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Comparison Of Kinetic Models For The Sorption Of Lead(II) Ion From Aqueous Solutions Using Unmodified And Thioglycolic Acid Modified Guinea Corn Wastes

*Corresponding Author*

A.A.Abia
 Department of Pure and Industrial
 Chemistry, University of Port Harcourt,
 P.M.B. 5323, Choba, Port Harcourt,
 (NIGERIA)
 Ph.: (+234)-08036685125
 E-mail: abiauniport2005@yahoo.com

*Received: 23rd January, 2007**Accepted: 28th January, 2007**Web Publication Date : 5th June, 2007**Co-Authors***E.D.Asuquo¹, I.G.Lawal²**¹Department of Pure and Industrial Chemistry, University of Port Harcourt, P.M.B. 5323, Choba, Port Harcourt, (NIGERIA)²Eleme Petrochemicals Company Ltd. Port Harcourt, Rivers State, (NIGERIA)

ABSTRACT

A comparison was made on the sorption efficiency of an unmodified(UGC) and chemically modified(TGC) guinea corn waste used to remove Pb²⁺ from aqueous solutions. The removal efficiencies of the two adsorbents were: 71.2% and 73.3% for the UGC and TGC adsorbents respectively. Also an analysis of six kinetic models: pseudo-second order, pseudo-first order, Elovich, intraparticle diffusivity, mass transfer and intraparticle diffusion equations was also used to characterize the metal ion transport mechanism. The sorption of Pb²⁺ was found to best fit the pseudo-second order equation. Thereby indicating that the sorption of Pb²⁺ followed a second order mechanism with chemical sorption as the rate limiting step. The two adsorbents were found to be efficient in the sorption of Pb(II) ions. © 2007 Trade Science Inc. - INDIA

KEYWORDS

Lead(II) ion;
 Kinetic modeling;
 Sorption wastewater;
 Guinea corn.

INTRODUCTION

Heavy metal influx into the environment has been increasing continuously as a result of industrial activities and technological development, posing a sig-

nificant threat to the environment and public health because of their toxicity, accumulation in the food chain and persistence in nature.

These toxic metals are often discharged by a number of industrial processes and this can lead in turn

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to the contamination of freshwater and marine environment. These heavy metals are major pollutants in marine, ground, industrial and even treated waste waters. Industrial waste constitutes the major source of various kinds of metal pollution in natural waters. The prominent toxic metals like, Cd, Zn, Ni and Pb find their way to water bodies through wastewaters^[1].

Lead is ubiquitous in the environment as a result of its natural occurrence and its industrial use. The decreased use of leaded gasoline over the past two decades has resulted in decreased concentrations of lead in blood in human beings. However, today the primary sources of environmental exposure to lead are leaded paint and drinking water. Also, most of the over toxicity from lead results from environment and industrial exposure^[2].

In order to meet water quality standard for most countries, the concentration of heavy metals in waste water must be controlled. Conventional physico-chemical treatment methods for removing heavy metals include; precipitation, filtration, oxidation-reduction, ion-exchange and membrane separation^[3]. However, when metals are dissolved in huge volumes at relatively low concentrations, these methods become generally ineffective or expensive^[4-7].

However, recent studies has shown that adsorption has now been recognized as an effective and economic method for removal of pollutants from wastewaters^[8]. Some by-products of agricultural materials like soybean, cotton seed, rice-straw and sugarcane have been evaluated as metal ion adsorbent in aqueous solutions^[9-10]. In these studies it had also been discovered that kinetics of metal ion sorption is an important parameter in the metal ion removal. The study of kinetics in waste water treatment is used to predict the rate of pollutant removal from aqueous solutions and it aids in the design of appropriate sorption treatment plants^[11].

In this study, the kinetics of lead(II) ion removal from aqueous solutions using unmodified and chemically modified guinea corn waste will be examined. Different kinetic models such as pseudo-first order^[12], Elovich^[13-14], intraparticle diffusion^[15], mass transfer^[16], pseudo-second order^[17] and intraparticle diffusivity^[18-19] will be used to analyze the kinetics of Pb(II) ion removal by the guinea corn wastewater

adsorbent. This will provide insights into the reaction pathways and mechanism of sorption reaction^[11].

EXPERIMENTAL

Guinea corn waste obtained from the processing of guinea corn was obtained from gusau, zamfara state. The guinea corn waste was washed with deionized water, air dried and ground using a national grinder.

The powered guinea corn waste was sieved through a 500 μ m sieve(Gilson Company Inc.). The sieved guinea corn waste was later soaked in excess 0.3M trioxonitrate(v) acid(HNO₃) solution for 24 hours. Thereafter, the guinea corn waste was filtered using a EB3A vacuum pump(Edwards Inc) and rinsed with deionized water and later air dried.

After wards, the air dried guinea corn waste was divided into two parts(A and B) each weighing 40g. Part 'A' was left untreated. Part 'B' was soaked and stirred in 0.3M thioglycolic acid solution and left for 24 hours according to the method described by^[20]. The untreated guinea corn waste was labeled as unmodified guinea corn[UGC] while the thioglycolic acid modified guinea corn was labeled as thioglycolic acid modified guinea corn(TGC).

Kinetic sorption studies of Pb(II) ion removal was carried out using the two adsorbents(UGC and TGC). 1000mg l⁻¹ stock solution of lead (II) nitrate (Pb NO₃)[BDH] was prepared using distilled deionized water. 100ml of Pb(II) ion solution of initial concentration 20mg dm⁻³ was measured into different labeled conical flask containing 0.5g of each adsorbent(UGC and TGC).

The different flasks were corked uniformly and agitated in a EFLI-Mk3 shaker at a speed of 25rpm at a temperature of 28°C and pH of 5.0 for 5 minutes. The experimental set up was repeated for various time. Infinity intervals of 10, 15, 20, 25 and 30 minutes sorption(α) was carried out for 24 hours. At the end of each contact time, the contents of each flask were filtered using a EB3A vacuum pump (Edwards Inc). The concentration of Pb²⁺ in each filtrate was determined using a UNICAM-919-solar atomic absorption spectrophotometer.

Data analysis

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The adsorption capacity (q_t) of each of the two adsorbent (UGC and TGC) for Pb(II) ions can be computed using the relationship^[21]

$$q_t = \frac{(C_i - C_t)}{ms} v \quad (1)$$

Also the percentage of Pb(II) ions removed (%RE) from solution by each adsorbent (UGC and TGC) was calculated from eqn 2:

$$\% RE = \frac{(C_i - C_t)}{C_i} \times 100 \quad (2)$$

The fraction of adsorption of Pb(II) ions by the UGC and TGC adsorbents was determined from the equation below^[22]:

$$Y_t = \frac{C_i - C_t}{C_i - C_t} \quad (3)$$

Where:

q_t is the metal sorption capacity of the adsorbent (mg/g)

C_i is the initial metal ion concentration in solution (mg/L)

C_t is the metal ion concentration in solution at time t (mg/L)

Y_t is the fraction of the metal adsorbent at time t

Ms is the weight of the adsorbent (g)

V is the volume of the metal ion solution used for sorption (dm^3)

C_e is the concentration of metal ion when sorption is complete: infinity sorption [$\infty = C_{e24 \text{ hr}}$]

Kinetic modeling

The sorption of Pb(II) ions by UGC and TGC adsorbents was analysed using different kinetic equations.

These are: pseudo-first order^[12], pseudo-second order^[17], Elovich equation^[13-14], intraparticle diffusion^[18-19], intraparticle diffusivity^[15] and mass transfer equation^[16]. The coefficient of determination, r^2 was used as the fitting parameter in determining which of these models best fits the sorption of Pb(II) ions by the two adsorbents^[23].

Pseudo-first order equation

The pseudo-first order equation^[12] expressed as eqn. (4):

$$\frac{dq_t}{dt} = K_1 (q_e - q_t) \quad (4)$$

where q_e and q_t are the sorption capacities, at equilibrium and at time t, respectively ($mg \cdot g^{-1}$), while K_1 is the rate constant of the pseudo-first order sorption

($L \cdot min^{-1}$). After integration and applying boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$, the integrated form of eqn. (4) is expressed as:

$$\log (q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad (5)$$

If sorption of Pb^{2+} follows this equation, then a plot of $\log(q_e - q_t)$ versus time, should give a linear relationship from where k , and q_e can be determined from the slope and intercept of the plot respectively.

Pseudo-second order equation

The pseudo-second order chemisorption^[17] is expressed as:

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

where q_e and q_t are the sorption capacities at equilibrium and at time t, respectively ($mg \cdot g^{-1}$) while K_2 is the rate constant of the pseudo-second order sorption ($g \cdot mg^{-1} \cdot min^{-1}$). For the boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$, the integrated form of eqn. (6) becomes:

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

which is the integrated rate law for a pseudo-second order sorption. Eqn. (7) can be rearranged to obtain:

$$q_t = \frac{1}{\frac{1}{K_2 q_e^2} + \frac{1}{q_e} t} \quad (8)$$

Which has a linear form:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (9)$$

where h ($mg \cdot g^{-1} \cdot min^{-1}$) can be regarded as the initial sorption rate as $q_t/t \rightarrow 0$, hence:

$$h = K_2 q_e^2 \quad (10)$$

Equation (9) can be written as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (11)$$

A plot of t/q_t versus time of eqn. (11) should give a linear relationship, if sorption of Pb^{2+} follows this model. From where q_e , K_2 and h can be obtained

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from the slope and intercept of the plot.

The elovich equation

The elovich equation^[13-14] is generally expressed as eqn. (II):

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (12)$$

where q_t is the sorption capacity at time t (mgg^{-1}) α is the initial sorption rate ($\text{mgg}^{-1}\cdot\text{min}^{-1}$) and β is the desorption constant ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$) during any one experiment.

To simplify the elovich equation^[13] it was assumed $\alpha \beta \gg 1$ and by applying boundary conditions

$$q_t = 0 \text{ at } t = 0 \text{ and } q_t = q_t \text{ at } t = t \quad (13)$$

A plot of q_t versus $\ln t$ should give a linear relationship with the constants α and β calculated from the slope and intercept of the plot respectively.

The intraparticle diffusion equation

The intraparticle diffusion^[18-19] is expressed as eqn. 13.

$$R = K_{id} (t)^a \quad (14)$$

A linearized form of the equation is:

$$\log R = \log K_{id} + a \log t \quad (15)$$

Where R is the percent Pb(II) ions adsorbed t is the contact time, 'a' depicts the adsorption mechanism.

K_{id} is the intraparticle diffusion rate constant (min^{-1}). K_{id} may be taken as a rate factor, this is percent Zn (II) ions adsorbed per unit time^[21].

Plotting $\log R$ versus $\log t$ of eqn. (14) will give a linear relationship, from which the constants "a" and K_{id} can be determined from the slope and intercept of the plot, respectively.

Intraparticle diffusivity equation

The intraparticle diffusivity^[15] equation for description of sorption kinetics of Pb(II) ions is expressed as:

$$qt = X_i + K^i \sqrt{t} \quad (16)$$

where K^i gives the initial rate of sorption controlled by intraparticle diffusivity ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$), where X_i depicts the boundary layer thickness. If the kinet-

ics of Pb(II) ion sorption follows the intraparticle diffusivity equation then a plot of q_t versus \sqrt{t} should give a linear relationship from where K^i and X_i can be obtained from the slope and intercept of the plot, respectively.

The mass transfer equation

The mass transfer equation^[16] is expressed as:

$$C_0 - C_t = D \exp(K_0 t) \quad (17)$$

Where C_0 is the initial metal ion concentration (mgdm^{-3}) and C_t is the metal ion concentration ion at time t , t is the shaking time (min), D is a fitting parameter and K_0 is the adsorption constant which is related to the mass transfer adsorption coefficient, $K_0 = kM$, where M is the mass of adsorbent (g): A linearized form of eqn. (16) is:

$$\ln(C_0 - C_t) = \ln D + K_0 t \quad (18)$$

If the sorption of Zn(II) ions is depicted by the mass transfer model, then a plot of $\ln(C_0 - C_t)$ versus time should give a linear relationship from where $\ln D$ and K_0 can be determined from the intercept and slope of the plot, respectively.

Analysis of each of the kinetic models for the sorption of Pb(II) ion was examined using a fitting parameter known as the coefficient of determination, r^2 ^[23].

RESULTS AND DISCUSSION

Time-dependent sorption of lead (II) ion

The uptake rate of Pb(II) ions from aqueous solution by the unmodified guinea corn (UGC) and thioglycolic acid modified guinea corn waste (TGC) was studied for agitation times varying from 5 to 30 minutes. The percentage removal of Pb(II) ions with time for the two adsorbents is illustrated in figure 1.

While the sorption capacity of the two adsorbents for the Pb(II) is presented in figure 2. From figure 1 it can be seen that adsorption of Pb(II) was fast in the first 5-15 minutes, this was then followed by a slow adsorption reaching a maximum at 30 minutes. The removal efficiencies at 30 minutes for the two adsorbents were 71.2% (UGC) and 73.3% (TGC) adsorbents. The initial faster rate of removal of Pb(II)

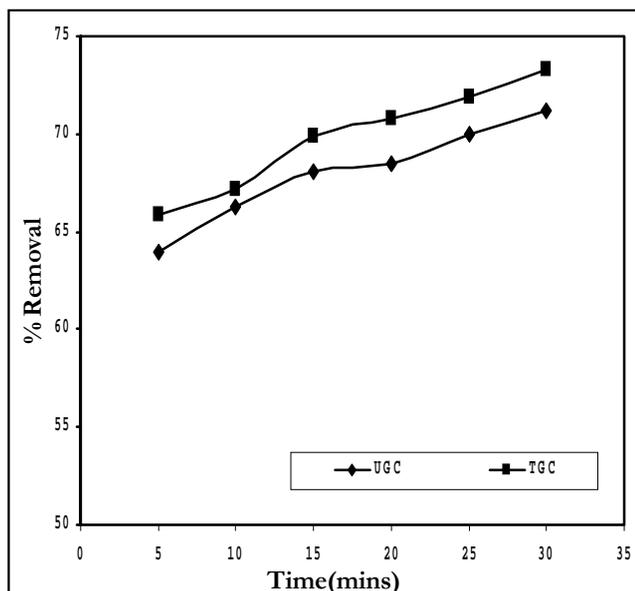


Figure 1: Percentage removal of Pb²⁺ with time for different adsorbents

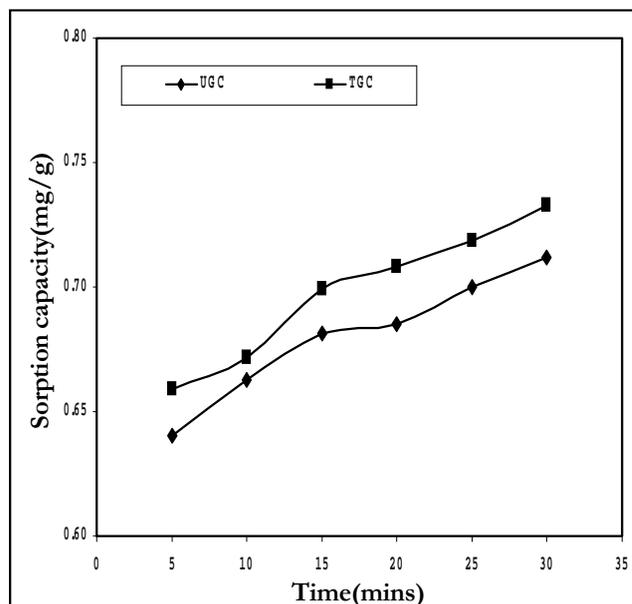


Figure 2: Pb²⁺ Sorption capacity (q_t) variation with contact time for adsorbents

ion at the commencement of sorption may be due to the availability of the uncovered surface area of the adsorbent, this trend is due to the phenomenon that adsorption kinetics depend on the surface area of the adsorbent^[24].

Figure 3 represents the time-dependence of the fraction of adsorption of Pb²⁺ by the UGC and TGC adsorbents. The shape of the curves shows three different stages. The initial stage relates to the transfer of Pb²⁺ from the bulk of the solution to the boundary film of the adsorbent and later to its surface. The second stage corresponds to the transfer of the Pb(II) ions from the surface to the intraparticle active sites of the adsorbent. The third stage shows the trend towards sorption equilibrium. The enhanced sorption of the Pb(II) ion by the two adsorbents with increase in agitation time may be due to the decrease in boundary layer resistance to mass transfer in the bulk and an increase in the kinetic energy of hydrated metal ions^[25].

Kinetic modeling of lead(II) ion sorption

Kinetics studies are important in determining the time needed to reach equilibrium and examinations into the rates of adsorption can be used to develop models and an understanding of solutes sorption on adsorbent surface. Kinetics is so important that, it can also be used to predict the rate of pollutant removal from aqueous solutions in the design of ap-

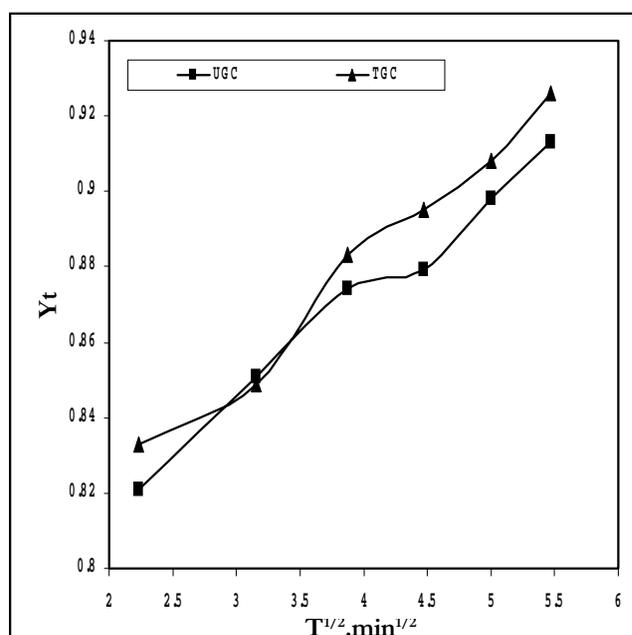


Figure 3: Time-dependence of the fraction of adsorption of Pb²⁺ for various adsorbents

propriate sorption treatment plants^[11].

Examination of literature reveals the existence of different opinions concerning the diffusion, giving place to various models for the prediction and the description of the process. However, these approaches converge at an identical total sight concerning the adsorption mechanisms. These mechanisms are grouped into 4 phases^[26]:

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- (1) Transfer of matter of the solution towards the boundary layer surrounding the particle.
- (2) Transfer of the boundary layer towards adsorbent surface: external diffusion.
- (3) Transfer of surface towards the adsorbent sites: intraparticle diffusion (in the solid and the various pores).
- (4) Adsorption, complexation and precipitation of metal species.
- (5) Chemical reaction (chemisorption).

However, it is quite common that more than one process can contribute to the system performance at the same time. In this case, the extensive interrelationships among the various equations make the overall kinetic model exceedingly complicated to evaluate. A rather simplifying approach to circumvent this problem is to assume that each one of the concurrent processes dominates over the others at specific time regimes of the process that is the rate-controlling step and, so study them independently^[27].

Hence the kinetic models that were used to analyze the sorption of lead(II) ions by the UGC and TGC adsorbents were; pseudo-first order, pseudo-second order, Elovich, intraparticle diffusivity, mass transfer and intraparticle diffusion equations.

The pseudo-first order kinetics of Pb(II) ions on the two adsorbents is illustrated in figure 4. From the graph the kinetic parameter for the pseudo-first order equation is presented in TABLE 1. From the table it is seen that the sorption capacity, q_c decreased

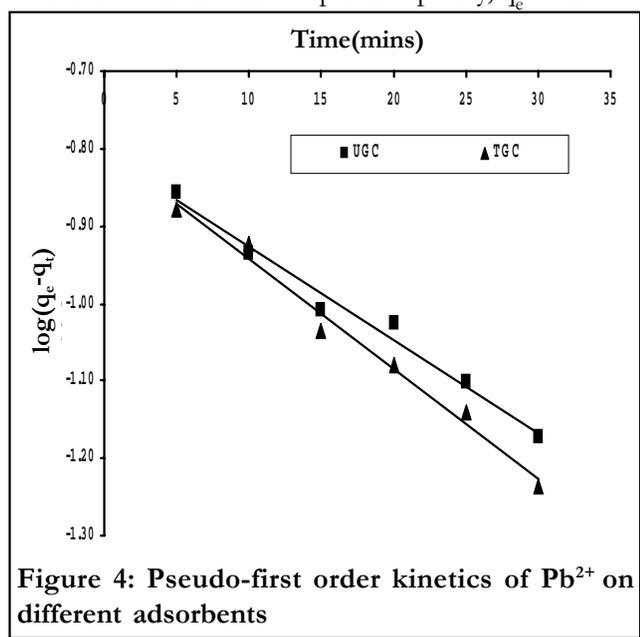


Figure 4: Pseudo-first order kinetics of Pb²⁺ on different adsorbents

TABLE 1: Kinetic parameters for pseudo-first order equation

Adsorbent	K_1 (Pseudo-first order rate constant) [L·min ⁻¹]	q_c (Sorption capacity) (mg·g ⁻¹)	r^2
UGC	2.76×10^{-2}	6.401	0.9825
TGC	3.27×10^{-2}	6.327	0.9866

with chemical modification, while the pseudo-first order rate constant, K_1 increased with chemical modification figure 5 indicates the pseudo-second order kinetics of Pb(II) ions on the UGC and TGC adsorbents. The kinetic constants, pseudo-second order constants, K_2 , the initial adsorption rate, h and the sorption capacity, q_c computed from figure 2 are presented in TABLE 2.

From the table, it is seen that the values of K_2 and h decreased with chemical modification, while the sorption capacity, q_c increased with chemical modification.

The plot of t/q_t versus $\ln t$ of the Elovich sorption model for Pb(II) ion sorption is illustrated in figure 6. From where the constants α , initial adsorption rate and β , the desorption capacity computed from the slope and intercept of the graph are presented in TABLE 3. It is seen that β decreased with chemical modification, while the values of α increased with chemical modification. Thereby, indicating that for the chemically modified adsorbent TGC the ini-

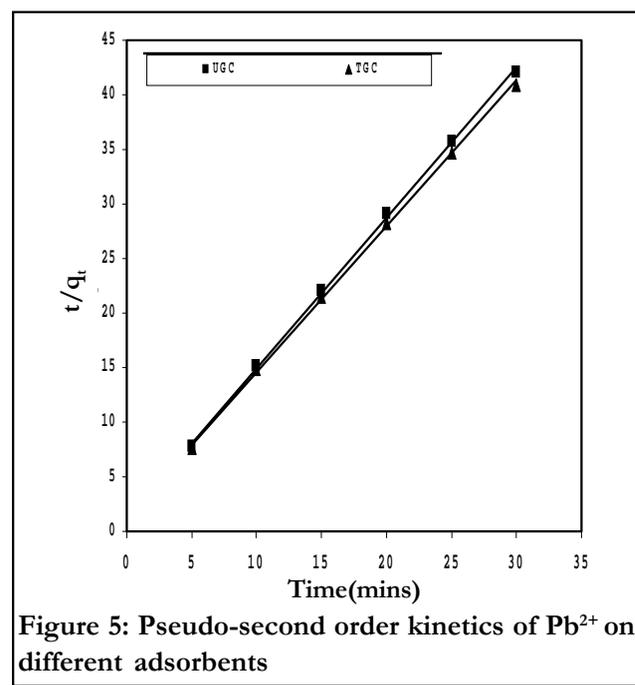


Figure 5: Pseudo-second order kinetics of Pb²⁺ on different adsorbents

TABLE 2: Kinetic parameters for pseudo-second order equation

Adsorbent	K_2 (Pseudo-second order rate constant) (g.mg.min ⁻¹)	h(initial adsorption rate)(mg.g ⁻¹ . min ⁻¹)	q _e (Sorption capacity) (mg.g ⁻¹)	r ²
UGC	1.503	7.94×10^{-1}	0.727	0.9994
TGC	1.335	7.52×10^{-1}	0.7505	0.9994

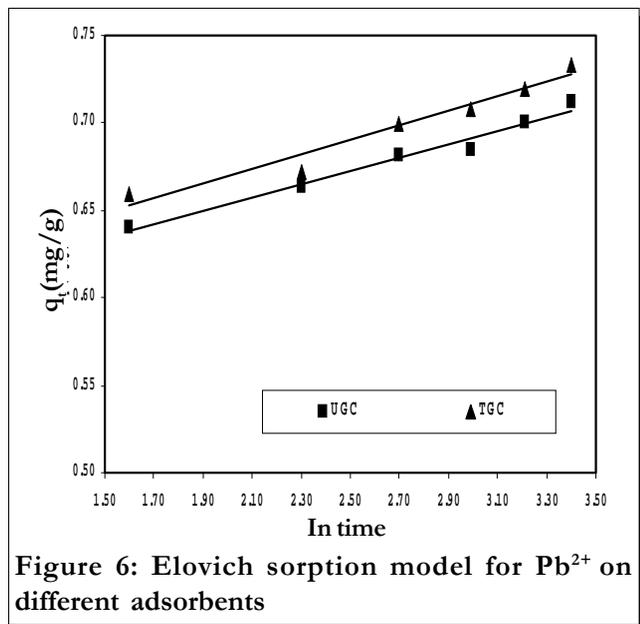


Figure 6: Elovich sorption model for Pb²⁺ on different adsorbents

TABLE 3: Kinetic parameters for elovich equation

Adsorbent	α (Initial adsorption rate) [mg.g ⁻¹ . min ⁻¹]	q _e (Sorption capacity) [mg.g ⁻¹ .min ⁻¹]	r ²
UGC	3.93×10^{-2}	25.974	0.9783
TGC	4.25×10^{-2}	24.096	0.9565

tial adsorption rate increased. The intraparticle diffusion kinetic sorption plot for Pb(III) ion removal by the UGC and TGC adsorbents is illustrated in figure 7. From the figure, the values of the intraparticle diffusion constant, K_{id} and the adsorption mechanism, α computed from the slope and intercept are presented in TABLE 4. From the table it is seen that the values of K_{id} and α increased with chemical modification.

Figure 8 describes the plot of the mass transfer kinetic equation for the description of sorption of Pb(II) ions by the two adsorbents. The values of the constants; the adsorption constant(K_o), the fitting parameter(lnD) and the mass transfer adsorption coefficient(K_m) computed from the plot are presented in TABLE 5. It can be seen that the values of K_o , lnD and k_m increased with chemical modification.

The intraparticle diffusivity equation was also used to fit the experimental data for the sorption of

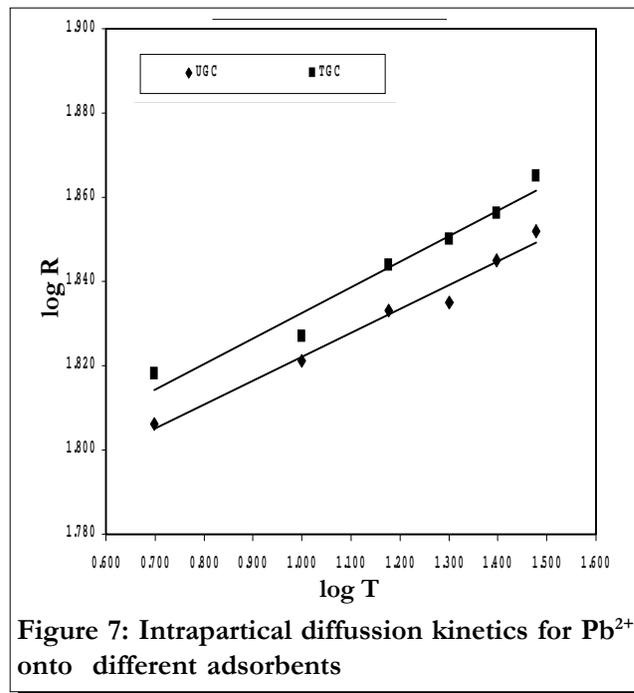


Figure 7: Intraparticle diffusion kinetics for Pb²⁺ onto different adsorbents

TABLE 4: Kinetic parameters for intraparticle diffusion equation

Adsorbent	K_{id} (Intraparticle diffusion constant) (min ⁻¹)	A (adsorption mechanism)	r ²
UGC	58.21	5.70×10^{-2}	0.9791
TGC	59.16	6.06×10^{-2}	0.9628

Pb(II) ions by the UGC and TGC adsorbents. Figure 9 illustrates the plot of the intraparticle diffusivity model. From the graph the values of the initial sorption rate K^1 and the boundary layer thickness X_i were computed from the slope and intercept of the plot and are presented in TABLE 6. Examination of TABLE 6 indicates that the values of the constants, K^1 and X_i increased with chemical modification.

Analysis of coefficient of determination of kinetic models

Examination of the 6 kinetic equations used to model the sorption of Pb(II) ions from aqueous solutions onto the unmodified guinea corn(UGC) and thioglycolic acid modified guinea corn(TGC) adsorbents shows that all the models fits the kinetic

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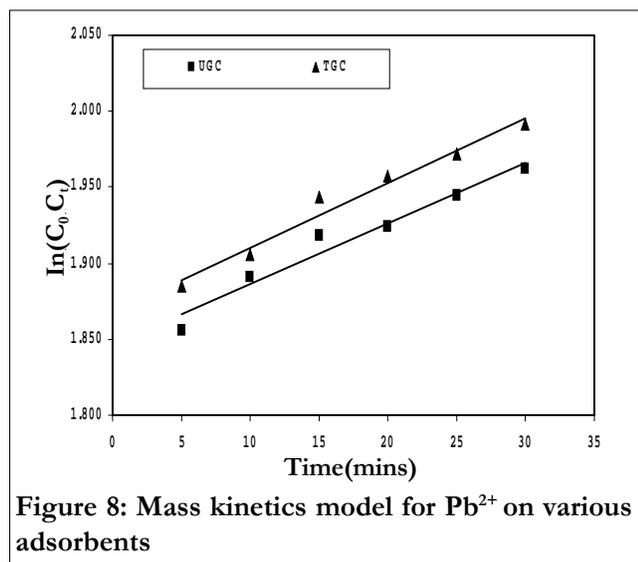


Figure 8: Mass kinetics model for Pb^{2+} on various adsorbents

TABLE 5: Kinetic parameters for mass transfer equation

Adsorbent	K_0 (adsorption constant) (min^{-1})	K_m (transfer coefficient) ($\text{gl}.\text{min}^{-1}$)	$\ln D$ fitting parameter	r^2
UGC	4.0×10^{-3}	8.0×10^{-3}	1.846	0.9600
TGC	4.3×10^{-3}	8.6×10^{-3}	1.868	0.9706

data for Pb^{2+} sorption.

However, to determine the most appropriate kinetic model that describes the mechanism of transport of $Pb(II)$ ions from the aqueous solution onto the two adsorbents a model selection criteria was used to determine their level of suitability and consistency^[28]. In this study, the coefficient of determination, r^2 was used to test the best-fitting of the kinetic models to the experimental data^[23].

Comparing the r^2 values of the six models in TABLE 1-6 shows that the coefficient of determination values for the pseudo-second order kinetic equation were highest(0.999). Since its values were closest to unity. Thus it was taken that the pseudo-second order kinetic equation was the model that best describes the mechanism of sorption of $Pb(II)$ ions onto the unmodified and thioglycolic acid modified guinea corn wastes(UGC and TGC).

The pseudo-second order model is based on the assumption that sorption follows a second order mechanism. So the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites and has the rate uniting step as a

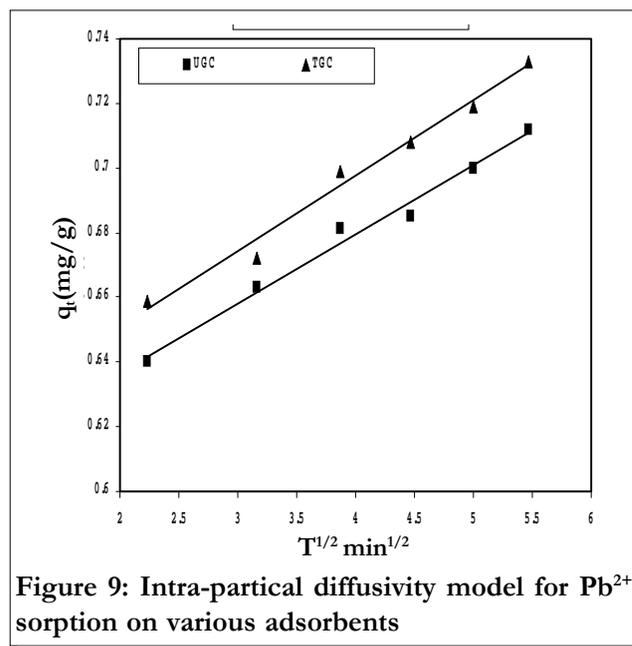


Figure 9: Intra-particle diffusivity model for Pb^{2+} sorption on various adsorbents

TABLE 6: Kinetic parameters for intraparticle diffusivity equation

Adsorbent	K^1 (Initial sorption rate) [$\text{mg}.\text{g}^{-1}.\text{min}^{-0.57}$]	X_1 (Boundary layer thickness)	r^2
UGC	2.13×10^{-2}	5.94×10^{-2}	0.9863
TGC	2.32×10^{-2}	6.04×10^{-2}	0.9828

chemical sorption (Chemisorption step)^[29].

Furthermore, the agreement between the values of the sorption capacity, q_c from the pseudo-second order model and the experimental observed values of the sorption capacity also lend credence to the assumption that the pseudo-second order equation is the best fitting model for the description of Pb^{2+} sorption onto the two adsorbents.

Hence, it can be said that sorption of $Pb(II)$ ions from aqueous solution onto unmodified and chemically modified guinea corn waste followed a pseudo-second order kinetic mechanism. This view was also observed for the sorption of some heavy metals using various adsorbents^[30-33].

CONCLUSION

The aim of this work was to determine the kinetics of $Pb(II)$ ion sorption from aqueous solution using two agricultural by-products(unmodified and chemically modified guinea corn waste). It was observed that the chemically modified guinea corn

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waste(TGC) had a higher efficiency than the unmodified for Pb^{2+} . Also different kinetic models were used to characterize the metal ion transport mechanism. The pseudo-second order kinetic model was found to best correlate the experimental data. The result also indicates that the two guinea corn waste adsorbents showed a great ability to adsorb $Pb(II)$ ions, and so can be successfully used in the environmental applications.

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