

Article

Kinetics and Physical Mechanism of Pb (II) and Cd (II) Ions Uptake from Aqueous Solution using Unmodified and Modified *Cola lepidota* Seed Extract as Adsorbents

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Abstract: The kinetics of Pb (II) and Cd (II) removal from aqueous media using unmodified *Cola lepidota* extract (UCE) and ethanedioic acid-modified *Cola lepidota* extract (ECE) was evaluated. The time-dependency tests on the adsorbent characteristics of the unmodified and modified propanone extract of *Cola lepidota* seed were performed at temperatures of 30, 40, 50, 60 and 70 °C. The experimentally resolved data between 10 and 90 min were applied to pseudo first-order, pseudo second-order and Elovich kinetic models. The pseudo second-order equation gave the best fit with correlation coefficient (R^2) of 0.9990 to 0.9998 within the tested range, indicating the greater influence of chemical adsorption in the process. The exothermic trend of the chemisorption process was reflected by the negative values of activation energy in the order: Pb (II) onto ECE > Cd (II) onto UCE > Pb (II) onto UCE > Cd (II) onto ECE. The physical mechanism of the process at 30 °C was verified by applying the generated data into film, mass transfer and intra-particle diffusion models. Results showed that the rate controlling step was mass transfer mechanism judging from its highest values of R^2 ; which signified that the energetics of the system experienced negligible resistance from the external and internal diffusion.

Keywords: pseudo second-order; *cola lepidota*; mass transfer; activation energy; ethanedioic acid; chemisorption

1. Introduction

The industrial revolution that started in Britain with the textile, iron and steel, transportation, communication, and other industries in the 18th and 19th century; spreading through Europe, USA and to the whole world brought about improved standard of living and pollution among other things [1]. The pollution resulting from industrialization gave rise to the introduction of both inorganic and organic pollutants into the environment; contaminating land, water and air, negatively affecting both the flora and fauna in the habitat. The inorganic pollutants are mainly metal ions while organic pollutants are usually dyes [2-4]. The metal ions are naturally distributed in the environment and very beneficial to plants and animals. However, above the permissible limits, these metal ions cause serious health challenges [5-7]. Cadmium and lead metal ions in particular causes hepatic encephalopathy, anemia, hearing loss, infertility, nephropathy, etc. [8]. Hence, the need to reduce metal ions contaminants to the permissible limit or to remove them completely from the environment especially from wastewater has become very necessary. Many methods like; electrolysis, coagulation, precipitation, solvent extraction, reverse osmosis, adsorption using activated carbon have been adopted for the remediation of heavy metal ions from wastewaters, but they are either too expensive or energy consuming or not environmentally friendly [9-12]. As such, in the recent past, research effort has been channeled towards the usage of agricultural waste and biological materials as adsorbents for the removal of metal ion contaminants from waste or heavy metal ions contaminated waters due to their effectiveness, ecologically friendly nature and cheapness among other advantages [13-15]. *Cola lepidota* of the malvaceae family and sterculioidae sub-family [16-17] are popularly called monkey kola; the bark, leaves and cotyledon are used for medicinal purposes while the fruit are consumed as food in West Africa [18]. Despite these uses, the fruit is still under-utilized especially for economic purposes considering its abundance during rainy season in West Africa [19]. Kinetic feasibility and mechanism characteristics of metal ion adsorption unraveled successfully at laboratory level with eco-compatible conditions using accessible low cost agro-waste are crucial to process design and management of the scale up application. The main goal of this study is to determine the reaction order and physical mechanism of *Cola lepidota* seed extract in the unmodified (UCE) and modified (ECE) forms as adsorbent in the removal of Pb (II) and Cd (II) ions from aqueous solutions; through studies using pseudo first-order, pseudo second-order, Elovich, film diffusion, mass transfer and intra-particle diffusion models. Resolutions from this investigation will be employed to abate the negative impacts on aquatic systems laden with Pb (II) and Cd (II) ions.

2. Materials and Methods

2.1. Pretreatment and Extraction of UCE

Large quantity of *Cola lepidota* were purchased from the mile-1 market in Port Harcourt, and identification of the fruit was carried out at the Herbarium of the Department of Plant Science and Biotechnology, University of Port Harcourt, Nigeria. The fruits were washed with de-ionized water and then cut open. The seeds were removed from the fruit, sorted and cut into smaller pieces. These seeds were air-dried for three weeks, pulverized, sieved (Newark, U.S.A standard test sieve: ASTM E-11 specification) to obtain an average particle size of 150 μm ; and labeled as Unmodified *Cola lepidota* seed powder (UC).

UC sample of 2550 g was subjected to extraction using soxhlet extractor, with propanone as the extractant. The propanone extract yield was approximately 10.03%. The extract was concentrated to obtain pasty sample by evaporation of the propanone from the propanone-extract mixture using rotor evaporator. The paste was transferred onto a filter paper, washed firstly with n-hexane and finally with water. The residue was dried at 50°C for 12hrs in an oven (JP Selecta Digiheat oven). The dried solid extract obtained was crushed into smaller particles, preserved in a tightly corked container and labeled as Unmodified *Cola lepidota* Extract (UCE).

2.2. Modification of Extract

Unmodified *Cola lepidota* Extract (UCE) of 22.5 g was weighed into a 500 ml beaker and 150 ml of de-ionized water was added and stirred for 30 min at 28 °C. 1.35 g of ethanedioic acid was added while stirring for another 10 min at an increased temperature of 50 °C. Then 37.5 ml of iodine solution (5 %w/v) was added with constant stirring at 50 °C for another 80 min and then cooled to 28 °C. Subsequently, 65 ml of saturated sodium thiosulphate pentahydrate was added and allowed to stand for 12 hrs at room temperature, which developed into two layers. The organic layer was decanted into a filter paper, and washed with 500 ml of distilled water. The residue was dried in an oven at 50 °C for 24 hrs. The product was stored in tightly capped bottle and labeled as Ethanedioic acid *Cola lepidota* Extract (ECE); and the infrared spectroscopic characterization was discussed previously [20].

2.3. Metal Ions Stock Solution Preparation

Stock solutions of 1,036.219 mgdm^{-3} Pb (II) ions and 1,124.4 mgdm^{-3} Cd (II) ions were prepared by dissolving $\text{Pb}(\text{NO}_3)_2$ (1.6564 g) and CdCl_2 (1.8336 g) in de-ionized water respectively, and made up to 1000 ml mark in separate volumetric flasks. The working solutions were further prepared into desired concentrations using the dilution formula. All the reagents used in this study were of analytical grade.

2.4. Kinetics Studies

UCE and ECE adsorption efficiency was determined by keeping concentration at 30 °C, while the time of agitation of the sorbents was varied. This was performed by adding 50 ml of 12.51 mgdm⁻³ Pb (II) ion (12.27 mgdm⁻³ Cd (II) ion) into a conical flask containing 50 mg of the UCE (or ECE). The mixture was firmly corked and attached to JP Selecta Vibromatic 7000384. The vibrator was set to 200 vibrations per min, and the samples were disengaged at the time intervals: 10, 20, 30, 40, 50, 60, 70, 80 and 90 min. The mixture was filtered and the concentration of the final metal ions quantified using Atomic Absorption Spectrophotometer (Buck scientific, model 210 VGP). This process was repeated at temperatures of 40, 50, 60 and 70 °C for the UCE and ECE. Thereafter, the percentage adsorption of Pb (II) and Cd (II) ions at equilibrium and adsorption capacity of UCE or ECE was calculated using equations 1 and 2 respectively [21-24].

$$\Delta[M^{n+}] = \left(\frac{C_i - C_f}{C_i}\right) \times 100 \quad (1)$$

Where $\Delta[M^{n+}]$ is the percentage adsorption of metal ion (%) or percentage concentration of metal ions removed, C_i and C_f are initial and final concentration in mg/L.

$$Q_t = \left(\frac{C_i - C_t}{m}\right) \times V \quad (2)$$

Where Q_t is the adsorption capacity of UCE or ECE at time, t (in mol/g), C_t is the remaining metal ions in the liquid phase after adsorption at t , m is mass of adsorbent in g, and V is the volume of adsorbate in L.

3. Results and Discussion

3.1. Contact Time Evaluation

The evaluation of equilibrium adsorption time was carried out with studies on the time of contact between 5 mg adsorbent and 50 ml adsorbate at 30 °C. The plots of effect of time on the uptake of Pb (II) and Cd (II) ions are presented in Figure 1.

Results in figure 1 revealed that the percentage adsorption was relatively fast and directly related to contact time at the initial stage of the process (that is, from 68.27 to 72.50 % within 60 min for Pb (II) onto UCE, from 72.34 to 78.10 % within 60 min for Pb (II) onto ECE, from 70.82 to 74.74 % within 50 min for Cd (II) onto UCE and from 79.63 to 84.52 % within 40 min for Cd (II) onto ECE). This is evidently due to the presence of vacant active sites on the adsorbent surface which were available for the

uptake of Pb (II) and Cd (II) ions. This period was followed by the saturation level, which is synonymous with equilibrium attainment. The saturation level reflected the maximum percentage uptake of metal ions with time ($\approx 73.78\%$ Pb (II) onto UCE at 70 min, $\approx 78.82\%$ Pb (II) onto ECE at 70 min, $\approx 75.88\%$ Cd (II) onto UCE at 60 min and $\approx 85.00\%$ Cd (II) onto ECE at 50 min), since no appreciable change in percentage adsorption was observed after this steadiness with increase in contact time. The trend on influence of contact time is: Pb (II) onto UCE < Cd (II) onto UCE < Pb (II) onto ECE < Cd (II) onto ECE. The higher rate of adsorption of Pb (II) and Cd (II) by ECE could be due to the increased number of active sites resulting from the modification of UCE with ethanedioic acid.

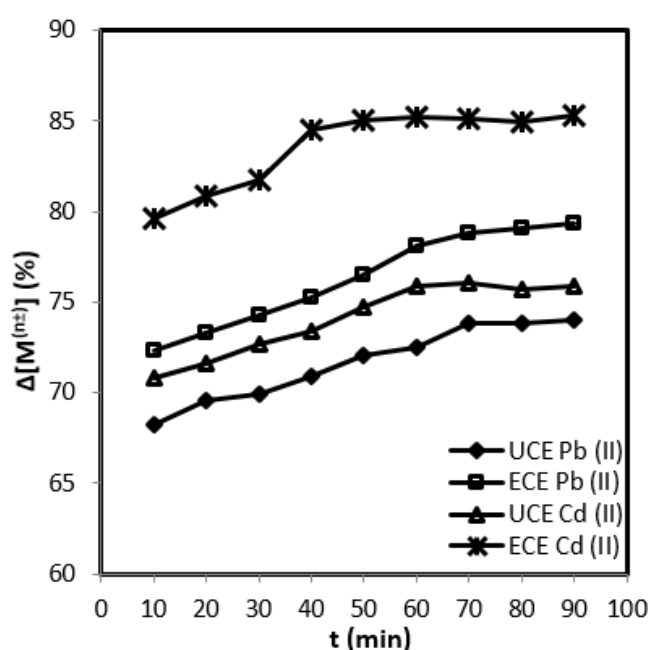


Figure 1. Percentage metal ion adsorption versus time for the adsorbents

3.2. Kinetic Modelling

Kinetic models were employed in this study to determine the rate of adsorption of Pb (II) and Cd (II) onto UCE and ECE. In view of this, the experimentally recorded data at temperatures of 30, 40, 50, 60 and 70 °C were subjected to the pseudo first-order, pseudo second-order and Elovich models.

The linearized form of the pseudo first-order kinetic model proposed by Lagergren [25-26] for adsorption is given as:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} t \quad (3)$$

Where Q_t and Q_e are adsorption capacity at time, t and equilibrium (mol g^{-1}) and k_1 (min^{-1}) is the rate constant. Q_e and k_1 were determined from the intercept and slope of the plot of $\log(Q_e - Q_t)$ versus time (Figures 2 to 5).

The pseudo second-order kinetic model equation was proposed by Ho and McKay [27-29] and is given in the linearized form as:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e} t \quad (4)$$

Where k_2 ($\text{g mol}^{-1} \text{min}^{-1}$) is the rate constant, the values of k_2 and Q_e were deduced from the slope and intercept of the plots of $\frac{t}{Q_t}$ versus time as presented in Figures 6 to 9.

The linearized form of Elovich model [30-31] is written as:

$$Q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (5)$$

The study was carried out by plotting Q_t versus $\ln t$ (Figures 10 to 13), from which the values of α and β were determined from the intercept and slope of the plots at different temperatures. The α is associated with chemisorption rate ($\text{mol g}^{-1} \text{min}$), while β is associated with extent of surface coverage and activation energy for chemisorption (g mol^{-1}) [32-33].

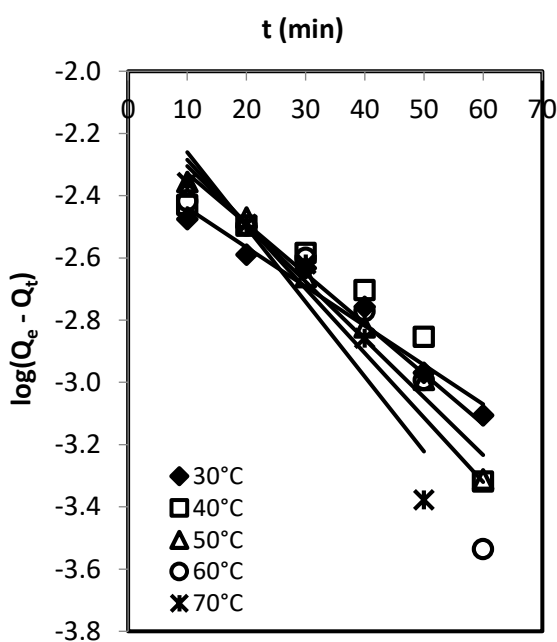


Figure 2. Pseudo first-order models for Pb (II) ion uptake by UCE

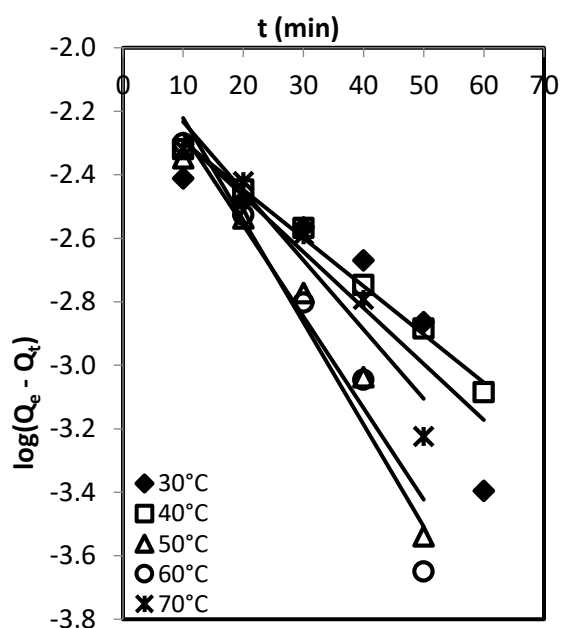


Figure 3. Pseudo first-order models for Pb (II) ion uptake by ECE

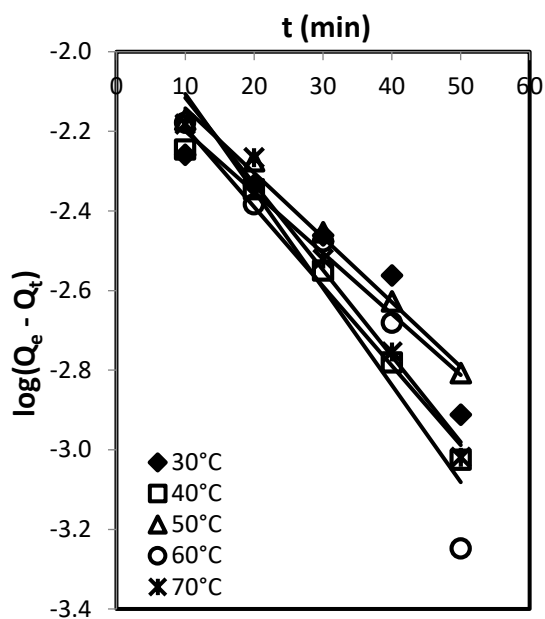


Figure 4. Pseudo first-order models for Cd (II) ion uptake by UCE

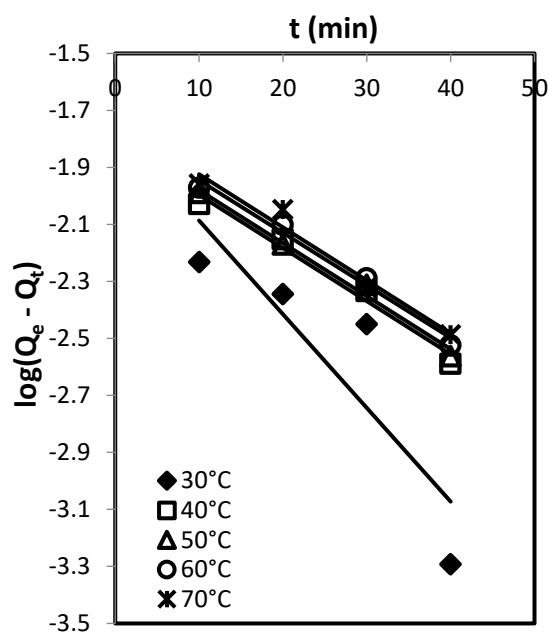


Figure 5. Pseudo first-order models for Cd (II) ion uptake by ECE

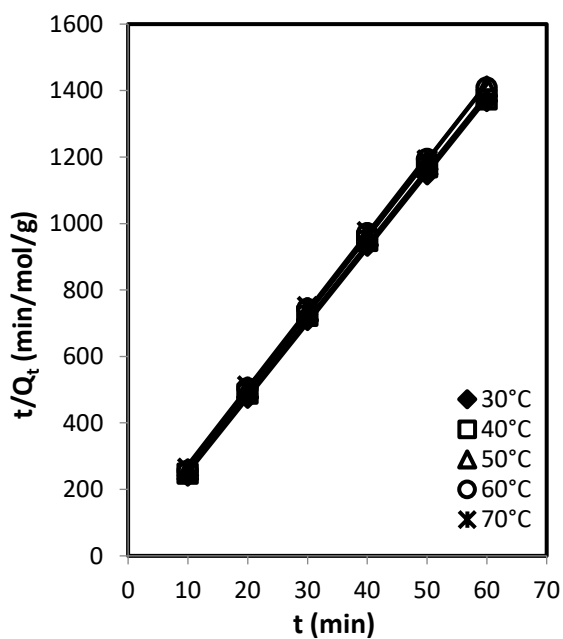


Figure 6. Pseudo second-order models for Pb (II) ion uptake by UCE

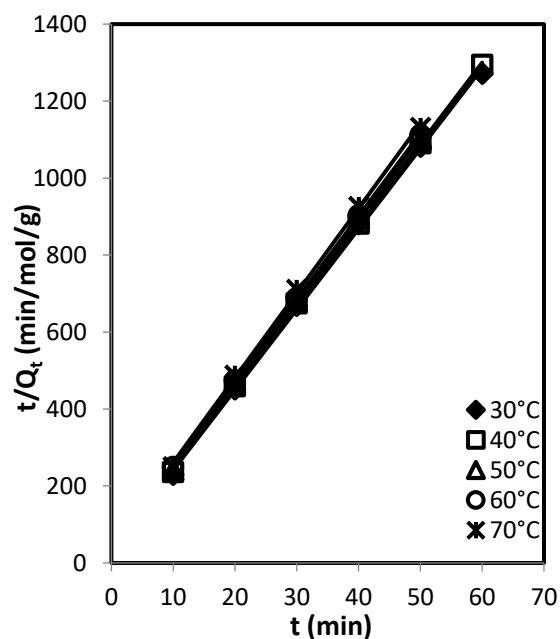


Figure 7. Pseudo second-order models for Pb (II) ion uptake by ECE

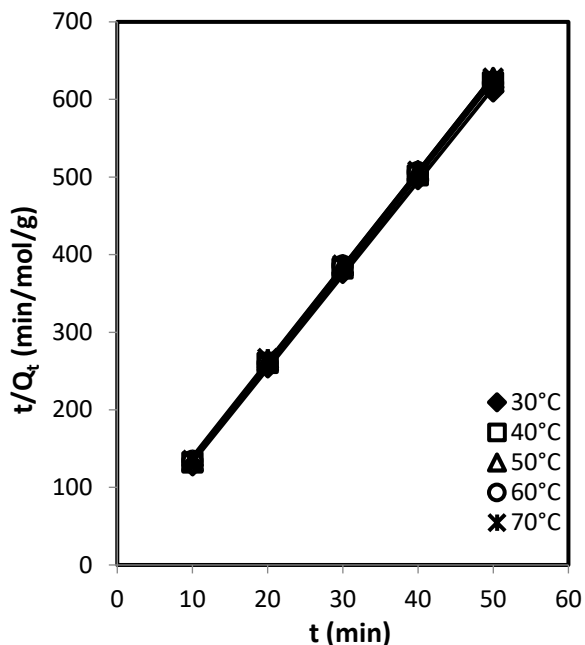


Figure 8. Pseudo second-order models for Cd (II) ion uptake by UCE

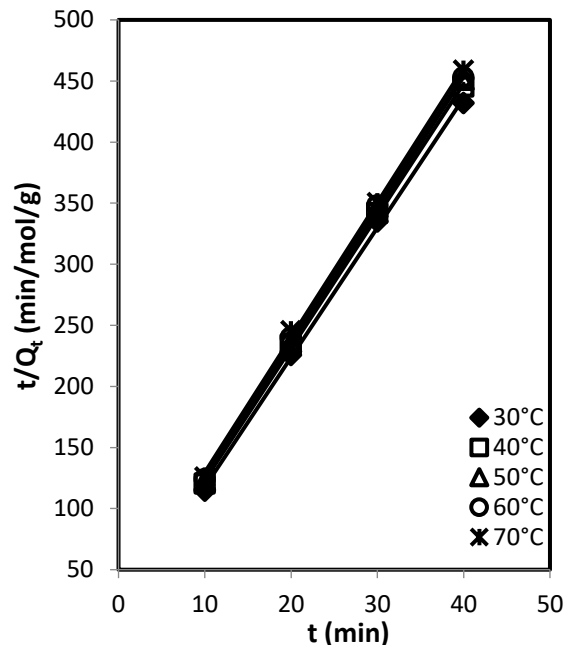


Figure 9. Pseudo second-order models for Cd (II) ion uptake by ECE

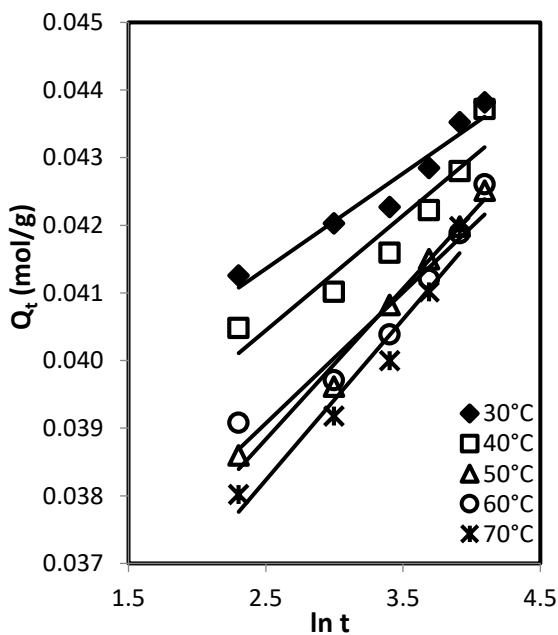


Figure 10. Elovich models for Pb (II) ion uptake by UCE

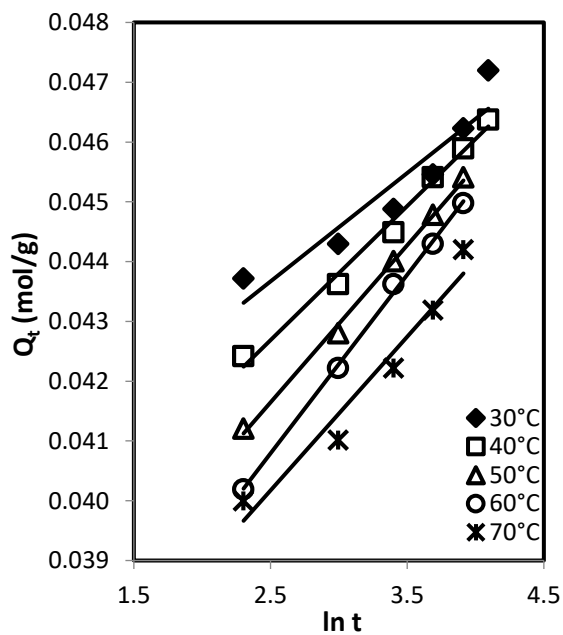


Figure 11. Elovich models for Pb (II) ion uptake by ECE

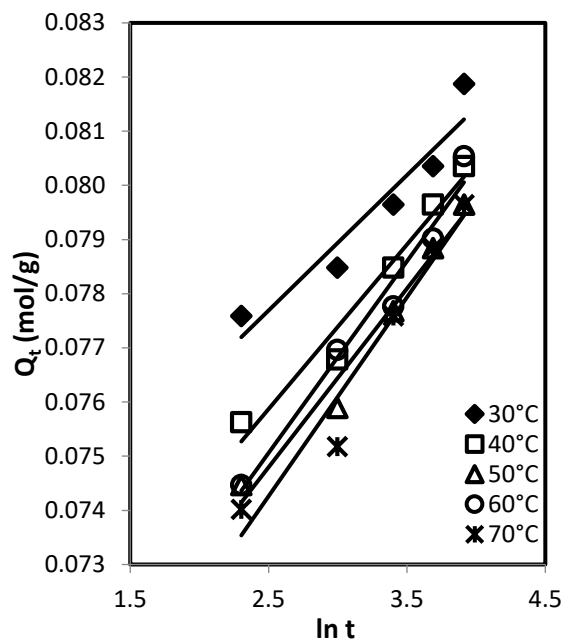


Figure 12. Elovich models for Cd (II) ion uptake by UCE

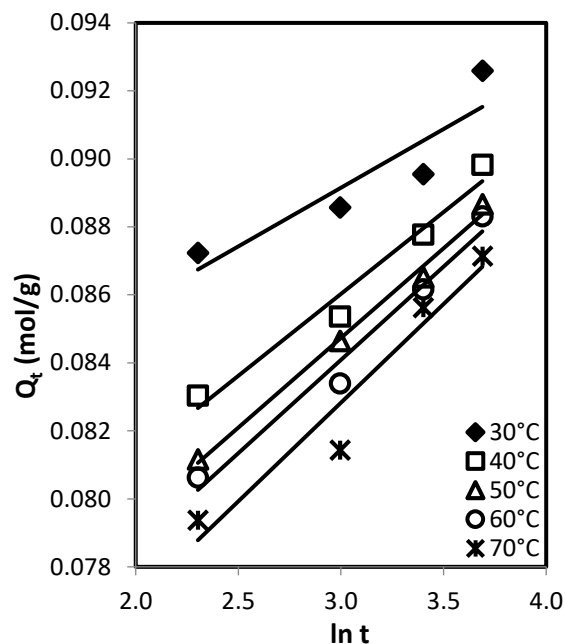


Figure 13. Elovich models for Cd (II) ion uptake by ECE

Table 1. Kinetic model constants and their R^2 values

Adsorbent	Temp. (°C)	$Q_e^{(calc)}$ (molg ⁻¹)	Pseudo 1 st order			Pseudo 2 nd order			Elovich		
			$Q_e^{(expt)}$ (molg ⁻¹)	k_1 (min ⁻¹)	R^2	$Q_e^{(expt)}$ (molg ⁻¹)	k_2 (gmol ⁻¹ min ⁻¹)	R^2	α (molg ⁻¹ min)	β (gmol ⁻¹)	R^2
UCE Pb (II)	30	0.0446	0.0049	0.029	0.9620	0.0444	19.834	0.9997	7.45E+08	714.29	0.9418
	40	0.0442	0.0068	0.037	0.8590	0.0443	14.740	0.9993	3.01E+06	588.24	0.8954
	50	0.0430	0.0076	0.043	0.9773	0.0435	13.455	0.9997	8.24E+03	454.55	0.9852
	60	0.0429	0.0084	0.048	0.8757	0.0434	13.304	0.9993	1.25E+05	526.32	0.9239
	70	0.0424	0.0096	0.055	0.9006	0.0431	12.909	0.9992	1.68E+03	416.67	0.9565
ECER Pb (II)	30	0.0476	0.0077	0.041	0.8310	0.0479	13.585	0.9992	4.89E+06	555.56	0.8825
	40	0.0472	0.0072	0.035	0.9929	0.0474	13.449	0.9998	4.64E+04	454.55	0.9889
	50	0.0457	0.0104	0.066	0.9598	0.0467	13.362	0.9998	1.90E+03	384.62	0.9972
	60	0.0452	0.0126	0.074	0.9537	0.0464	12.081	0.9998	1.99E+02	333.33	0.9983
	70	0.0448	0.0097	0.050	0.9266	0.0454	11.858	0.9992	1.11E+03	384.62	0.9525
	30	0.0831	0.0090	0.035	0.9032	0.0829	12.328	0.9996	6.33E+09	400.00	0.9125
UCE Cd (II)	40	0.0813	0.0102	0.046	0.9801	0.0818	11.178	0.9998	2.32E+07	333.33	0.9641
	50	0.0812	0.0105	0.037	0.9918	0.0812	10.390	0.9998	1.86E+06	303.03	0.9750
	60	0.0811	0.0137	0.056	0.8918	0.0820	9.558	0.9996	5.73E+05	285.71	0.9233
	70	0.0806	0.0126	0.050	0.9770	0.0815	9.080	0.9997	1.62E+05	270.27	0.9506
ECER Cd (II)	30	0.0931	0.0175	0.076	0.7711	0.0942	9.767	0.9990	2.10E+07	285.71	0.8300
	40	0.0924	0.0155	0.043	0.9759	0.0924	7.849	0.9995	1.44E+04	208.33	0.9684
	50	0.0914	0.0161	0.043	0.9866	0.0914	7.590	0.9997	2.34E+03	188.68	0.9930
	60	0.0913	0.0173	0.042	0.9843	0.0913	6.872	0.9995	1.20E+03	181.82	0.9764
	70	0.0904	0.0183	0.043	0.9680	0.0906	6.318	0.9992	4.58E+02	172.41	0.9343

The generated plots (Figures 2 to 13) using the three models were straight lined, and their fitness to the resolved data assessed based on the correlation coefficient (R^2) values which were found to be greater than 0.77 within the temperature range tested as presented in Table 1. The R^2 values for the pseudo second-order equation were highest, suggesting chemisorption as the rate determining step of the kinetic process at temperatures of 30, 40, 50, 60 and 70 °C.

Further perusal of the tabulation (Table 1), revealed that the experimentally deduced equilibrium adsorption capacity $\{Q_{e(\text{exp})}\}$ for the pseudo second-order process conformed relatively closer to the calculated equilibrium adsorption capacity $\{Q_{e(\text{calc})}\}$ when compared with that of pseudo first-order. This also confirmed the adsorption process to be in line with the assumptions of pseudo second-order model. The relatively high values of α and β at the studied temperatures for the adsorbents, suggest the controlling influence of chemical adsorption on the metal ions uptake process.

3.3. Activation Energy of Adsorption

The Arrhenius plot (Figure 14) of $\ln k_2$ against inverse temperature using equation 6 [34-35] was performed to deduce the values of activation energy (E_a) and pre-exponential factor (A) for the process.

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

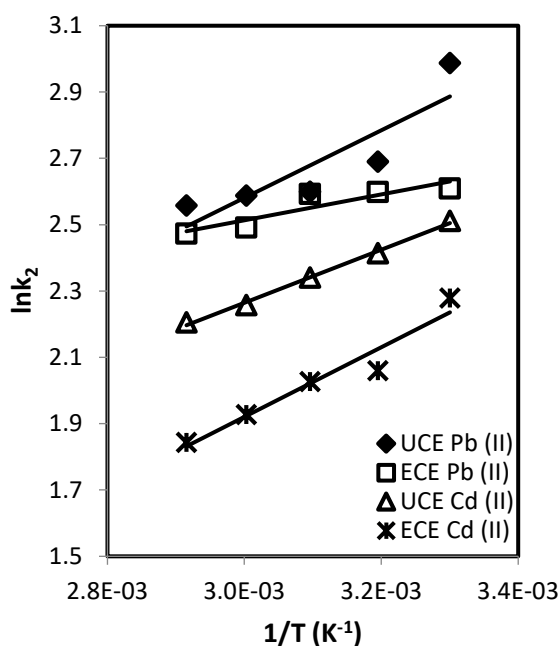


Figure 14. Arrhenius equation plots for the adsorbents

The values of E_a and A were computed from the slope and intercept of the plots of $\ln k_2$ against $1/T$ with universal gas constant (R) as $8.314 \text{ JK}^{-1}\text{mol}^{-1}$ for the adsorbents. The negative values of E_a (Table 2) for the Pb (II) and Cd (II) ions adsorption on UCE and ECE indicate the exothermic affinity of the chemisorption process [37]. The values of A are in the order: Pb (II) onto ECE > Cd (II) onto UCE > Pb (II) onto UCE < Cd (II) onto ECE.

Table 2. Values of Ea and A for the adsorption process

Adsorbent	Ea (Jmol ⁻¹)	A (gmol ⁻¹ min ⁻¹)
UCE Pb (II)	-8466.98	0.62
ECER Pb (II)	-3243.62	3.83
UCE Cd (II)	-6652.86	0.87
ECER Cd (II)	-8725.54	0.29

3.4. Adsorption Mechanism

The film, mass transfer and intra-particle diffusion models (equations 7, 8 and 9 respectively) were utilized to adequately correlate the experimental results at 30 °C to the determination of the mechanism of adsorption.

Boyd and co-workers [37] developed the film diffusion model given in equation 7 as follows:

$$\ln(1 - F) = D_f - k_p t \quad (7)$$

Where F is the fractional attainment of equilibrium at time, t ($F = \frac{Q_t}{Q_e}$), k_p (min⁻¹) is the film diffusion constant and D_f is the intercept. k_p and D_f were resolved from the slope and intercept of the linear plots of $\ln(1 - F)$ against t for the Pb (II) and Cd (II) ions uptake at 30 °C.

The mass transfer model [38] by Lo and his research team is given as:

$$\ln(C_o - C_t) = \ln D + K_o t \quad (8)$$

Where D is fitting parameter and K_o is a constant equal to $k_o m$; k_o is the mass transfer adsorption coefficient, while m is mass of UCE or ECE.

The intra-particle diffusion equation was proposed by Webber and Morris [39] as:

$$Q_t = k_{int} t^{1/2} + C \quad (9)$$

Where k_{int} (g/mol.min^{1/2}) is intra-particle diffusion rate constant and C is the possible boundary layer thickness [40]. C is zero when the adsorption is purely by intra-particle diffusion and large value of C reflects greater boundary layer effect on ion diffusion [41]. k_{int} and C were both determined from the slope and intercept of the plot of Q_t versus $t^{1/2}$.

The corresponding linear plots are depicted in Figures 15, 16 and 17 for film, mass transfer and intra-particle diffusion models respectively; while the values of R^2 and constants computed from the slopes and intercepts are presented in Table 3.

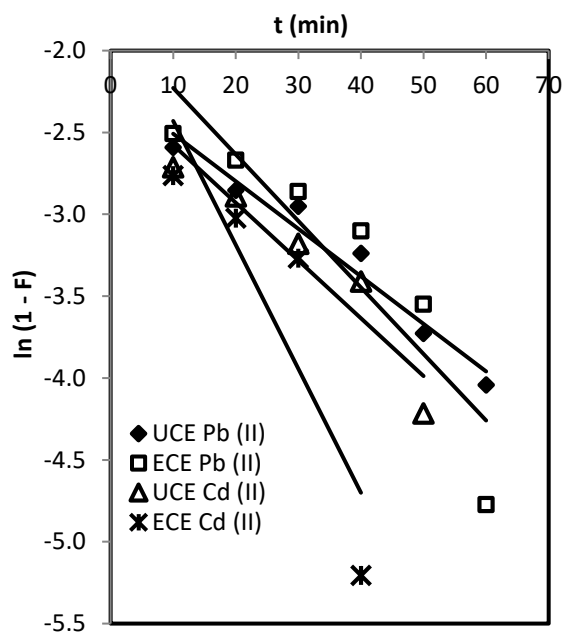


Figure 15. Film diffusion models for the adsorbents

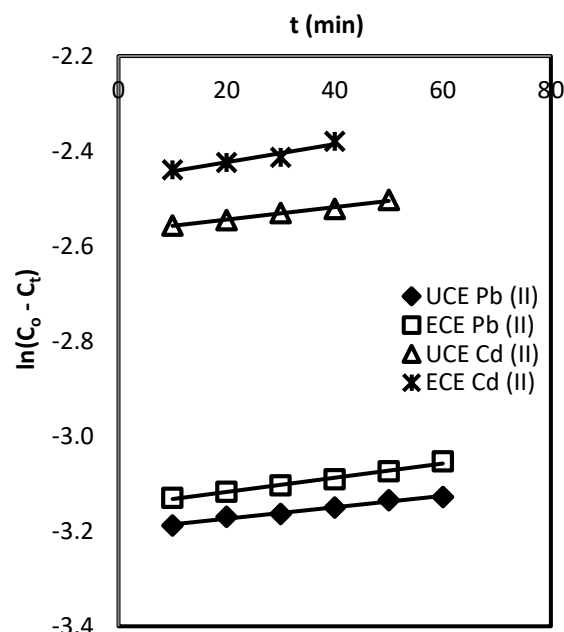


Figure 16. Mass transfer models for the adsorbents

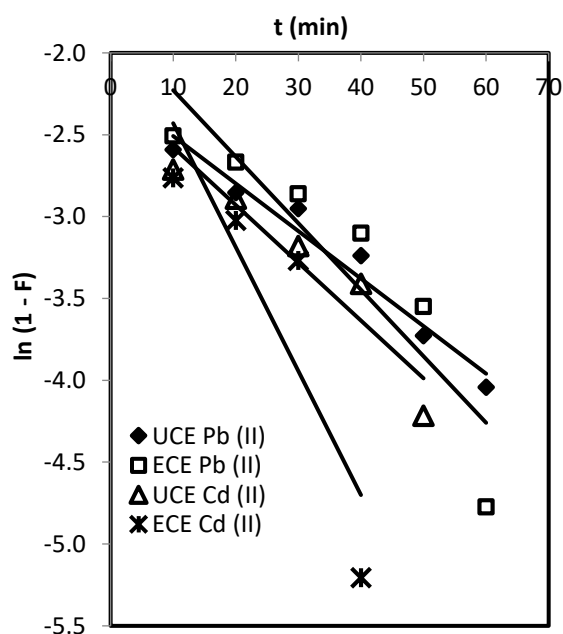


Figure 15. Film diffusion models for the adsorbents

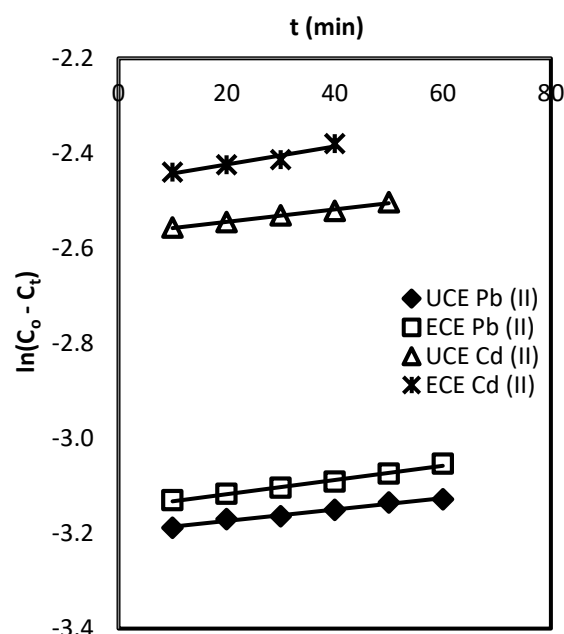


Figure 16. Mass transfer models for the adsorbents

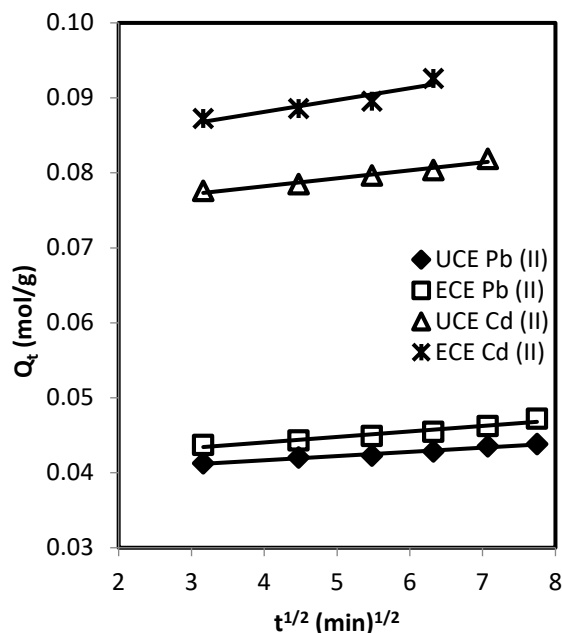


Figure 17. Intra-particle models for the adsorbents

Table 3. Values of R^2 and constants for the adsorption process

Adsorbent	Film diffusion			Mass transfer				Intra-particle diffusion		
	k_p (min^{-1})	D_f	R^2	K_o (min^{-1})	k_o (gmin^{-1})	D	R^2	k_{int} ($\text{molg}^{-1}\text{min}^{-1/2}$)	C (molg^{-1})	R^2
UCE Pb (II)	0.0290	-2.218	0.9620	0.0012	6.0×10^{-5}	0.0409	0.9833	0.0006	0.0394	0.9786
ECER Pb (II)	0.0406	-1.822	0.8310	0.0015	7.5×10^{-5}	0.0430	0.9900	0.0007	0.0411	0.9501
UCE Cd (II)	0.0353	-2.224	0.9032	0.0013	6.5×10^{-5}	0.0765	0.9894	0.0011	0.0740	0.9629
ECER Cd (II)	0.0757	-1.673	0.7711	0.0019	9.5×10^{-5}	0.0853	0.9390	0.0016	0.0818	0.8894

The observed trend for the R^2 values is: mass transfer > intra-particle diffusion > film diffusion, which suggested that the energetics of the system was in line with diffusion and mass transport by convection during the process of adsorption [42]. The trend of the values of mass transfer adsorption coefficient are 6.0, 7.5, 6.5 and 9.5×10^{-5} gmin^{-1} for Pb (II) onto UCE, Pb (II) onto ECE, Cd (II) onto UCE and Cd (II) onto ECE respectively. However, the values of intercept from the linear patterned intra-particle diffusion plots are above zero and in the order: 0.0394 {Pb (II) onto UCE} < 0.0411 {Pb (II) onto ECE} < 0.0740 {Cd (II) onto UCE} < 0.0818 {Cd (II) onto ECE}. These findings indicate the occurrence of boundary layer diffusion to some extent and that the rate controlling mechanism is not purely intra-particle diffusion, since the plot of Q_t versus $t^{1/2}$ for the adsorbents did not pass through the point of origin. On the whole assessment, the mass transfer mechanism was predominant, indicating that the driving force for collision and movement of molecular species were not obstructed or hindered in the reaction medium.

4. Conclusion

This batch studies have revealed the capability of unmodified and ethanedioic acid-modified *Cola lepidota* seed extract in the removal of Pb (II) and Cd (II) ions from aqueous media at different temperatures and times of contact. The optimal percentage removal at 30 °C was achieved within contact time of 70, 70, 60 and 50 min for Pb (II) onto UCE, Pb (II) onto ECE, Cd (II) onto UCE and Cd (II) onto ECE respectively. In all cases studied, the adsorption of Pb (II) and Cd (II) ions were found to decrease with increase in temperature in the order: 30 > 40 > 50 > 60 > 70 °C. The kinetics of contact between the adsorbent (5 mg) and adsorbate (50 ml) was best described by pseudo second-order model. The Arrhenius plots using the kinetic data gave pre-exponential factor of the process as 0.62, 3.83, 0.87 and 0.29 $\text{gmol}^{-1}\text{min}^{-1}$ for Pb (II) onto UCE, Pb (II) onto ECE, Cd (II) onto UCE and Cd (II) onto ECE respectively. The minimum amount of energy required for the process of metal ion uptake was reflected in the values of activation energy as -8.467, -3.244, -6.653 and -8.726 kJmol^{-1} for Pb (II) onto UCE, Pb (II) onto ECE, Cd (II) onto UCE and Cd (II) onto ECE respectively. Analyses of R^2 values from modeled plots of film, mass transfer and intra-particle diffusion, indicated the predominance of mass transfer mechanism of ions in the process.

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References

- [1] Giri, S.; Singh, A.K. Risk assessment, statistical source identification and seasonal fluctuation of dissolved metals in the Subarnarekha River, India. *J. Hazard. Mater.* **2014**, 265: 305-314.
- [2] Yang, M. A current global view of environmental and occupational cancers. *J. Environ. Sci. Health C* **2011**, 29: 223-249.
- [3] Saadi, R.; Saadi, Z.; Fazaeli, R.; Fard, N.E. Monolayer and multilayer adsorption isotherm models for sorption from aqueous media. *Korean J. Chem. Eng.* **2015**, 32: 787-799.
- [4] Ibezim-Ezeani, M.U.; Akaranta, O. Diffusion dynamics of metal ions uptake at the carboxylated-epichlorohydrin red onion skin extract resin-aqueous interface. *Int. J. Eng. Res. Application*, **2017**, 7: 46-52.

- [5] Dada, A.O.; Olalekan, A.P.; Olatunya, A.M.; Dada, O. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms studies of equilibrium sorption of Zn^{2+} unto phosphoric acid modified rice husk. *IOSR J. Appl. Chem.* **2012**, 3: 38-45.
- [6] Ibezim-Ezeani, M.U.; Okoye, F.A.; Akaranta, O. Equilibrium studies of metal ions onto modified orange mesocarp extract in aqueous solution. *American Chem. Sci. J.* **2012**, 2: 25-37.
- [7] Sekar, M.; Sakthi, V.; Rengaraji, S. Kinetics and equilibrium adsorption Study of lead (II) onto activated carbon prepared from coconut shell. *J. Colloid Interface Sci.* **2004**, 279: 307-313.
- [8] Menke, A.; Muntner, P.; Silbergeld, E.K.; Platz, E.A.; Guallar, E. Cadmium levels in urine and mortality among US adults. *Environ. Health Perspectives*, **2009**, 117: 190.
- [9] Xiangliang, P.; Jialong, W.; Daoyong, Z. Biosorption of Pb(II) by *Pleurotus ostreatus* immobilized in calcium alginate gel. *Process Biochem.* **2005**, 40: 2799-2803.
- [10] Gurgel, L.V.A.; Freitas, R.P.D.; Gil, L.F. Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by sugarcane bagasse and mercerized sugarcane bagasse chemically modified with succinic anhydride. *Carbohydrate Polymer*, **2008**, 74: 922-929.
- [11] Ng, C.Y.; Cheung, W.H.; McKay, G. Equilibrium studies of the sorption of Cu(II) ions onto chitosan. *J. Colloid Interface Sci.* **2002**, 255: 64-74.
- [12] Singha, A.S.; Guleria, A. Utility of chemically modified agricultural waste okra biomass for removal of toxic heavy metal ions from aqueous solution. *Eng. Agric. Environ Food*, **2015**, 8: 52-60.
- [13] Wan N.W.S.; Hananfiah, M.A.K.M. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. *Bioresour. Technol.* **2008**, 99: 3935-3948.
- [14] Abdel-Halim, E.S.; Al-Deyab, S.S. Removal of heavy metal ions from aqueous solution through adsorption onto natural polymers. *Carbohydrate Polymer* **2011**, 84: 454-258.
- [15] Dhiraj, S.; Mahajan, G.; Kaur, M.P. Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – a review. *Bioresour. Technol.* **2008**, 99: 6017-6027.
- [16] Akinnifesi, F.K.; Sileshi, G.; Ajayi, O.C.; Tchoundjeu, Z. Indigenous fruit tree domestication. Indigenous fruit trees in the tropics: Domestication, utilization and commercialization. *Wallingford, UK, CABI*, **2007**.
- [17] Ogbu, J.U.; Umeokechukwu, C.E. Aspects of fruit biology of three wild edible monkey kola species fruits (*Cola spp: Malvaceae*). *Annual Res. Review Bio.* **2014**, 4: 2007-2014.
- [18] Egbe, A.E.; Tabot, P.T.; Fonge, B.A. Ethnobotany of some selected tree species in southwest Cameroon. *Ethnobotany Res. Applications* **2012**, 10: 235-246.

- [19] Ogbu, J.U.; Essien, B.A.; Kadurumba, C.H. Nutritional value of wild *Cola spp.* (monkey kola) fruits of southern Nigeria. *Nigeria J. Horticultural Sci.* **2007**, 12: 113-117.
- [20] Ibezim-Ezeani, M.U.; Pat-Okunbor, A.E.; Obi, C. Comparative investigation on fourier transform infrared spectra of unmodified, extract and modified *Cola lepidota* seed. *J. Scientific Eng. Res.* **2017**, 4: 1-6.
- [21] Fasoto, T.S.; Arawande, J.O.; Akinnusotu, A. Adsorption of Zinc and Chromium ions from aqueous solution onto sugarcane bagasse. *Int. J. Modern Chemistry* **2014**, 6: 28-47.
- [22] Chandra, T.C.; Mirna, M.M.; Sudaryanto, Y.; Ismadji, S. Adsorption of basic dye onto activated carbon prepared from durian shell: Studies of adsorption equilibrium and kinetics. *Chem. Eng. J.* **2007**, 127: 121-129.
- [23] Orji, I.; Ibezim-Ezeani, M.U.; Akaranta, O. Utilisation of red onion skin extract for remediation of lead (II) and cadmium (II) ions from aqueous solution. *Int. J. Enhanced Res. Sci. Technol. Eng.* **2016**, 5: 283-291.
- [24] Coskun, A.; Yildiz, A.; Delibas, A. Removal of methylene blue using fast sucking adsorbent. *J. Mater. Environ. Sci.* **2017**, 8: 398-409.
- [25] Qu, Y.; Zhang, C.; Li, F.; Bo, X.; Liu, G.; Zhou, Q. Equilibrium and kinetics study on the adsorption of perfluorooctanoic acid from aqueous solution onto powdered activated carbon. *J. Hazard. Mater.* **2009**, 169: 146-152.
- [26] Kumar, N.S.; Min, K. Phenolic compounds biosorption onto *schizophyllum commune* fungus: FTIR analysis, kinetics and adsorption isotherms modeling. *Chem. Eng. J.* **2011**, 168: 562-571.
- [27] Liu, W.; Yang, L.; Xu, S.; Chen, Y.; Liu, B.; Li, Z.; Jiang, C. Efficient removal of hexavalent chromium from water by an adsorption-reduction mechanism with sandwiched nanocomposites. *RSC Advances*, **2018**, 8: 15087-15093.
- [28] Ho, Y. S.; McKay, G. Pseudo-second order model for sorption processes. *Process biochem.* 1999, 34: 451-465.
- [29] Tang, B.; Lin, Y.; Yu, P.; Luo, Y. Study of aniline / ϵ -caprolactam mixture adsorption from aqueous solution onto granular activated carbon: Kinetics and equilibrium. *Chem. Eng. J.* **2012**, 187: 69-78.
- [30] Bulut, E.; Özacar, M.; Şengil, İ.A. Adsorption of malachite green onto bentonite: equilibrium and kinetic studies and process design. *Microporous Mesoporous mater.* **2008**, 115: 234-246.
- [31] Sánchez-Galván, G.; Ramírez-Núñez, P.A. Cationic dye biosorption by *salvinia minima*: Equilibrium and kinetics. *Water Air Soil Pollut.* **2014**, 225: 2008.
- [32] Teng, H.; Hsieh, C.T. Activation energy for oxygen chemisorption on carbon at low temperatures. *Ind. Eng. Chem. Res.* **1999**, 38: 292-297.

- [33] Aroua, M.K.; Leong, S.P.P.; Teo, L.Y.; Yin, C.Y.; Daud, W.M.A.W. Real-time determination of kinetics of adsorption of lead (II) onto palm shell-based activated carbon using ion selective electrode. *Bioresour. Technol.* **2008**, 5786-5792.
- [34] Chakraborty, S.; Chowdhury, S.; Saha, P.D. Insight into biosorption equilibrium, kinetics and thermodynamics of crystal violet onto *ananas cosmosus* (pineapple) leaf powder. *Appl. Water Sci.* **2012**, 2: 135-141.
- [35] Kara, A.; Osman, B.; Göçenoğlu, A.; Beşirli, N. Kinetic, isothermal, and thermodynamic studies of Cr(VI) adsorption on L-tryptophan-containing microspheres. *Environ. Eng. Sci.* **2014**, 31: 261-271.
- [36] Ibezim-Ezeani, M.U.; Orji, I. Kinetic and equilibrium studies on lead(II) ion removal from aqueous solution using succinic acid modified red onion skin extract. *Int. J. Sci. Eng. Technol. Res.* **2017**, 6: 367-374.
- [37] Al-Anber, M.A. Adsorption properties of aqueous ferric ion on natural cotton fiber: kinetic and thermodynamic studies. *Desalin. Water Treat.* **2013**, 1-12.
- [38] Qadeer, R.; Akhtar, S. Kinetics study of lead ion adsorption on active carbon. *Turk J. Chem.* **2005**, 29: 95-99.
- [39] Li, Y.; Du, Q.; Liu, T.; Sun, J.; Jiao, Y.; Xia, Y.; Xia, L.; Wang, Z.; Zhang, W.; Wang, K.; Zhu, H.; Wu, L. Equilibrium, kinetic and thermodynamic studies on the phenol onto graphene. *Mater. Res. Bull.* **2012**, 47: 1898-1904.
- [40] Quiton, K. G.; Doma, B.; Futalan, C.M.; Wan, M. Removal of chromium (VI) and zinc (II) from aqueous solution using kaolin-supported bacterial biofilms of gram-negative *e.coli* and gram-positive *staphylococcus epidermidis*. *Sustainable Environ. Res.* **2018**, 28: 206-213.
- [41] Munagapati, V.S.; Yarramuthi, V.; Nadavala, S.K.; Alla, S.R.; Abburi, K. Biosorption of Cu(II), Cd(II) and Pb(II) by *acacia leucocephala* bark powder: Kinetics, equilibrium and thermodynamics. *Chem. Eng. J.* **2010**, 157: 357-365.
- [42] Aikpokpodion, P.E.; Osobamiro, T.; Atewolara-Odule, O.C.; Oduwole, O.O.; Ademola, S.M. Studies on adsorption mechanism and kinetics of magnesium in selected cocoa growing soils in Nigeria. *J. Chem. Pharm. Res.* **2013**, 5: 128-139.