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STUDY OF THE ADSORPTION OF Cr, Ni, AND Pb FROM TANNERY WASTEWATER USING MODIFIED RICE HUSK AND CASSAVA PEEL POWDER

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ABSTRACT

Over the years, water pollution due primarily to the discharge of toxic heavy metals from industrial activities has served as a major challenge in the quest to provide a safe environment. Key among the technologies used for the treatment of wastewater contaminated with heavy metals is adsorption. In this study, mixed rice husk and cassava peel powder were used to develop microporous adsorbent with chemical modification by Sulphuric acid (H_2SO_4) for the batch adsorption of hexavalent chromium [Cr (VI)], Nickel(Ni), and Lead(Pb). Using adsorption equilibrium isotherms and adsorption kinetic study, a positive correlations (better fit) was obtained for Redlich-Peterson isotherm and Pseudo second order kinetic models. A maximum adsorption capacity of 139.18 mg/g, 3.66mg/g, and 5.58mg/g and a maximium removal of 93.60%, 98.20% and 93.80% were obtained for Chromium, Nickel, and Lead respectively. Therefore, rice husk and cassava peel usage were found to has a high chance of reducing solid waste management problems as well as having the potential to be effective in the removal of heavy metals from industrial effluents.

Keywords: Adsorption, Adsorption capacity, Percentage adsorption removal, Isotherms, Equilibrium, Kinetic models

INTRODUCTION

One of today's environmental challenges is the excessive use of heavy metals for industrial and domestic activities which often contaminates the ground and surface water; therefore, it is vital to remove these elements from water and wastewater before discharge into the environment. (Yari *et al*., 2016). Metals and their derivatives are potential pollutants that could be particularly problematic due to their stability and mobility. Chromium Cr(VI), Nickel (Ni), and lead(Pb) containing wastewater discharged from various industries including mining, tanning, cement, production of steel and other metal alloys, electroplating operations, photographic material and corrosive painting industries (Yao *et al*., 2010).

Health related issues have increased rapidly over the recent years due to environmental pollution which has decreased the quality of life duration and diversity of both plants and animals (Faleye *et al*., 2024) . The carcinogenic, mutagenic, and toxicity of Cr(VI) and Pb can negatively affect the life cycle; thus, there is a significant need to remove this element for the elimination of this element (Rao *et al*., 2010). Moreover, contaminants when found in soil can be readily absorbed by plants, which, when consumed by humans and animals, pose significant health risks and hazards (Ramadan *et al*., 2024).

Several conventional techniques, including adsorption, electrochemical precipitation, reverse, ion exchange, activated sludge osmosis, etc. are used for the treatment of effluents containing metal ions. For one reason or the other, most, of these techniques are not suitable for large-scale wastewater treatment, especially in developing countries. (Malakootain *et al*.,2014).

Adsorption is a versatile and effective method for removing chromium, particularly when it is combined with appropriate regeneration steps. This reduces the problem of sludge disposal and renders the system economically viable, especially when the adsorbent used is of low cost. The adsorption process is used, in a variety of important industrial applications and now it is increasingly used on a large scale as an economical and efficient separation technique for metal ion removal from wastewater (Zvinowanda *et al.*, 2009). Activated carbon has been used as an adsorbent in wastewater treatment throughout the world, but this is not an economical adsorbent due to its high operation and regeneration costs (Mohanty *et al*., 2006).

Many studies have been made on the use of different adsorbents like peat, coir pith, chitin, Azolla, Lemna minor, hardwood sawdust, bagasse pith, paddy straw, and various blends of these (Gupta *et al*., 2001). However, the studies are continuing for cost-effective and efficient adsorbent. The use of agricultural waste such as cassava peel, orange peel, maize cob, and rice husk has been identified as a paramount alternative because it is conveniently available in many countries like Nigeria (Yari *et al*., 2016).

MATERIALS AND METHODS

Materials

The carbonaceous raw material used for the preparation of the adsorbent sample is rice husk and cassava peel sourced from Zaria, Kaduna state, Nigeria. The cassava peel and rice husk sample was washed with ordinary water and sun-dried for 5-7 days to drastically reduce its moisture content and then crushed for size reduction. All chemical reagents were of analytical grade.

The dried cassava peels and rice husk were crushed manually into powder form (250 micrometer) using a mortar and pestle. Chemical activation was done using a 0.5M sulphuric acid to soak the adsorbent sample for 24 hours after which they were filtered and washed with distilled and de-ionized water until a pH of 7 was attained. The samples were further sun-dried for 3 days and oven dried after which they were kept till usage.

The wastewater sample used was obtained from the Tannery Department of the Nigeria Institute of Leather and Science Technology (NILEST) Extension Center, Kano, Nigeria. It was transported in a container packed with ice to the Water Resources and Environmental Engineering Laboratory of Ahmadu Bello University Zaria, Kaduna state, Nigeria.

Characterization of Adsorbent and wastewater Sample

The adsorbents were subjected to different characterization to establish properties that are relevant to adsorption. Some of the characterization tests carried out include bulk density, moisture content, scanning Electron Microscopy (SEM), Fourier Transformed Infrared Spectroscopy (FTIR), point of zero charge, and specific surface area.

The physicochemical analysis carried out using standard methods includes Heavy metal ion concentration, Biological Oxygen Demand(BOD), Chemical Oxygen Demand(COD), pH, Total Dissolved Solid(TDS), turbidity, electrical conductivity, Dissolved oxygen(DO), Total Suspended Solid(TSS), oil and grease, nitrate, sulphide, and chloride ion test.

Experimental conditions

Reactions were carried out using Standard Methods (APHA, 1995).

Since adsorption is affected by physical and chemical variables, the influence of adsorbent mass, pH, and contact time were investigated in this study. The range of parameters used for the study is presented in Table 1.

Table 1: Range of parameters used for this study

Parameter	**Range**
pH	4 – 12
Contact time	10 – 120 min
Dosage	2 – 10g

Adsorption experiment

The batch adsorption studies process conditions employed as presented in Table 2 was generated based on Table 1. The experimental design matrix (Table 2) was obtained using Design Expert - Version 11.0 under a 3-level factor Box Behnken Design (BBD). pH, contact time, and adsorbent dosage were considered the independent variable, and the adsorptive capacity of the adsorbents for each of the heavy metals was studied as the response variable.

Table 2: Design of Experiment and its expected responses

Run	**Factor A: pH**	**Factor B: Contact time(mins)**	**Factor C: adsorbent dosage (g)**	**Response 1: chromium adsorptive capacity Qe(mg/g)**	**Response 2: Nickel adsorptive capacity Qe(mg/g)**	**Response 3: lead adsorptive capacity Qe(mg/g)**
1	4.00	120	6.00			
2	12.00	10	6.00			
3	12.00	65	2.00			
4	4.00	65	10.00			
5	8.00	120	2.00			
6	4.00	10	6.00			
7	4.00	65	2.00			
8	8.00	65	6.00			
9	8.00	65	6.00			
10	8.00	10	10.00			
11	12.00	65	10.00			
12	8.00	65	6.00			
13	12.00	120	6.00			
14	8.00	10	2.00			
15	8.00	65	6.00			
16	8.00	120	10.00			
17	8.00	65	6.00			

100ml of the wastewater sample was treated with the modified mixed adsorbent (1:1 mass of cassava peel and rice husk) under various conditions of contact time, pH, and adsorbent dosage as presented in table 2. The mixing of the adsorbent material was done by the use of a mechanical stirrer and the adjustment of the sample pH was done with the addition of either HCL or NaOH in the appropriate portion until the required pH was obtained.

The mixture (adsorbent and wastewater sample) was placed in a 250ml Ermeleyer flask and subjected to shaking at 150 rpm for the various required time (10, 65, and 120 minutes). It was left undisturbed for 24 hours to allow the system to equilibrate. Afterwhich, the mixture was filtered through a Whiteman filter paper (150mm) into another plastic bottle. The residual heavy metal concentrations in the filtrate were determined using an atomic absorption spectroscopy machine.

The heavy metal removal and adsorption capacity under equilibrium conditions were determined using equations 1 and 2 respectively.

$$\% \text{ Removal } = \frac{Ci - Ce}{Ci} \times 100 \quad (1)$$

$$\text{Adsorptive capacity } Qe = \frac{V(Ci - Ce)}{W} \quad (2)$$

Where; C_i is the initial concentration of heavy metal, C_e is the final concentration/equilibrium concentration, V is the volume of solution used, W is the weight of adsorbent used and Q_e is the equilibrium adsorption capacity. Finally, before the spent adsorbent was disposed of, it was soaked in hydrochloric acid and sodium hydroxide to remove the adsorbate from its surface.

Adsorption Isotherms relationship

Isotherm data are basic requirements for the design of adsorption reactors. Moreover, analysis of adsorption Isotherm is an important thing in environmental pollution control, the key thing is to develop an equation that will accurately represent the result and which can be used for design purposes, (Volesky, 2001).

Langmuir, Freundlich, Temkin, and Redlich-Peterson Isotherms are some Isotherms used commonly in Engineering. However, for this study, emphasis is restricted to the use of Langmuir, Freundlich, and Redlich Peterson isotherms.

Langmuir Isotherm

Langmuir isotherm presents the interaction between adsorbate and adsorbent. It is essential for the design of the adsorption process as it applies to homogeneous adsorption processes where each adsorbate on the surface has equal adsorption activation energy. The linear form is provided as:

$$\frac{Ce}{qe} = \frac{1}{Kl} + \frac{1}{K}Ce \qquad (3)$$

Where k and L are Langmuir constants.

qe is the amount of solute removed or adsorbed at equilibrium.

Ce is the equilibrium concentration of the mixture.

Thus, K, L and the squared of the regression coefficient (R^2), are adsorption parameters estimated by the Langmuir model, which are used to suggest whether the adsorption of a metal ion can be modeled by Langmuir Isotherm.

It has been well documented that the essential characteristic of the Langmuir Isotherm may be expressed in terms of the dimensionless parameter (RL). RL has been defined as an Isotherm shape that predicts if an adsorption system is favorable or unfavorable. RL is considered a reliable indicator of the adsorption process. Mamdouth et al (2004), stated that RL indicates the Isotherm shape according to the following assumption characteristics:

RL (is unfavorable); RL = 1 (linear adsorption); 0<RL<1 (is favorable);

RL is as expressed in the equation

$$RL = \frac{1}{1+lCo}$$

where, C_O, is the initial concentration of the mixture

Freundlich Isotherm

For heterogeneous surfaces, this model is the most relevant, especially for multilayer adsorption isotherm, and is generally characterized by the heterogeneity factor $(\frac{1}{n})$. The expression applied to the experimental data for the linear form

$$\text{Ln } Q_e = \text{Ln } K_f + \frac{1}{n}\text{Ln } C_e \qquad (4)$$

Ce and Qe are equilibrium concentration, and adsorption capacity at the equilibrium stage. Kf and n are Freundlich constants that incorporate all factors affecting the adsorption process (adsorption capacity and intensity). Values of Kf and n can be obtained from the intercept and slope of a plot of adsorption capacity, qe against equilibrium concentration Ce. Both parameters K_f and 'n' affect the adsorption Isotherm. The larger the K_f and 'n' values, the higher the adsorption capacity. Furthermore, the magnitude of the exponent n indicates the favorability of the adsorption process.

Redlich-Peterson (R-P) Adsorption Isotherm.

R-P isotherm proposed by Redlich and Peterson is a combined form of Langmuir and Freundlich expressions. It can be used for predicting homogenous and heterogeneous adsorption systems. The equation is as follows:

$$qe = \frac{KR\ Ce}{1 + aR\ Ce\beta} \qquad (5)$$

Where KR (L/g) and αR (L/mg) β are the adsorption R-P constants and β is the exponent and ranges between 0 and 1. When β = 0, the R-P equation reduces to Henry's equation which is a linear isotherm, and to the Langmuir isotherm for β = 1. For high adsorbate concentration, the R-P equation reduces to the Freundlich isotherm.

Adsorption Kinetic Study

The importance of adsorption kinetics cannot be overstated as the rate and mechanism of adsorption can be determined from kinetic studies. Adsorption kinetic study seeks to determine the efficiency of adsorption. The kinetics study is defined as the rate of solute removal that controls the residence time of the adsorbate in the solution–solute interface.

Pseudo First Order Kinetic Model

Two vital relevant for adsorption are the mechanism and the reaction rate. The residence time required for completing the reaction is determined by the solute uptake and enumerated from kinetic analysis. Lagergren, in 1898, postulated the first order rate equation for oxalic acid and malonic acid adsorption onto charcoal to describe the liquid-solid interactions based on solid capacity as

$$\text{Log (Qe-Qt)} = \text{Log Qe} - \frac{K1}{2.303}t \qquad (6)$$

2.5.2. Pseudo Second Order (PSO) Kinetic Model

This model assumes that the rate of site occupation is proportional to the square of unoccupied sites. The linear PSO kinetic equation is presented as:

$$\frac{t}{Qt} = \frac{1}{K2Qe2} + \frac{1}{Qe}t \qquad (7)$$

The Elovich Rate Equation

The Elovich equation was initially used to describe the chemisorption of gas molecules on solids.

(Low, 1960). Nevertheless, the Elovich equation was successfully used to describe the sorption of zinc on solids (Taylor *et al.*, 1995).

The model equation is

$$\frac{dqt}{dt} = aexp(-bqt) \qquad (8)$$

where *a* (*mg g*−1min−1) and *b* (*g mg*−1) are the model parameters.

The integration of Eq. (2.8) with the boundary conditions q = 0 at t = 0 and qt = qt at t = t, gives:

$$qt = \frac{1}{b}\ln(1 + abt). \qquad (9)$$

Model applicability test for isothermal and kinetic studies

Prediction of the best-fit model can be based on the criteria of Regression analysis using the correlation of applicability (R^2) test, Precision test comparing qe experiment and qe calculated, and Statistical Sum of Error test (SSE) which shows the error and was calculated using the equation 10

$$SSE(\%) = \sqrt{\frac{(qe\ exp - qe\ cal)2}{N}} \qquad (10)$$

Where N is the number of data points, qe exp is the experimented qe, and qe cal is the calculated qe.

RESULTS AND DISCUSSION

Characterization of Adsorbents and Wastewater Sample

Characterization of the adsorbent

Table 3 shows some of the physical characterization of the adsorbent used in this study.

Table 3: Characterization of adsorbents

Sample	Characterization of Adsorbent			
	Bulk density (g/cm^3)	**Moisture content (%)**	**Surface area (m^2/g)**	**Point of zero charge**
Acid-treated cassava peel	0.33	-	-	3.57
Acid-treated rice husk	0.28	-	-	4.21
Ordinary cassava peel	0.43	-	579	4.9
Ordinary rice husk	0.43	-	825	5.5
Mixed ordinary adsorbents	-	20	1453	-
Mixed acid-modified adsorbents	-	15	1575	-
Mixed adsorbents after adsorption	-	-	826	-

The bulk density may be used to identify several particle classes. The macro-porous particle has a bulk density >1 g/cm^3 (pore space volume for gram of carbon). The mesoporous particle has a bulk density in the range of 0.85–1.0 g/cm^3. While the microporous particle presents a value be < 0.85 g/cm^3. Generally, macroporous or mesoporous particles are used for the removal of large molecules while, microporous, are more suitable for the removal of small molecules (Tchobanoglous *et al*., 2003). Based on the values obtained as presented in Table 3, since they are less than 0.85g/cm^3 the adsorbent can be categorized as a microporous material which is often the ideal fit for the adsorption of the heavy metals from wastewater. The reduction of bulk density obtained between the treated and untreated adsorbents is due to the increase of pore volume as a result of the chemical activation thus leading to the reduction in the weight of the adsorbents and consequently a decrease in its mass-to-volume ratio. The smaller the particle size, the more the surface area available for adsorption.

The reduction of moisture content in the treated adsorbent can be attributed to the reaction between the acid and water thereby leading to a reduction of moisture in the adsorbent. The lower the moisture content, the better the adsorption performance of a material (Singh *et a*l., 2012).

It has been reported that acid modification provides an adsorbent with a larger surface area and a smaller porosity so that the binding of metal ions may occur on the surface of the adsorbent (Horsfall *et al*., 2004). Thus, the increase in the specific surface area of the mixed adsorbent from 1453$m^3g/$ to 1575m^3/g with acid treatment is expected to enhance the adsorption of metal from the tannery wastewater since more site would be available to adsorb the metal. On mixing the adsorbents, a greater surface area was obtained as presented in Table 3 as against the single adsorbents. On the other hand, the decrease in the surface area of the adsorbents after the adsorption process can be attributed to the binding of the heavy metals on the surface of the adsorbent thus covering the active sites involved in metal adsorption (Swantches *et al*., 2016).

The point of zero charge of the adsorbent is the pH at which its surface has no charge. It provides information about the metal sorption mechanism. The point of zero charge of the treated and original adsorbents was determined using the salt addition method.

The point of zero charge for both treated and untreated rice husk was 4.21 and 5.5, respectively while that of treated and untreated cassava peel was 3.57 and 4.9, respectively. It has been reported by earlier researchers (Anirdvan and Krishan, 2004) that the point of zero charge of an adsorbent decreases with an increase in the acidic groups on the surface of the adsorbents. From the results, it can be concluded that acid modification of the adsorbent gave a positive (acidic) surface charge since the point of zero charge for the treated adsorbents was found to be lower than that of the untreated surface. Therefore, these results confirm that more acidic functional groups were incorporated into the cassava waste biomass and rice husk as a result of the acid treatment.

We can further see that the surface of the treated adsorbents is positively charged at solution pH below that obtained 3.57 and 4.21 for cassava peel and rice husk respectively. This causes competition between proton and metal ions for adsorption sites. Above the values of the point of zero charge, a negative charge is present on the surface of the adsorbent leading to better heavy metal adsorption through electrostatic attractions (Seepe., 2015).

FTIR Analysis

The functional groups present in the adsorbents (treated conditions) were identified by subjecting them to the Fourier Transfer Infrared analysis and the results obtained are presented in Figure 1 and Figure 2.

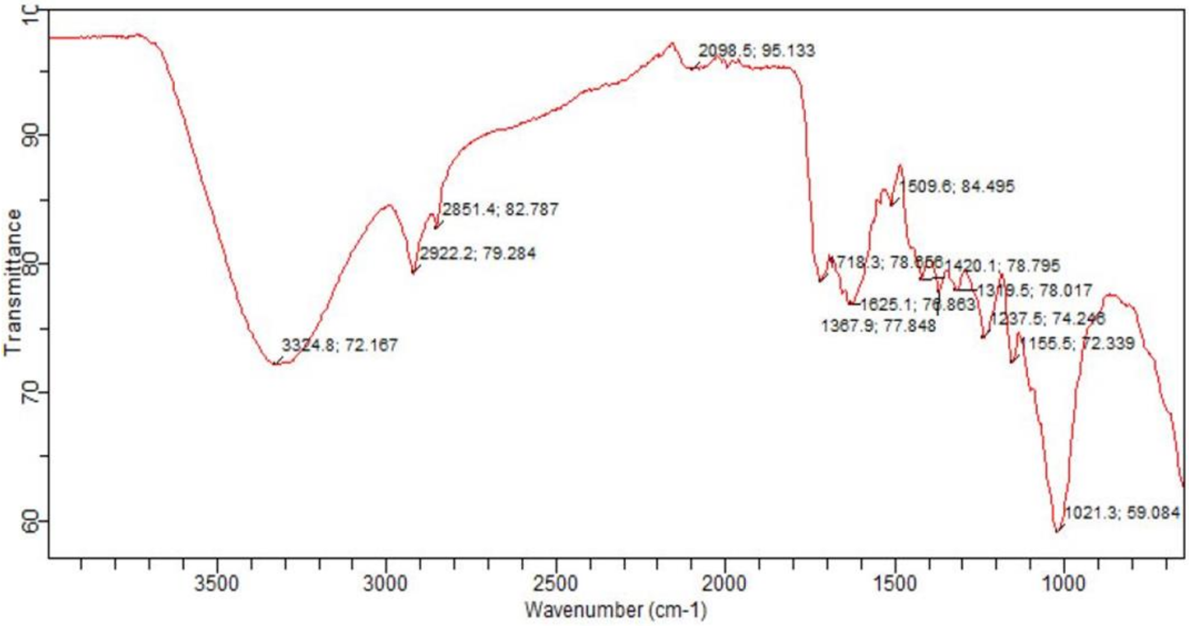

Figure 1: FTIR for acid modified cassava peel

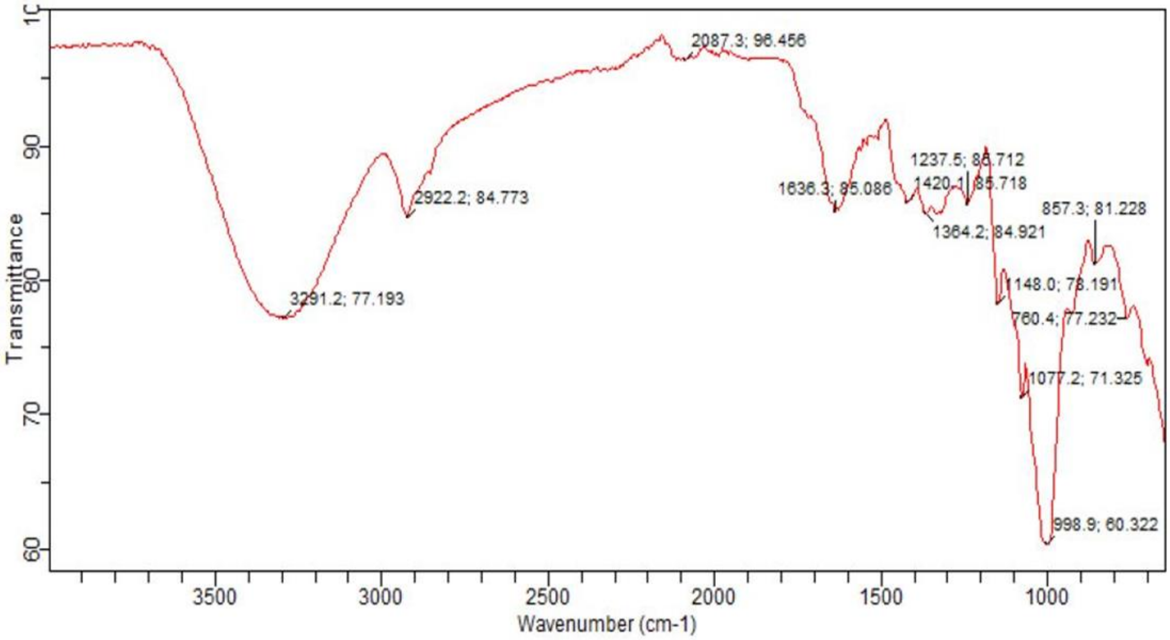

Figure 2: FTIR for acid-modified Rice husk

Various functional groups such as amine (-NH), carboxylate anions (-COO-), hydroxyl (-OH), and others (-C=C), (-C-C), (-C=O), (-C-O), (-C-N), (-C-H) have been proposed to be responsible for sorption metal binding by different biosorbents and their importance for metal uptake depends on factors such as the number of sites, its accessibility, chemical State or affinity between site and metal (Masood *et al.*, 2009). The FTIR was found to be in the range of 4000 - 650 cm^{-1} region with a resolution of 8 cm^{-1}. According to the illustration of Singh et al., (2012) of the functional groups corresponding to a range of wave numbers, the largest peak of wave number 3336 cm^{-1} shown in Figures 1 and 2, corresponds to either free or H-bonded O-H groups that could be present in carboxylic acids on the surface of rice husk and cassava peel. The peak at 1625.1 and 1628.8 cm^{-1} wave number corresponds to the C=O that could exist in the carboxylic acids. Peaks of wave numbers in the range of 1367.9 to 1021.3 cm^{-1} on the treated adsorbents are an indication of the C-O bond, and bands of wave number 2922 cm^{-1} are an indication of the presence of the C-H bond. C-O bond may be due to carboxylic acids, alkoxyl groups, or fiber carbonaceous that are present in the structure of rice husk that is composed of lignin and cellulose. These groups probably act as proton donors that once get deprotonated, the hydroxyl or carboxyl group adsorbs the heavy metal ions. (Singh *et al.*, 2012). All the hetero-atoms (functional groups such as –OH, C=C, and C=N) can be involved in the adsorption process via an ion exchange mechanism or complexation mechanism.

SEM Analysis

The surface morphology was identified by the use of the SEM as presented in plate I to plate II.

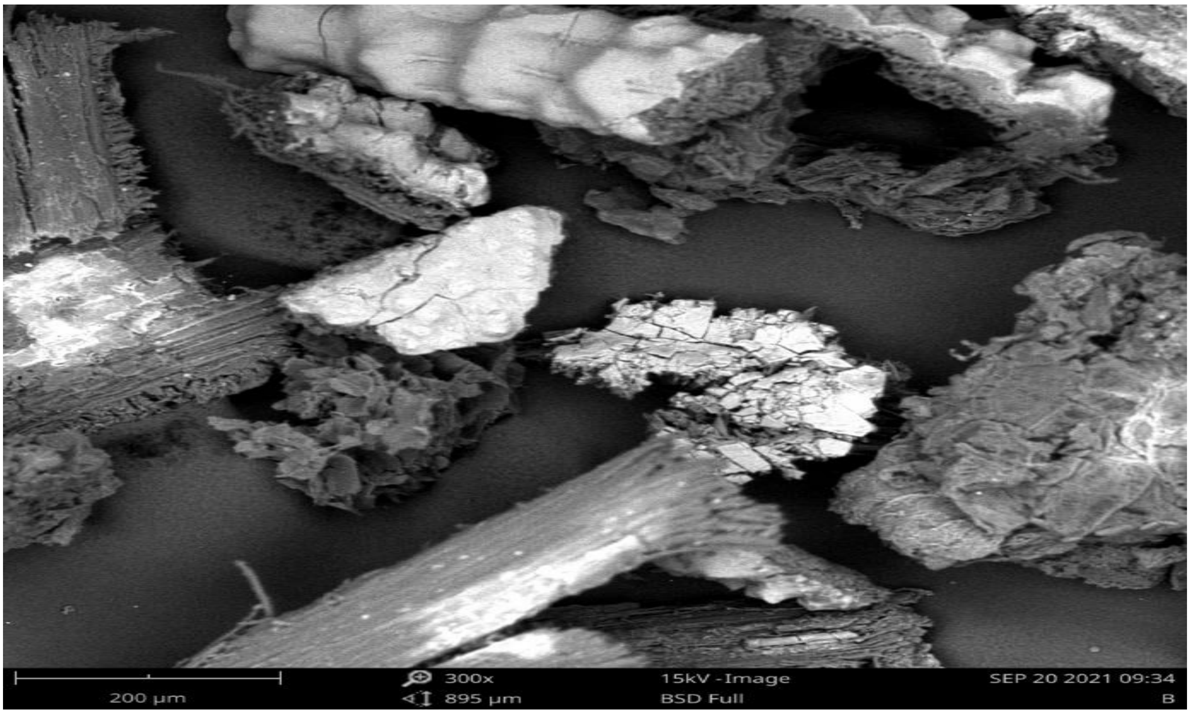

Plate 1: SEM image of the mixed (mass 1:1) cassava peel and rick husk (modified) 1500x magnification

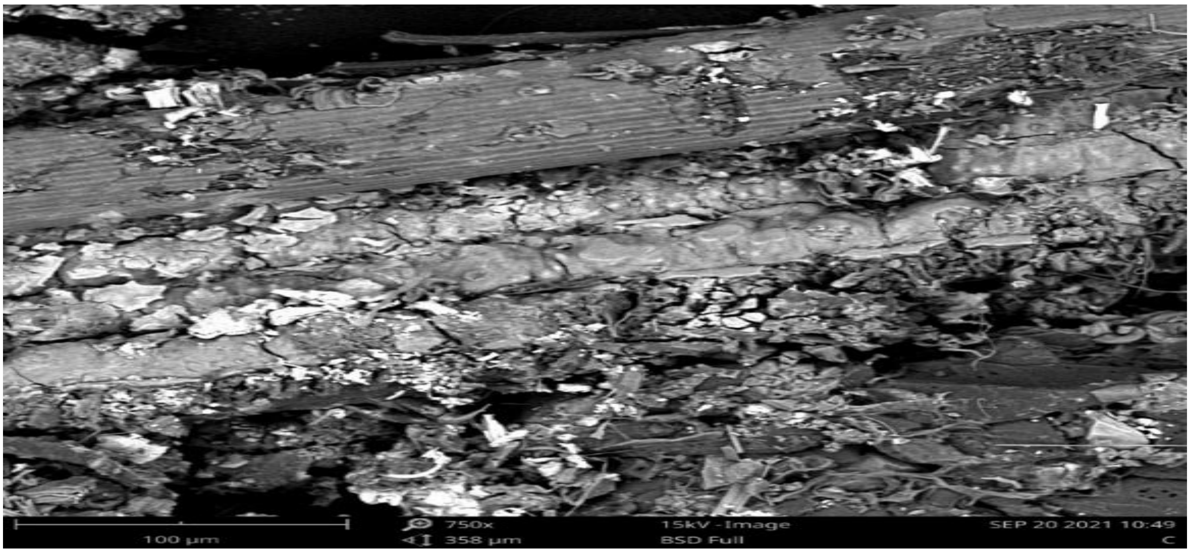

Plate 2: SEM image of the mixed (mass 1:1) cassava peel and rick husk after the adsorption study 750x magnification

The scanning Electron Microscopy (SEM) image displays the surface structure or morphology of a given material. Rice husk and cassava peel powders were mixed in equal proportions and subjected to SEM under specific magnification. In plate I, the cell crystallization is reduced, and more pore formation occurs by the binding or the coming together of the adsorbent thereby creating more surface porosity which further leads to more adsorption capacity (Mahmood *et al.*, 2014). The bright spots on plate I also show the rough and porous surface of the adsorbent, which is one of the factors that increases adsorption capacity (Feka., 2017). Plate II shows the adsorption of the heavy metal depicting the surface of the adsorbent after adsorption. It is seen that the caves, pores, and surface of the adsorbent were covered by the adsorbed heavy metal consequently the surface has become smooth. It is evident that upon adsorbing the heavy metal the adsorbent structure has changed (Feka., 2017).

Wastewater sample characterization

The wastewater sample was characterized using standard conditions and the findings are presented in Table 4.

Table 4: Physicochemical characterization of Wastewater from NILEST Study Cente, Kano

S/no	**Parameters**	**Values**	**Unit**	**Standard**	
				NESREA(2009)	**WHO (2006)**
1	Initial color	Brown			Light permeable
2	Odor	Objectionable (unpleasant)		Odourless	
3	pH	9.83		6.0-9.0	6.5- 9.5
4	Temperature	28.3	^{O}C	40	30
5	Electrical conductivity	12.70	ms/cm	<400	250
6	TDS	28200	mg/L	2000	2100
7	BOD	480	mg/L	<30	30
8	COD	5500	mg/L	<60	250
9	Turbidity	4800	NTU	<10	5
10	Chloride	549.83	mg/L	600	250
11	TSS	11500	mg/L	30	
12	Oil and grease	3000	mg/L	10	
13	Nickel	0.07395	mg/L	0.02	0.1
14	Lead	0.137	mg/L	0.05	0.2
15	Chromium	3.298	mg/L	0.05	0.1
16	Cupper	0.085	mg/L	0.5	1.0
17	Zinc	0.150	mg/L	2.0	3.0
18	Iron	0.683	mg/L	0.5	0.3
19	Maganesse	0.147	mg/L	5	1.0

*Source : NESREA 2009, WHO 2006(Feka., 2017)

pH value for the wastewater as presented in Table 4 is 9.83 and is outside the WHO and NESREA acceptable limits for the discharge of wastewater into both surface waters and sewers. This value (9.83) implies that the NILEST study center wastewater is alkaline in nature. A pH of 6.0 – 9.0 is the recommended range for effluent to be discharged, alkaline wastewater cannot be discharged because it will be harmful to man, and aquatic animals and will alter the biological activity of the steam if added (Oke *et al*., 2006). If the surface water pH shifts too far either way from the pH range of 6.5-7.5, sensitive fish and plant life may be lost (UNIDO, 2016).

The presence of dissolved solids in water may affect its taste; the palatability of wastewater for aquatic life is controlled by the amount of dissolved solids inside it (WHO, 1996). TDS concentration (28200 mg/L) as presented in Table 4 for this work exceeds WHO (2100 mg/L) and NESREA (2000 mg/L) discharge limit. This could be the major source of sediments which reduces the light penetration into water bodies and ultimately decreases photosynthesis. Alongside this, the high value of total suspended solids implies that there would be the adsorption of heat from sunlight causing an increase in the water temperature and subsequently decreasing the level of dissolved oxygen available for aquatic activities.

From related literature, (Oke *et al*., 2006) wastewater with suspended solids is classified as weak (less than 100mg/L), medium (less than 220mg\L), and strong (greater than 220mg/L). From the result obtained (11,500mg/L) as presented in Table 4, it can be classified as a strong wastewater and cannot be discharged into the stream as it will encourage sludge formation which in turn supports anaerobic reaction that will further affect the self-purification ability of the stream.

The Chemical Oxygen Demand (COD) is the amount of oxygen required for degradation of the compound in the wastewater to occur. The higher the COD value of the wastewater the more oxygen demand to discharge the water bodies. The value of COD obtained is 5500mg/L as presented in Table 3.3, it is above the discharge limit and this shows that the effluent has high oxygen-demanding waste which causes the depletion of DO which is a key requirement for aquatic life.

Biological Oxygen Demand (BOD) measures the amount of oxygen required by bacteria to break down simpler substances, the decomposable organic matter present in any wastewater or treated effluent (WHO, 2002). A BOD of 480mg/L was obtained as presented in Table 4. The higher level of BOD as compared to the permissible limit are indication of the pollution strength of the wastewater and is often associated with low dissolved oxygen thus making the stream unfit for aquatic life.

The chemical oxygen demand (COD) and the biological oxygen demand (BOD) are the most important parameters commonly used to examine wastewater quality since they reflect the organic load in wastewater. The BOD value of 480 mg/L from Table 4 was much higher than the WHO and NESREA standard of less than 30 mg/L. COD recorded (Table 4) was 5500 mg/L as against the WHO standard of 250 mg/L. High BOD and COD levels are other indicators of an increased load of organic pollutants in any wastewater.

Adsorption study

The adsorption process was carried out under various conditions of pH, adsorbent dosage, and time as generated by the design of the experiment (Design Expert 11.0 version software) as presented in Table 2. The adsorption study was carried out using both the treated and ordinary adsorbent. The ordinary adsorbent was used as the control for the adsorption process.

At the end of the adsorption process, the filtrate obtained was analyzed to determine the concentration of chromium, lead, and nickel. Table 5 presents the removal percentage and adsorption capacity (Qe) for each of the heavy metals studied.

Table 5: Heavy metal removal and adsorption capacity for modified mixed (1:1 mass) adsorbent (cassava and rice husk)

Run	pH	Contact time (min)	Dosage (g)	Cr Qe (mg/g)	Cr removal (%)	Ni Qe (mg/g)	Ni Removal (%)	Pb Qe (mg/g)	Pb removal (%)
1	4	120	6.00	46.448	84.50	0.2330	18.90	1.7767	77.80
2	12	10	6.00	21.712	39.50	0.6778	55.00	0.3933	17.20
3	12	65	2.00	48.480	29.40	1.9275	52.10	1.0300	15.00
4	4	65	10.00	30.935	93.60	0.1475	20.00	1.2360	90.20
5	8	120	2.00	126.825	76.80	3.6625	90.50	3.0900	45.06
6	4	10	6.00	47.990	87.30	0.3158	25.50	2.1420	93.80
7	4	65	2.00	139.175	84.40	0.5325	14.40	5.5750	81.40
8	8	65	6.00	34.630	63.00	1.1708	95.00	1.400	61.30
9	8	65	6.00	34.740	63.20	1.1708	94.90	1.1680	51.20
10	8	10	10.00	25.329	76.80	0.7265	98.20	0.8080	59.00
11	12	65	10.00	14.413	43.70	0.4375	59.20	0.7330	53.50
12	8	65	6.00	24.965	45.40	1.1675	94.70	1.1530	50.50
13	12	120	6.00	24.350	44.30	0.9925	80.50	1.1780	51.60
14	8	10	2.00	90.695	55.00	2.5875	70.00	2.9750	43.40
15	8	65	6.00	34.850	63.40	1.1808	95.80	1.1733	51.40
16	8	120	10.00	26.120	79.20	0.6615	89.50	0.9340	68.20
17	8	65	6.00	34.900	63.50	0.9975	80.90	1.1720	51.30

The volume of solution used (V) = 100 mL, Initial concentration (Ci) of chromium = 3.298mg/L, Nickel = 0.07395mg/L, and Lead = 0.137mg/L.

Adsorption Equilibrium Isotherm

For the equilibrium isotherm study, the isotherm models discussed in section 2.4 were used to analyze the experimental data.

Langmuir Isotherm

The linearized form of the Langmuir isotherm model as presented by equation 3 in section 2.4.1 was used by plotting 1/Qe versus 1/Ce. Equilibrium isotherm parameters for the model were obtained from the slope and intercept of the plot for chromium, Nickel, and Lead.

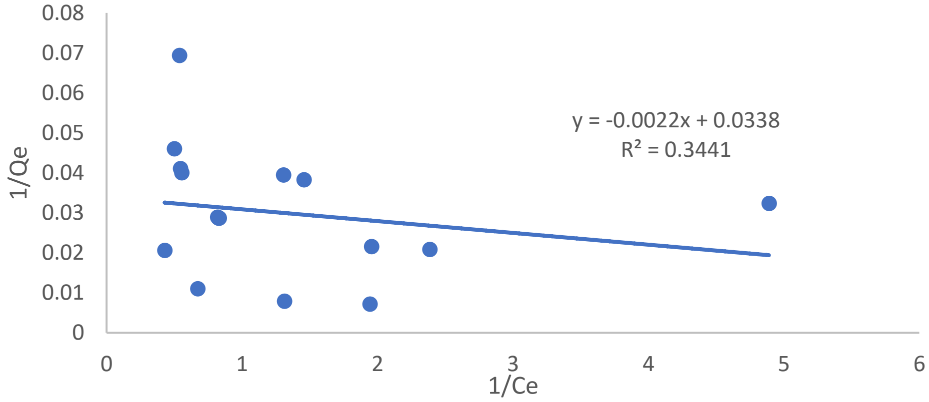

Figure 3: Langmuir isotherm plot for Chromium adsorption

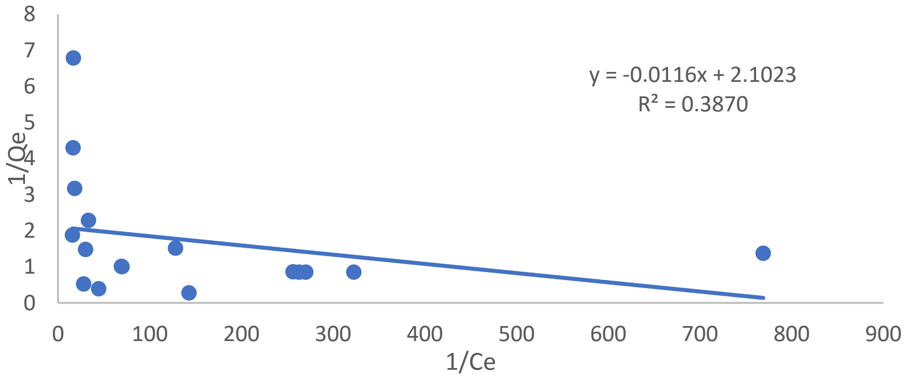

Figure 4: Langmuir isotherm plot for Nickel adsorption

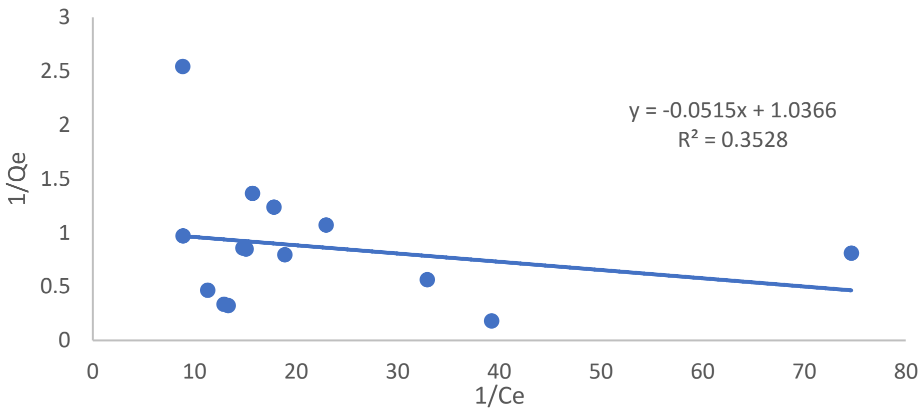

Figure 5: Langmuir isotherm plot for Lead adsorption

Freundlich Isotherm

The linearized form of the Freundlich isotherm model given in equation 4 under section 2.4 was used by plotting against Log qe versus Log Ce. Equilibrium isotherm parameters for the model were obtained from the slope and intercept of the plot chromium, nickel, and lead.

Similarly, the Freundlich isotherm model for the adsorption of chromium, nickel, and lead is presented in Figure 6 to Figure 8

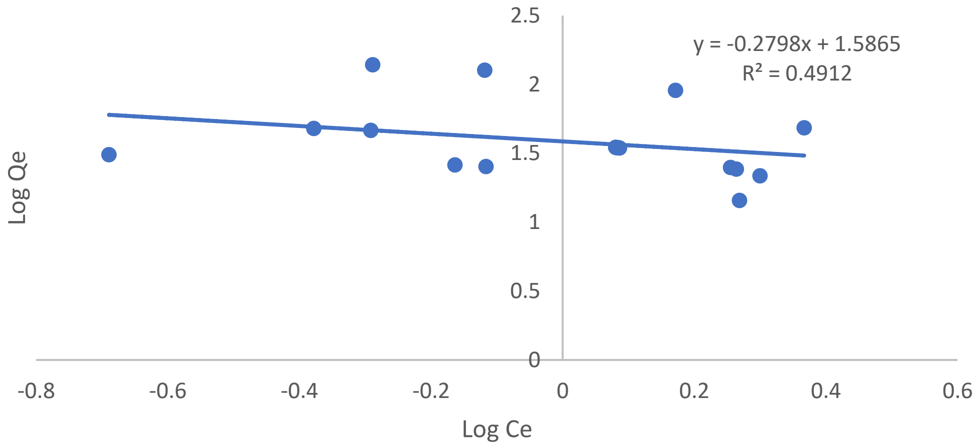

Figure 6: Freundlich isotherm plot for chromium adsorption

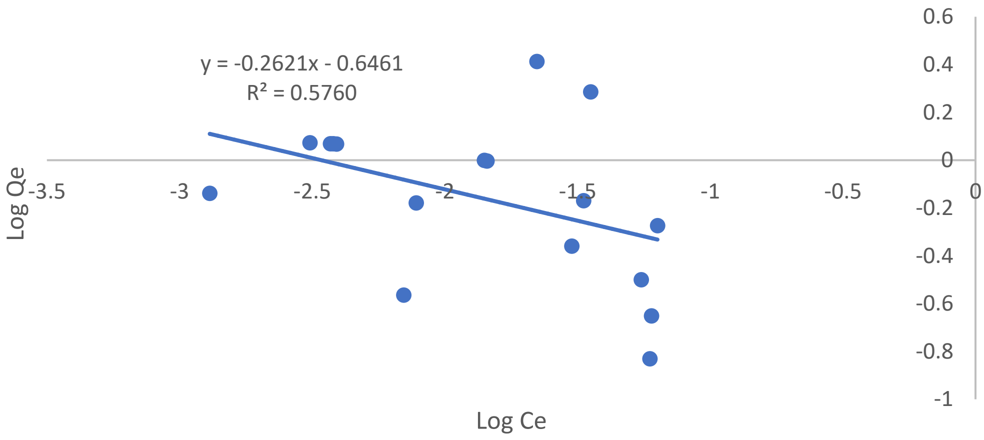

Figure 7: Freundlich isotherm plot for Nickel adsorption

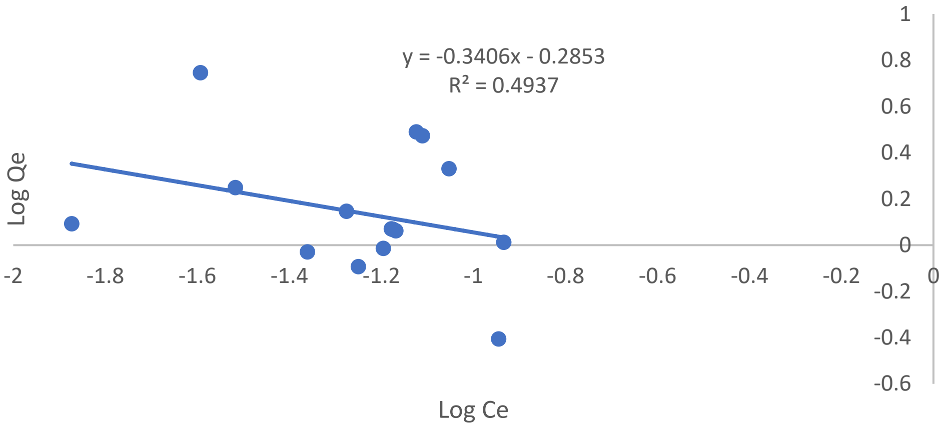

Figure 8: Freundlich isotherm plot for Lead adsorption

Redlich-Peterson Isotherm

This model is presented by equation 5 in section 2.4. A plot of $\ln(Ce/qe)$ versus ln Ce was obtained to enable the determination of Redlich-Peterson constants, where β is the slope and A is the intercept on chromium, nickel, and lead axis. The Redlich- Peterson isotherm model plot for the adsorption of chromium, nickel, and lead respectively are presented in Figure 9 to Figure 11

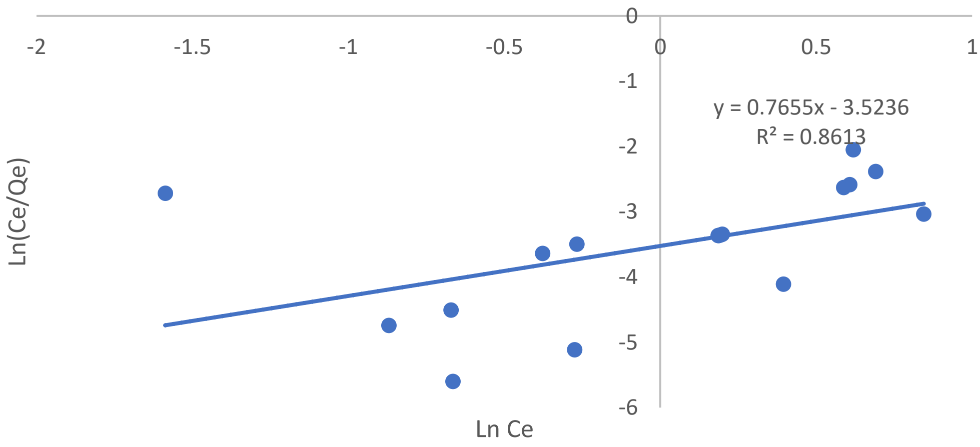

Figure 9: Redlich-Peterson isotherm plot for Chromium adsorption

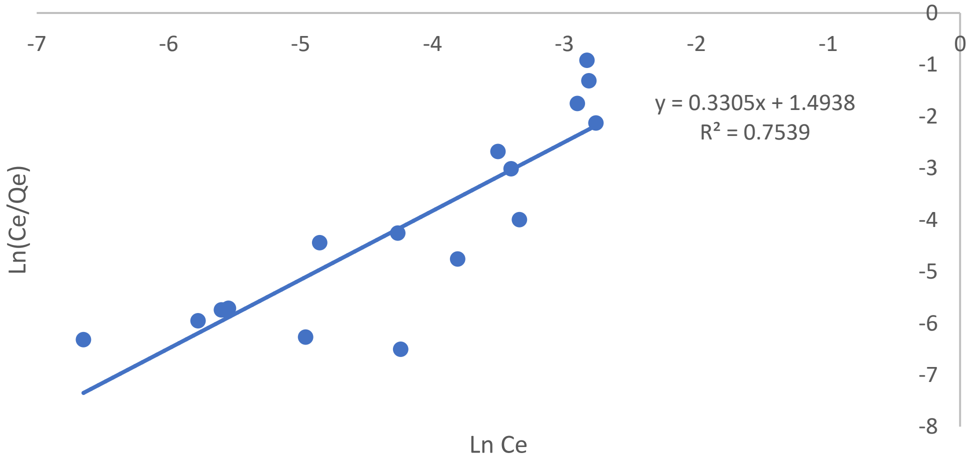

Figure 10: Redlich –Peterson isotherm plot for Nickel adsorption

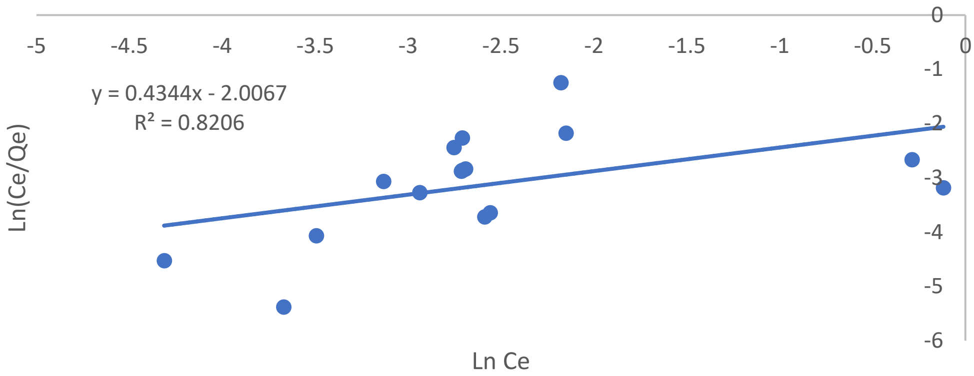

Figure 11: Redlich – Peterson isotherm plot for Lead adsorption

A summary of the experimental constant for the studied isotherm models is presented in Table 6, 7, and 8 for chromium, nickel, and lead respectively.

Table 6: Isotherm Experimental Constants for Adsorption of Chromium

Isotherm model	Constants	Values
Langmuir	R^2	0.344
	B	119.9
	Qm	3.7921
Freundlich	R^2	0.4912
	Kf	$3.5 X10^8$
	1/n	0.6636
Redlich- Peterson	R^2	0.8613
	β	0.7655
	A	-3.5236

Table 7: Isotherm Experimental Constants for Adsorption of Nickel

Isotherm model	Constants	Values
Langmuir	R^2	0.387
	B	806.17
	Qm	0.1069
Freundlich	R^2	0.5760
	Kf	$1.3 X 10^2$
	1/n	1.166
Redlich- Peterson	R^2	0.7539
	β	0.3305
	A	1.4938

Table 8: Isotherm Experimental Constants for Adsorption of Lead

Isotherm model	Constants	Values
Langmuir	R^2	0.3528
	B	134.23
	Qm	0.1448
Freundlich	R^2	0.4937
	Kf	$3.18 X 10^1$
	1/n	0.5572
Redlich Peterson	R^2	0.8206
	β	0.4344
	A	-2.0067

The low R^2 values obtained for both the Langmuir and Freundlich isotherm models in all the heavy metals studied indicate an unfavorable applicability for the adsorption process. The high 1/n value obtained for the various heavy metals based on the Freundlich model is meant to be favorable at $0.1<1/n<1$, implying a non-favorable applicability which is in agreement with previous related studies (Feka., 2017).

The R^2 values 0.8613, 0.7539, and 0.826 were obtained for chromium, nickel, and lead using the Redlich- Peterson isotherm model as presented in Table 6 to Table 8 shown to be the highest among all the isotherm models studied showing that the model of good applicability in describing the adsorption process. This implies that the adsorption process does not follow the ideal monolayer mechanism but that of a hybrid.

Adsorption Kinetics

The adsorption kinetics were studied using the pseudo-first-order, pseudo-second-order, and Elovich model reaction. The results obtained for each of the studied metal is presented in Table 9 to Table 11. a plot for each of the studied kinetic mechanisms is presented in Figure 12 to Figure 14.

Table 9: Kinetic studies experimental constants for Chromium adsorption study

Kinetic model	Constants	Values
Pseudo-first-order	R^2	0.717
	$K_1(min^{-1})$	0.007
	qe exp (mg/g)	30.935
	qe cal (mg/g)	46.13
	SSE(%)	3.69
Pseudo-second-order	R^2	0.981
	$K_2(g\ mg^{-1}min^{-1})$	0.4167
	qe exp (mg/g)	30.935
	qe cal (mg/g)	25.641
	SSE(%)	1.284
Elovich	R^2	0.975
	α (mg g^{-1} min $^{-1}$)	2.69×10^4
	β(mg g^{-1})	0.1190

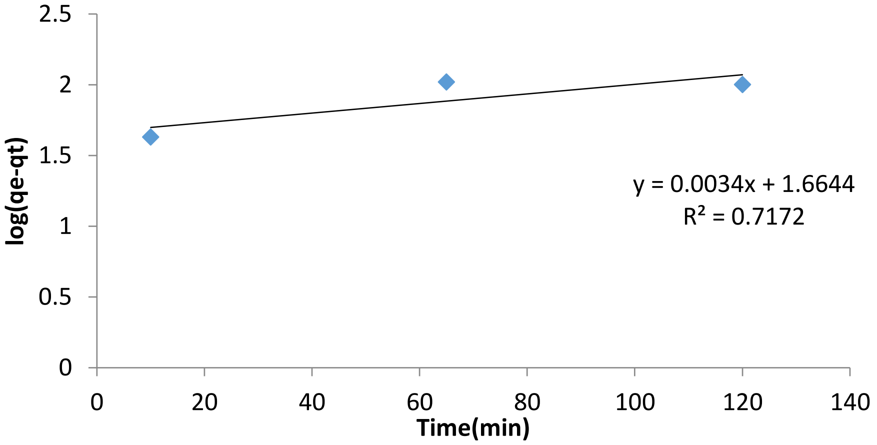

Figure 12: Pseudo-first-order kinetic plot for Chromium adsorption

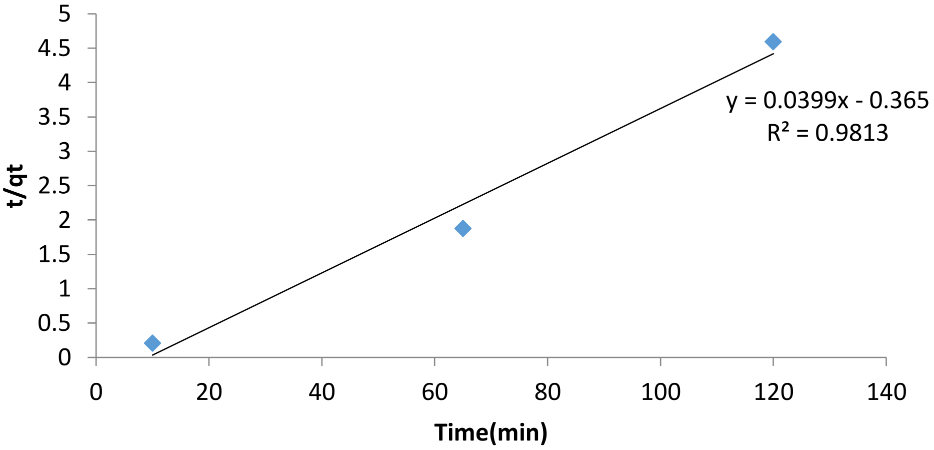

Figure 13: Pseudo-second-order kinetic plot for Chromium adsorption

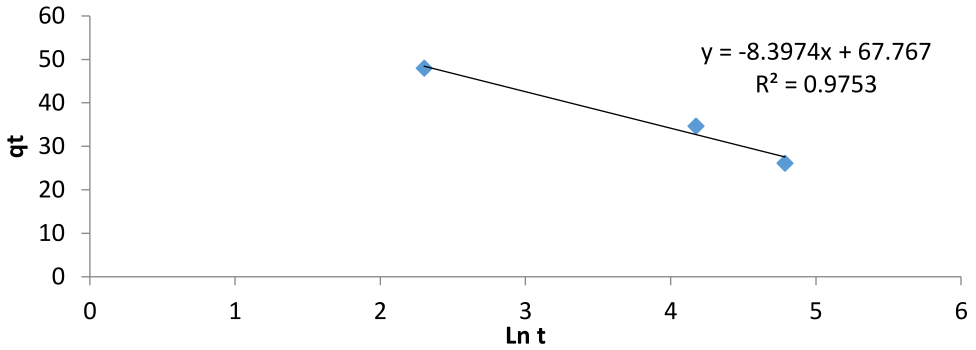

Figure 14: Elovich kinetic plot for Chromium adsorption

Table 10: Kinetic studies experimental constants for Nickel adsorption

Kinetic model	Constants	Values
Pseudo first- order	R^2	0.111
	$K_1(min^{-1})$	0.0023
	qe exp (mg/g)	0.7265
	qe cal (mg/g)	1.762
	SSE(%)	0.25
Pseudo-second order	R^2	0.866
	$K_2(g\ mg^{-1} min^{-1})$	1.781
	qe exp (mg/g)	0.7348
	qe cal (mg/g)	0.7348
	SSE(%)	0.0020
Elovich	R^2	0.413
	α (mg g^{-1} min $^{-1}$)	0.3175
	β(mg g^{-1})	4.694

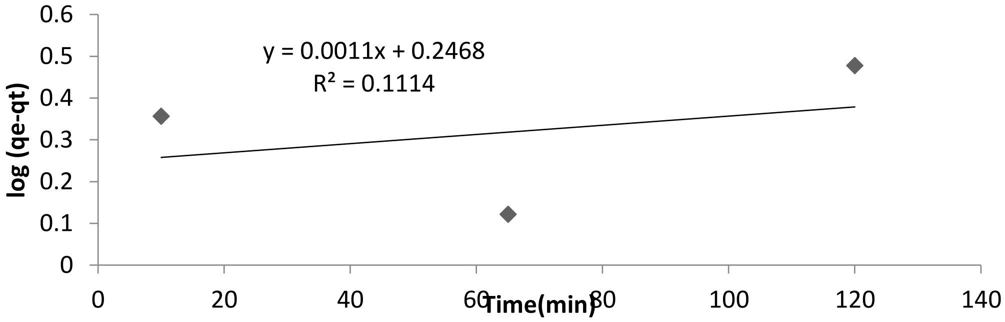

Figure 15: Pseudo-first-order kinetic plot for Chromium adsorption

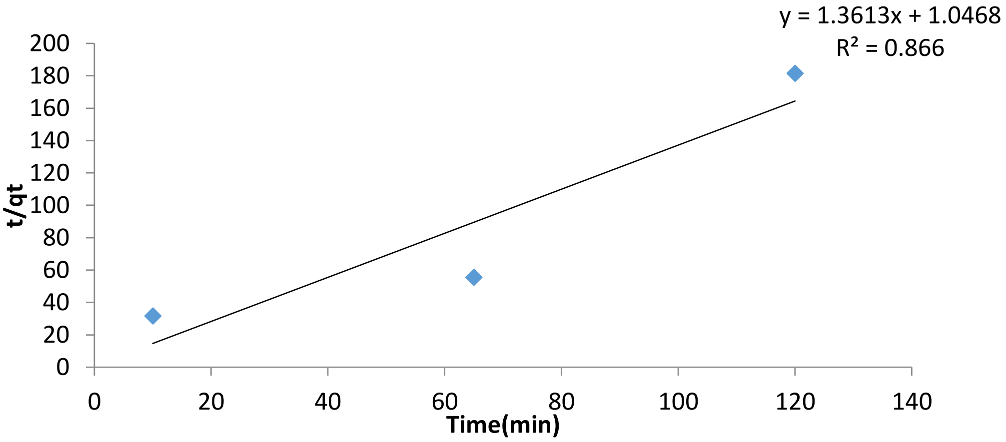

Figure 16: Pseudo-second-order kinetic plot for Nickel adsorption

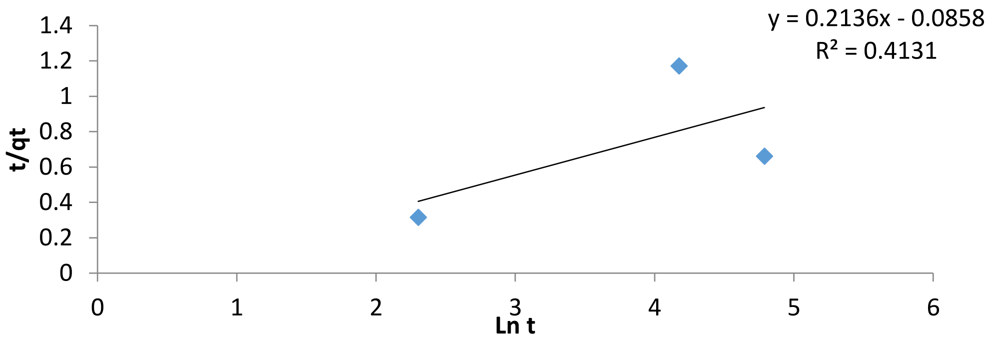

Figure 17: Elovich kinetic plot for Nickel adsorption

Table 11: Kinetic studies experimental constants for Lead adsorption

Kinetic model	Constants	Values
Pseudo first -order	R^2	0.172
	$K_1(min^{-1})$	0.0023
	qe exp (mg/g)	2.1420
	qe cal (mg/g)	1.7258
	SSE(%)	0.100
Pseudo-second - order	R^2	0.951
	$K_2(g\ mg^{-1}min^{-1})$	0.1937
	qe exp (mg/g)	2.1420
	qe cal (mg/g)	2.187
	SSE(%)	0.0011
Elovich	R^2	0.232
	α (mg g^{-1} min $^{-1}$)	3.65 x 10^1
	β(mg g^{-1})	9.2593

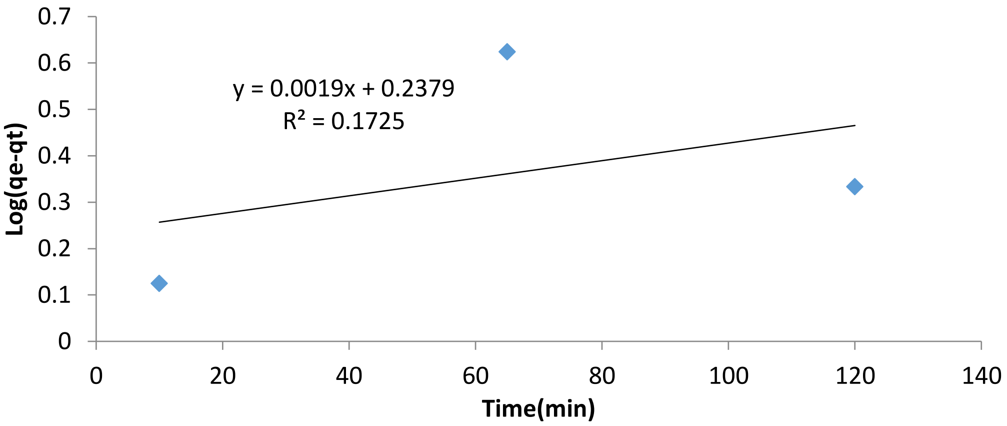

Figure 18: Pseudo first - order kinetic plot for Lead adsorption

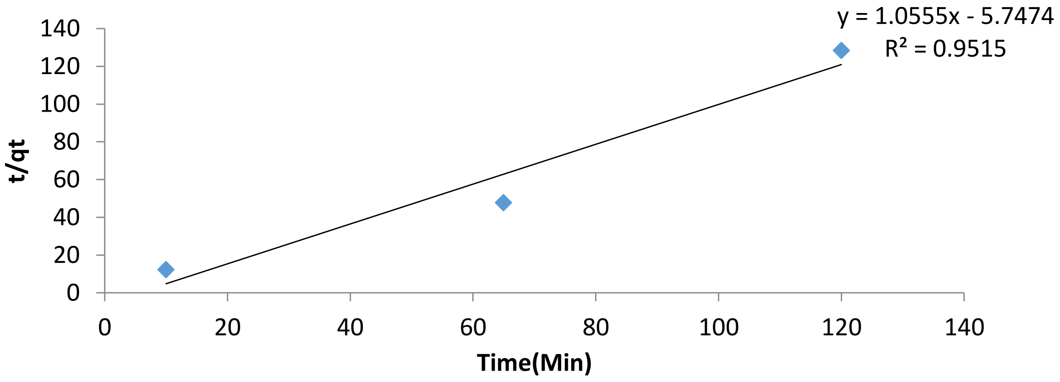

Figure 19: Pseudo second order kinetic plot for Lead adsorption

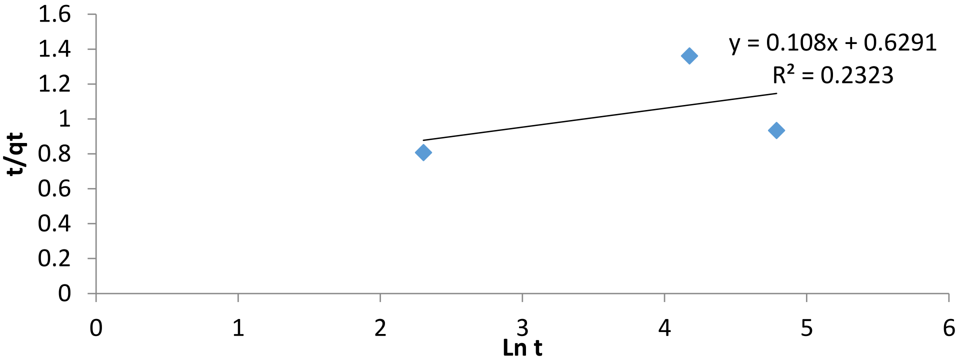

Figure 20: Elovich kinetic plot for Lead adsorption

The study of adsorption kinetics describes the solute uptake rate and evidently, this rate controls the residence time of adsorbate uptake at the solid-solution interface. Taha *et al*., (2014), inferred that a kinetic model helps in the study of the adsorption rate, models the process, and predicts information about adsorbent/adsorbate interaction (physisorption or chemisorption).

The R^2 values for the first-order kinetics and Elovich model as well as the high SSE (%) value obtained as presented in Table 9 to Table 11 show that they are not the best fit in describing the adsorption kinetics. The low correlation coefficient value obtained from the pseudo-first-order kinetic model as presented in Table 9 to Table 11 for the studied metals indicates that sorption is not occurring exclusively onto one site per ion (Nuhoglu and Malkoc, 2009). This model is not applicable and does not explain the mechanism of adsorption kinetics. The coefficient of regression (R^2) for the pseudo-second-order model for the studied heavy metals suggested the applicability of the pseudo-second-order kinetic model, this shows that the overall rate of the adsorption process was controlled by chemisorption and involves valence forces, through sharing or exchange of electrons between the sorbent and the sorbate (Ho and McKay, 1999). The second-order kinetics applies to the system; since the plot of t/qt versus t (Figure 13,16 and 19) for the heavy metal studied gave a linear relationship (Itodo *et al*., 2011). Very low error function (1.284%, 0.0020%, and 0.0011 %) for chromium, nickel, and lead respectively was recorded which implicates this model as suitable for describing the rate of the heavy metal (Cr, Pb, and Ni) uptake by the adsorbent.

The poor extent of linearity (R^2) as presented in Table 9 to Table 11 for both the pseudo-first-order and Elovich kinetic model in all the cases of the studied metals, could not explain the sorption rate in this study. The Elovich equation is mainly applicable to chemisorption kinetics. The Elovich equation is often valid for systems in which the adsorbing surface is heterogeneous (Namasivayam and Kavitha 2002). In reactions involving the chemisorption of adsorbate on a solid surface without desorption of products, the adsorption rate decreases with time due to an increased surface coverage (Panida and Xianshe., 2016).

CONCLUSION

A maximum adsorption capacity of 139.175mg/g, 3.6625mg/g, and 5.5750mg/g with a final concentration of 0.5145 mg/L, 0.0070mg/L and 0.0255mg/L and a maximum percentage removal of 93.60%, 98.20% and 93.80% for Chromium, Nickel and Lead respectively from the Tannery Wastewater was obtained.

The adsorption isotherm better fitted to the Redlich Peterson isotherm model with a highest R^2 value of 0.8613, 0.7539, and 0.8206 for Chromium, Nickel and lead respectively implying that the adsorption process does not follow the ideal monolayer mechanism but that of a hybrid.

The adsorption kinetics was better modelled using pseudo-second-order kinetics with a highest R^2 value of 0.981, 0.866, and 0.951 with a corresponding least Sum Squared Error SSE (%) of 1.284, 0.0020, and 0.297 for Chromium, Nickel and Lead respectively. The correlation coefficient, R^2, favoring the pseudo-second-order model with a very negligible percentage sum of square error is an indication of a chemisorption mechanism.

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