Equilibrium and Thermodynamic Studies using Eco-Friendly *Cola lepidota* Seed Resins as Novel Adsorbents in the Removal of Pb (II) and Cd (II) Ions from Aqueous System

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**Abstract.** This study reveals the removal of Pb (II) and Cd (II) ions from aqueous system using unmodified *Cola lepidota* extract (UCE) and modified *Cola lepidota* extract resin (ECER). The modification was achieved by using ethanediolic acid and the adsorption process was carried out with respect to initial concentrations, temperature and pH. Phytochemical analysis of the seeds was done by Gas Chromatography Mass Spectrometry (GC-MS). The zero point charge was evaluated and Pb (II) and Cd (II) ions equilibrium concentration was determined using Atomic Absorption Spectrophotometer (AAS). The GC-MS spectra suggested the seed contained 22 compounds. The zero point charge of UCE and ECER was found to be 4.0 and 7.0, respectively. Percentage removal of Pb (II) and Cd (II) ions onto ECER and UCE gave 89.35%, 83.45%, 75.32% and 80.11%, respectively. Optimal temperatures were 313 K and 303 K for Pb (II) and Cd (II) ions onto UCE, 303 K and 353 K for Pb (II) and Cd (II) ions onto ECER with 97.60%, 91.04%, 97.44% and 90.22% metal ions removal. Optimal pH was 4.0 for Pb (II) ion onto UCE and ECER, 8.0 for Cd (II) ion onto UCE and 6.0 to 8.0 for Cd (II) ion onto ECER with 98.40%, 98.40%, 95.11% and 98.37% removal. Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Redlich-Peterson isotherm model equations were tested and the result showed that Freundlich adsorption isotherm model equation fitted well with the removal of the metal ions onto UCE and ECER. Adsorption of Pb (II) ion onto UCE and ECER and Cd (II) ion onto UCE was exothermic with negative entropy while Cd (II) ion onto ECER was endothermic with positive entropy. The change in Gibbs free energy, $\Delta G^\circ$, was negative for all the metal ions. The unmodified *Cola lepidota* extract (UCE) and the ethanediolic acid *Cola lepidota* extract resin (ECER) can be recommended empirically as surfaces for heterogeneous reactions.

**Keywords:** *Cola lepidota*, seed resin, adsorption, equilibrium, heavy metals thermodynamics

**Introduction**

The increasing environmental pollution occasioned by unchecked human activities especially with heavy metal ion contamination in the environment is a major world health challenge which requires adequate attention (Gupta *et al.*, 2015; Alok *et al.*, 2010). Most automobiles in Nigeria emit lead which is a component additive in petroleum motor spirit from the exhaust pipes. Again, due to the current power shortage, an average family, institution and company or firm in Nigeria has at least one power generating plant which uses mainly leaded petroleum products. Along the roads, streets and markets are found milling machines, tyre-vulcanizing equipment, furniture making and spraying machines, car panel-biting and spraying equipment that are operated with leaded fuel which release lead contaminated fumes into the atmosphere in an uncontrollable manner.

Mining of minerals, petroleum exploration and production, iron and steel manufacturing industries largely contributed to the unprecedented pollution of the environment by heavy metals and metalloids such as iron, chromium, nickel, cadmium, mercury, lead, zinc, arsenic, etc. (Saleh *et al.*, 2014; Giri and Singh, 2014). Menke *et al.* (2009) stated that exposure to cadmium is a major cause of cancer, prevalence of cardiovascular diseases in the masculine gender and mortality of both male and female at very high dose. Jurasovic *et al.* (2004) noted that cadmium and lead poisoning have been linked to cause endocrine infection which affect mostly men’s sexual performance (Davies, 1987). The illegal mining of lead has caused the death of nothing less than four hundred (400) children in Zamfara State of Nigeria (Horsfall, 2011).

In recent times, there has been a conscious effort to use biological materials or agricultural produce and agricultural waste for bioremediation either in
bioaccumulation or biosorption (Ahmaruzzaman and Gupta, 2011). The use of non-biological materials or waste such as active alumina, zeolites, silica gel, activated carbon, etc. as adsorbents to remove heavy metal ions from contaminated source are not cost effective and environmentally friendly due to the generation of chemical sludge and other challenges.

Hence, the need for alternative approach in removing the metal ions from contaminated environment has become imperative (Gupta et al., 2014; Vinod et al., 2011). Hence, an invention arising from the challenges associated with the regular approach of heavy metal ions removal is the use of biological materials or/and agricultural wastes in the treatment of heavy metal ions in contaminated environment (Gupta et al., 2015).

*Cola lepidota* is an indigenous fruit found in West and Central African forests which is commonly called Monkey cola. It belongs to the family of Malvaceae and sub-family of Sterculioideae (Ogbu and Umeokechukwu, 2014). *Cola lepidota* has local names such as Achicha or Ochicha, Ohihia, Ndiya, Tuwo-biri, by the Ibos, Ikweres, Ibibios and the Hausas, respectively (Ibezim-Ezeani et al., 2017). The nutritive values of *Cola lepidota* reveal that every 100 g of the mesocarp of *Cola lepidota* is composed of the following average contents: moisture content 82.60 g; fibre ash 1.58 g; energy value 55 kcal, fats 0.00 g; carbohydrate 25.8 g; crude protein 1.75 g; vitamin C 11.28 mg; vitamin A 0.25 IU; phosphorus 0.09 mg; potassium 0.19 mg; calcium 0.42 mg; and magnesium 0.09 mg (Ogbu et al., 2007).

There is little or no information on the application of *Cola lepidota* as sorbent for decontamination of trace metals, inorganic and organic materials from aqueous solutions, wastewaters and stimulated waters or heterogeneous surfaces for catalysis.

Therefore, this research was carried to determine the removal efficiency of the extract of *Cola lepidota* seed in the unmodified and modified forms for Pb (II) and Cd (II) ions from aqueous system.

**Materials and Methods**

**Sample collection and pre-treatment.** The *Cola lepidota* fruits were purchased from Sanganal market at mile 1 market, Port Harcourt, Nigeria, and identified at University of Port Harcourt Herbarium. They were washed properly using de-ionized water to remove potential particulate contaminants, then cut open and the seeds removed from the fruits. The seeds were cut into tiny sizes, sun-dried for twenty one days and milled using an electric grinder. The powdered *Cola lepidota* seeds were sieved at Geology Department of University of Port Harcourt using a set of Newark U.S.A standard test sieve (ASTM E-11 specification) until an average particle size of 150 μm was obtained. It was then kept in an air-tight container made of polyethylene, and labeled as Unmodified *Cola lepidota* seed powder (UC).

The following analytical grade chemicals were used for this research; propanone, ethanediolic acid, *n*-hexane, hydrochloric acid, sodium hydroxide, sodium thiosulphate pentahydrate, lead (II) nitrate, cadmium (II) chloride and iodine crystals.

**Extraction and modification of *Cola lepidota* seed powder.** The extraction was achieved using Soxhlet extractor and propanone as solvent. The extract paste was placed in a filter paper, firstly washed with *n*-hexane to remove the esters and residual propanone, and then finally washed with water to remove any left over *n*-hexane. The residue was dried at 323 K in an oven for 12 h. A solid extract obtained was crushed into tiny particles and labelled Unmodified *Cola lepidota* Extract (UCE). Then, the extract (22.5 g) was weighed into 500 mL beaker and 150 mL of de-ionized water was added and stirred for 30 min. Ethanediolic acid (1.35 g) was added while stirring for another 10 min at an increased temperature of 323 K. Ethanediolic acid in this modification was used because it is very hydrophilic i.e. readily absorbs water and equally the acid is a good binder and chelating agent. After that 37.5 mL of iodine solution (5% w/v) was added, while still stirring at 323 K for another 80 min until the reaction was brought to an end by quenching techniques (rapid cooling to room temperature). Subsequently, 75 mL of saturated sodium thiosulphate pentahydrate was added and allowed to stand for 12 h at room temperature which gave rise to two layers. The organic layer was decanted into a filter paper, and washed with 500 mL of distilled water. The modified extract was dried in an oven at 323 K for 24 h. The resin prepared was labeled ‘Ethanediolic *Cola lepidota* Extract Resin (ECER)’.

**Metal ions stock solution preparation.** A 1.6564 g sample of Pb(NO₃)₂ was weighed into 250 mL beaker, 100 mL of de-ionized water was added to dissolve the salt. The dissolved lead (II) nitrate was transferred into 1000 mL volumetric flask and made up to mark to prepare 1.036219 mg/L of lead (Pb (II)) stock solution.
CdCl₂ (1.8336g) was dissolved in a 250 mL beaker and 100 mL of de-ionized water was added to dissolve the salt. The dissolved cadmium (II) chloride was transferred into 1000 mL volumetric flask and made up to mark to obtain 1,124.4 mg/L of cadmium (Cd (II)) stock solution.

**Metal ions working solutions.** Aliquots of the stock solution were transferred into various volumetric flasks, and made up to their respective marks to prepare different concentrations of the calibration standards and working solutions as required. This was achieved by applying the serial dilution equation 1.

\[
C_1 V_1 = C_2 V_2 \quad \text{..........................................................} \quad 1
\]

where:

\(C_1\) and \(C_2\) represent the concentration of stock and working solutions while \(V_1\) and \(V_2\) represents the volume of stock and working solutions, respectively.

**Characterization: Gas chromatography-mass spectrometry (GC-MS).** UCE was subjected to GC-MS analysis using Shimadzu GC-MS-QP 2010 to determine various components of the propanone extract and elucidate their possible structures.

**Zero point charge (pHZpc) determination.** The zero point charge UCE and ECER were determined by dispensing 0.01 M NaCl (50 mL) solution into fourteen conical flasks (100 mL) and the pH of the solution adjusted in duplicates to 2.0, 4.0, 6.0, 8.0, 10.0, 11.0 using 0.1 M NaOH or 0.1 M HCl. Some samples of UCE and ECER (50 mg) were dispersed into each of the flask, corked properly, agitated mechanically (180 rpm) for 1 h and then allowed to stand for 48 h at room temperature. At the end, the mixtures were subjected to filtration using a filter paper. The pH of supernatant were measured and various changes in each pH value between initial (pH<sub>i</sub>) and final (pH<sub>f</sub>) obtained. Plots of changes between initial and final pH (ΔpH) against initial pH were performed, the point(s) of intersection was taken as the zero point charge (Vieira et al., 2014).

**Effect of initial concentration (IC) and adsorption studies at equilibrium.** The adsorption on the surface of the UCE and ECER with Cd (II) and Pb (II) was carried out by adding 50 mg of the resins into separate 100 mL conical flask containing 50 mL (each of 0.1 mol/L – 0.7 mol/L) of Cd (II) and Pb (II) ions, and adjusted the pH of UCE to 4.0, while ECER was adjusted to pH 7.0. The flasks were corked and the mixtures agitated mechanically (180 rpm) for 1 h and left to stand for 48 h at room temperature. The mixtures in the flasks were filtered through Whatmann filter paper after the shaking period. The supernatants were analyzed using Atomic Absorption Spectrophotometer (Buck scientific-model 210 VGP) to quantify the metal ions at wavelengths of 228.9 nm for Cd (II) and 283.2 nm for Pb (II) ions. Thereafter, the removal of the ions at equilibrium and the adsorption capacity were calculated using equations 2 and 3.

\[
\% \Delta \left[ M^{\text{eq}} \right] = \left( \frac{C_i - C_e}{C_i} \right) \times 100 \quad \text{..........................................................} \quad 2
\]

where:

\(\% \Delta \left[ M^{\text{eq}} \right]\) represent percentage metal ion removed, \(C_i\) and \(C_e\) are initial and equilibrium concentration in mg/L.

\[
Q_e = \left( \frac{C_i - C_e}{W} \right) \times V \quad \text{..........................................................} \quad 3
\]

where:

\(Q_e\) is the equilibrium amount adsorbed by the metal ions on the adsorbent (which is the ratio of adsorbate to sorbent in mol/g), \(C_i\) and \(C_e\) are initial and equilibrium concentration in mol/L and \(W\) is weight of sorbent in grams and \(V\) is volume of adsorbate in litres.

**Temperature studies.** A 0.1 mol/L solution of 50 mL each of Pb (II) and Cd (II) ions were added into several flasks containing 50 mg of UCE and ECER at pH of 4.0. These were subjected to heating on Präcis dig (6001197) JP Selecta water bath at the following temperatures; 303 K, 313 K, 323 K, 343 K and 353 K for 10 min each. Each sample mixture was then filtered at the end of the 10 min and the supernatant was analyzed to quantify the equilibrium concentration of the metal ion using Atomic Absorption Spectrophotometer. The percentage S metal removal and equilibrium adsorption capacity was determined using equations 2 and 3.

**Thermodynamic parameters determination.** The values of Δ\(S^o\), Δ\(H^o\), Δ\(G^o\) were determined by the application of equations below at varying temperatures of 303 K, 313 K, 323 K, 343 K and 353 K (Crini and Badot, 2008).

\[
\Delta G = -RT \ln \left( \frac{Q_e}{C_e} \right) \quad \text{..........................................................} \quad 4
\]
\[ \Delta G^o = \Delta H^o - T \Delta S^o \] ……………………………………….. 5
\[ \ln \left( \frac{q_e}{C_e} \right) = - \frac{\Delta H}{RT} + \frac{\Delta S}{R} \] ……………………………………….. 6
\[ \ln K = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \] ……………………………………….. 7
\[ \ln K_{abs} = \frac{E_a}{RT} + \ln K_a \] ……………………………………….. 8
\[ \Delta H = - \frac{RT}{T_2 - T_1} \left( \ln C_i - \ln C_e \right) \] ……………………………………….. 9

where:

K_{abs} and K_a represent the absorption and dissociation constants.

Plot of ln K_{abs} versus \frac{1}{T} is linear and from the slope and intercept: \Delta S^o \Delta H^o, \Delta G^o were calculated.

Effect of pH. A 50 mg of UCE and ECER was weighed into several 150 mL flasks and 50 mL each of 0.1 mol/L Pb (II) and Cd (II) ions was added to the flasks. The pH of the samples was adjusted using either 0.1 M NaOH or 0.1 M HCl to the following pH of 2.0, 4.0, 6.0, 8.0, 10.0 and 11.0 for UCE and ECER, respectively. The flasks containing the mixtures were shaken mechanically (180 rpm) for 1 h. The samples were then filtered using Whatman filter paper and the concentration of metal ions in the supernatant determined using Atomic Absorption Spectrophotometer. Equations 2 and 3 were used to evaluate the percentage ion removed and adsorption capacity, respectively.

Results and Discussion

Gas chromatography–mass spectrometer spectrum of UCE. The GC-MS spectrum of the UCE is presented in Fig. 1. The spectrum indicated the presence of twenty two compounds, which are presented in Table 1.

Zero point charge. Zero point charge (pH_{zpc}) is an important characteristic of adsorbents. It is the pH at which the surface of adsorbent has neither positive nor negative charges.

Hence, at the zero point charge, the sorbent is said to be electrically neutral (Coskun et al., 2017). The zero point charge plots of UCE and ECER in Fig. 2 showed that the zero point charge of UCE was obtained at a pH of approximately 4.0 while that of ECER was obtained at a pH of approximately 7.0. This finding showed that the adsorption of Pb (II) and Cd (II) ions onto UCE and ECER surfaces were optimal at these pH values.

Effect of concentration on adsorption of Pb (II) and Cd (II) ions onto UCE and ECER. The effect of concentration on the adsorption of Pb (II) and Cd (II) ions onto UCE and ECER are presented in Fig. 3.

The results showed that there was a general increase in the adsorption of adsorbates from the aqueous media by UCE and ECER. This could be attributed to the

<table>
<thead>
<tr>
<th>Table 1. New compounds discovered from GC-MS analysis</th>
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<tbody>
<tr>
<td>Name of compounds</td>
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<tr>
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</tr>
<tr>
<td>Octylacetylene (1-decyne)</td>
</tr>
<tr>
<td>Glycerin (1, 2, 3-Propanetriol)</td>
</tr>
<tr>
<td>Pelargonic acid (Non-anonic acid)</td>
</tr>
<tr>
<td>Undec-10-ynoic acid</td>
</tr>
<tr>
<td>Phenol, 3, 5-bis (1, 1-dimethylethyl)</td>
</tr>
<tr>
<td>1-Pentadecene (Pentadec-1-ene)</td>
</tr>
<tr>
<td>Ethyl ester (Decanoic acid)</td>
</tr>
<tr>
<td>n-Butyl laurate (Dodecanoic acid)</td>
</tr>
<tr>
<td>1, 2-Benzenedicarboxylic</td>
</tr>
<tr>
<td>Methyl 14-Methyl Pentadecanoate (Pentadecanoic acid)</td>
</tr>
<tr>
<td>Ethyl hexadecanoate (Hexadecanoic acid)</td>
</tr>
<tr>
<td>Palmitic acid (n-Hexadecanoic acid)</td>
</tr>
<tr>
<td>Linolelaidic acid (9, 12-Octadecadienoic acid)</td>
</tr>
<tr>
<td>10-Octadecenoic acid</td>
</tr>
<tr>
<td>Cyclopentaneundecanoic acid</td>
</tr>
<tr>
<td>Linoleic acid (Ethyl cis, cis-9, 12-Octadecadienoate)</td>
</tr>
<tr>
<td>Spireo [2, 4] heptane</td>
</tr>
<tr>
<td>Grape seed oil (9, 12-Octadecadienoic acid (Z, Z) 9, 12-Tetradecadien-1-ol</td>
</tr>
<tr>
<td>(Z), (Z)-9-Pentadecadien-1-ol</td>
</tr>
<tr>
<td>Di-n-octyl phthlate</td>
</tr>
<tr>
<td>Squalene (2, 6, 10, 14, 18, 22-Tetracosahexaene)</td>
</tr>
</tbody>
</table>
driving force which may be increasing due to the increasing initial concentrations of Pb (II) and Cd (II) ions (Coskun et al., 2017). The percentage removal of Pb (II) ion onto ECER was observed to be highest at 0.5 mol/L and the sequence of removal followed as: Pb (II) ion < Cd (II) ion onto UCE < Cd (II) ion < Pb (II) ion onto ECER.

**Adsorption equilibrium isotherms.** The experimental data were applied to the adsorption isotherm models in order to determine the nature of sorbent surface (either homogeneous or heterogeneous) and adsorption (physisorption, chemisorptions or ion exchange). The isotherm models tested include Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Redlich-Peterson.

**Langmuir isotherm model.** The linearized Langmuir equation was given by Langmuir (1918) as:

\[
\frac{C_e}{Q_{eq}} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m}
\]

where:

\(C_e\) (mol/L) is the concentration of adsorbate at equilibrium, \(K_L\) (L/g) is the Langmuir isotherm constant related to sorption energy, \(Q_{eq}\) (mol/g) is the adsorption capacity at equilibrium, \(Q_m\) (mol/g) is the maximum coverage of the monolayer.

The data were investigated by plotting \(C_e/Q_{eq}\) vs \(C_e\) presented in Fig. 4. The result showed that adsorption...
of Pb (II) ion onto ECER had RL value of 0.03 and $R^2$ value 0.696 which implied that the adsorption process was feasible and was best fitted into the Langmuir isotherm model. The adsorption of Pb (II) ion onto UCE, Cd (II) ion onto UCE and ECER all had better $R^2$ values but negative RL values suggesting that the adsorptions were not feasible. Hence, it can be inferred that the layer of UCE was homogeneous.

**Freundlich isotherm model.** The linearized form of the Freundlich equation was given as equation 11 (Freundlich, 1907) as:

$$\log Q_{eq} = \log K_f + \frac{1}{n} \log C_e$$  

where:

$Q_{eq}$ (mol/g) is the adsorption capacity at equilibrium, $K_f$ (L/g) the Freundlich constant, $C_e$ (mol/L) is the concentration of adsorbate at equilibrium, $\frac{1}{n}$ is the intensity of adsorption, $n$ is the factor for heterogeneity which indicates the distribution of bonds and it is not dependent on the concentrations of adsorbents.

The investigation was carried out by the plot of $\log Q_{eq}$ vs $\log C_e$ presented in Fig. 5. The summary of the values of the constants and the $R^2$ values is presented in Table 2. The experimental data fitted very well for the adsorption process. The increasing order of fitness was as follows: Cd (II) ion onto UCE < Cd (II) ion onto ECER < Pb (II) ion onto UCE < Pb (II) ion onto ECER. The $R^2$ values showed that the adsorption of Pb (II) and Cd (II) ions onto UCE and ECER fitted very well into the Freundlich adsorption model and thus suggesting that the adsorbent surface were heterogeneous in nature and the adsorption of adsorbates onto the adsorbent was multilayered (Apemiye et al., 2017). This correlated with the kinetic plots obtained from Intra-particle and Boyd model. Also, adsorption of Cd (II) ion onto ECER had higher $R^2$ value for Langmuir than for Freundlich adsorption isotherm model further suggesting that the modification of UCE to ECER increased the homogeneous nature of ECER’s surface.

**Temkin isotherm model.** The Temkin equation used in this study was presented by Temkin (1934) and expressed as:

$$Q_{eq} = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e$$  

where:

$R$ is the universal gas constants (8.314 J/K/mol), $T$ is temperature in Kelvin (absolute temperature), $K_T$ is the Temkin binding equilibrium constant (L/mol) the values obtained from this corresponds to the highest possible binding energies, $b_T$ is related to the heat of adsorption.

The investigation was carried out by plotting $Q_{eq}$ vs $\ln C_e$, and the $b_T$ and $K_T$ were determined from the slope and intercerpt of the curve (Fig. 6). The values were presented in Table 2. The result showed that the $R^2$ values obtained where less than that obtained for Freundlich adsorption equilibriuim isotherm. However, the $b_T$ and $K_T$ values obtained were high for all the adsorption processes.

**Dubinin-Radushkevich (D-R) isotherm model.** To resolve the adsorption mechanism, the deduced data were tested with the D-R adsorption isotherm (Dubinin, 1960). The equation is given as:

![Fig. 5. Freundlich plots for UCE and ECER.](image1)

![Fig. 6. Temkin plots for UCE and ECER.](image2)
Table 2. Summary of isotherm equilibrium constants

<table>
<thead>
<tr>
<th></th>
<th>UCE Pb (II) ion</th>
<th>UCE Cd (II) ion</th>
<th>ECER Pb (II) ion</th>
<th>ECER Cd (II) ion</th>
</tr>
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<tbody>
<tr>
<td>$R^2 = 0.171$</td>
<td></td>
<td></td>
<td>0.696</td>
<td>0.999</td>
</tr>
<tr>
<td>$K_L$ (g/L)</td>
<td>$-7306.06$</td>
<td>$-17142.83$</td>
<td>160162.21</td>
<td>$-14899.82$</td>
</tr>
<tr>
<td>$Q_m$ (mol/g)</td>
<td>$-0.000065$</td>
<td>$-1.28E-05$</td>
<td>5.63E-05</td>
<td>$-2.51E-05$</td>
</tr>
<tr>
<td>$R_t = -3.1$</td>
<td></td>
<td></td>
<td>-0.22</td>
<td>-0.25</td>
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<thead>
<tr>
<th></th>
<th>Langmuir</th>
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<th>Frendlich</th>
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<tr>
<td>$R^2 = 0.943$</td>
<td>0.896</td>
<td>0.951</td>
<td>0.932</td>
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<tr>
<td>$1/n = 0.174$</td>
<td>0.198</td>
<td>0.141</td>
<td>0.184</td>
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</tr>
<tr>
<td>$n = 5.75$</td>
<td>5.05</td>
<td>7.09</td>
<td>5.43</td>
<td></td>
</tr>
<tr>
<td>$K_F$ (L/g) = 6.50E-6</td>
<td>1.14E-5</td>
<td>1.18E-5</td>
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<thead>
<tr>
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<th>Temkin</th>
<th>Dubinin-Radushkevich</th>
<th>Redlich-Peterson</th>
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<tr>
<td>$R^2 = 0.717$</td>
<td>0.895</td>
<td>0.659</td>
<td>0.972</td>
</tr>
<tr>
<td>$Q_m$ (mol/g)</td>
<td>6.50E-6</td>
<td>1.18E-5</td>
<td>1.31E-5</td>
</tr>
<tr>
<td>$K_T$ (L/g)</td>
<td>22026.47</td>
<td>22026.47</td>
<td>25191420</td>
</tr>
<tr>
<td></td>
<td>12595710</td>
<td>125957100</td>
<td>1202604.28</td>
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<tr>
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<td>0.659</td>
<td>0.972</td>
</tr>
<tr>
<td>$Q_m$ (mol/g)</td>
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<td>1.18E-5</td>
<td>1.31E-5</td>
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<tr>
<td>$K_T$ (L/g)</td>
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<tbody>
<tr>
<td>$R^2 = 0.174$</td>
<td>0.940</td>
<td>0.655</td>
<td>0.533</td>
</tr>
<tr>
<td>$g = -0.2768$</td>
<td>-3.0043</td>
<td>0.4927</td>
<td>-1.5997</td>
</tr>
<tr>
<td>$K_T$(L/g) = -2.4967</td>
<td>-3.0335</td>
<td>4.567</td>
<td>-16.313</td>
</tr>
</tbody>
</table>

\[
\log Q_{eq} = \log Q_m K \varepsilon^2
\]

where:

$Q_{eq}$ and $Q_m$ represent adsorption capacity at equilibrium and D-R monolayer capacity (mol/g) respectively, $\varepsilon$ represents the Polanyi potential associated with the concentration at equilibrium (J/mol) and $K$ describes the constant associated with energy of adsorption (mol/J)^2.

The D-R adsorption equilibrium isotherm was investigated by plotting $\log Q_{eq}$ vs. $\varepsilon^2$ (Fig. 7) and the values of $\log Q_{eq}$ and $K$ were determined from the intercept and slope.

$\varepsilon$ was calculated using the equation.

\[
\varepsilon = R T \ln \left(1 + \frac{1}{C_e} \right)
\]

The mean free energy was calculated using the equation given as:

\[
E = (2K)^{0.5}
\]

The D-R isotherm results presented in Table 2 showed that all the adsorption was by physisorption. However, the $Q_m$ was quite high as well as the $R^2$ values except for the adsorption of Pb (II) ion onto ECER. The increasing order of the $R^2$ values was as follows: Pb (II) ion onto ECER < Pb (II) ion onto UCE < Cd (II) ion onto ECER < Cd (II) ion onto UCE.

In general, the D-R model suggest that the adsorption mechanism was by physical adsorption which also correlated with what was observed for the adsorption of Pb (II) and Cd (II) ions onto UCE, as well as Pb (II) ion onto ECER while investigating temperature effect on adsorption. The only exception was the adsorption of Cd (II) ion onto ECER. This suggests that all the adsorption process was a combination of physisorption and chemisorption but physisorption dominated all the processes since the chemical interactions between the adsorbates and adsorbent surface was weak.

Redlich-Peterson isotherm model. The Redlich-Peterson adsorption equilibrium isotherm was a combination of the Langmuir and Freundlich equation (Redlich and Peterson, 1959).
Dubinin-Radushkevich plots for UCE and ECER.

\[
Q_{eq} = \frac{C_e}{1 + K_R C_e^g}
\]

\[
\ln\left(\frac{C_e}{Q_{eq}}\right) = g \ln C_e - \ln K_R
\]

where:

The constants KR (L/g) and a, represent the Redlich-Peterson (R-P) adsorption equilibrium isotherm constants, g represents the exponent taking values between 1 and 0, as g approaches 0, Henry’s law; and g = 1 changes the R-P equation into the Langmuir form.

The investigation was carried out by plotting \(\ln\left(\frac{C_e}{Q_{eq}}\right)\) vs \(\ln C_e\) as shown in Fig. 8. The g values obtained for the adsorption process was negative except for Pb (II) ion onto ECER with a value of 0.493 and this further suggest that the active surfaces of adsorption of the Pb (II) ion onto ECER was a combination of heterogeneous (multilayer) and homogeneous (monolayer) surfaces probably due to the modification process. Also, the ‘g’ value obtained for Pb (II) ion onto ECER also fell between 0 and 1 which also confirmed that the adsorption was favorable. The \(R^2\) values for Cd (II) ion onto UCE and ECER was high but still below that for Freundlich. Hence, this model was not the best fit for the adsorption process in this study.

**Effect of temperature.** The temperature studies on the adsorption of Pb (II) and Cd (II) ions onto the sorbents are presented in Fig. 9. Adsorption of Pb (II) ion onto UCE reached a maximum between 303 K to 313 K similar to what was reported by Seker et al. (2004), after which a further increase in temperatures above 313 K resulted in a decrease in the adsorption and percentage removal of adsorbates suggesting an endothermic process below 313 K and exothermic process above 313 K.

Adsorption of Pb (II) and Cd (II) ions onto UCE and ECER decreased with increase in temperature suggesting that physisorption probably occurred (Ibezim-Ezeani et al., 2012). This observation may be due to an increasing weak interaction occurring between the adsorbates and the sorbent binding sites; the deformation of the active sites may also have occurred as a result of increased temperature leading to distortion of the sorbents structural arrangement (Saravanan et al., 2013). However, the adsorption of Cd (II) ion onto ECER and the percentage removal gradually increased as the temperature increased from 303 K to 353 K suggesting that the process was endothermic and probably chemisorption occured similar to what was reported.

**Fig. 7.** Dubinin-Radushkevich plots for UCE and ECER.

**Fig. 8.** Redlich-Peterson plots for UCE and ECER.

**Fig. 9.** Plots of metal ions removed (%) against temperature (K).
by Nethaji et al. (2013). From the data generated, effect of temperature on adsorption and percentage removal of adsorbate from aqueous medium was not really pronounced (Coskun et al., 2017). Generally, the order of adsorption from aqueous medium at lower temperature was as follows: Cd (II) ion onto ECER < Cd (II) ion onto UCE < Pb (II) ion onto UCE < Pb (II) ion onto ECER while the increasing order of removal and adsorption of adsorbate at higher temperature was as follows: Cd (II) ion onto UCE < Cd (II) ion onto ECER < Pb (II) ion onto ECER < Pb (II) ion onto UCE.

**Thermodynamic analysis.** The thermodynamic parameters were presented in Table 3 while the Van’t Hoff plot was shown in Fig. 10. The values obtained suggest that the adsorption of Pb (II) and Cd (II) ions onto UCE and Pb (II) ion onto ECER was exothermic while Cd (II) ion onto ECER was endothermic. The negative values of ΔS° also suggest that the degree of randomness for the adsorption of Pb (II) and Cd (II) ions onto UCE and Pb (II) ion onto ECER reduced while that of Cd (II) ion on ECER increased on the surfaces of the sorbents (Mohammadi et al., 2011). Also, the negative values of ΔG° suggest that the adsorption processes were spontaneous and feasible.

**Effect of pH.** Adsorption process was greatly influenced by the pH of the medium (Coskun et al., 2017; Kalemmbkiewicz, 2016).

The pH analysis presented in Fig. 11 showed that at lower pH, adsorption of Pb (II) and Cd (II) ions onto UCE and ECER were low which could be as a result of charge repulsion between the positively charged metal ions and hydrogen ions (Soco and Kalemmbkiewicz, 2016). However, at pH 4.0, the adsorption and percentage removal of Pb (II) ion onto UCE was higher than for Pb (II) ion onto ECER. Also, the adsorption of Cd (II) ion onto ECER was higher than adsorption of Cd (II) ion onto UCE at 6.0 to 8.0. The pH 4.0 for UCE adsorption coincided with the zero point charge of UCE. However, adsorption of Pb (II) ion onto UCE and ECER was the same and highest at pH 6.0 to 7.0 coinciding with the zero point charge of ECER suggesting that at zero point charge, there was little or no competition between the hydrogen ions and the metal ions for the adsorbents active binding sites as the H⁺ on the adsorbents surfaces has been overshadowed by the Pb (II) ion. The decrease in the percentage metal ions removal from pH 8.0 to 11.0 may also be as a result of the amphoteric nature of Pb(OH)₃ thereby leading to precipitation of the slightly insoluble Pb(OH)₂ (Soco and Kalemmbkiewicz, 2016). Thus, the high pH values must be avoided in this kind of metal ions removal. Soco and Kalemmbkiewicz (2016) also reported similar observation for Cd (II) ion and this could be attributed

**Table 3.** Thermodynamic values for Pb (II) and Cd (II) ions onto UCE and ECER

<table>
<thead>
<tr>
<th>Parameter</th>
<th>UCE Pb (II)</th>
<th>UCE Cd (II)</th>
<th>UCER Pb (II)</th>
<th>UCER Cd (II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH° (kJ/mol)</td>
<td>-11.201</td>
<td>-14.633</td>
<td>-20.671</td>
<td>10.613</td>
</tr>
<tr>
<td>ΔS° (kJ/mol)</td>
<td>-9.69E-03</td>
<td>-0.029</td>
<td>-0.043</td>
<td>0.047</td>
</tr>
<tr>
<td>ΔG° (kJ/mol)</td>
<td>-8.265</td>
<td>-5.846</td>
<td>-7.642</td>
<td>-3.628</td>
</tr>
</tbody>
</table>

**Fig. 10.** Van’t Hoff plots for UCE and ECER.

**Fig. 11.** Plots of metal ions removed (%) against pH.
to the likely formation of Cd(OH)$_2$ and Cd(OH)$^+$ since there was almost little or no competition from H$^+$ at pH 6.0 to 9.0.

**Conclusion**

*Cola lepida*da seeds are composed of twenty two chemical compounds confirmed from the GC-MS phytochemical analysis. The modification of *Cola lepida* seeds was successfully done using ethanediol acid as the modifying agent. The resins of *Cola lepida* in the unmodified and modified forms were very good, efficient and feasible adsorbents. All the adsorption process was mainly physisorption with mean free energy less than 8 kJ/mol. The adsorption process fitted well with the Freundlich adsorption isotherm model equation indicating that the resin had heterogeneous surface. The thermodynamic parameters showed that adsorption of Pb (II) and Cd (II) ions onto UCE and Pb (II) ion UCER was exothermic while the adsorption of Cd (II) ion onto ECER was endothermic and the standard entropy values for the adsorption of Pb (II) and Cd (II) ions onto UCE and Pb (II) ion on UCER was negative indicating that the degree of randomness reduced on the surfaces of the adsorbents while the adsorption of Cd (II) ion onto ECER was positive indicating that the degree of randomness increased on the surface of the adsorbent. The Gibbs free energy for the adsorption process was negative indicating that the adsorption process was reversible, spontaneous and feasible. The unmodified *Cola lepida* recorded a higher percentage removal of Pb (II) ion onto UCE than onto ECER at pH 4.0 while adsorption of Cd (II) ion onto ECER occurred at pH 6.0 to 8.0 and also recorded a higher percentage removal of Cd (II) ion onto ECER than UCE. However, for selective and quick removal of Pb (II) ion at pH 6.0 in the presence of competing metal ions that can be removed below pH 6.0, the ECER is recommended the best option for the adsorption. The difference in the adsorption of Cd (II) ion onto UCE and ECER was more pronounced especially under the influence of pH; hence Cd (II) ion onto ECER was significantly better than Cd (II) ion onto UCE at pH 6.0 to 8.0. However, UCE is best used in the adsorption of Cd (II) ion from aqueous medium at pH of 6.0 while above 6.0; ECER is a better option for the adsorption.

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**Conflict of Interest.** The authors declare no conflict of interest

**References**


