

Equilibrium Isotherm and Adsorption Kinetics Models for Heavy Metals Removal Using a Carboxymethylated Phosphorus Oxochloride Crosslinked Peanut Testa Extract

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Abstract- Adsorption of heavy metals from aqueous solutions on a previously synthesized cation exchange resin derived from crosslinking of peanut testa catechin units with phosphorus oxochloride (PPTE) is the subject of investigation in this study. The H^+ forms of the developed crosslinked PPTE cation exchange resins have been exchanged with the divalent metal ions: Fe^{2+} , Ni^{2+} , Pb^{2+} , Cu^{2+} and Zn^{2+} respectively in aqueous solutions in separate batch experiments. The effect of various operational parameters (concentration of metal ions, contact time and temperature) was studied and the batch adsorption data were subjected to isotherm and kinetic model fits. The modeling results quite reasonably suit the examined isotherm (Langmuir, Tempkin and Freundlich) models as well the pseudo-first order PFO, pseudo second order PSO and Elovich kinetic models. A comparison of the isotherm models has revealed that Langmuir isotherm provides the best fit among all the models used, with R^2 values in the range 0.9728.... 0.9883, followed by Tempkin model with the coefficient of determination values in the interval $0.9061 \leq R^2 \leq 0.9567$, and lastly the Freundlich isotherm model whose R^2 values lie in the range 0.8705.... 0.9582. The kinetic data model fits, however, have shown specific behavior with respect to the metal ion being adsorbed, while the PFO model gave a far better fit for the adsorption of Zn^{2+} ions ($R^2 = 0.9607$) as compared to Ni^{2+} ($R^2 = 0.8615$) or Fe^{2+} ions ($R^2 = 0.8477$), the PSO, on the other hand, gave a far better fit for Fe^{2+} ($R^2 = 0.9688$) as compared to Zn^{2+} ions ($R^2 = 0.8384$) or Ni^{2+} ions ($R^2 = 0.8292$). This study thus provides a good evidence for successful application of economic viable peanut testa based crosslinked PPTE resins in adsorptive removal of heavy metals from wastewater.

Keywords- Adsorption Isotherms, Kinetics, Chemical Modification, Heavy Metals, Peanut Testa Polyphenols

I. INTRODUCTION

Pollution of water sources due to indiscriminate dumping of heavy metals and their aqueous solutions has triggered global concern for over fifty years. Some metals, especially heavy metals characterized by an atomic weight that overages 40.04 are toxic or poisonous to man and the general environment.

Iron (Fe), nickel (Ni), chromium (Cr), copper (Cu), lead (Pb), zinc (Zn) and mercury (Hg) are among the most toxic metals and hazardous priority substances on the list of pollutants contained in the Water Framework Directive [1]. Metals such as Fe, Cu and Zn which are known to be essential to humans, plants and animals are also known to be relatively immobile, presenting adverse effects if their availability to the organs surpasses certain threshold values [2,3]. The toxicity of Pb, for example results to partial blindness, hormonal dysfunctions and poor judgment in humans [4] while hypoglycemia, asthma, nausea, headache and cancer of the lungs are signs of Ni contamination in animals [5,6].

Awareness of the toxicity of heavy metals to the environment necessitates their removal both from domestic water supply sources and wastewater before discharge in order that they meet WHO permissible limits [7]. This has inspired huge interest and motivation towards the removal of heavy metal ions from water sources [8].

The use of abundant, tannin-rich and easy to process agricultural by-products for the purification of heavy metal polluted water has become the focus of current scientific researches because they offer inexpensive and environmentally friendly techniques which are based on the interactions between pollutant metal ions and polar constituents, usually the COOH and multiple hydroxyl ($-OH$) groups of polyphenolic compounds in plants' chemical structure [9,10,11]. The groups demonstrate special affinity for metal ions and possess the capacity to remove large quantities of such in aqueous solutions, thus, can be used as alternative, effective and efficient adsorbents for the concentration and recovery of heavy metal ions in polluted water [12,13,14].

Unfortunately, agricultural by-products cannot be used directly to purify water because the constituent tannins are water-soluble compounds which leach out soluble matter in water thereby imparting colouration to the water and creating secondary pollution. As a way to overcome this constraint, scientists immobilized [15] the chemical constituents of tannins by converting to water-insoluble polymeric substrates. Agiri and Akaranta [15]; Ozacar et al., [16] and many other researchers have synthesized various adsorbents from

commercial tannins and organic dyes and used same to remove heavy metal pollutants such as: Cr, Cu, Zn, Pb, Th, Au, and Pd from water.

Peanut (*Arachis hypogaea* L.) is an economically valuable crop that is universally cultivated. Sequel to the acknowledgment of the ability of peanut shells fibre to bind toxic metals by Henderson et al. [17], Wilson et al. [18] and Chamorthy et al. [19] investigated and attested to the current enhancement of its metal ions binding capacity from industry waste by heat treatment or chemical modification. Approximately one million metric tonnes of polyphenol-rich peanut skin or testa waste generated globally from peanut processing [20, 21] is under-utilized as additives to functional foods [22] and additives [23] or litter to distort the landscape and infest the environment [24, 25].

In this study, peanut testa polyphenols (tannins) converted to highly effective cation exchange resins have been used to remove the heavy metal ions of Fe²⁺, Ni²⁺, Pb²⁺, Cu²⁺ and Zn²⁺ in water. Furthermore, the equilibrium adsorption data as well as the kinetics and mechanism for the removal of the metal ions have been investigated.

II. EXPERIMENTAL PROCEDURE AND ANALYSIS

A. Ion Exchange and Adsorption Experimental Procedures

The H⁺ forms of the crosslinked PPTE cation exchange resins whose synthesis and characterization have been duly reported in previously reported works [26, 27] were exchanged with the divalent metal ions: Fe²⁺, Ni²⁺, Pb²⁺, Cu²⁺ and Zn²⁺ respectively in aqueous solutions in separate batch experiments. 1g of HNO₃ activated Crosslinked-PPTE was suspended in separate 50 mL laboratory simulated single metal ion solutions containing 10 ppm of the metal ions in a plastic bottle. The metal ion solutions were prepared by dissolving 0.0880, 0.0320, 0.0996, 0.0628 and 0.1346 g respectively of ZnSO₄·7H₂O, Pb(NO₃)₂, FeSO₄·7H₂O, Cu(CH₃COO)₂·H₂O and (NH₄)₂SO₄·NiSO₄·6H₂O in a little quantity of DI H₂O in separate 2 L standard flasks and diluting to volume with DI H₂O. The individual resins (5 g) was also stirred in 50 mL of a multi-elements solution containing 10 ppm of each of the metal ions in five separate batch set-ups. The multi-element solution was prepared by dissolving the same amount of the respective metal salts in a little quantity of DI H₂O in a 250ml standard flask and diluting to volume with DI H₂O.

The pH of the metal ion solutions which were administered by means of delivery pipettes was determined and adjusted to 6 ± 0.5 with 0.1 M HCl or NaOH before introducing the adsorbents. The caps were immediately screwed on, the bottles positioned on the shaker and agitated at 150 rpm (revolutions per minute) for 2 hrs at room temperature (RT). At the end of the process, the bottles were disengaged and the suspensions rapidly filtered on whatman No. 2V folded filter paper. The concentration of each metal ion present in the filtrates was determined by Atomic Absorption Spectrophotometry.

The amount of each metal ion (in ppm) taken out of the solution by each of the adsorbents at equilibrium Q_e, was computed using the model:

$$Q_e = \left[\left(\frac{C_o - C_e}{W} \right) \right] \times V \quad (1)$$

Where; C_o and C_e are the initial concentration and concentration (in ppm) of the metal ion left in the solution at equilibrium while V and W are the volume of the solution and the weight of the adsorbent (g) respectively used in the experiment. Atomic absorption measurements were carried out in triplicate and the average of two readings reported in their percentages.

B. Parametric study of the adsorption process

The adsorption study was repeated at different metal ion concentrations in the range of 5...30 mg/l, temperatures ranging from 25...80°C, and various contact times from 30 until 150 minutes in order to investigate the effect of these various parameters on the adsorption of Fe²⁺, Ni²⁺, Pb²⁺, Cu²⁺ and Zn²⁺ from aqueous solutions onto the surface of crosslinked-PPTE. In all these experiments the adsorbent dose of 1g, pH=6±0.5, and agitation speed = 150rpm was employed.

C. Adsorption Isotherms

Equilibrium isotherm equations are used to describe the experimental sorption data. The equation parameters are the underlying thermodynamic assumptions of these equilibrium modes often provide some insight into both the sorption mechanisms and the surface properties and affinities of the adsorbent. Langmuir [28] developed a relationship between the amount of gas absorbed onto an adsorbent and the pressure of that gas. Such equations are now referred to as langmuir sorption isotherms, a theoretically based sorption isotherm in the idea case.

Three most common isotherms for describing solid-liquid sorption systems have been employed in this study, namely: the Langmuir, Tempkin and the Freundlich, adsorption isotherms (Table 1). Linear regression has been used to determine the best fitting model. The coefficient of determination, the Sum of the Squared Error (SSE), the average relation error and the sum of the absolute errors are used to evaluate isotherm data as linear model [29, 30, 31].

TABLE I. COMMON ISOTHERMS FOR DESCRIBING SOLID-LIQUID ADSORPTION SYSTEMS [32]

| Isotherm | Equation | Linearized Equation |
|------------|---|---|
| Langmuir | $q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$ | $\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e$ |
| Freundlich | $q_e = K_f C_e^{1/n}$ | $\log q_e = \log K_f + \frac{1}{n} \log C_e$ |
| Tempkin | $q_e = \frac{RT}{b_T} \ln A_T C_e$ | $q_e = B_T \ln A_T + B_T \ln C_e$ |

D. Adsorption Kinetic Studies

Analysis of chemical kinetics is of pertinent importance to understand the reaction rate. The first order kinetic equation for a batch adsorption process could be expressed as:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \tag{2}$$

Upon solving the first order differential equation (2) by means of separating the variables and integration the following linear dependence popularly known as the pseudo first order adsorption (PFO) kinetic equation emerges after replacing the natural logarithm with the decimal:

$$\log(q_e - q_t) = \log q_e - (K_1/2.303)t \tag{3}$$

Where q_e and q_t are the amount of adsorbed metal ions (mg/g) at equilibrium and at any time t respectively;

K_1 = the first order rate constant (min^{-1}).

Therefore plotting $\log(q_e - q_t)$ versus time gives the slope $K_1/2.303$ and intercept $\log q_e$

Pseudo second order equation could be expressed as;

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \tag{4}$$

Similar integration and simplification of this first-order differential equation (4) yields the linearized form of the pseudo second order (PSO) adsorption kinetic equation:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

Where K_2 = rate constant of second order adsorption .

Thus the linear plot of t/q_t against t should give a slope corresponding to $1/q_e$ and $1/K_2 q_e^2$ as intercept.

This PSO kinetic model is more likely to predict the behaviour for the range of concentration studied for adsorption and represents chemisorptions.

Another commonly used kinetic model is the Elovich equation firstly proposed by Roginsky and Zeldovich [32] for the description of CO adsorption behavior MnO_2 . This model is based on the assumption that solid surfaces are actually energetically heterogeneous [33]. The linearized form of this equation could be expressed as follows]:

$$q_e = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \tag{6}$$

III. RESULTS AND DISCUSSION

A. Parametric study of the adsorption process

The influence of various parameters such as contact time of the process, metal ion concentration as well as temperature on the on the adsorption of various heavy metals (Fe, Ni, Pb, Cu and Zn) on Crosslinked-PPTE has been studied in this work.

It is obvious that the contact time between the crosslinked PPTE and contaminated water solution is an important parameter because it directly controls the target pollutant

removal efficiency, adsorption capacity, and enunciates the kinetic behavior. The effect of contact time on the adsorption of Fe, Ni, Pb, Cu and Zn on Crosslinked-PPTE was therefore studied at room temperature with the initial metal ion concentration fixed at 5mg/l, pH=6±0.5, adsorbent dose= 1g, agitation speed= 150rpm, while the contact time was varied from 30 to 150 minutes. The results are presented in Table 1. The results in Table 1 have revealed that the adsorption process for all the heavy metals follows a similar trend with an initial fast adsorption stage up to 0...30 minutes, a slower stage from 30...60 minutes and peak adsorption values attained 60...90. For all the cases considered, it is evident that further increase in the contact time after 90 minutes yielded no significant changes in the adsorption capacity.

The initial concentration of metal ions in aqueous solutions determines the amount of adsorbent which will be required to attain acceptable removal efficiency, which could give a clue to the process cost-effectiveness. This necessitates the study of the effect of metal ion concentrations in the range 5...30 mg/l on the adsorption of Fe, Ni, Pb, Cu and Zn on Crosslinked-PPT while maintaining adsorbent dose = 1g, pH=6±0.5, contact time = 1hr, agitation speed = 150rpm at room temperature. At constant adsorption equilibrium time of 60 min, it was found that the removal efficiency steadily decreased in all cases with increasing metal ion concentration from 5 mg/l to 30 mg/l. This could be ascribed to the accessibility of less adsorption sites in higher dosage, which leads to the decrease in the removal rate. Increasing the metal ions concentration while maintaining the adsorbent dosage at 1g limits the number of adsorbent sites available for the removal process. However, considering the fact that the number of pollutant molecules on these fixed number of adsorbent sites has increased, this will obviously lead to a drop in their removal efficiency [34, 35].

TABLE II. EFFECT OF CONTACT TIME ON THE ADSORPTION OF FE, NI, PB, CU AND ZN ON CROSSLINKED-PPTE, INITIAL METAL ION CONCENTRATION 5MG/L, PH 6±0.5, ADSORBENT DOSE = 1G, AGITATION SPEED= 150RPM @RT

| Time (min) | %Fe | %Ni | %Pb | %Cu | %Zn |
|------------|------|------|------|------|------|
| 30 | 21.7 | 19.7 | 18.5 | 24.7 | 23.1 |
| 60 | 52.8 | 42.5 | 26.8 | 41.2 | 39.8 |
| 90 | 69.8 | 63.7 | 49.4 | 61.2 | 61.7 |
| 120 | 68.6 | 65.4 | 51.7 | 60.1 | 60.9 |
| 150 | 69.2 | 66.2 | 50.9 | 60.6 | 61.3 |

TABLE III. EFFECT OF METAL ION CONCENTRATION ON THE ADSORPTION OF FE, NI, PB, CU AND ZN ON CROSSLINKED-PPTE

| Conc(mg/l) | %Fe | %Ni | %Pb | %Cu | %Zn |
|------------|------|------|------|------|------|
| 5 | 79.3 | 76.3 | 51.3 | 73.4 | 66.8 |
| 10 | 69.9 | 67.4 | 49.6 | 69.6 | 61.1 |
| 15 | 61.2 | 58.6 | 38.3 | 59.7 | 53.7 |
| 20 | 53.6 | 51.3 | 31.4 | 51.2 | 50.3 |
| 25 | 42.4 | 40.1 | 27.6 | 40.4 | 42.7 |
| 30 | 37.2 | 34.7 | 27.3 | 38.9 | 42.8 |

Adsorbent dose = 1g, pH=6±0.5, contact time = 1hr, agitation speed = 150rpm @RT

Another parameter of significance is the process temperature, which that may positively or negatively influence the efficiency of the adsorption process. As a consequence, the effect of temperature on the adsorption process was investigated at various temperatures ranging from room temperature (RT) 25 to 50 °C. The removal process was conducted at equilibrium state, initial metal ion concentration of 5mg/l, pH=6±0.5, adsorbent dosage of 1g, contact time of 1hr and agitation speed = 150rpm (Table 4).

The data presented in Table 4 have shown that with increasing temperature increased from 25 °C to 50 °C, the percentage removal of all the heavy metals under study consistently increased, with the highest percentage removal attainable at 50 °C, after which the removal efficiency dropped. This could be explained by the fact that the elevation of metal ion solution temperature to nearly 50 °C could provide suitable driving force to raise their mobility, and therefore lead to enhanced interaction level with the adsorbent binding sites [34, 35]. The Increase in the temperature in adsorption processes has been generally observed to yield enhanced diffusion rate of the adsorbate molecules across the external boundary layer and internal pores of the adsorbent particle. Ozer et al. [36] observed the increase of the adsorption yield and adsorption capacity at elevated temperature and concluded on the endothermic nature of adsorbate molecules adsorption which may involve not only physical adsorption but also chemisorption.

TABLE IV. EFFECT OF TEMPERATURE ON THE ADSORPTION OF FE, NI, PB, CU AND ZN ON CROSSLINKED-PPTE, INITIAL METAL ION CONCENTRATION =5MG/L, PH=6±0.5, ADSORBENT DOSE= 1G, CONTACT TIME=1HR @ AGITATION SPEED= 150RPM

| Temp., °C | %Fe | %Ni | %Pb | %Cu | %Zn |
|-----------|------|------|------|------|------|
| 25 | 68.3 | 60.2 | 44.2 | 55.2 | 45.3 |
| 40 | 72.7 | 68.4 | 52.1 | 61.7 | 56.3 |
| 50 | 79.1 | 73.3 | 64.4 | 76.3 | 68.1 |
| 60 | 74.6 | 68.9 | 61.3 | 78.2 | 65.2 |
| 70 | 68.1 | 65.4 | 59.9 | 71.6 | 64.8 |
| 80 | 59.6 | 53.8 | 59.3 | 69.8 | 62.7 |

B. Adsorption Isotherms and Models

In this work, conventional two-parametric models, namely Langmuir, Freundlich and Tempkin isotherm models have employed for the experimental data analysis involving heavy metal removal from aqueous solutions using cross-linked PPTE. The data obtained from the variation of process parameters on the adsorption process have been fitted to the linearized equation of Langmuir, Freundlich and Tempkin isotherms (Table 1).

The Langmuir model is derived from the presumptions that sorption occurs at finite number of sites within the adsorbent at a constant temperature. Langmuir isotherm is valid for a monolayer disposition of adsorbates. The constants q_m and K_L are characteristics of the langmuir equation and can be determined from a linearized form of this equation (Table 1). Typical Langmuir isotherm plots of the process involving all the heavy metals under consideration are shown in Fig. 1. Thus, a plot of C_e / q_e versus C_e indicates a straight line of slope $1/q_m$ and an intercept of $1/(K_L q_m)$. The linear plot of Langmuir Isotherm at room temperature is shown in Fig 2 and the corresponding model parameters are listed in Table 5.

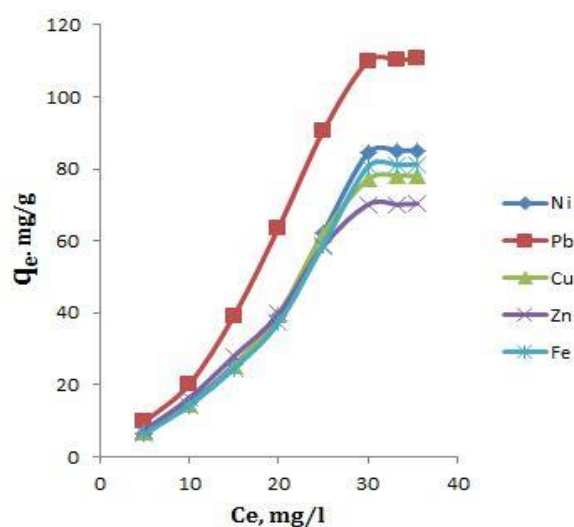


Figure 1. Langmuir Isotherm Plots for Heavy Metal Adsorptions on crosslinked PPTE.

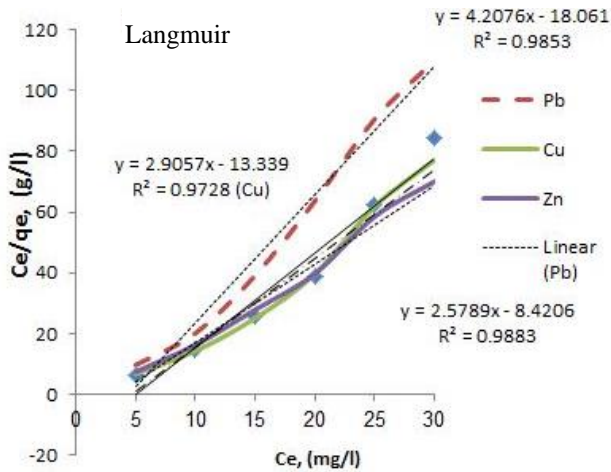


Figure 2. plot of C_e / q_e versus C_e

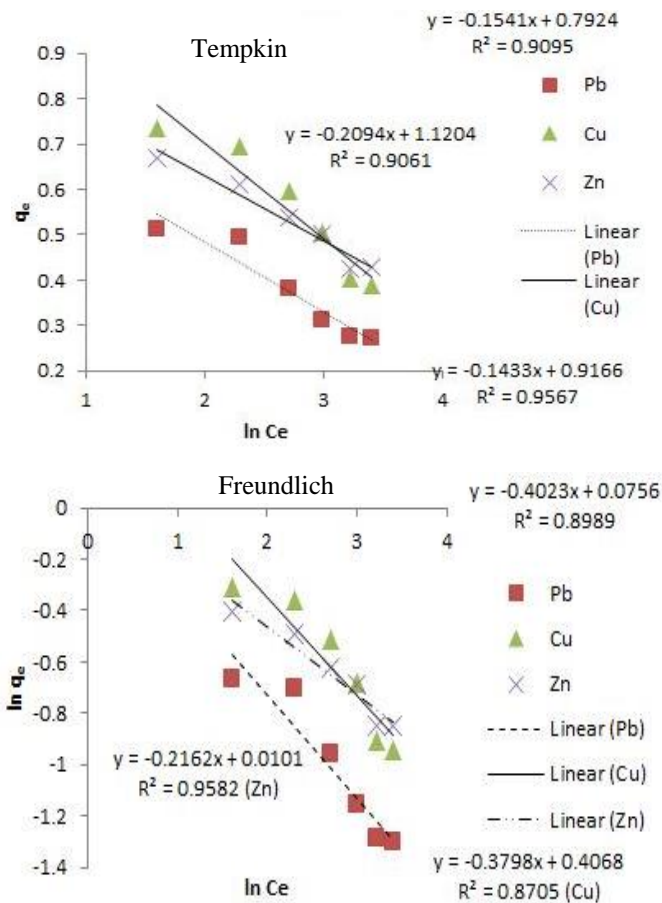


Figure 3. Isotherm model plots for heavy metal adsorption on crosslinked PPTE.

All the adsorption isotherm plots for heavy metal adsorption on crosslinked PPTE as shown in Fig. 3 gave a relatively good agreement to the obtained experimental data with the linear correlation coefficient, R^2 values in the range

0.87.... 0.988. A comparison of the specific isotherm models has revealed that Langmuir isotherm provides the best fit among all the models used, with R^2 values in the range 0.9728.... 0.9883, followed by Tempkin model with the coefficient of determination values in the interval $0.9061 \leq R^2 \leq 0.9567$, and lastly the Freundlich isotherm model whose R^2 values lie in the range 0.8705.... 0.9582 (Fig. 3). The best-fit equilibrium model arising from the Langmuir isotherm could further buttress the fact the adsorption process of the heavy metals under study on the surface of peanut testa extract based ion exchange substance was a monolayer adsorption over a homogeneous surface. These results are in accordance with those obtained with similar adsorbents reported in literature [37, 38, 39].

TABLE V. COMPARISON OF LANGMUIR MODEL PARAMETERS FOR ADSORPTION OF VARIOUS HEAVY METALS ON CROSSLINKED PPTE.

| Parameters | Fe | Ni | Pb | Cu | Zn |
|--------------|--------|-------|--------|--------|--------|
| q_m , mg/g | 3.574 | 2.493 | 11.943 | 13.864 | 10.792 |
| K_l | 0.0133 | 0.017 | 0.026 | 0.0290 | 0.0041 |
| R_l | 0.7505 | 0.706 | 0.003 | 0.6256 | 0.9067 |
| R^2 | 0.988 | 0.976 | 0.975 | 0.957 | 0.942 |

C. Adsorption Kinetic Models

The adsorption kinetic data have been employed to elucidate on the interaction between the adsorbate and adsorbent by using kinetic models of PFO, PSO and Elovich in their linear forms (equations 3, 5 and 6 respectively). The resulting plots are presented in Fig.4 a,b and c. The most appropriate kinetic model has been selected by applying the coefficient of determination (R^2). adsorption capacity were considered. It is also essential to point out that all the kinetic models considered are suitable to a large extent for predicting the adsorption rate of the heavy metals on the crosslinked PPTE surface.

A unique feature of this kinetic studies, however, is its selectivity with respect to some individual metal ions. As an example, while the PFO model gave a far better fit for the adsorption of Zn^{2+} ions ($R^2 = 0.9607$) as compared to Ni^{2+} ($R^2 = 0.8615$) or Fe^{2+} ions ($R^2 = 0.8477$), the PSO, on the other hand, gave a far better fit for Fe^{2+} ($R^2 = 0.9688$) as compared to Zn^{2+} ions ($R^2 = 0.8384$) or Ni^{2+} ions ($R^2 = 0.8292$). The corresponding adsorption capacity for Fe^{2+} calculated by employing PSO correlates well with the experimentally observed adsorption capacity, and this together with higher R^2 values point out the fact that PSO is far more suitable than PFO in its case. PFO has been generally established to be ideal during the initial stage of the adsorption process, even though PSO could be more pronounced for within the whole range of the remaining process. PSO has been believed to be more accurate for adsorbent/adsorbate systems wherein chemisorption plays a predominant role.

These results therefore all attest to the variation in the prevalence of physical adsorption and/or chemisorption depending on the metal ion being adsorbed. For instance, the higher significance of the PSO reaction kinetics could infer the

predominance of chemical reactions between the Fe^{2+} ions and the active adsorbent sites.

According to the observed experimental data modelled with Elovich kinetic equation (6) for all the metal ions under study an excellent fit has been exhibited with sufficiently high coefficient of determination R^2 values above 0.92 (Fig. 4c). This further buttress the fact that adsorption kinetics tends more towards chemical adsorption mechanism in nature to a great extent.

TABLE VI. COMPARISON OF KINETIC MODEL PARAMETERS FOR THE ADSORPTION OF VARIOUS HEAVY METALS ON CROSSLINKED PPTE RESINS.

| Metal Ion | PFO | | PSO | |
|------------------|---------|--------|---------|--------|
| | K_1 | R^2 | K_2 | R^2 |
| Fe^{2+} | 0.00299 | 0.8477 | 0.01160 | 0.9688 |
| Ni^{2+} | 0.00875 | 0.8615 | 0.00006 | 0.8292 |
| Pb^{2+} | 0.00422 | 0.7004 | 0.00014 | 0.8832 |
| Cu^{2+} | 0.00412 | 0.8568 | 0.00002 | 0.8338 |
| Zn^{2+} | 0.00622 | 0.9607 | 0.00009 | 0.8384 |

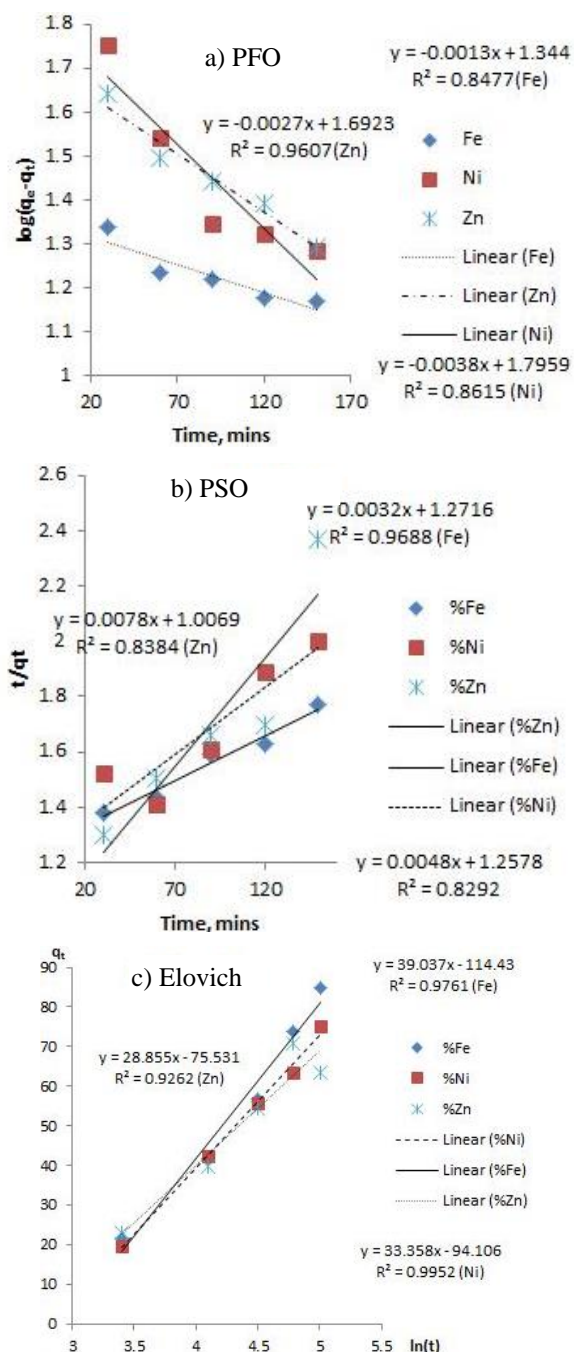


Figure 4. Kinetic Model Plots for Heavy Metal Adsorption on Crosslinked PPTE.

IV. CONCLUSIONS

The equilibrium isotherm and adsorption kinetics studies have been conducted to investigate the effect of various factors on the adsorption of heavy metals from aqueous solutions on the surface of a peanut testa extract based crosslinked PPTE ion exchange resin. The experimental data have been suitably modeled with existing adsorption isotherm and kinetic models. A comparison of the specific isotherm models has revealed that Langmuir isotherm provides the best fit among all the models used, with R^2 values in the range 0.9728.... 0.9883, while the kinetic data model results attest to the variation in the prevalence of physical adsorption and/or chemisorption depending on the metal ion being adsorbed. The Elovich kinetic model, however, provided the best fit indicating that adsorption kinetics tends more towards chemical adsorption mechanism in nature to a great extent. Thus, economic viable peanut testa based crosslinked PPTE resins have been proved to be efficient alternatives in adsorptive removal of heavy metals from wastewater.

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