

Kinetic Study of Pb^{2+} , Cr^{6+} , Zn^{2+} and Fe^{3+} from Aqueous Solution Using Unmodified and Oxalic Acid Modified Cassava (*Manihot esculenta crantz*) Peel Waste Powder

Kanu Chidinma Queeneth, Adowei Pereware*

Department of Pure and Industrial Chemistry, Faculty of Science, University of Port Harcourt, Choba Port Harcourt, Nigeria

Email address:

pereware.adowei@uniport.edu.ng (Adowei Pereware)

*Corresponding author

To cite this article:

Kanu Chidinma Queeneth, Adowei Pereware. Kinetic Study of Pb^{2+} , Cr^{6+} , Zn^{2+} and Fe^{3+} from Aqueous Solution Using Unmodified and Oxalic Acid Modified Cassava (*Manihot esculenta crantz*) Peel Waste Powder. *Advances in Applied Sciences*.

Vol. 8, No. 3, 2023, pp. 60-69. doi: 10.11648/j.aas.20230803.11

Received: May 28, 2023; Accepted: June 20, 2023; Published: July 6, 2023

Abstract: Adsorption kinetic study provides understanding into reaction rate and mechanism of sorption during adsorption process. This research investigated the adsorption kinetics of the removal of Pb^{2+} , Cr^{6+} , Zn^{2+} and Fe^{3+} in aqueous solution using unmodified and oxalic acid modified cassava peel waste powder (CPP) using standard methods. Data obtained for the effect of agitation time revealed that within 30-60 minutes, both the unmodified and oxalic acid modified cassava peel powder (CPP) were able to remove 94% Pb^{2+} , 80% Cr^{6+} , 96% Zn^{2+} and 82% Fe^{3+} respectively. The experimental data were evaluated in terms of intra-particle diffusion coefficient and rate of adsorption, thus comparing transport mechanism and sorption process and found it to be 7.55 ± 0.05 mg/g for Pb^{2+} , 6.4 mg/g and 6.39 ± 0.05 mg/g for Cr^{6+} , 7.32 mg/g and 7.45 ± 0.01 mg/g for Zn^{2+} , 6.74 mg/g and 6.48 ± 0.12 mg/g for unmodified and differentially modified respectively. Results from the experiment shows that the pseudo-second order model appropriately describes the kinetic process which supports chemisorption ($R^2 > 0.99$) value. There was no significant effect on removal by oxalic acid modification. The result further revealed that cassava peel powder can remove heavy metal ions from solution and this can be applied in waste water treatment operations.

Keywords: Adsorption, Kinetics Study, *Manihot esculenta crantz*, Cassava Peel Wastes

1. Introduction

Heavy Metals are a threat to the environment and public health. Various industrial applications [1] and natural occurrences [2] have caused widespread distribution of heavy metals in the environment; and this has raised anxieties over their bad effects on man and his environment. Heavy metals, unlike organic pollutants, are nonbiodegradable and are persistent in the environment making their treatment a challenge [3]. Because of their toxicity, heavy metals are currently faced with rigorous measures for maximum allowable limits of their discharge into the environment [4]. Authorities imposing these measures require that treatment methods should be environmentally friendly so as to safeguard public health and the environment [5]. Conventional techniques for removing heavy metals in wastewater such as membrane separation, chemical

precipitation, ion-exchange, extraction, electro-dialysis and electrolytic extraction have limited applications such as incomplete removal, high cost, huge energy requirements and production of secondary waste [6]. These methods are costly and not too proficient in meeting treatment objectives. Adsorption came as a better substitute [7]. Agricultural waste products have been extensively studied in relation to the adsorption process. These agro-by-products are used in the natural and modified form. In the natural form, the product is washed, ground and sieved until reaches the desired particle size and subsequently used in adsorption tests. While, in the modified form, the product is pre-treated by-means of well-known modification techniques [8]. The goal of these pretreatments is to enhance and reinforce the functional group potential and, consequently, increase the number of active sites. Several researchers and co-workers [9-15] investigated the use of many unmodified and modified

agricultural wastes as adsorbents for the removal of inorganic (heavy metals) and organic (dyes) contaminants from wastewater. Other agricultural solid wastes from cheap and readily available resources such as orange peel [16-20], pomelo peel [21], garden grass [22], mandarin peel [23], garlic peel [24], grapefruit peel [25], mango peel waste [26], muskmelon peel [27], potato peel [28], rice straw [29, 30], and almond shell [31] have also been investigated for the removal of numerous heavy metals and dyes from aqueous solutions.

However, information on the use of unmodified and modified cassava wastes [32] are scanty. Cassava (*manihot esculenta crantz*) is the third-largest source of starch. It is a significant essential food in unindustrialized nations [33]. More than 228 million tons of cassava were produced worldwide in 2007, of which Africa accounted for 52%. In 2007, Nigeria produced 46 million tons making it the world's largest producer, because of its highly varied applications, processing of cassava gained remarkable consideration in recent years [34]. The preparation of cassava for consumption purposes produces wastes such as peelings which create a lot of conservational problems. So far, not much effort is made to manage the enormous waste arising from processing cassava tuber into its various products, which are abundant all seasons.

Hence, the objective of this study is to evaluate kinetic study for the removal of Pb²⁺, Cr⁶⁺, Zn²⁺ and Fe³⁺ from aqueous solution using unmodified and oxalic acid modified cassava (*Manihot esculenta crantz*) peel powder.

2. Materials and Method

Sample Collection: The cassava tubers used for this project work were got from traders in Choba market near University of Port Harcourt in Rivers State and identified in the department of plant science and Biotechnology University of Port Harcourt.

Sample Preparation: The obtained cassava was cut into small pieces, washed to get rid of sand and dirt particles and were peeled to get the powders. The air-dried cassava peel powder was further dried in oven (Gallenkamp, model OV-160 England) at 105°C to a particular weight and pulverized with a grinder to get a standardized particle size.

Preparation of Cassava Peel Powder: The ground cassava peel powder (CPP) was soaked in 0.1M HNO₃ acid for 48 hours so that all metals contained in the CPP could be removed, followed by a thorough wash with distilled water. The washing continued until the filtrate gave a negative EDTA test for heavy metal ions, by adding 5 drops of 0.01M EDTA solution and 2ml of NH₄Cl buffer to 5ml of the filtrate. Blue color of EDTA solution showed no presence of metal ions. The Cassava peel paste was dried at 45°C in oven, and meshed. The portion with size <100µm was taken for use and was kept in clean air-tight plastic containers for use.

Preparation of Modified Cassava Peel Powder: 10 ± 0.12 grams of the cassava peel powder (CPP) was weighed into 250ml beakers and was modified with 250ml of 0.5 M of

oxalic acid solution respectively with one portion left unmodified. The mixture was shaken for six hours at 30°C and was kept stable overnight, discarding the filtrate and the Cassava Peel paste was air-dried to obtain the modified cassava peel powder (CPP).

Effect of Contact Time: Exactly one gram (1.0 g) of unmodified and oxalic acid modified samples were weighed separately and placed in six 100 mL plastic bottles. 20 mL of metal ions solution of concentration 200 mg/L of pH 6.02 was added to the plastic bottles and tightly closed. The plastic bottles were agitated for 5 seconds. The mixtures of adsorbent and metal solutions were then shaken together at the allowed contact times of 10, 20, 30, 40, 50, and 60 minutes at 100rpm. At the end of each agitation time, the solutions centrifuged for 10 min at 1500 rpm and filtered. The remaining metal ions concentration in 5 ml of the filtrates was evaluated using a flame Atomic Absorption Spectrometer (AA-7000 Shimadzu). The wavelength at which lead, Cr⁶⁺, zinc and Fe³⁺ were analyzed was 283.9 nm, 350 nm, 213.9 nm, and 510 nm respectively. Standard solution of 1000 mg/L of Pb, Cr, Zn and Fe was used to create a standard calibration curve. The calibration curve was determined using serial dilution (0.0, 0.5, 1.0, and 2 mg/L).

Experimental Data Evaluation

The metal uptake capacity (q_e) and the adsorption percentage (R) were calculated using the following equations:

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

The percentage metal ion adsorbed by CPP i.e. adsorption efficiency

$$\% R = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

Where

C_o = initial heavy metal concentration (mg/l),

C_e = equilibrium or final heavy metal concentration in the solution (mg/l),

q_e = metal adsorbed at equilibrium (mg/g),

M = Adsorbent mass (g),

V = Solution Volume in (L).

Kinetic Treatment of Experimental Data: Adsorption kinetics were investigated to determine the adsorptive absorption of metal ions from aqueous at various time intervals. In this study, the adsorption of heavy metal ions was modeled using pseudo-first order, pseudo-second order kinetic and intraparticle diffusion models on waste rubber tires adsorbent [30]. When plotted, the linear form of each model indicates if the model is favorable to define the sorption process or not.

Pseudo-First Order: The pseudo –first order kinetic equation is as follows:

$$dq_t = k_1 \frac{q_e - q_t}{dt} \quad (3)$$

Integrating equation 3 using boundary conditions t = 0 and q_t = q_e gives.

$$\log(q_e - q_t) = \log \frac{q_e}{2.303} - k_1 t \quad (4)$$

Where q_e is the amount of metal ion adsorbed per gram of CPP (mg/g), q_t , amount of metal ion adsorbed at time t (mg/g) and k_1 is the rate constant of pseudo first order (min^{-1}). To determine the rate constants, plots of $\log (q_e - q_t)$ against t for metals at 30°C were made. The rate constants, k_1 and correlation coefficients (R^2) values of the metals were calculated from the plots.

Pseudo-Second Order Model: The adsorption capacity is relative to number of binding spots occupied on the adsorbent; the kinetic rate law can be written as:

$$dq_t = k_2 (q_e - q_t)^2 \quad (5)$$

k_2 is rate constant of adsorption ($\text{g/mg} \cdot \text{min}.$), q_e , amount of metal ion adsorbed at equilibrium (mg/g), q_t = amount of metal ion adsorbed at time, t (mg/g).

Separation of the variables in equation 5.

$$dq_t = \frac{k_2}{(q_e - q_t)^2} dt \quad (6)$$

Integrating equation 6 gives

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_t} t \quad (7)$$

Which is Pseudo-Second order rate law. The initial adsorption rate, is described by the constant (h_0) as;

$$h_0 = k_2 q_e^2 \quad (8)$$

The initial rate, h_0 , amount adsorbed at equilibrium, q_e , rate constant, K_2 and the coefficient of determination (R^2) were calculated from slope and intercept of plot of t/q_t versus t .

Weber-Morris Intra-Particle Diffusion Model: Intra-particle diffusion was analyzed using the Weber-Morris model equation.

$$q_t = kt^{0.5} + C \quad (9)$$

Where k is the rate constant ($\text{mg g}^{-1} \text{min}^{-0.5}$) and C , is thickness of boundary layer, if Weber- Morris plot of q_t versus $t^{0.5}$ is linear, adsorption is measured by surface diffusion only. However multiple plots show two or more steps are responsible for adsorption.

Elovich Model: In adsorption, decreases in rate due to increase in surface coverage is a function of time, the Elovich Model explains such conditions [28, 35].

$$q_t = \frac{1}{k} \ln(t + t_0) - \frac{1}{k} \ln t_0 \quad (10)$$

Where $t_0 = a \frac{1}{k}$ If $t > t_0$, this is further simplified as

$$q_t = \frac{1}{k} \ln(ab) + \frac{1}{k} \ln t \quad (11)$$

The Elovich model equation was applied to results from experiment by plotting q_t versus $\log t$, after simplifying natural log of equation 11 to \log_{10} as;

$$\log q_t = a + 2.303 k \log t \quad (12)$$

Statistical Evaluation of Experimental Data: Mean, Standard deviation and Analysis of Variance (ANOVA) was employed in the evaluation of experimental data.

3. Results and Discussion

Elemental Composition of Cassava Peel Powder: The data in table 1 shows the detected elements originally present in the cassava peel powder ascertained using Atomic Adsorption spectroscopy, which shows the amount of different metals in microgram per gram sample.

Table 1. Elemental Composition of Cassava Peel Powder.

Elements	Concentration $\mu\text{g g}^{-1}$
Calcium (Ca)	420.50
Potassium (K)	141.22
Cadmium (Cd)	0.32
Manganese (Mn)	9.50
Magnesium (Mg)	195.57
Lead (Pb)	0.01
Chromium (Cr)	0.01
Zinc (Zn)	1.90
Iron (Fe)	3.28

Effect of Contact Time on Removal Efficiency of Unmodified and Modified Cassava Peel Powder for Fe^{3+} , Zn^{2+} , Cr^{6+} and Pb^{2+} : The removal efficiency of unmodified and oxalic acid modified cassava peel powder for Fe^{3+} , Zn^{2+} , Cr^{6+} and Pb^{2+} from aqueous solution was studied at different contact time; 10, 20, 30, 40, 50, 60 minutes respectively. Effect of contact time on removal of metal ions with unmodified and modified CPP is shown in Figures 1 and 2 respectively. The data from the time- dependent experiments for removal of metal ions with unmodified CPP in figure 1 Showed that Zn^{2+} reached equilibrium in 30 minutes with 96.8% removal, followed by desorption in 40 minutes which remained constant, this is credited to number of active sites on adsorbent surface being completely used up [11]. Pb^{2+} , Fe^{3+} and Cr^{6+} attained equilibrium in 60 minutes with 94%, 84% and 80% removal respectively, their adsorption increased as contact time increased, and this % removal was in agreement with Chowdhury [36] who reported 88.84% to 94.23% for these metals using palm oil fuel ash as adsorbent.

In Figure 2, adsorption onto 0.5M modified CPP showed that Pb^{2+} equilibrium was reached in 50 minutes with 93.5% adsorption, followed by desorption. Cr^{6+} and Zn^{2+} attained equilibrium in 60 minutes with 80.7% and 92.3% sorption respectively, Fe^{3+} attained equilibrium in 30 minutes, the decrease in percentage sorption of Fe^{3+} after attainment of equilibrium is because the site for adsorption is completely occupied, adsorption is controlled by rate at which adsorbate moves from the external to internal sites of adsorbent, therefore flow rate is relative to time [37].

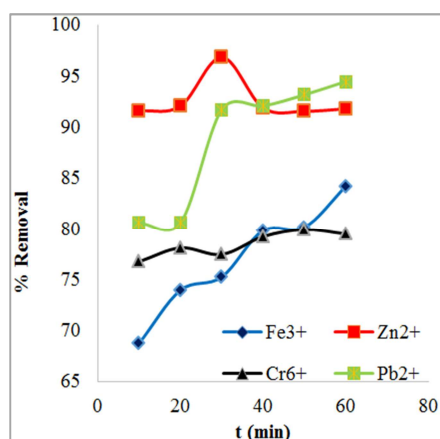


Figure 1. Effect of time on % Removal of amount of metal ions removed by unmodified CPP at different contact time.

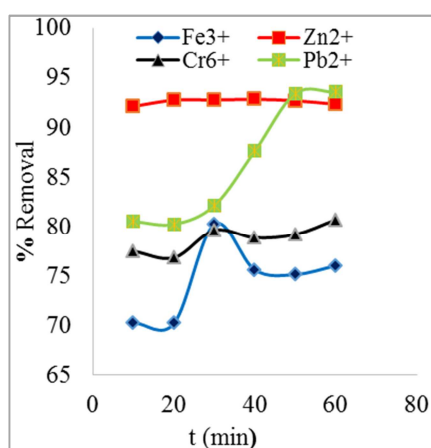


Figure 2. Effect of time on % Removal of amount of metal ions removed by 0.5 M modified CPP at different contact time.

The percentage removal of Cr^{6+} and Fe^{3+} onto the unmodified CPP and in the different modified CPP were relatively low compared to Pb^{2+} and Zn^{2+} because of high ionic radius and low charge density [38, 39]. As such the affinity of Cr^{6+} and Fe^{3+} ion towards the active binding site is lower. Equilibrium for Fe^{3+} in the 0.5M, 1M and 2M modified CPP clearly shows that equilibrium was reached in approximately 30 min irrespective of acid modification, because the adsorption sites took up available metal ions quickly at low concentrations. The plots are single and continuous indicating saturation, this suggests monolayer coverage of metal ions on adsorbent surface [40]. Mechanism of metal removal from solution involve different stages which includes migration of metal ions from solution to the surface of adsorbent, diffusion through boundary layer to adsorbent surface, adsorption at a binding site and intra-particle diffusion on interior of biomass [41]. The boundary layer resistance is affected by rate of sorption and increasing the contact time will reduce this resistance and increase the mobility of ions [42]. The higher metal ion uptake with increased contact time is because of reduction in boundary layer resistance to mass transfer in solution and increase in kinetic energy of metal ions [43]. Rapid metal removal occurred within 30–40 minutes, and remained relatively

constant after. A long contact time for equilibrium shows that predominant step is physisorption, while short contact time shows chemisorption. The contact time observed for the CPP – metal ion sorption specifies that the predominant mechanism is physisorption [44, 33].

Modification with oxalic acid reduced the sorption of prepared CPP because of protonation of sorption sites of CPP surface due to modification with acid. This will tend to leave metal ions in solution rather than being adsorbed on the surface [45]. Rate of metal sorption on CPP from solution depends on the nature of the metal. This relates to the ability to makes complexes with functional groups on CPP surface [36]. In addition different sorption of ions may be credited to variations in ionic radii. The lesser the ionic radius, the greater its tendency to hydrolyze, which further leading to decrease in sorption [46].

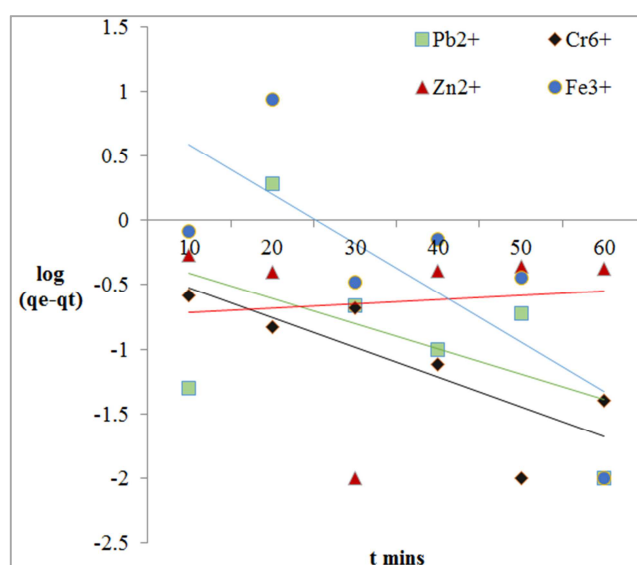


Figure 3. Pseudo-first order plot for removal of metal ions investigated by unmodified CPP.

Generally, the adsorbed amounts of oxalic acid modified adsorbent were relatively low compared to that of unmodified CPP. This may be due to negative charge of dissociated acid anions repelled by thiol-functional group, and this might have strong repulsion forces with metal ions [47].

Kinetic Studies for the Removal of Pb^{2+} , Cr^{6+} , Zn^{2+} and Fe^{3+} in aqueous solution using Unmodified and Modified Cassava Peel Powder: Process design, operation control and adsorption kinetics are essential for any practical application [48]. Adsorption kinetics during wastewater treatment is important as it gives valuable insights into the reaction pathways and mechanism controlling the rate of reaction [49]. Kinetics also describes the metal uptake which in turn controls the residence time of adsorbate at the solid-solution interface. Adsorption kinetics were investigated to determine the adsorptive absorption of metal ions from wastewater at various time intervals. Kinetic study is useful in predicting the rate of sorption for a given system. Adsorption kinetics depends so much on adsorbent material, which also influences the removal and mechanism [50]. To examine the kinetics of heavy metal

ions removal by unmodified and oxalic acid modified adsorbents, four kinetic models were tested: Pseudo-First order, Pseudo-Second order, Elovic Model and Intra-Particle diffusion models were applied to the data.

Pseudo-first order kinetic model: The pseudo-first-order kinetic rate model which describes the rate of adsorption of the adsorbate by the adsorbent are presented in figures 3 and 4 for removal of Pb^{2+} , Cr^{6+} , Zn^{2+} and Fe^{3+} in aqueous solution of by unmodified and oxalic acid modified CPP respectively. According to pseudo-first-order model, K_1 and q_e (Table 2) were calculated from the slope and intercept from the plots of

$\log (q_e - q_t)$ versus t . It was discovered that experimental q_e values did not correlate with the calculated q_e for the unmodified and modified CPP, first-order model does not reproduce the adsorption of metal ions on unmodified and different modified CPP. Also, coefficient of determination R^2 was less than ($<$) 0.99 which indicates no fit for the model. Non-linear plots were observed for all metals, meaning that adsorption between these metals and CPP was not appropriately evaluated by pseudo – first order model, this relates with the findings [51-53] in the adsorption of heavy metals using different adsorbents.

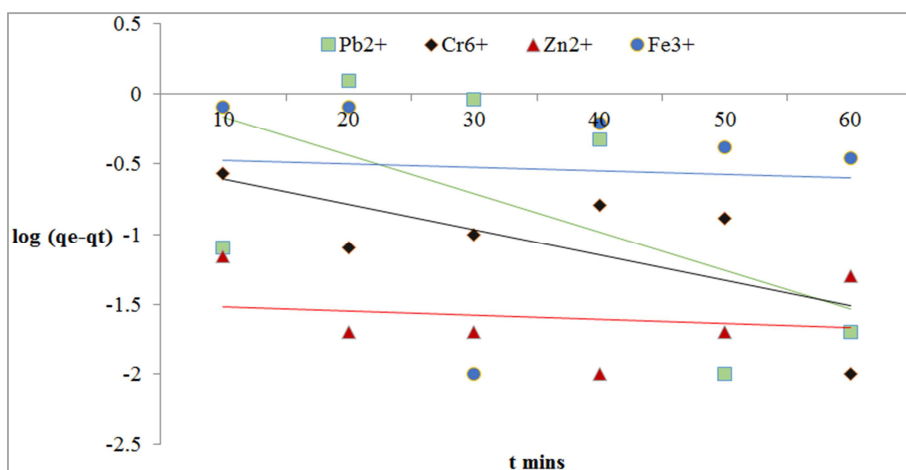


Figure 4. Pseudo-first order plot for removal of metal ions investigated by 0.5M Modified CPP.

Table 2. Data for computation of Pseudo-first order rate constant and correlation coefficient for adsorption of metal ions onto unmodified CPP and 0.5M Modified CPP.

Metal ions	unmodified CPP				0.5M oxalic acid Modified CPP			
	q_e (mg/g) experimental	q_e (mg/g) calculated	K_1 (min^{-1})	R^2	q_e (mg/g) experimental	q_e (mg/g) calculated	K_1 (min^{-1})	R^2
Pb^{2+}	0.6088	7.550	0.0451	0.2334	1.3004	7.48	0.0631	0.3343
Cr^{6+}	0.5047	6.400	0.0527	0.6494	0.3748	6.47	0.0417	0.4638
Zn^{2+}	0.1777	7.450	0.0078	0.0090	0.7097	7.44	0.0067	0.0319
Fe^{3+}	9.330	6.740	0.0882	0.568	0.3555	6.43	0.0058	0.0042

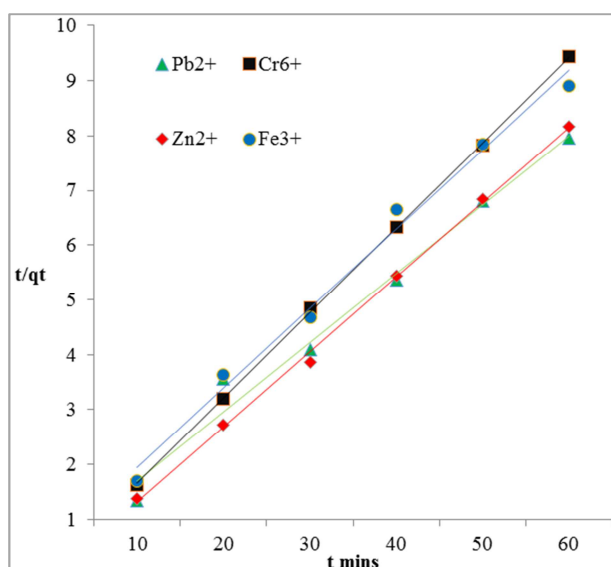


Figure 5. Pseudo – second order plot for metals ions onto unmodified CPP.

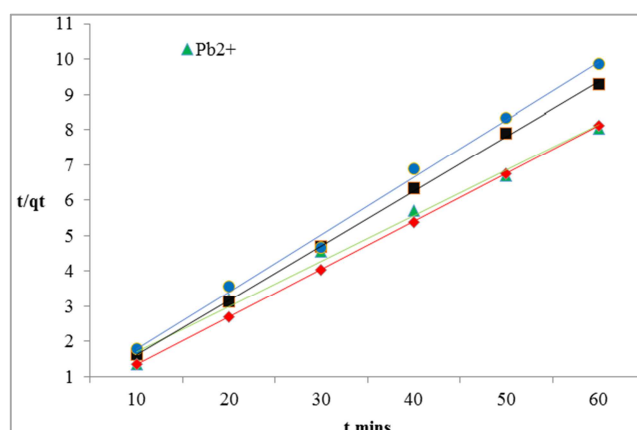


Figure 6. Pseudo second plot for metal ions on 0.5M modified CPP.

Pseudo-Second Order Model: Pseudo-second order model also described the adsorption kinetics of metal ions on CPP, it's known that adsorption capacity is equivalent to number of binding sites occupied on the adsorbent [54]. Plots of

Pseudo-second order for adsorption of metal ions on unmodified and oxalic acid modified CPP are shown in figures 5 and 6 respectively. The values of initial sorption rate h_0 , the sorption capacity q_e , the pseudo- second order rate constant K_2 and correlation coefficient (R^2) were calculated from slope and intercept from plot of t/q_t versus t . The data plotted showed a better fit for all metals, this indicates that adsorption can be suitably explained using pseudo- second order kinetic model with $R^2 > 0.99$ for all metals which is a good fit for unmodified and oxalic acid modified CPP. As a fit becomes more perfect, R^2 becomes

closer to 1.0. The values of calculated q_e (Table 3) from the second order model compared favorably with the experimental values which indicates a good fit for kinetic data. This result is consistent with [55-57], amongst many others using various adsorbent for heavy metal removal. As seen in tables 4, Cr⁶⁺ had a higher initial sorption rate (g/mg./min) than other metal ions for both the modified and the different modified CPP, this implies that adsorption of Cr⁶⁺ metals was quicker and in a mixed metal ion system of these four metals, Cr⁶⁺ might be adsorbed before others quantitatively [53].

Table 3. Data for computation of Pseudo-second order rate constant and correlation coefficient for adsorption of metal ions.

Metal ions	Unmodified CPP					0.5M oxalic acid modified CPP				
	q_e (mg/g) (experimental)	q_e (mg/g) calculated	K_2 (g/mg/min ⁻¹)	h_0	R^2	q_e (mg/g) (experimental)	q_e (mg/g) calculated	k_2	h_0	R^2
Pb ²⁺	7.930	7.550	0.0364	2.292	0.9818	7.77	7.48	0.039	2.362	0.9894
Cr ⁶⁺	6.440	6.400	0.2294	9.515	0.9998	6.45	6.47	0.371	15.432	0.9996
Zn ²⁺	7.315	7.450	0.0381	2.037	0.9987	7.40	7.44	0.323	18.18	1
Fe ³⁺	6.906	6.740	0.0420	2.003	0.9903	6.75	6.43	0.172	6.494	0.9956

Elovich Model: In adsorption reactions in aqueous system, the rate decreases with time due to increase in surface coverage [58]. Elovich model explains such condition. Elovich kinetic model may be suitable when the adsorbate ions and the surface sites interact chemically through a second-order mechanism. Elovich plots of metal ion sorption on unmodified and oxalic acid modified CPP are shown in figures 7 and 8 respectively.

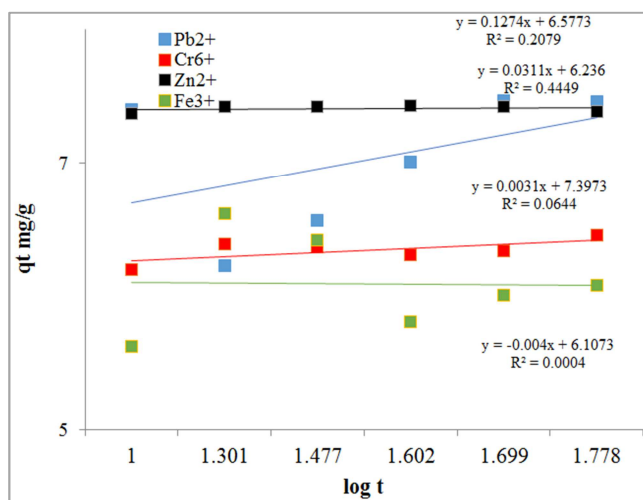


Figure 7. Elovich plot for metal ions onto unmodified CPP.

According to values obtained for coefficient of

determination R^2 for all metal ions, for unmodified and different modified CPP ($R^2 < 0.99$), it was detected that Elovich model failed to give good fitting to the experimental figures for adsorption of Pb²⁺, Cr⁶⁺, Zn²⁺, Fe³⁺ on unmodified and oxalic acid modified CPP unlike [59] that reported R^2 values 0.9978 using chemically activated carbon production from agricultural waste of chickpea and its application for heavy metal adsorption and [60] that R^2 values of 0.903 using Activated Plantain Peel Biochar As Adsorbent For Sorption of Zinc (II) Ions.

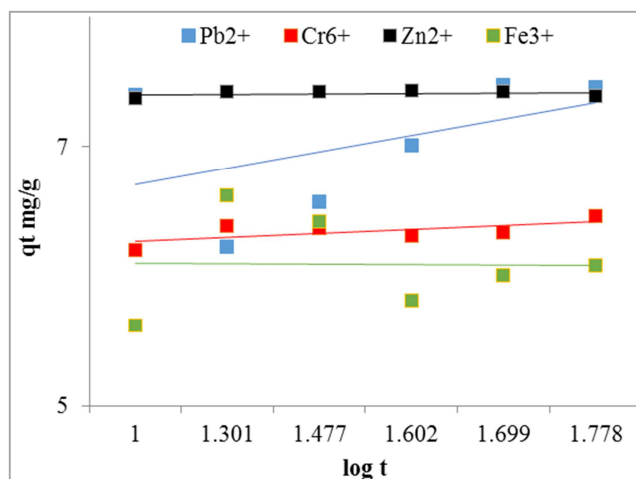


Figure 8. Elovich plot for metal ions onto oxalic acid modified CPP.

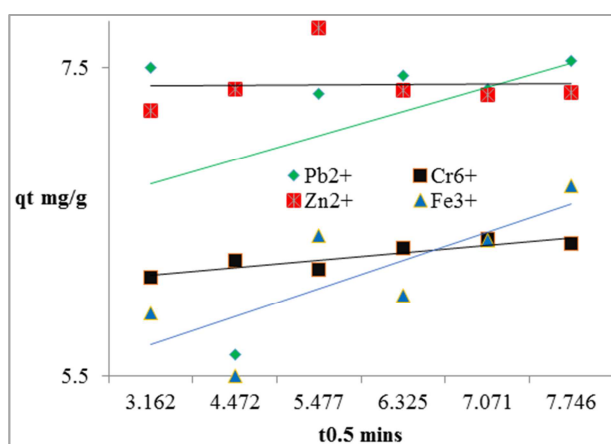
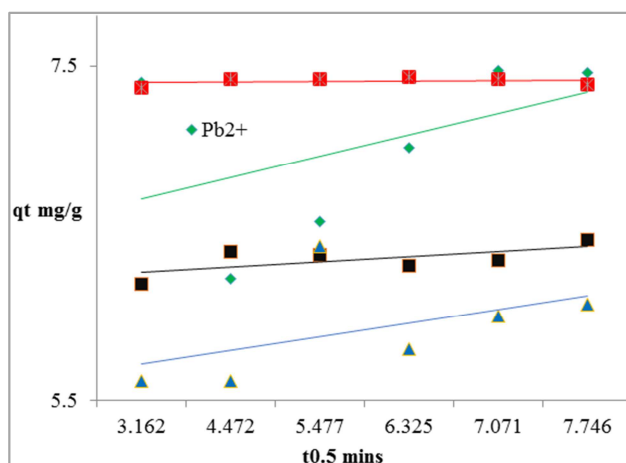
Table 4. Data for computation of Elovich rate constant and correlation coefficient for adsorption of metal ions.

Metal ions	Unmodified CPP			0.5M oxalic acid modified CPP		
	K_1 (min ⁻¹)	A: mg/g	R^2	K_1 (min ⁻¹)	a mg/g	R^2
Pb ²⁺	3.188	6.076	0.0801	5.08	6.35	0.063
Cr ⁶⁺	7.520	5.831	0.7839	10.55	6.02	0.5171
Zn ²⁺	18.77	7.210	0.037	59.51	7.33	0.2308
Fe ³⁺	2.180	4.600	0.4867	2.69	5.82	0.0196

Table 5. Data for computation of Weber-Morris rate constant and correlation coefficient for adsorption of metal ions onto Unmodified CPP and onto 0.5 M modified CPP.

Metal ions	K1 (min ⁻¹)	C	R2	K1 (min ⁻¹)	C	R2
Pb ²⁺	0.152	6.268	0.1231	0.112	6.385	0.1323
Cr ⁶⁺	0.052	5.977	0.8028	0.036	6.142	0.4786
Zn ²⁺	0.011	7.325	0.0112	0.005	7.380	0.1351
Fe ³⁺	0.192	5.665	0.0556	0.097	5.279	0.02851

Intra-Particle Diffusion Model: Diffusion rate cannot be obtained from the kinetic models, because of this, intra-particle diffusion model [61] was employed. Weber-Morris plots for metal ion sorption onto unmodified and oxalic acid modified CPP are shown in figures 9 and 10 respectively.

**Figure 9.** Weber-Morris plot for metal ion sorption on unmodified CPP.**Figure 10.** Weber-Morris plot for metal ion sorption on oxalic acid modified CPP.

In Weber-Morris plot, k is rate constant $\text{mg g}^{-1} \text{min}^{0.5}$ and C is a constant that gives idea about thickness of boundary layer. If the Weber-Morris plot of q_t versus $t^{0.5}$ remains straight, then adsorption is controlled by surface diffusion, however if the data display multi-linear plots, then two or more steps influences adsorption [62] (Tsibranska, 2012). The plots show a curvature at the beginning for some metals, this is typically related to boundary layer diffusion or exterior mass transfer effects [63] (Srivastava *et al.*, 2006). The multi-linear plot reveals two consecutive adsorption steps. The first stage is faster than the second, and it is external surface

adsorption referred to as boundary layer diffusion, the second stage is slow adsorption stage where intra-particle diffusion is rate limiting. Closer examination to these steps shows that the second step is the rate limiting step. Extrapolating the linear portions of the y-axis gives the intercept which proposes the measure of boundary layer thickness. The deviancy of plots from origin might be due to change in rate of mass transfer in the initial and final stages of adsorption [33]. (Horsfall and Vicente, 2007). Such deviation from origin designates that pore diffusion is not the rate-controlling step. The greater value of C , the larger the boundary layer effect. If C is zero, the only rate-controlling step is intra-particle diffusion. However, if C is not 0, this indicates that adsorption comprises more than a single diffusive resistance [64] (Nady *et al.*, 2013). The figures for unmodified and different modified CPP shows that boundary effect for Zn^{2+} is higher than other metal because of larger ionic radius compared to other investigated metals. This result is in agreement with the findings [65, 66] Jean-Pierre and Bouté, (2016), Tsibranska and Hristova, (2012) on adsorption of heavy metals onto activated carbon from apricot stones.

4. Conclusions

The physicochemical evaluation of the cassava peel showed that the CPP is a good adsorbent based on its volume activity, suspension in liquid phase and affinity for cations. The laboratory experiments showed that cassava peel powder can remove Pb^{2+} , Zn^{2+} , Cr^{6+} and Fe^{3+} from aqueous system with acid modified and unmodified biomass within 30-60 minutes contact time, the kinetic data revealed that the reaction followed pseudo-second order with R^2 value of > 0.99 for all metal ions and the rate limiting step is intra-particle diffusion. Large quantities of agricultural waste are produced by agro-industry and their metal ion adsorption capacities are recognized as possible substitutes to existing heavy metal elimination methods. One of such agricultural waste is the cassava peel.

References

- [1] Arruti, A.; Fernández-Olmo, I. and Irabien, A. (2010): Evaluation of the contribution of local sources to trace metals levels in urban PM_{2.5} and PM₁₀ in the Cantabria region (Northern Spain). *J. Environ. Monitor.* 12 (7): 1451–1458.
- [2] Goyer RA. (2011): Toxic effects of metals. In: Klaassen CD, editor. *Cassarett and Doull's Toxicology: The Basic Science of Poisons*. McGraw-Hill Publisher; New York. pp. 811–867.

- [3] Cherono, Faith; Mburu, Njenga; Kakoi, Beatrice (2021). Adsorption of lead, copper and zinc in a multi-metal aqueous solution by waste rubber tires for the design of single batch adsorber. *Heliyon* 7 (2021) e08254 1–12.
- [4] UNEP (1989). United Nations Environmental Programme, Industry and Environment Office, 1989. Paris.
- [5] Nema, K (2003). Environmental Protection (Standards for Effluents Discharge) Regulations, 2003.
- [6] Agwaramgbo, L.; Magee, N.; Nunez, S. and Mitt, K. (2013): Biosorption and chemical precipitation of lead using biomaterials, molecular sieves, and chlorides, carbonates, and sulfates of Na & Ca. *J. Environ. Protect.* 4: 1251–1257.
- [7] Oluyemi, E. A., Adewale F. A., and Iyabo O. O. (2012): Removal of Pb^{2+} and Cd^{2+} Ions from Wastewaters Using Palm Kernel Shell Charcoal (Pksc). *Res. J. Eng. Appl. Sci.* 1 (5): 308–313.
- [8] Bhatnagar, A; M. Sillanpää (2010). Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—a review, *Chem. Eng. J.* 157 (2–3): 277–296.
- [9] Horsfall, M. Jnr; and Spiff, A. I. (2004a). Studies on the Effect of pH on the sorption of Pb^{2+} and Cd^{2+} ions from aqueous solutions by *Caladium bicolor* (Wild Cocoyam) biomass. *Elec. Journal of Biotechnology*, Vol 7 (3), pp 310–320.
- [10] Horsfall, M. Jnr; and Spiff, A. I. (2004b). Adsorption of Metal ions from Mixed Solutions by *Caladium bicolor* (Wild Cocoyam) Biomass. *Journal of Corrosion Sci. & Technol.* Vol. 2, pp 120–126.
- [11] Horsfall, M. Jnr and Spiff, A. I. (2005a). Effect of metal ion concentration on the biosorption of Pb^{2+} and Cd^{2+} by *Caladium bicolor* (wild cocoyam). *African J. of Biotech.* Vol. 4 (2) pp 191–196.
- [12] Horsfall, M. Jnr and Spiff, A. I. (2005b). Kinetic Studies on the Sorption of Lead and Cadmium Ions from Aqueous Solutions by *Caladium bicolor* (Wild Cocoyam) Biomass. *Bull. Chem. Soc. Ethiop.* 19 (1), 89–102.
- [13] Horsfall, M. Jnr.; and Spiff, A. I. (2005c). Sorption of Lead, Cadmium, and Zinc on Sulfur-Containing Chemically Modified Wastes of Fluted Pumpkin (*Telfaria occidentalis*) HOOK f.). *Chem. & Biodiversity*; Vol. 2; pp 373–385.
- [14] Horsfall, M. Jnr.; and Spiff, A. I. (2005d). Equilibrium sorption study of Al^{3+} , Co^{2+} and Ag^{+} in aqueous solutions by fluted pumpkin (*Telfaria occidentalis* HOOK f) waste biomass. *Acta Chim. Slov.* 52 171–181. Slovakia.
- [15] Horsfall, M. Jnr, F. E. Ogban, and E. E. Akporhonor (2005). Biosorption of Pb^{2+} from Aqueous Solution by *Rhizophora mangle* Aerial Root Waste Biomass. *Chemistry & Biodiversity* Vol 2 No 9 1246–1255.
- [16] Li, X; Y. Tang, Z. Xuan, Y. Liu, F. Luo, (2007). Study on the preparation of orange peel cellulose adsorbents and biosorption of Cd^{2+} from aqueous solution, *Sep. Purif. Technol.* 55 69–75.
- [17] Feng, N; X. Guo, S. Liang, (2009) Adsorption study of copper (II) by chemically modified orange peel, *J. Hazard. Mater.* 164 1286–1292.
- [18] Liang, S; X. Guo, N. Feng, Q. Tian, Isotherms, kinetics and thermodynamic studies of adsorption of Cu^{2+} from aqueous solutions by Mg^{2+}/K^{+} type orange peel adsorbents, *J. Hazard. Mater.* 174 (2010) 756–762.
- [19] Guo, X. Y; S. Liang, Q. H. Tian, (2011) Removal of heavy metal ions from aqueous solutions by adsorption using modified orange peel as adsorbent, *Adv. Mater. Res.* 236–238 237–240.
- [20] Liang, S; X. Guo, Q. Tian, (2011) Adsorption of Pb^{2+} and Zn^{2+} from aqueous solutions by sulfured orange peel, *Desalination* 275 212–216.
- [21] Tasaso, P (2014), Adsorption of copper using pomelo peel and depectinated pomelo peel, *J. Clean Energy Technol.* 2: 154–157.
- [22] Hossain, A. A. (2012). H. H. Ngo, W. S. Guo, T. Setiadi, Adsorption and desorption of copper (II) ions onto garden grass, *Bioresour. Technol.* 121: 386–395.
- [23] Husein, D. Z (2013) Adsorption and removal of mercury ions from aqueous solution using raw and chemically modified Egyptian mandarin peel, *Desalin. Water Treat.* 51: 6761–6769.
- [24] Liu, W; Y. Liu, Y. Tao, Y. Yu, H. Jiang, H. Lian, (2014). Comparative study of adsorption of Pb(II) on native garlic peel and mercerized garlic peel, *Environ. Sci. Pollut. Res.* 21 (2014) 2054–2063.
- [25] Zou, W; L. Zhao, L. Zhu, (2012). Efficient uranium (VI) biosorption on grapefruit peel: Kinetic study and thermodynamic parameters, *J. Radioanal. Nucl. Chem.* 292: 1303–1315.
- [26] Iqbal, A. Saeed, I. Kalim, (2009). Characterization of adsorptive capacity and investigation of mechanism of Cu^{2+} , Ni^{2+} and Zn^{2+} adsorption on mango peel waste from constituted metal solution and genuine electroplating effluent, *Sep. Sci. Technol.* 44 (2009) 3770–3791.
- [27] Huang, K; H. Zhu, (2013). Removal of Pb^{2+} from aqueous solution by adsorption on chemically modified muskmelon peel, *Environ. Sci. Pollut. Res.* 20 (2013) 4424–4434.
- [28] Aman, T; A. A. Kazi, M. U. Sabri, Q. Bano, (2013). Potato peels as solid waste for the removal of heavy metal copper (II) from waste water/industrial effluent, *Colloids Surf. B: Biointerfaces* 63 (2008) 116–121.
- [29] Ding, Y; D. Jing, H. Gong, L. Zhou, X. Yang, (2012). Biosorption of aquatic cadmium (II) by unmodified rice straw, *Bioresour. Technol.* 114 20–25.
- [30] Yadav, D; M. Kapur, P. Kumar, M. K. Mondal, (2015). Adsorptive removal of phosphate from aqueous solution using rice husk and fruit juice residue, *Process. Saf. Environ.* 94 (2015) 402–409.
- [31] Horsfall, M. Jnr. And Vicente J. L (2007): Kinetic study of liquid-phase adsorptive removal of heavy metal ions by almond tree (*Terminalia catappa* L.) leaves waste. *Bull. Chem. Soc. Ethiop.* 21 (3), 349–362.
- [32] Horsfall, M. Jnr; Abia, A. A, and Spiff A. I. (2006): Kinetic studies on the adsorption of Cd^{2+} , Cu^{2+} , Zn^{2+} ions from aqueous solutions by cassava (*Manihot esculenta crantz*) tuber bark waste. *Bioresource Technology* 97 (2): 283–291.
- [33] Salahudeen, N., Ajinomo, C. S. and Omaga, O. (2014): Production of activated carbon from cassava peel. *J. Appl. Phytotech. Environ. Sanit.* 3 (2) 72–80.

- [34] Gin, W. A.; Jimoh, A.; Abdulkareem, A. S and Giwa, A. A. (2014): Utilization of cassava peel waste as a raw material for activated carbon production; approach to environmental protection in Nigeria. *Inter. J. Eng. Res. Tech.* 3 (1): 112–120.
- [35] Goswami, S. and Ghosh, U. C. (2005): Studies on adsorption behavior of Cr (VI) onto synthetic hydrous stannic oxide. *Water SA.* 31 (4), 597–602.
- [36] Chowdhury, Z. Z.; Zain, S. M. and Rashid, A. K. (2011): Equilibrium Isotherm Modeling, Kinetics and Thermodynamics Study for Removal of Lead from Waste Water. *E-J. Chem.* 8 (1), 333–339.
- [37] Seepe, L N, Simate, G. S.; Shemi, A.; Sibanda, V. and Van D. L. (2015): Removal of CO_3^{2+} , V^{3+} , and Cr^{3+} , from synthetic waste water using cassava waste. *SA J. Chem. Eng.* (18): 51–69.
- [38] Horsfall, M. Jnr.; Abia, A. A; and Spiff, A. I. (2003). Removal of Cu (II) and Zn (II) ions from wastewater by Cassava (*Manihot esculenta Cranz*) waste biomass. *Africa Journ. Biotech.* 2 (10) 360–364.
- [39] Abia, A. A. and Asuquo, E. D., (2008): Sorption of Pb (II) and Cd (II) ions onto chemically unmodified and modified oil fruit fibre adsorbent: Analysis of Pseudo second order kinetics model. *Indian J. Chem. Tech.* 15: 341–348.
- [40] Pimentel, P. M.; Melo, M. A., Melo, D. M. A; Assução, A. L., Henrique, D. M.; Silva Jr. C. N. and González, G. (2008): Kinetics and thermodynamics of Cu (II) adsorption on oil shale wastes. *Fuel Proc. Tech.* 89 (1): 62–67.
- [41] Igwe J. C. and Abia A. A., (2005). Comparative adsorption of Zn (II), Cd (ii) and Pb (ii) ions from aqueous and non-aqueous solution by maize cob and husk. *Afr. J. Biotech.* 4 (10): 1113–1116.
- [42] Horsfall, M. Jnr. and Abia, A. A (2003): Sorption of cadmium (II) and Zinc (II) ions from aqueous solutions by cassava waste biomass (*Manihot esculenta crantz*). *J. Wat. Resource*, 37: 4913–4923.
- [43] Gerdea-Torresdey, J. L., Tang, L. and Salvador J. M, (1996) Phyto-filtration of hazardous cadmium, chromium, lead, and zinc ions by biomass of *Medicago sativa* (alfalfa). *J. Hazard. Mat.* 57, 29–39.
- [44] Ozturk, G.; Kuralay, B. and Gizli, N. (2017): Removal of Cu (II) ions from industrial wastewater by chemically modified natural plant wastes. The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM) in International Conference on Technology, Engineering and Science 1: 96–103.
- [45] Stojanovic, D. M.; Aleksandra, Z.; Milovan, P.; Danijela, B.; Tatjana, A.; Aleksandar L. B. (2011): Biosorptive removal of Pb^{2+} , Cd^{2+} and Zn^{2+} ions from water by *Lagenaria vulgaris* shell". *Water SA*, 37, 82–89.
- [46] Kong, Q; Xie, B.; Preis, S.; Hu, Y.; Haizhen, W. and Wei, C. (2018): Adsorption of Cd^{2+} by an ion-imprinted thiol-functionalized polymer in competition with heavy metal ions and organic acids. *RSC Adv.* 8: 8950–8960.
- [47] Ho, Y. S; J. C. Y. Ng, G. McKay, Kinetics of pollutant sorption by biosorbents: Review, *Separ. Purif. Methods* 29 (2) (2000) 189–232.
- [48] Kalmykova, Y; A. M. Strömvall, B. M. Steenari, Adsorption of Cd, Cu, Ni, Pb and Zn on Sphagnum peat from solutions with low metal concentrations, *J. Hazard Mater.* 152 (2) (2008) 885–891.
- [49] Badmus O., Audu, K. and Anyata, U. (2010). "Removal of Lead Ion from Industrial Wastewaters by Activated Carbon Prepared from Periwinkle Shells (*Typanotonus fuscatus*)." *Turkish J. Environ. Eng. Sci. Ind. Res.* 53, (5) 251–263.
- [50] Ramesh, S. T., Rameshbabu, N., Gandhimathi, R., Nidheesh, P. V., Srikanth, K. (2012): Kinetics and equilibrium studies for the removal of heavy metals in both single and binary systems using hydroxyapatite. *Appl. Wat. Sci.* 2, 187–197.
- [51] Kumar, P. S; S. Ramalingam, S. D. Kirupha, A. Murugesan, T. Vidhyadevi, S. Sivanesan, Adsorption behavior of nickel (II) onto cashew nut shell: equilibrium, thermodynamics, kinetics, mechanism and process design, *Chem. Eng. J.* 167 (2011) 122–131.
- [52] Sivakuman, V., Asaithan, M. and Sivakumar, P. (2012): Physico-chemical and adsorption studies of activated carbon from agricultural waste. *Adv. Appl. Sci. Resource.* 3 (1); 219–226.
- [53] Kundu, S. and Gupta, A. K., (2006). Arsenic adsorption onto iron oxide-coated cement (IOCC): regression analysis of equilibrium data with several isotherm models and their optimization. *Chem. Eng. J.* 122 (1–2), 93–106.
- [54] Horsfall, M., Abia, A. A. and Spiff, A. J. (2003) Removal of Cu (II) and Zinc ions from waste water by cassava (*Manihot esculenta crantz*) waste Biomass. *Afr. J. Biotech.* 2: 360–364.
- [55] Emenike, P. C., David, O. O., Ngene, B. U and Imokhai, T. T. (2017) Assessment of KOH-activated unripe *Musa paradisiaca* peel for adsorption of copper from aqueous solution *Cogent Eng.* 4: 1376488.
- [56] Mokhesur, M. R.; Mohd, A.; Alias, M. Y.; Yunus, B. K. and Rezaul, H. A. (2014): Removal of Heavy Metal Ions with Acid Activated Carbons Derived from Oil Palm and Coconut Shells *Mat.* 7, 3634–3650.
- [57] Gamzenur, Ö. Murat, K., Esin, A. and Ayşe, E. P., (2019). Chemically activated carbon production from agricultural waste of chickpea and its application for heavy metal adsorption: equilibrium, kinetic, and thermodynamic studies. *Appl. Wat. Sci.* 9: 56.
- [58] Horsfall, M. Jnr.; Fred, O. and Eyitemi, E. A. (2006): Sorption of chromium (VI) from aqueous solution by cassava (*Manihot esculenta crantz*). *J. Chem. Biodiv.* 3 (2): 161–174.
- [59] Nworie, F., Nwabue, F., Ikelle, I., Ogah, A., Elom, N. and Illochi, N. (2018); Activated Plantain Peel Biochar as Adsorbent for Sorption of Zinc (II) Ions: Equilibrium and Kinetics Studies. *J. Turkish Chem. Soc.* 5 (3): 1257–70.
- [60] Lin, J. X., Zhan, S. L., Fang, M. H., Qian, X. Q and Yang, H. (2011): Adsorption of basic dye from aqueous solution onto fly ash. *J. Environ. Manage.* 87 (1): 193–200.
- [61] Tsibranska, E. H., (2012) Comparison of different kinetic models for adsorption of heavy metals onto activated carbon from apricot stones *Bulgarian Chem. Comm.* 43, (3) 370–377.
- [62] Srivastava, V. C.; Agarwal, N. K. and Mishra, I. M. (2006): Removal of Congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analyses. *Chemosphere*, 61 (4): 492–501.

- [63] Horsfall, M. J. and Spiff A. I., (2005) Equilibrium sorption study of Al^{3+} , Co^{2+} and Ag^{+} in aqueous solutions by fluted pumpkin (*Telfairia Occidentalis* HOOK f) waste biomass. *Acta Chim. Slov.* 52 174–181.
- [64] Nady, A. F.; El-Shafey, O. I. and Laila, B. K. (2013): Effectiveness of Alkali-Acid Treatment in Enhancement of the Adsorption Capacity for Rice Straw for the Removal of Methylene Blue Dye. *ISRN Physical Chemistry*. Article <http://dx.doi.org/10.1155/2013/208087>.
- [65] Jean-Pierre, S. and Bouté, J., (2016) Intraparticle diffusion-adsorption model to describe liquid/solid adsorption kinetics. *Revista Mexicana De Ingenieria Quimica*, 15 (1), 161–173.
- [66] Chavali, V and Kandare, E (2016): Rigid biofoam composites as eco-efficient construction materials. *Biopolymers and Biotech Admixtures for Eco-efficient Construction Materials*. Pp 275–304.