



ADSORPTION ISOTHERMS AND KINETICS OF HEAVY METALS REMOVAL FROM TANNERY EFFLUENT USING COMPOSITE AGRICULTURAL WASTE AS ADSORBENT

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Tannery waste waters are very complex and characterized by high content of organic, inorganic and nitrogenous compounds which include heavy metals. In this study, the adsorption Isotherm and kinetics of a composite adsorbent produced from the chemical activation of groundnut shell and rice husk were utilized as agricultural waste in the removal of Pb, Cr and Cd from tannery effluent. The experimental data were fitted to Langmuir, Freundlich and Temkin isotherms, while the kinetics were studied using Pseudo-First-Order and Pseudo-Second-Order kinetic models. The results revealed that Langmuir isotherm model showed excellent fit to the experimental data for all the heavy metal adsorption onto Groundnut shell activated carbon (GR-AC). This can be seen from the high correlation coefficients R^2 . The Langmuir monolayer adsorption capacity (q_m) value was found to be 9.81 mg/g (Pb), 5.72 mg/g (Cr) and 4.25 mg/g (Cd) respectively. The equilibrium adsorption capacity (q_e) values calculated from the Second Order kinetics model agreed well with the experimental values for Pb and Cd. In addition, the First Order Kinetic rate constant decreased with increase in initial metal ion concentration. The excellent correlation between the calculated q_e and experimental q_e values and higher regression coefficient R^2 shows clearly that the adsorption of these heavy metals onto GR-AC followed Pseudo-Second-Order kinetic model. Therefore, groundnut shell and rice husk can effectively be utilized as agricultural waste to produce a composite adsorbent to remove Pb, Cr and Cd from tannery effluent.

1.0 Introduction

Recently, the fast growth of industrialization causes a large amount of heavy metal-laden disposal to the environment which is highly toxic, mutagenic, and oncogenic (Başaran et al., 2008). The rate of contaminated wastewater has kept on increasing intensively as a result of rapid urbanization and industrialization (Beyan, et al., 2022). Among industries, leather industry is recognized as a potential source to generate a significant amount of heavy metals into the environment (Islam et al., 2021). Tannery wastewaters are very complex and are characterized by high content of organic, inorganic and nitrogenous compounds, chromium, sulphides, suspended solids, and dissolved solids (Durai and Rajasimman 2011). The performance of treatment technologies varies with the types, sources and complexity of wastewater, and the kinds of technologies used. Basically, the selection of wastewater treatment methods depends on the durability, sustainability, efficiency and reliability of technologies. The development of appropriate and effective wastewater treatment technologies is progressing (Bedada et al., 2020).

Various conventional methods had been developed and tested for the removal of heavy metals from wastewater so that their environmental and health effects are minimized. Removal of metals from wastewater can be achieved by the application of several methods such as sedimentation, electrochemical processes, ion exchange, biological operations, cementation, coagulation/flocculation, filtration, membrane processes, chemical precipitation and adsorption (Dagmawi and Dawit, 2013). Adsorption, among these techniques, is widely accepted due to ease of use in operation, low cost and high efficiency. However, selection of a suitable adsorbent is critical. Biochar has recently been established as an effective adsorbent for a variety of environmental applications and got a huge attention of the researchers for heavy metals' removal from wastewater. Biochar is a black, solid, stable, and porous carbonaceous compound with a large surface area and is derived from waste biomass through slow or fast pyrolysis (Amin et al., 2019). For the adsorption of various pollutants, there has been a lot of success for Rice Husk (Abbas et al., 2013; Dikdima et al., 2022) and Groundnut shell (Tegegn et al., 2022; Kothai et al., 2019).

Isotherms and kinetics studies play an important role in understanding the nature and mechanism of adsorption process. In this study, the equilibrium and dynamics characteristics of the adsorption of heavy metals from tannery effluents using agricultural waste as adsorbents were evaluated. The Experimental equilibrium adsorption data were modelled using Langmuir, Freundlich and Temkin models. In addition, pseudo first and pseudo second order kinetics models were also fitted to the adsorption data to further describe the adsorption mechanism.

2. Materials and Methods

2.1 Adsorbent Preparation and adsorption Experiment

Rice husks and Groundnut Shells were obtained from a local rice mill and a local groundnut shelling mill in Gamboru, Maiduguri, Borno state. The raw groundnut shell and rice husks were ripped off to remove dusts and washed with distilled water to remove the adhered particles dried for 24 hours in an oven at 105°C. It was then carbonized at temperature of 400°C for 1 hour to obtain bio char and then refined into powder form which was stored for uses.

The adsorption experiments were performed in a series of flasks containing 50 ml solutions tannery wastewater at 50 – 250 mg/L concentrations and adsorbent dosages of 0.5g. The mixtures were agitated for 60 min at 250 rpm using a shaker mixer. The resulting mixtures were filtered, and the concentrations of heavy metals were determined using Atomic Adsorption Spectrometer (AAS). The adsorption equilibrium was investigated for different metal concentrations between 50 and 250mg/L. In addition, kinetics experiments were conducted with 250 mg/L metal and 0.5 g of adsorbent at 30, 40 and 50°C temperature with stirring at 250 rpm for 60 min. The amount of adsorption at equilibrium was obtained using Equation (1)

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

where: V is the solution volume in L, m is the amount of adsorbent used in g and q_e is metal ion uptake in mg/g at time, t

2.2 Adsorption isotherm determination

Adsorption isotherms are commonly used to describe the interaction of the adsorbate with the adsorbent. It also furnishes information for the understanding of the nature of reaction which is fundamental to optimizing the design of adsorption system. Several isotherm models have been developed and utilize for the analysis of equilibrium data. The adsorption data was analyzed by fitting to Langmuir, Freundlich and Temkin Isotherm models (Manikandan, 2016).

Langmuir isotherm model is representative of monolayer adsorption occurring on energetically homogenous surface (Foo and Hameed., 2010). The Linear form of the model is expressed by Equations (2) and (3)

$$\frac{C_e}{q_e} = \frac{1}{kQ_0} + \frac{C_e}{Q_0} \quad (2)$$

$$\text{or } \frac{1}{Q_e} = \frac{1}{Q_0} + \frac{1}{kQ_0C_e} \quad (3)$$

The non- linear form is expressed by:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad (4)$$

where: C_e is the equilibrium concentration in (mg/L), Q_0 is the Maximum adsorption Capacity, k is the Adsorption equilibrium constant (L/mg) and q_e is the equilibrium adsorption capacity.

Freundlich isotherm is widely applied in heterogeneous systems especially for organic compounds or highly interactive species on activated carbon and molecular sieves. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface (Foo and Hameed., 2010)

The Equation is given by Equation (5) and the non-linear form is expressed by Equation (6):

$$Q_e = k_f C_e^{1/n} \quad (5)$$

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (6)$$

where: n is Adsorption intensity, k_f is the Freundlich coefficient related to adsorption capacity. The Freundlich isotherm constants K_f , $1/n$ can then be calculated from the slopes and intercepts of $\ln (q_e)$ versus $\ln C_e$.

Temkin isotherm is based on the hypothesis that, due to the interaction between adsorbent and adsorbate. The heat of adsorption of all the molecules in the layer reduce linearly with coverage due to adsorbate–adsorbate interactions. It is based on the assumption that the free energy of adsorption is a function of surface coverage (Samuel et al, 2015). The Temkin isotherm model is represented by Equation (7):

$$q_e = B \ln AT + B \ln C_e \quad (7)$$

The non- linear form is expressed by Equation (8):

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \quad (8)$$

Where $\frac{RT}{b_T}$ is related to the heat of adsorption, and AT is the maximum binding energy of the adsorbate to the adsorbent, b_T is Temkin constant. The constants of the model B_T and K_T were obtained from the slope and intercept of the graph of the q_e versus $\ln C_e$, respectively.

2.3 Adsorption kinetics

Kinetic modeling for adsorption processes involves studying the rate of adsorption of a species under particular condition before attaining equilibrium, it involves studying the mechanisms of the adsorption processes (Vunain et al., 2021). The adsorption experimental data were

evaluated for their suitability using Pseudo-First Order and Pseudo-Second-Order models as presented by Equation (9) and (10).

$$\log(q_e - qt) = \log q_e - \frac{k_1}{2.303} t \tag{9}$$

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{10}$$

where: q_e and q_t (mg/g) are the adsorption capacities at equilibrium and time t (min), respectively. k_1 and k_2 are the pseudo-first-order and pseudo-second-order rate constants (Samuel et al., 2015).

3. Results and Discussion

3.1 Adsorption Isotherm Models

The adsorption data were analyzed by fitting to isotherm models into Langmuir, Freundlich and Temkin isotherm models. The adsorption isotherm of Lead, Chromium and Cadmium onto GR-AC are presented in Figure 1 (a-c). The parameters and correlation coefficients obtained from the plots are shown in Table 1. It can be observed from Figure 1(a-c) and Table 1 that Langmuir isotherm model showed excellent fit to the experimental data for all the heavy metal adsorption onto GR-AC. This can be seen from the high correlation coefficients in Table 1. The R_L value was found between 0 and 1, which indicated the favorability of the adsorption process under the studied conditions. The Langmuir monolayer adsorption capacity (q_m) value was found to be 9.8039 mg/g (Pb), 5.7175 mg/g (Cr) and 4.2535 mg/g (Cd) respectively. Lead adsorption onto GR-AC showed the highest maximum adsorption capacity. Similar result was reported in the literature (Bayuo et al., 2018). Langmuir isotherm connotes homogeneous distribution of active sites on the adsorbents, hence, the surface of GR-AC is homogeneous with monolayer coverage. This demonstrates that the adsorbent surface is homogeneous for Pb, Cr and Cd adsorption. The monolayer adsorption is accomplished via chemical adsorption and the active sites of GR-AC were uniformly disseminated.

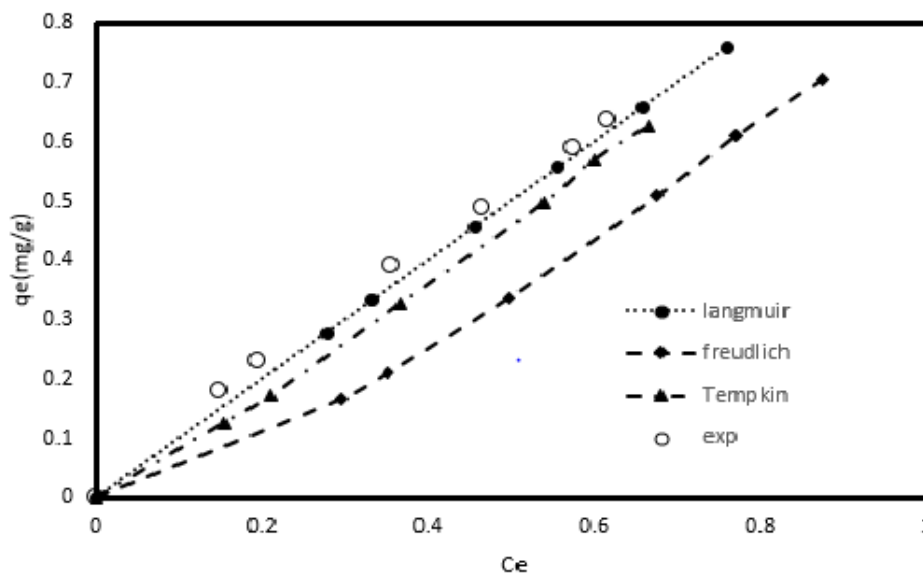


Figure 1a: Langmuir, Freundlich and Temkin Isotherm for Lead Adsorption

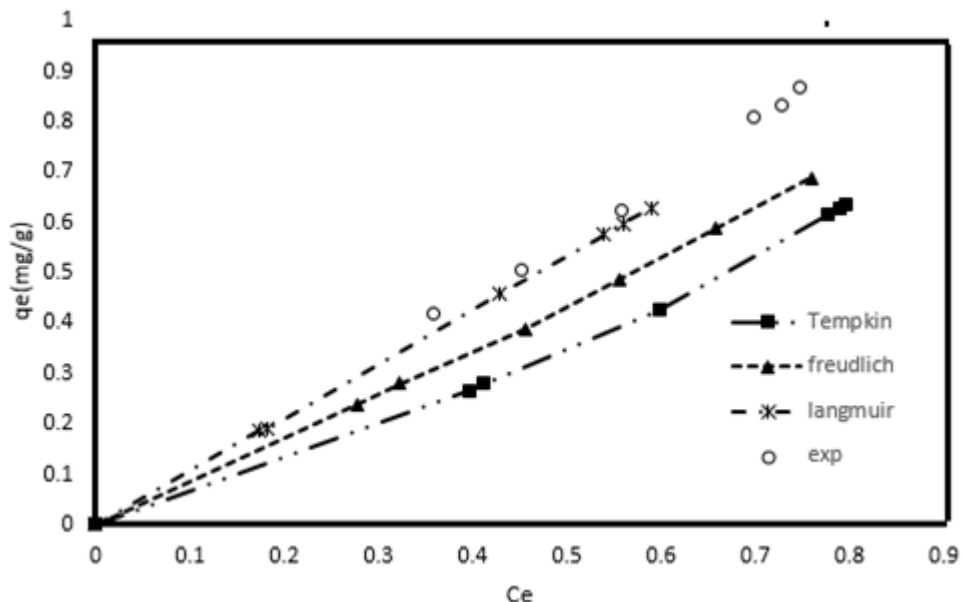


Figure 1b: Langmuir, Freundlich and Temkin Isotherm for Chromium Adsorption

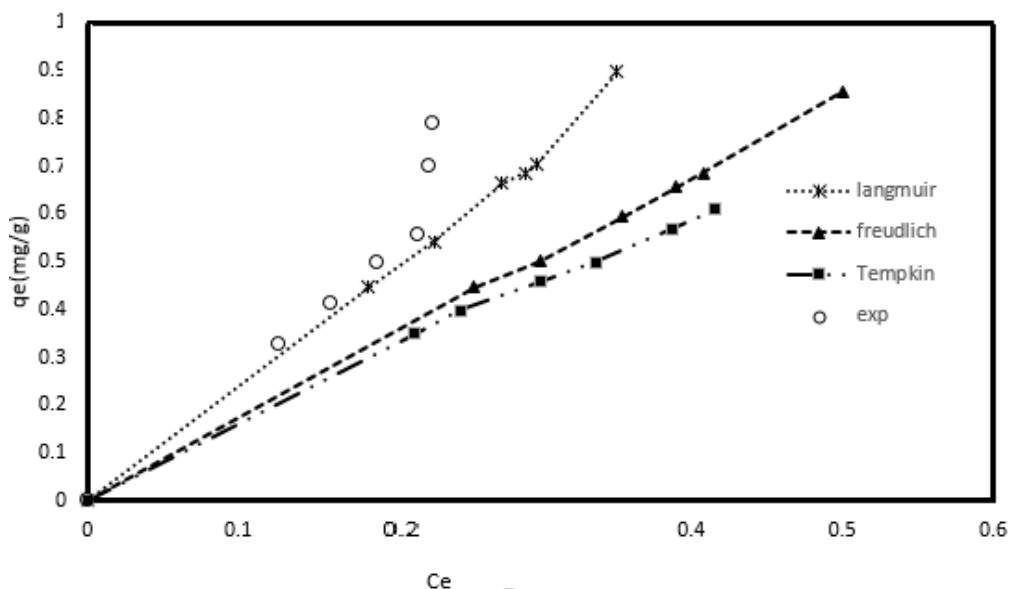


Figure 1c: Langmuir, Freundlich and Temkin Isotherm for Cadmium Adsorption

Table 1: Isotherm Parameters for the Adsorption of Heavy Metals onto GR-AC

Models	Lead	Chromium	Cadmium
Langmuir			
$q_{max}(mg/g)$	9.8039	5.7175	4.2535
$b(L/mg)$	10.38	6.1823	3.5078
R_L	0.09786	0.0618	0.0387
R^2	0.9993	0.9979	0.9873
Freundlich			
$K_f(L/g)$	-0.0057	-0.9914	0.0825
$1/n$	0.98700	1.0592	1.2094
R^2	0.9831	0.9673	0.9789
Temkin			
$K_T(L/mg)$	10.6956	1.5299	14.3586
$b_T(J/mol)$	2.3698	2.1729	2.0371
R^2	0.9965	0.9890	0.9504

3.2 Adsorption Kinetics Model

The experimental data were examined with Pseudo-First-Order model and Pseudo-Second-Order kinetic models in order to understand the mechanism of adsorption. Figures 2(a-f) and Tables 2(a-c) presents the plot and kinetic parameters for Pb, Cr and Cd onto GR-AC respectively. The results revealed that the correlation coefficients, R^2 of the First and Second Order models in all the metal ions adsorptions are near 0.99 indicating good correlation with the experimental data. The q_e values calculated from the Second Order kinetics model agree well with the experimental values for Pb and Cadmium and the First Order Kinetic rate constant decreased with increase in initial metal ion concentration. The Pseudo-second-order models assume that there is strong interaction between the adsorbate and adsorbent with chemisorption as the rate controlling step. The excellent correlation between the calculated q_e and experimental q_e values and higher regression coefficient (R^2) shows clearly that the adsorption of these heavy metals onto GR-AC followed Pseudo-Second-Order kinetic model. Similar result has been reported by (Samuel et al., 2015).

Table 2a: Kinetic Model Parameters for Lead adsorption onto GR-AC

C_o (mg/L)	q_e exp (mg/g)	Pseudo first-order			Pseudo second		
		K_1 (1/h)	$q_{e\text{ cal}}$ (mg/g)	R^2	K_2 (g/mg.min)	$q_{e\text{ cal}}$ (mg/g)	R^2
50	1.238	0.406	0.215	0.9828	27.091	2.959	0.718
100	5.791	0.331	1.756	0.9956	7.563	5.071	0.9960
150	3.126	0.340	1.139	0.9996	8.241	3.968	0.9956
200	3.126	0.339	1.139	0.9996	5.116	3.395	0.9985
250	5.791	0.331	1.756	0.9956	5.080	4.762	0.9986

Table 2b: Kinetic Model Parameters for Chromium adsorption onto GR-AC

C_o (mg/L)	q_e exp (mg/g)	Pseudo first-order			Pseudo second		
		K_1 (1/h)	$q_{e\text{ cal}}$ (mg/g)	R^2	K_2 (g/mg.min)	$q_{e\text{ cal}}$ (mg/g)	R^2
50	1.898	0.312	0.641	0.9965	18.198	3.948	0.907
100	2.883	0.266	1.059	0.9998	33.053	2.547	0.9867
150	2.800	0.235	1.029	0.9997	313.111	1.428	0.9992
200	2.821	0.202	1.037	0.9992	181.133	2.708	0.9961
250	2.930	0.161	1.075	0.9996	67.518	2.217	0.9949

Table 2c: Kinetic Model Parameters for Cadmium adsorption onto GR-AC

C_o (mg/L)	q_e exp (mg/g)	Pseudo first-order			Pseudo second		
		K_1 (1/h)	$q_{e\text{ cal}}$ (mg/g)	R^2	K_2 (g/mg.min)	$q_{e\text{ cal}}$ (mg/g)	R^2
50	1.917	0.844	0.651	0.9939	5.474	8.518	0.9705
100	1.676	0.678	0.516	0.9985	1.347	7.007	0.9987
150	2.052	0.573	0.719	0.9983	20.488	6.863	0.9955
200	1.668	0.454	0.511	0.996	8.0267	6.325	0.9950
250	1.7864	0.4399	0.580	0.9972	3.681	5.678	0.9828

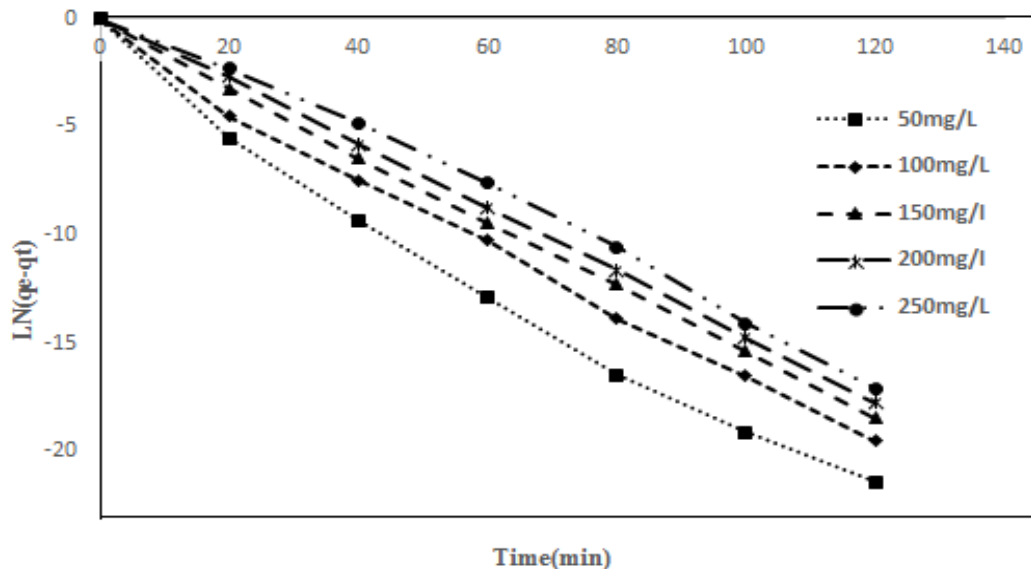


Figure 2a: Pseudo-First-Order plot of Lead onto GR-AC

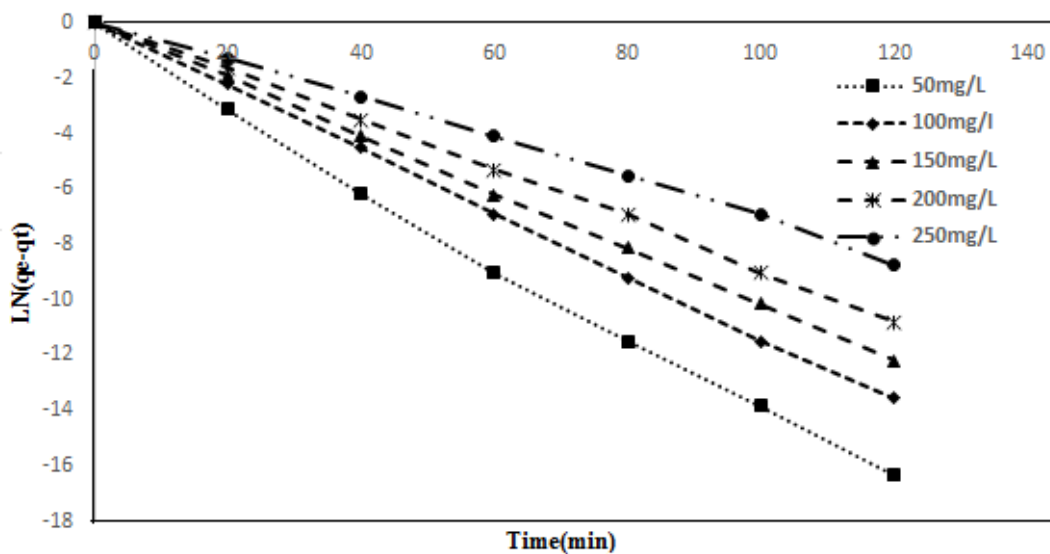


Figure 2b: Pseudo-First-Order plot of Chromium onto GR-AC

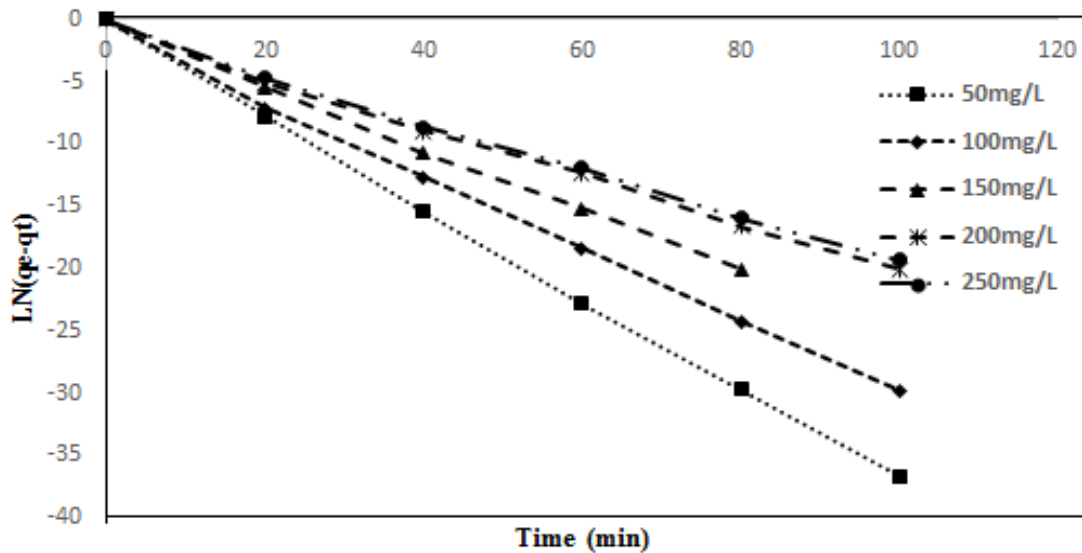


Figure 2c: Pseudo-First-Order plot of Cadmium onto GR-AC

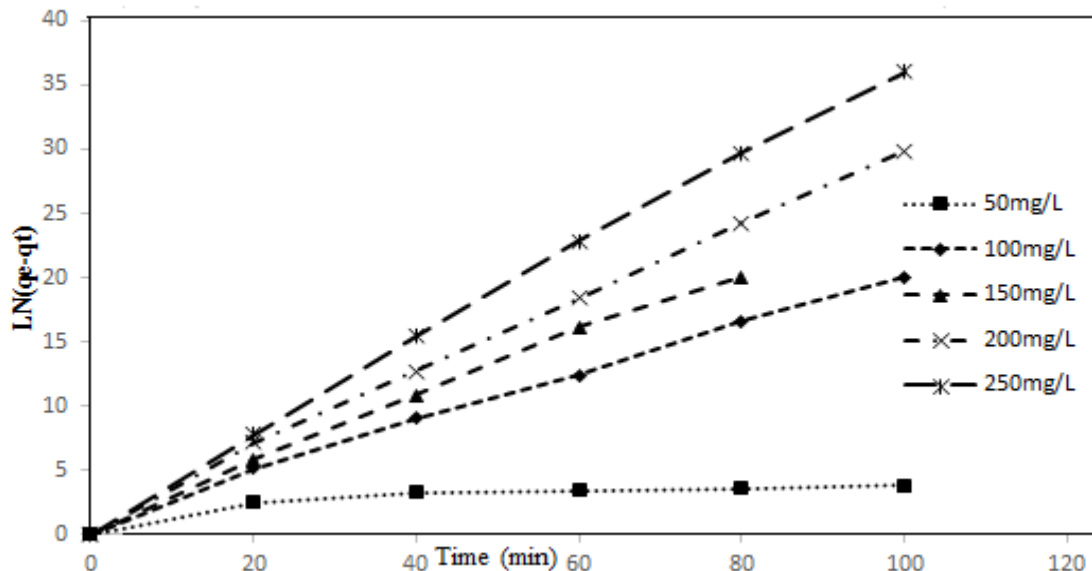


Figure 2d: Pseudo-Second-Order plot of Lead onto GR-AC

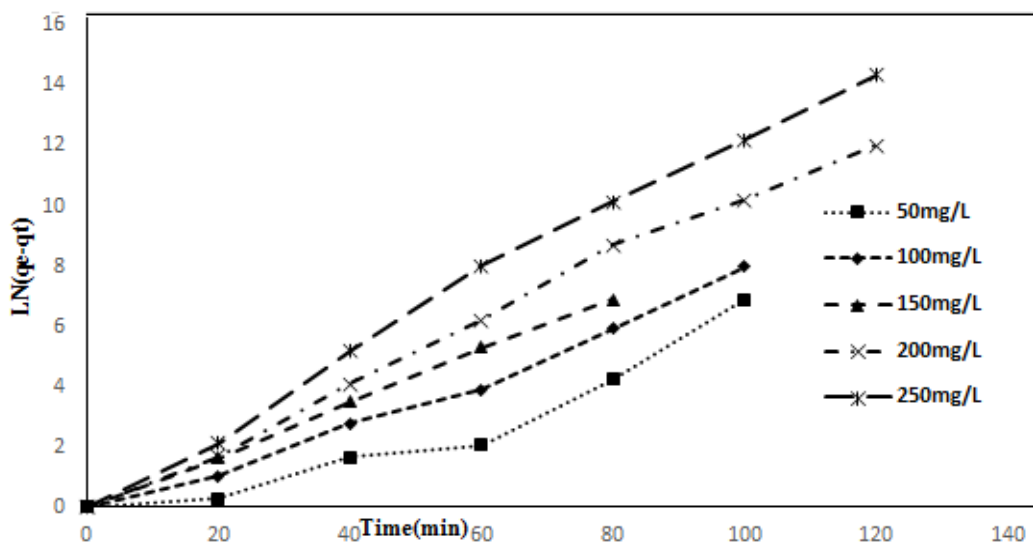


Figure 2e: Pseudo-Second-Order plot of Chromium onto GR-AC

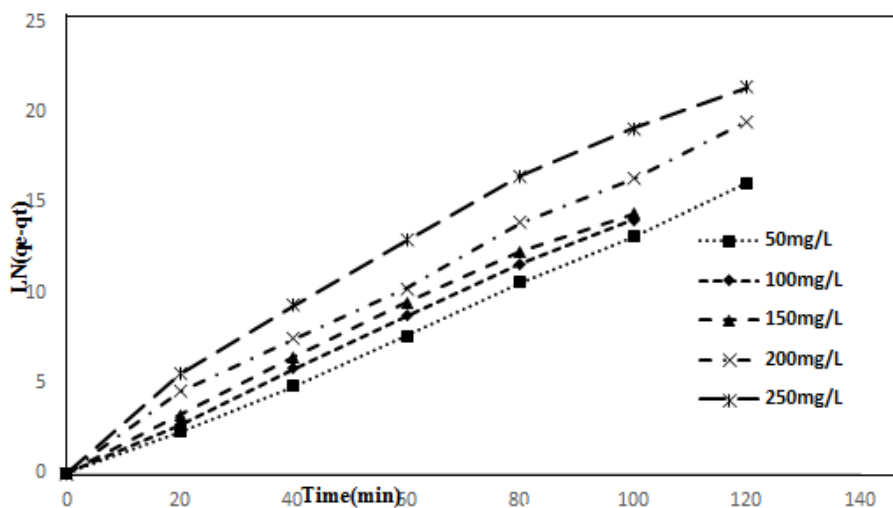


Figure 2f: Pseudo-Second-Order plot of Cadmium onto GR-AC

4. Conclusion

Groundnut shells and rice husks were utilized as agricultural waste to produce a composite adsorbent via chemical activation for the removal of Pb, Cr and Cd from tannery effluent. The adsorption Isotherm was evaluated by fitting the experimental data with Langmuir, Freundlich and Temkin isotherm while the kinetics studies were evaluated using Pseudo-First-Order and Pseudo-Second-Order kinetic models. Results shows that the adsorption of Lead, Chromium and Cadmium were well fitted to Langmuir model due to higher value of Regression coefficient (R^2). The R_L value was found between 0 and 1, which indicated the favorability of the adsorption process under the studied conditions. The Langmuir monolayer adsorption capacity (q_m) were 9.81, 5.72 and 4.25 mg/g for Lead, Chromium and Cadmium respectively. Lead adsorption onto GR-AC showed the highest maximum adsorption capacity. Pseudo-Second-Order Kinetic model provided a better correlation for the experimental data studied in comparison to the Pseudo-First-Order thus indicating a heterogeneous process. Therefore, the GR-AC can be effectively utilized for the removal of heavy metals in tannery wastewater.

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