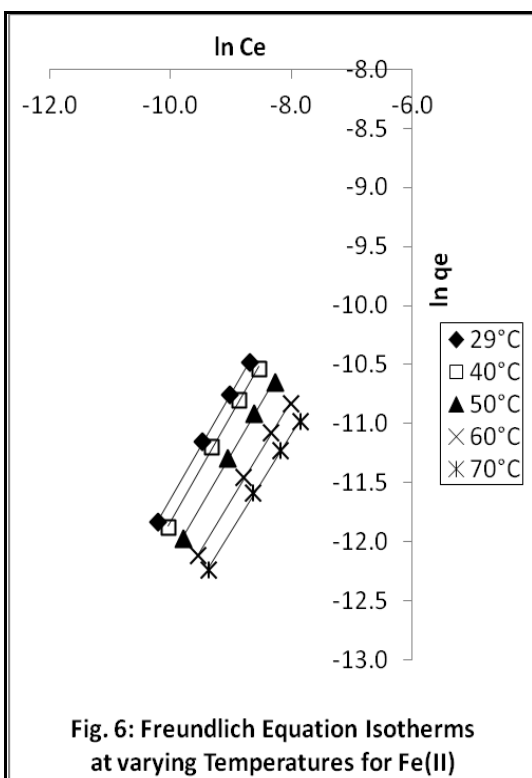
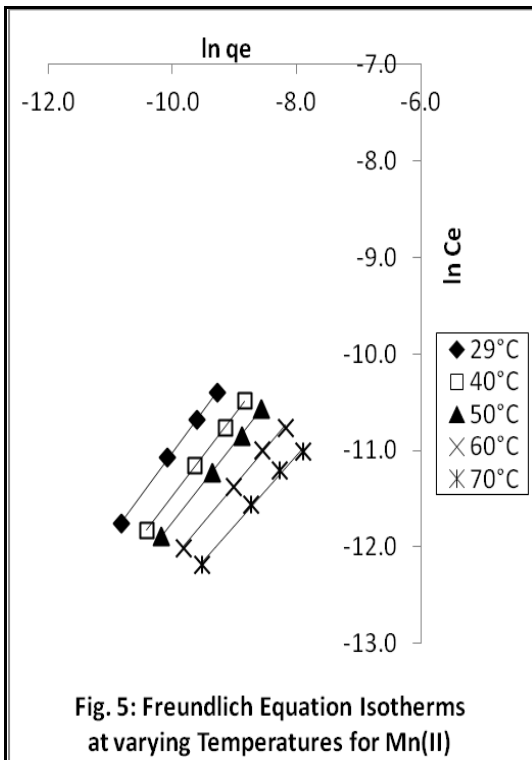


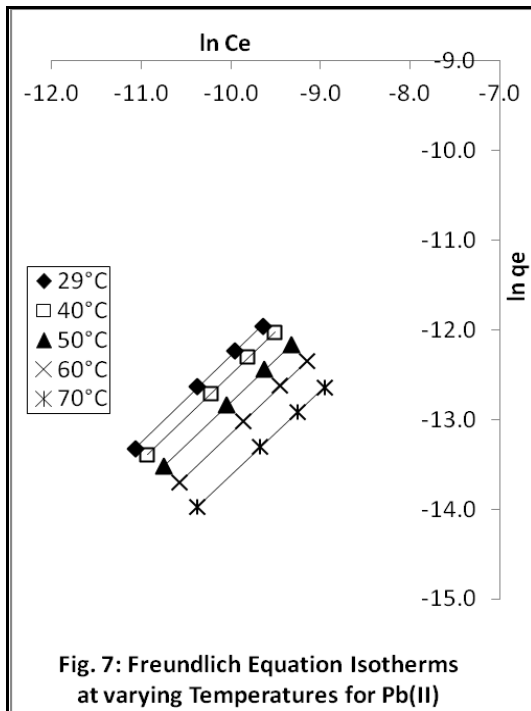


The Freundlich expression is an empirical equation based on sorption on a heterogeneous surface suggesting that binding sites are not equivalent<sup>31</sup>. The linearized form of Freundlich equation<sup>34-35</sup> is:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{3}$$

where 1/n (ranges between 0 and 1) is a measure of the surface heterogeneity, which may become more heterogeneous when 1/n gets close to zero.  $K_f$  (mol/g) is the Freundlich constant related to the bond strength and  $n$  indicates the bond energies between metal ion and the sorbent. The plots of  $\ln C_e$  against  $\ln q_e$  are presented in Figures 5, 6, and 7 for  $Mn^{2+}$ ,  $Fe^{2+}$  and  $Pb^{2+}$  ions respectively.

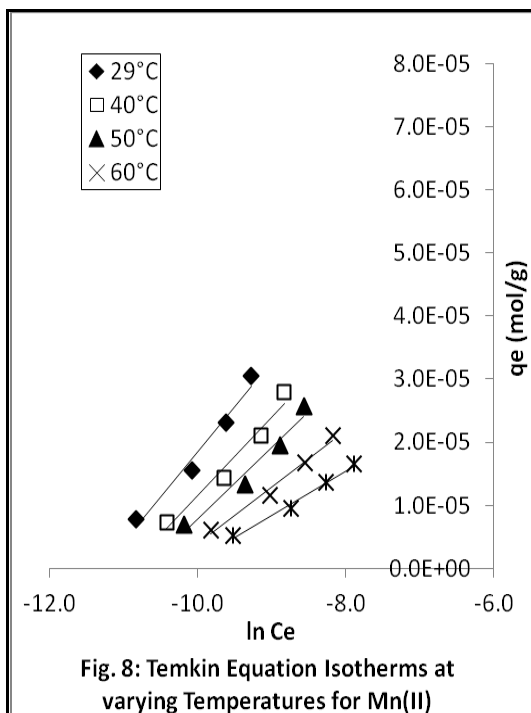




The Temkin isotherm assumes that decrease in the heat of sorption is linear and the sorption is characterized by a uniform distribution of binding energies<sup>36</sup>. The linearized form of Temkin equation<sup>37</sup> is:

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \tag{4}$$

where  $1/b_T$  (mol/J) is the sorption potential of the sorbent,  $K_T$  (mol/g) is the equilibrium binding constant,  $b_T$  (J/mol) is the Temkin constant related to the heat of sorption,  $R$  is the gas constant ( $8.314 \text{ JK}^{-1}\text{mol}^{-1}$ ) and  $T$  is the temperature in kelvin. The plots of  $q_e$  against  $\ln C_e$  are presented in Figures 8, 9, and 10 for  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Pb}^{2+}$  ions respectively.



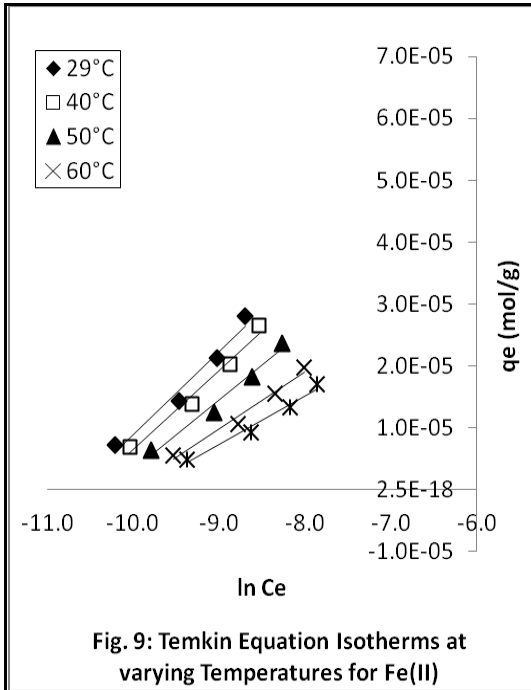


Fig. 9: Temkin Equation Isotherms at varying Temperatures for Fe(II)

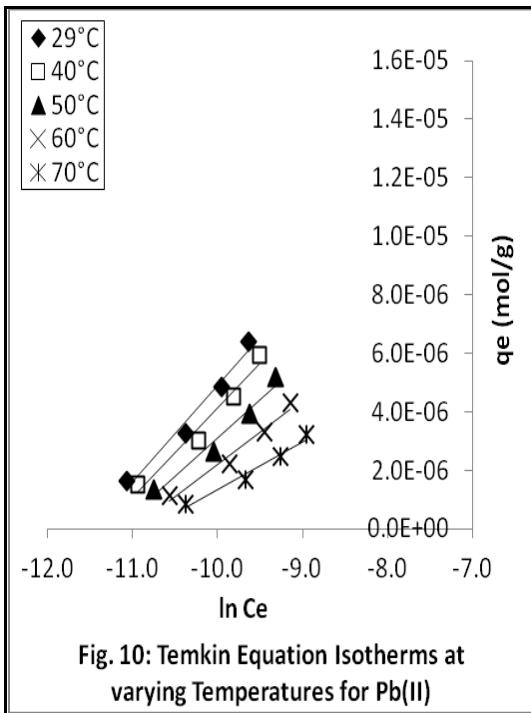


Fig. 10: Temkin Equation Isotherms at varying Temperatures for Pb(II)

The isothermal plots obtained at different temperatures and concentrations are linear, testifying to the applicability of Langmuir, Freundlich and Temkin models to the experimental data. The values of the slopes and intercepts of the plots were utilized in evaluating the Langmuir, Freundlich and Temkin constants. The correlation coefficients<sup>38-39</sup> and isotherm constants are presented in Tables 1 and 2 respectively.



**Table 1: Comparison of Coefficient of Determination (R<sup>2</sup>) Values and Linear Equations for the Isotherms**

Metal Ion	Temp (°C)	Langmuir		Freundlich		Temkin	
		R <sup>2</sup>	Linear Equation	R <sup>2</sup>	Linear Equation	R <sup>2</sup>	Linear Equation
Mn(II)	29	0.9953	y = 7198x + 2.410	0.9997	y = 0.879x - 2.234	0.9688	y = 1.43E-05x + 1.61E-04
	40	0.9464	y = 10226x + 3.851	0.9990	y = 0.837x - 3.096	0.9635	y = 1.25E-05x + 1.37E-04
	50	0.9374	y = 12463x + 5.205	0.9997	y = 0.811x - 3.624	0.9591	y = 1.13E-05x + 1.21E-04
	60	0.9925	y = 19025x + 7.999	0.9977	y = 0.764x - 4.494	0.9810	y = 9.06E-06x + 9.44E-05
	70	0.9931	y = 27225x + 12.23	0.9935	y = 0.731x - 5.197	0.9908	y = 7.03E-06x + 7.17E-05
Fe(II)	29	0.9931	y = 6906x + 4.834	0.9998	y = 0.892x - 2.711	0.9677	y = 1.34E-05x + 1.43E-04
	40	0.9901	y = 7848x + 5.942	0.9987	y = 0.895x - 2.875	0.9755	y = 1.28E-05x + 1.35E-04
	50	0.9872	y = 9901x + 8.263	0.9980	y = 0.873x - 3.406	0.9793	y = 1.12E-05x + 1.15E-04
	60	0.9953	y = 13798x + 12.22	0.9991	y = 0.844x - 4.047	0.9760	y = 9.22E-06x + 9.28E-05
	70	0.9984	y = 17407x + 16.11	0.9988	y = 0.830x - 4.444	0.9789	y = 7.88E-06x + 7.81E-05
Pb(II)	29	0.9008	y = 11901x + 9.306	0.9995	y = 0.962x - 2.669	0.9702	y = 3.28E-06x + 3.77E-05
	40	0.9693	y = 12981x + 11.50	0.9998	y = 0.959x - 2.904	0.9665	y = 3.03E-06x + 3.44E-05
	50	0.9829	y = 17556x + 15.70	0.9997	y = 0.952x - 3.285	0.9689	y = 2.63E-06x + 2.94E-05
	60	0.9635	y = 21853x + 22.27	0.9996	y = 0.950x - 3.648	0.9700	y = 2.20E-06x + 2.42E-05
	70	0.9915	y = 33379x + 35.78	0.9997	y = 0.942x - 4.195	0.9704	y = 1.63E-06x + 1.77E-05

**Table 2: Isotherm Constants and ΔG Values at Different Temperatures**

Metal Ion	Temp. (°C)	Langmuir constants			Freundlich constants		Temkin constants	
		- ΔG (kJ / mol)	b (l/mol)	X <sub>m</sub> (mol/g)	n	K <sub>f</sub> (mol/g)	b <sub>T</sub> (J/mol)	K <sub>T</sub> (mol/g)
Mn(II)	29	20091.5	2986.725	1.389E-04	1.138	1.070E-01	1.7571E+08	80387.3
	40	20516.9	2654.947	9.779E-05	1.194	4.521E-02	2.0768E+08	54710.8
	50	20894.6	2394.078	8.024E-05	1.232	2.667E-02	2.3828E+08	44399.2
	60	21523.3	2378.391	5.256E-05	1.309	1.118E-02	3.0568E+08	33545.9
	70	21979.3	2224.853	3.673E-05	1.368	5.533E-03	4.0559E+08	26879.5
Fe(II)	29	18240.0	1428.716	1.448E-04	1.120	6.644E-02	1.8738E+08	43115.7
	40	18528.5	1236.553	1.361E-04	1.117	5.639E-02	2.0330E+08	36600.3
	50	19035.7	1198.166	1.010E-04	1.145	3.315E-02	2.3934E+08	29296.0
	60	19459.0	1128.384	7.247E-05	1.184	1.747E-02	3.0021E+08	23329.4
	70	19919.1	1080.286	5.745E-05	1.205	1.174E-02	3.6198E+08	20333.6
Pb(II)	29	17961.6	1278.790	8.403E-05	1.040	6.927E-02	7.6526E+08	97475.0
	40	18289.8	1128.208	7.704E-05	1.042	5.477E-02	8.5771E+08	85361.2
	50	18849.8	1118.015	5.696E-05	1.050	3.741E-02	1.0195E+09	71190.9
	60	19071.1	980.8833	4.576E-05	1.052	2.603E-02	1.2573E+09	60092.1
	70	19500.4	932.7579	2.996E-05	1.061	1.507E-02	1.7474E+09	50065.0

At the various temperatures and concentrations studied, the regression correlation coefficients are relatively high and in the order: Freundlich > Langmuir > Temkin, indicating that Freundlich model best described the ion exchange process. In reference to Freundlich assumption, the findings seem to imply that the surface of CERR is heterogenic, which is apparently due to uneven spatial positioning of active sites in the system. The tabulated results showed that the magnitude of K<sub>f</sub> decreased with increase in temperature from 29 to 70 °C, indicating the enhancement of ion exchange capacity at lower temperature of 29 °C. In the whole analysis, the values of n are in the range of 1.138 to 1.061, and increased with temperature. If n < 1, bond energies increase with the surface density; if n > 1, bond energies decrease with the surface density; and when n = 1, all surface sites are equivalent<sup>40</sup>. The deduced values of n indicate that the bond energies decreased with surface density, which becomes more pronounced as temperature is increased from 29 to 70 °C. The study on

Cadmium biosorption using green coconut shell powder, revealed values of  $n$  greater than unity, indicating favorable sorption at the temperature studied<sup>41</sup>.

The values of  $X_m$  and  $b$  at temperatures of 29 to 70 °C reflected the sequence:  $Mn^{2+} > Fe^{2+} > Pb^{2+}$ , which is in agreement with that of the ionic radii of the metal ions. The Langmuir constants,  $b$  with the regression coefficient values near 1.0 is an evidence of strong affinity of  $Mn^{2+}$ ,  $Fe^{2+}$  and  $Pb^{2+}$  ions to the binding sites of CERR.

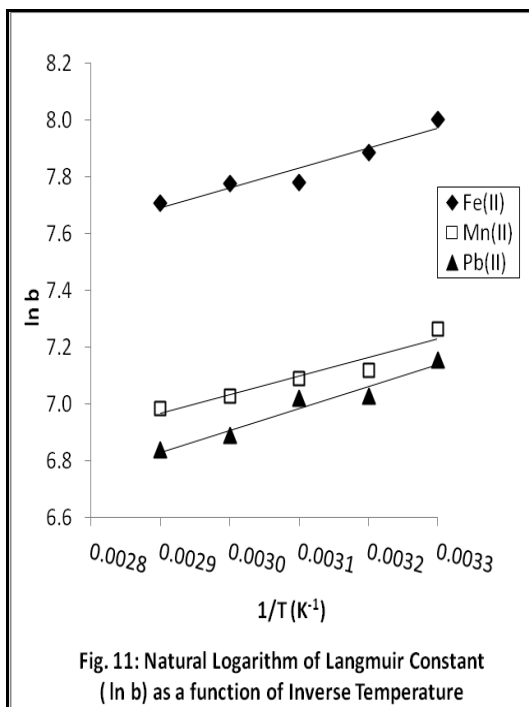
The listed values of  $K_T$  and  $b_T$  varied with increase in temperature from 29 to 70 °C, indicating that the ion exchange potential of CERR is dependent on the temperature of the investigated system.

The magnitude of the change in the Gibbs free energy,  $\Delta G^\circ$ , enthalpy,  $\Delta H^\circ$  and entropy,  $\Delta S^\circ$  of the process proffers a description of the behavior of exchanging and exchangeable species during the operation of the system. The deduction of these thermodynamic parameters was based on the variation of the Langmuir constant,  $b$  with change in the temperature range of 29 to 70°C using equations 5<sup>42-43</sup> and 6<sup>44</sup>:

$$\Delta G^\circ = -RT \ln b \quad (5)$$

$$\ln b = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6)$$

The calculated values of  $\Delta G^\circ$  are listed in Table 2. These values are negative and decreased with increase in temperature from 29 to 70°C. The negative values of  $\Delta G^\circ$  indicate the spontaneity of the process within the investigated temperatures for the metal ions. The linearized plots of  $\ln b$  as a function of  $1/T$  are presented in Fig. 11.



The evaluations of  $\Delta H^\circ$  and  $\Delta S^\circ$  were conducted through the substitution of the values of slope and intercept of the plots into  $-\Delta H^\circ/R$  and  $\Delta S^\circ/R$  respectively. The values of  $\Delta H^\circ$  are -5.811, -5.409 and -6.410 kJ/mol for  $Mn^{2+}$ ,  $Fe^{2+}$  and  $Pb^{2+}$  respectively (Table 3). These values signify that the exchange reaction with CERR is exothermic. An exothermic reaction occurs when the initial energy of the reactant species is greater than that of the product species, while an endothermic reaction occurs when the initial energy of the reactant species is lesser than that of the product species<sup>45</sup>. The  $\Delta S^\circ$  values are 47.081, 42.238 and 38.208 J/K/mol for  $Mn^{2+}$ ,  $Fe^{2+}$  and  $Pb^{2+}$  respectively (Table 3). These positive values could imply some degree of structural rearrangement of the CERR molecule, which led to increased level of disorderliness at the resin-aqueous solution interface during the exchange process. In the adsorption of Cu(II), Ni(II) and Cr(VI) by modified oak sawdust, the negative values of  $\Delta G^\circ$  showed that the adsorption process is spontaneous and that the degree of

spontaneity of the reaction increases with increasing temperature. The process was endothermic with values of  $\Delta H^\circ$  as 4.33, 0.88 and 0.91 kJ/mol for Cu(II), Ni(II) and Cr(VI) respectively. The  $\Delta S^\circ$  values were positive as a result of redistribution of energy between the adsorbate and adsorbent. Before adsorption occurs, the heavy metal ions near the surface of the adsorbent will be more ordered than in the subsequent adsorbed state and the ratio of free heavy metal ions to ions interacting with the adsorbent will be higher than in the adsorbed state. As a result, the distribution of rotational and translational energy among a small number of molecules will increase with increasing adsorption by producing a positive value of  $\Delta S$  and randomness will increase at the solid – solution interface during the process of adsorption<sup>46</sup>.

**Table 3: Thermodynamic parameters for the exchange process with CERR**

Thermodynamic parameters	Mn(II)	Fe(II)	Pb(II)
Linear equation	$y = 698.9x + 5.662$	$y = 650.6x + 5.080$	$y = 770.9x + 4.595$
$\Delta H$ (kJ/mol)	-5.811	-5.409	-6.410
$\Delta S$ (J/K/mol)	47.081	42.238	38.208

## Conclusions

The CERR exhibited the ability for  $Mn^{2+}$ ,  $Fe^{2+}$  and  $Pb^{2+}$  ions uptake, with the rate increasing with increase in concentration, and attaining equilibrium at 0.04g/l of metal ion solution. Maximum ion exchange capacities of  $3.050 \times 10^{-5}$ ,  $2.804 \times 10^{-5}$  and  $6.404 \times 10^{-6}$  mol/g for  $Mn^{2+}$ ,  $Fe^{2+}$  and  $Pb^{2+}$  ions respectively were obtained with 0.04g/l metal ions concentration at 29°C. Isothermal studies involving the various exchange capacities for the metal ions at temperatures of 29 to 70°C were conducted with Langmuir, Freundlich and Temkin models. The linear plots of Freundlich model exhibited the highest correlation coefficient and best described the process. The computed values of the change in enthalpy,  $\Delta H$ , Gibbs free energy,  $\Delta G$ , and entropy,  $\Delta S$  showed that the exchange process was spontaneous, feasible, exothermic and favored interaction of metal ions at the exchange sites.

## Acknowledgement

The authors sincerely thank Prof. Leo Osuji (Head of Department of Pure and Industrial Chemistry, University of Port Harcourt, Nigeria) for supporting this research work with laboratory facilities. We also appreciate Mr. Nwagbo Okike, Ms. Yewande Johnson and other laboratory technologists for their assistance.

## References

- Holub, M., Balintova, M., Pavlikova, P. and Palascakova, L., Study of sorption properties of zeolite in acidic conditions in dependence on particle size, Chemical Engineering Transaction, 2013, 32, 559-564.
- Demim, S., Drouiche, N., Aouabed, A., Benayad, T., Couderchet, M. and Semsari, S., Study of heavy metal removal from heavy metal mixture using the CCD method, Journal of Industrial and Engineering Chemistry, 2014, 20, 512-520.
- Singha, A.S. and Guleria, A., Chemical modification of Cellulosic Biopolymer and its use in removal of heavy metal from wastewater, International Journal of Biological Macromolecules, 2014, 67, 409-417.
- Lakshmiopathy, R., Sarada N. C. and Jayaprakash N., Agricultural wastes as low cost adsorbents for sequestration of heavy metal ions and synthetic dyes from aqueous solution: A mini review, International Journal of ChemTech Research, 2015, 8(5): 25-31.
- Sangeetha, K., Vasugi, G. and Girija, E. K., Removal of lead ions from aqueous solution by novel hydroxyapatite/alginate/gelatin composites, International Journal of ChemTech Research, 2015, 8(5): 117-125.
- Ranjitha, J., Raj, A., Kashyap, R., Vijayalakshmi, S. and Donatus, M., Removal of heavy metals from industrial effluent using salvinia molesta, International Journal of ChemTech Research, 2016, 9(5): 608-613.

7. Figueiredo, H. and Quintelas, C., Tailored zeolites for the removal of metal oxyanions: Overcoming intrinsic limitation of zeolites, *Journal of hazardous materials*, 2014, 274, 287-299.
8. Sakizci, M. and Tanriverdi, L. Ö., Influence of acid and heavy metal cation exchange treatments on methane adsorption properties of mordenite, *Turkish Journal of Chemistry*, 2015, 39, 970-983.
9. Vinisha, V. P. and Janardanan, C., Ion exchange, adsorption and antimicrobial properties of tin(IV) molybdovanadosulphosalicylate composite material and its application in environmental remediation, *International Journal of ChemTech Research*, 2015, 8(9): 424-432.
10. Dzyazko Y.S., Volkovich Y.M., Ponomaryova L.N., Sosenkin, V.E., Trachevskii V.V., and Belyakov V.N., Composite Ion-exchangers based on flexible resin containing Zirconium Hydro-phosphate for electro-membrane separation, *Journal of Nanoscience and Technology*, 2016, 2(1): 43-49.
11. Alexandratos, S. A., Ion-exchange resins: A retrospective from industrial and engineering chemistry research, *Industrial and Engineering Research*, 2009, 48, 388-398.
12. Fu, F. and Wang, Q., Removal of heavy metal from wastewaters: A review, *Journal of Environmental Management*, 2011, 92, 407-418.
13. Siji, S. and Janardanan, C., Synthesis and characterization of Bismuth Based Novel Inorganic Ion-exchange materials and their analytical applications. *IOSR Journal of Applied Chemistry*, 2014, 7(1): 77-84.
14. Esmaeili, H. and Foroutan R., Investigation into Ion-exchange and adsorption methods for removing heavy metal from aqueous solution, *International Journal of Biology, Pharmacy and Allied Science*, 2015, 4(12): 620-629.
15. Mohamed, A. S., An economical dyeing process for cotton, polyester and cotton/polyester blended fabrics, *Journal of Textile and Apparel, Technology and Management*, 2010, 6(4): 1-11.
16. Hussein, I. and Elhassaneen, Y., Protection of humans from ultraviolet radiation (UVR) through the use of cotton clothes dyed with aqueous extracts of onion skin as the natural colorant, *Journal of American Science*, 2013, 9(8): 16-24.
17. Akaranta, O. and Akaho, A. A., Synergic effect of Citric Acid and Red Onion skin extract on the Oxidative stability of Vegetable Oil, *Journal of Applied Science and Environmental Management*, 2012, 16(4): 337-343.
18. Nnaji, N. J. N., Okoye, C. O. B., Obi-Egbedi, N. O., Ezeokonkwo, M. A. and Ani, J. U., Spectroscopic characterization of red onion skin tannin and its use as alternative aluminium corrosion inhibitor in hydrochloric acid solutions, *International Journal of Electrochemical Science*, 2013, 8, 1735-1758.
19. James, A. O. and Akaranta, O., Corrosion inhibition of aluminium in 2M sulphuric acid using acetone extract of red onion skin, *International Journal of Applied Chemical Sciences Research*, 2014, 2(1): 1-10.
20. Jebson, S. R. and Moses, A. N., Use of allium cepa (red onion skin) extract as indicator alternate in acid – base titrimetric analysis, *International Journal of Research in Applied, Natural and Social Sciences*, 2015, 3(7): 17-22.
21. Ibezim-Ezeani, M. U. and Anusiem, A. C. I., Effect of ionic charge on the adsorption of sodium-palmitate and sodium-laurate onto galena, hematite and cassiterite in aqueous solution, *E-Journal of Chemistry*, 2010, 7(4): 1491-1497.
22. Tadepalli, S., Murthy, K. S. R. and Vijay, P., Removal of copper and cadmium from industrial effluents using the mixed adsorbent in batch study, *International Journal of ChemTech Research*, 2016, 9(5): 691-704.
23. Lee, J. D., *Concise Inorganic Chemistry*, 5th ed. Blackwell Science Ltd, New York, 1996, 426-763.
24. Kosa, S. A., Al-Zhrani, G. and Salam, M. A., Removal of heavy metals from aqueous solutions by multi-walled carbon nanotubes modified with 8-hydroxyquinoline, *Chemical Engineering Journal*, 2012, 181-182, 159-168.
25. Ademiluyi, F. T. and Ujile, A. A., Kinetics of batch adsorption of iron(II) ions from aqueous solution using activated carbon from Nigerian bamboo, *International Journal of Engineering and Technology*, 2013, 3(6): 623-631.
26. Neto, V. O. S., Carvalho, T. V., Honorato, S. B., Gomes, C. L., Barros, F. C. F., Araújo-Silva, M. A. Freire, P. T. C. and Nascimento, R. F., Coconut bagasse treated by thiourea/ammonia solution for cadmium removal: Kinetics and adsorption equilibrium, *BioResources*, 2012, 7(2): 1504-1524.

27. Aydin, F. and Kuleyin, A., The effect of modification and initial concentration on ammonia removal from leachate by zeolite, *World Academy Science*, 2011, 54, 293-296.
28. Gulipalli, C. S., Prasad, B. and Wasewar, K. L., Batch study, equilibrium and kinetics of adsorption of Selenium using rice husk ash, *Journal of Engineering, Science and Technology*, 2011, 6(5): 586-605.
29. Zhao, G., Wu, X., Tan, X. and Wang, X., Sorption of heavy metal ions from aqueous solutions: A review, *The Open Colloid Science Journal*, 2011, 4, 19-31.
30. Sivaprakash, B., Rajamohan, N. and Sadhik, A. M., Batch and column sorption of heavy metal from aqueous solution using a marine alga *sargassum tenerrimum*, *International Journal of ChemTech Research*, 2010, 2(1): 155-162.
31. Karthika, C. and Sekar, M., Removal of mercury (II) ions from aqueous solution by acid acrylic resin. A study through adsorption isotherms analysis, *International Research Journal of Environmental Science*, 2012, 1(1): 34-41.
32. Ibezim-Ezeani, M. U. and Anusiem, A. C. I., Thermodynamics of the adsorption of Palmitate and laurate soaps onto some metal ore surfaces in aqueous media, *African Journal of Pure and Applied Chemistry*, 2011, 5(9): 272-277.
33. Lim, J., Kang, H., Kim, L. and Ko, S., Removal of heavy metals by sawdust adsorption: Equilibrium and kinetic studies, *Environmental Engineering Research*, 2008, 13(2): 79-84.
34. Dizadji, N., Rashtchi, M., Dehpouri, S. and Nouri, N., Experimental investigation of adsorption of copper from aqueous solution using vermiculite and clinoptilolite, *International Journal of Environmental Research*, 2013, 7(4): 887-894.
35. Abd.Hadi, N. B., Rohaizar, N. A. B. and Sien, W. C., Removal of copper(II) from water by adsorption on papaya seed, *Asian Transactions Engineering*, 2011, 1(5): 49-55.
36. Buasri, A., Chaiyut, N., Tapang, K., Jaroensin, S. and Panphrom, S., Biosorption of heavy metals from aqueous solutions using water hyacinth as a low cost biosorbent, *Civil and Environmental Research*, 2012, 2(2): 17-24.
37. Neto, V. O. S., Oliveira, A. G., Teixeira, R. N. P., Silva, M. A. A., Freire, P. T. C., Keukeleire, D. D. and Nascimento, R. F., Use of coconut bagasse as alternative adsorbent for separation of copper (II) ions from aqueous solutions: Isotherms, kinetics and thermodynamic studies, *BioResources*, 2011, 6(3): 3376- 3395.
38. Foo, k.Y. and Hameed, B. H., Insight into the modeling of adsorption isotherm systems, *Chemical Engineering Journal*, 2010, 156, 2-10.
39. Gupta, S., Dutta, G. and Mondal, D., Mechanism of fluoride mobilization in an alluvial aquifer: Akinetic approach, *International Journal of ChemTech Research*, 2016, 9(4): 270-278.
40. Kamel, N. H. M., Sayyah, E. M. and Abdel-aal, A. A., Removal of lead, cobalt and manganese from aqueous solutions using a new modified synthetic ion exchanger, *Archives of Applied Science Research*, 2011, 3(2): 448-464.
41. Pino, G. H., Mesquita, L. M. S., Torem, M. L. and Pinto, G. A. S., Biosorption of cadmium by green coconut shell powder, *Minerals Engineering*, 2006, 19, 380-387.
42. Manohar, D. M., Krishnan, K. A. and Anirudhan, T. S., Removal of mercury (II) from aqueous solutions and chlor-alkali industry wastewater using 2-mercaptobenzimidazole-clay, *Water Research*, 2002, 36, 1609-1619.
43. Jain, R., Gupta, V.K. and Sikarwar, S., Adsorption and desorption studies on hazardous dye naphthol yellow s, *Journal of Hazardous Materials*, 2010, 182, 749-756.
44. Achmad, A., Kassim, J., Suan, T. K., Amat, R. C. and Seey, T. L., Equilibrium, kinetics and thermodynamic studies on the adsorption of direct dye onto a novel green adsorbent developed from uncaria gambir extract, *Journal of Physical Science*, 2012, 23(1): 1-13.
45. Manilla, P. N., Ogali, R. E. and Uzoukwu, B. A., *Undergraduate chemistry: Fundamental principles*, Timi Hyacinth Publishers, Nigeria, 2001, 296.
46. Argun, M. E., Dursun, S., Ozdemir, C. and Karatas, M., Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics, *Journal of Hazardous Materials*, 2007, 144, 77-85.

\*\*\*\*\*