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EVALUATION OF MICROSOFT EXCEL SOLVER AS A TOOL FOR ADSORPTION KINETICS DETERMINATION

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ABSTRACT

The paper contains a study of adsorption kinetics of lead ions on powdered corn cobs (PCCS). Corn cobs were collected within Obafemi Awolowo University, Ile-Ife, Nigeria, washed with distilled water, air dried, powdered and sieved into different particle sizes (630 - 300μm, 300 - 212 μm, 212 - 150 μm and 150 -75 μm) and stored for use. Lead solutions were prepared from lead salt using standard methods. Physical and chemical properties of PCCS, and adsorption kinetics of lead onto PCCS were studied. Effects of pH, particle size and initial lead concentrations on the kinetics models and their constants were studied and analysed using Analysis of Variance (ANOVA). Kinetics models' constants were determined using least square, graphical and Microsoft Excel Solver (MES) methods. Statistical evaluations of the three methods were conducted using Akaike Information Criterion (AIC) and Model of Selection Criterion (MSC). The study showed that moisture content of the PCCS was 7.29 %, volatile solid at 550°C was 96.88 % and volatile solids at 1200°C was 99.44 %. Ash contents of the PCCS were 3.13 %, and 0.52 % at 550°C and 1200°C respectively. Kinetics constants varied with pH, particle size of the adsorbent and initial lead concentrations. The study showed that pH, particle size and initial lead concentrations were significant factors that influence adsorption kinetics of lead ions on PCCS at 95 % confidence level. It was concluded that the adsorption processes of Pb^{2+} onto the adsorbents followed two steps, mode of adsorption and transport are affected by more than one process. The order of accuracy of the methods was in Microsoft Excel Solver > Least Squared > Graphical method based on the value of MSC and AIC

Keywords: lead; adsorption kinetics; low-cost adsorbents; solution; adsorption

INTRODUCTION

The presence of heavy metals in wastewater at higher concentration is a significant environmental pollution problem due to the toxic effects and accumulation of these heavy metals throughout the food chain. Lead and cadmium are among the heavy metals that have higher priority for removal from aqueous environments than the other heavy metals (Amoko *et al*, 2016). The standard techniques for the removal of lead and cadmium from water and wastewaters include chemical precipitation, ion exchange, adsorption, membrane processes and distillation. Some of these techniques required high initial capital and operational costs (Ismail *et al.*, 2009; Adie *et al.*, 2009). These two factors make some of the techniques not practicable in developing countries like Nigeria and Kenya. These findings are the basis for the need for the development of innovative techniques with lower initial and operational cost. In the last three decade, efforts for new water and wastewaters treatment techniques had focused on adsorption and electrochemical methods (Amoko *et al*, 2016.

It has been reported that adsorption has many advantages over other treatment processes. The advantages are low capital and operational costs, the selective removal of metals, adsorbent regeneration and metal recovery potentiality, rapid kinetics of adsorption and desorption and small volume of sludge generation. Adsorption technology has been shown to be a feasible alternative for removing heavy metals from wastewater. This technology can utilize naturally abundant materials such as seaweeds (Amoko *et al*, 2016, Fehintola *et al.*, 2015a) and powdered egg shell (Oke *et al.*, 2008). Many researchers have studied adsorption of lead (II) and cadmium (II) from aqueous solutions using various biomasses. Yun *et al.* (1996) observed that the maximum uptake capacities of Durvillaea potatorum and

Ecklonia radiata for Pb^{2+} were 1.6 and 1.3 mmol/g, respectively. More information on adsorption can be found in literature such as Erhan *et al.* (2004), Hanafiah *et al.* (2006), Izanloo and Nasseri (2005); Otun *et al.* (2006a and 2006b); Alam *et al.* (2007); Wuyep *et al.* (2007); Ho (2007); Adie *et al.* (2009); Oke *et al.* (2016).

Generally, in adsorption, equilibrium analysis, adsorption kinetics and mechanism are critical parameters. Kinetics analysis is fundamental for the evaluation of the affinity or capacity of an adsorbent. It is therefore, important to determine adsorption rates and its relationship with the concentrations of adsorbate in a solution. Many studies have been carried out to formulate a general expression describing the kinetics of adsorption on adsorbent surfaces for liquid–solid phase sorption systems. In recent years, sorption mechanisms have been reported and involved kinetic-based models. Some of the cited adsorption kinetics in literature are first-order kinetics and second-order kinetics. They also include reversible reactions, pseudo-first-order and pseudo- second order; reactions based on solution concentration and the Elovich model. The main objective of this study is to investigate the adsorption of lead (II) from aqueous environments using powdered corn cobs, with a particular attention to the kinetics.

MATERIALS AND METHODS

Corncobs were collected from an agricultural farm in Obafemi Awolowo University, Ile-Ife, Nigeria. The corncobs were washed with distilled water to remove impurities. The corncobs were dried at room temperature, ground into powder, sieved and classified using British Standard (BS) sieve. Powdered corncobs (PCCS) were selected based on its availability and based on previous studies (Fehintola *et al.*, 2015a and b). Powdered corncob with sieve sizes of < 300 m ($PCCS_1$), 300 - 212 m ($PCCS_2$), 212 - 150 m ($PCCS_3$) and 150 - 75 m ($PCCS_4$) were separated and stored in different desiccators. The mineral contents of the PCCS were determined by using spectrophotometer (Jenway 7315) after acid digestion of 2 g samples (2.0 g of cleaned PCCS was soaked in acid, APHA, 2012; van Loosdrecht *et al.,* 2016). Selected properties (moisture content, ash content, and water and acid solubility) of the PCCS were determined using standard methods. Sample of PCCS was dried in an initially weighed dish at 105°C to a constant weight in an oven (APHA, 2012, Fehintola *et al.*, 2015b). The moisture content (M_c) of PCCS was computed as follows:

$$M_c\,(\%) = \quad 100\left(\frac{W_1 - W_2}{W_1}\right) \qquad (1)$$

Where: M_c is the moisture contents, W_1 and W_2 are the initial and final weights of the PCCS after drying at 105°C

A known weight of the dried PCCS samples used (individually) for the determination of moisture content was placed in crucibles of known masses and transferred into a muffle furnace (Brother Furnace, XD 1220N). The muffle furnace was heated to 550°C for 2 hours and weighed, then reheated to 1200°C for 2 hours and weighed finally. The PCCS samples were allowed to cool in the desiccators to the room temperature, and the final weights of the crucibles and PCCS were determined. Volatile solid and ash contents of PCCS were computed as follows:

$$V_S\ (\%) = \quad 100\left(\frac{W_2 - W_3}{W_2}\right) \qquad (2)$$

$$A_{sh}\ (\%) = 100 \quad \left(\frac{W_4}{W_1}\right) \qquad (3)$$

Where: W_3 and W_4 is the final weight of PCCS after 2 hours in the muffle furnace at 550 and 1200°C, A_{sh} and V_S are the ash and volatile solid contents of the PCCS.

A 5 gram each of the samples were soaked in 300 mL of distilled water and 300 mL of 0.25 M of HCl individually for 24 hours. The PCCS samples were filtered using pre-dried and weighed filter papers (number 1). The PCCS samples and the filter papers were dried in the oven at 105° C for 24 hours and allowed to cool in desiccators to the room temperature, and the final weights of the samples were determined. The water (W_s) and acid solubilities (A_s) of PCCS were computed as follows (Fehintola *et al.*, 2015):

$$W_S\ (\%) = \quad 100\left(\frac{W_2 - W_4}{W_2}\right) \qquad (4)$$

$$A_S\ (\%) = 100\left(\frac{W_2 - W_5}{W_2}\right) \qquad (5)$$

Where: W_S is the water solubility of PCCS, A_S is the acid solubility of PCCS, W_4 and W_5 are the dry weight of the PCCS after soaking in the distilled water and the 0.25 M of HCl acid for 24 hours respectively.

A 2.0 g of the PCCS was digested using trioxonitrate (V) acid digestion method as described in Standard Methods for Water and Wastewater Analysis (APHA, 2012, van Loosdrecht *et al.*, 2016). The chemical properties of the PCCS were determined using standard methods (APHA, 2012) and the total metal concentrations (M_{cc}) were determined using spectrophotometry method. Metal concentrations in the PCCS were computed as follows:

$$q_t = \left(\frac{(C_0 - C_t)}{M}\right)V \qquad (6)$$

Where: B is the dilution factor, A is the concentration of the metals (mg/L) in the PCCS obtained from the reading and M_{cc} is the actual concentration of the metal.

Working solutions of Pb^{2+} were regularly prepared from the stock solution. In order to ascertain the adsorptions kinetics, known quantities of PCCS were added to a known volume (300ml) of a solution containing 19.47 mg / L Pb^{2+} solution, stirred for 3 minutes and allowed to settle. The supernatants from the treatment process were filtered through a filter paper at an interval of 1 hour for 8 hours, and the filtrates were analyzed for Pb^{2+} concentration. For adsorptive rates of natural waters and raw water samples were collected from selected surface water in Ile-Ife. Pb^{2+} concentration the natural and raw water samples were determined. The natural and raw water samples (the water samples) were subjected to a similar treatment as for the synthetic Pb^{2+} solutions. The amount of solute removed (adsorbed) was computed using equation (7). The percentage of Pb^{2+} removed (R_t%) from the solution was calculated using equation (8) as follows:

$$q_t = \left(\frac{(C_0 - C_t)}{M}\right)V \qquad (7)$$

$$R_t(\%) = 100\left(\frac{(C_0 - C_t)}{C_0}\right) \qquad (8)$$

Where: q_t is the adsorption capacity at time t (mg/g), C_0 is the initial concentration of lead in the solution (mg/L), C_t is the concentration of lead in the solution at time t (mg/ L), and R_t *is* the percentage of the pollutant adsorbed (%).

Effects of pH on the removal of Pb^{2+} from synthetic Pb^{2+} solution was investigated using PCCS of particle size 300 - 212 m ($PCCS_1$) at different pH values (the pH of the solutions were controlled with either 0.01 M HCl or NaOH), at an initial lead concentration of 0.64 mg / L. pH of these solutions were determied using pH meter(Jenway 6051). The influence of adsorbent (PCCS) particle size on the Pb^{2+} removal from solution through batch adsorption processes was investigated using various particle sizes of PCCS ($PCCS_1$, $PCCS_2$, $PCCS_3$ and $PCCS_4$) at pH 7.2 and at an initial Pb^{2+} concentration of 0.64 mg / L. The effect of initial concentrations on the adsorptive rate of lead ion using batch adsorption experiments was investigated at initial concentrations between 0.13 mg / L and 19.47 mg / L. at particle size 75 m ($PCCS_1$) and pH 7.2. The laboratory analyses of pH and Pb^{2+} concentrations in both synthetic and natural water used were conducted as specified in APHA (2012, van Loosdrecht *et al.*, 2016) using pH meter (Jenway 6051) and spectrophotometer (Jenway 7315) method for Pb^{2+} concentrations. The adsorption kinetics of Pb^{2+} onto PCCS was analyzed using a pseudo second-order, Elovich, and intra-particle diffusion kinetic models through the use of Microsoft Excel Solver (MES), graphical and least square methods. Microsoft Excel Solver was used for the determination of the adsorption kinetics constants. The methods were evaluated statistically using Akaike Information Criterion, (AIC), Schwartz Criterion (SC), coefficient of Determination (CD) and Model of Selection Criterion (MSC). Expected concentrations were used as reference data. Procedures employed in the computations of model constants using Microsoft Excel Solver (MES) are as follows (Oke *et al.*, 2017):

a) Microsoft Excel Solver was added in on the toolbar of Microsoft Excel;

b) Target (limit) value of the iteration was set for the software based on square of difference as

$$\sum_{i=1}^{n}(q_t \quad - \quad a \quad + \quad bX)^2 \qquad (9)$$

c) Changing cells of the iterations were selected, number of iterations, degree of accuracy and maximum time for the iteration were set for the software to meet the target; and

d) The iteration started through Microsoft Excel Solver (Figure 1).

More on MES can be found in literature (Oke *et al.,* 2016; 2017, Barati, 2013; Tay *et al.,* 2014; Hui *et al.,* 2018). In the utilization of least square method, equations used are as follows:

$$Y \quad = \quad a \quad + \quad bX \qquad (10)$$

$$\sum_{i=1}^{n} Y_i \quad = \quad an \quad + \quad b\sum_{i=1}^{n} X_i \qquad (11)$$

$$\sum_{i=1}^{n} X_i Y_i \quad = \quad a\sum_{i=1}^{n} X_i \quad + \quad b\sum_{i=1}^{n} X_i^2 \qquad (12)$$

Using equations (11) and (12), a and b are determined as follows:

$$b \quad = \left(\frac{\sum_{i=1}^{n} X_i \sum_{i=1}^{n} Y_i - n\sum_{i=1}^{n} X_i Y_i}{\sum_{i=1}^{n} X_i \sum_{i=1}^{n} X_i - n\sum_{i=1}^{n} X_i^2} \right) \qquad (13)$$

$$a \quad = \quad \left(\frac{\sum_{i=1}^{n} Y_i - b\sum_{i=1}^{n} X_i}{n} \right) \qquad (14)$$

Linear transformation of the second-order pseudo adsorption kinetic equation is expressed as shown in equation (15):

$$\left(\frac{t}{q_t} \right) \quad = \quad \frac{1}{h} \quad + \quad \frac{1}{q_e} t \qquad (15)$$

Where: q_e is the equilibrium solid phase concentration of sorbate (mg/mg), t is the time, k_2 *is* the rate constant of second-order pseudo adsorption. Assuming the h (mg/g· h) is equal to $k_2(q_e)^2$

Erhan *et al.* (2004), Oke *et al.* (2008), Ismail *et al.* (2009) simplifies Elovich equation as follows:

$$q_t \quad = \quad \frac{1}{\beta}\log_e(\alpha\beta) \quad + \quad \frac{1}{\beta}\log_e(t) \qquad (16)$$

Where: β is the desorption constant during any experiment and is the initial adsorption rate

The intraparticle diffusion model is based on the theory proposed by Weber and Morris (1963). It was tested to identify the diffusion mechanism. It is an empirical functional relationship and is common to the most adsorption processes. The theory states that the uptake varies proportionally with $t^{0.5}$ rather than with the contact time t.

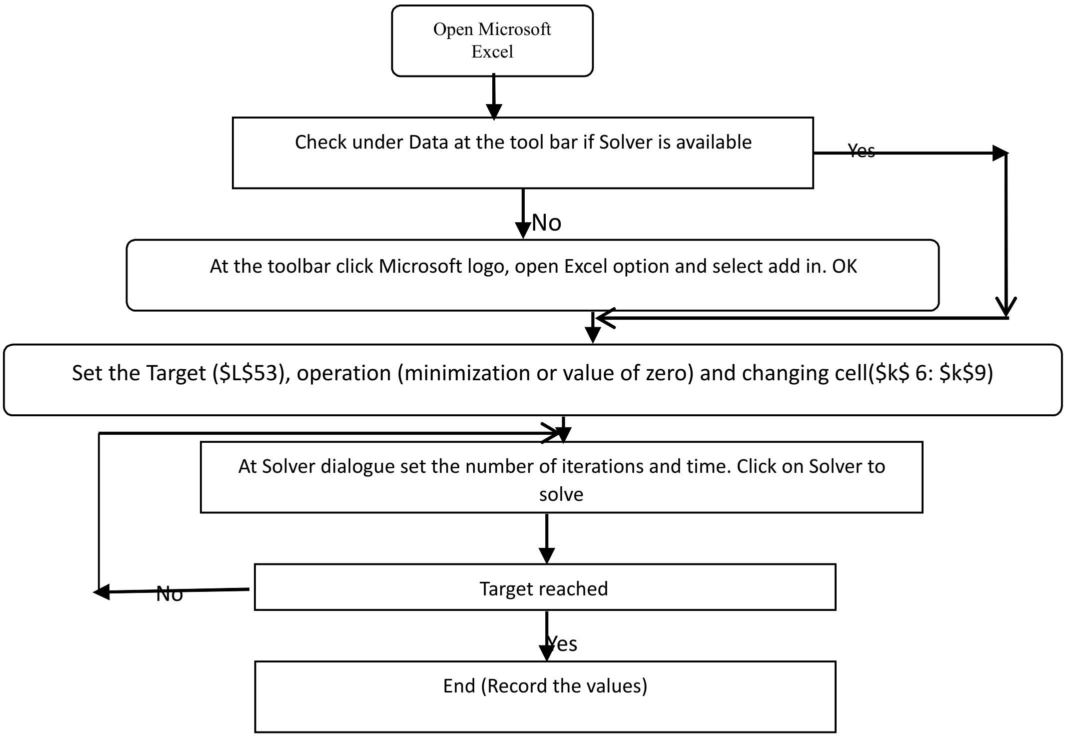


Figure 1: Procedure for using Microsoft Excel Solver in the computation of adsorption kinetics

According to this theory the equation can be expressed as follows (Edson *et al.*, 2011):

$$R = k_p (t)^{0.5} + I \qquad (17)$$

Where: R is the percentage of the pollutant adsorbed (%), 't' is the time, k_p is the intraparticle diffusion rate constant (/$h^{0.5}$) and I is a constant that describe the thickness of the boundary layer.

The Model of Selection Criterion (MSC) is interpreted as the proportion of expected chloride concentration and observed chloride concentrations variation that can be explained by the obtained chloride concentrations. Higher value of MSC indicates higher accuracy, validity and the good of fit of MSC. MSC method was computed using equation (18) as follows:

$$MSC = \ln \frac{\sum_{i=1}^{n} \left(Y_{obsi} - \bar{Y}_{obs}\right)^2}{\sum_{i=1}^{n} \left(Y_{obsi} - Y_{cali}\right)^2} - \frac{2p}{n} \qquad (18)$$

where, Y_{obsi} is the observed concentration; $_{obs}Y$ is the average of observed concentration; p is the total number of fixed parameters to be estimated in the equation; n is the total number of concentration, and Y_{cali} is the expected concentration.

The AIC was derived from the Information Criterion of Akaike (1976). It allows a direct comparison among models with a different number of parameters. The AIC presents the information on a given set of parameter estimates by relating the coefficient of determination to the number of parameters. The AIC values were computed using equation (19) as follows:

$$AIC = n\left(\ln \sum_{i=1}^{n} \left(Y_{obsi} - Y_{cali}\right)^2\right) + 2p \qquad (19)$$

The Schwartz Criterion (SC) is defined by the formula in equation (20). SC was computed as follows:

$$SC = n \ln\left(\sum_{i=1}^{n} \left(Y_{obsi} - Y_{cali}\right)^2\right) + p\ln(n) \qquad (20)$$

The more appropriate model is the one with the smaller SC value. Coefficient of determination (CD) can be interpreted as the proportion of expected data variation that can be explained by the obtained data. Higher values of CD indicate higher accuracy, validity and good fitness of the method. CD can be expressed as follows:

$$CD = \frac{\sum_{i=1}^{n}\left(Y_{obsi} - \overline{Y_{cali}}\right)^2 - \sum_{i=1}^{n}\left(Y_{obsi} - Y_{cali}\right)^2}{\sum_{i=1}^{n}\left(Y_{obsi} - \overline{Y_{cali}}\right)^2} \quad (21)$$

RESULTS AND DISCUSSION

The study revealed that that moisture content of the PCCS was 7.29 %, volatile solid at 550°C was 96.88 % (96.63 % based on the dried weight), and volatile solids at 1200°C was 99.44 % (99.44 % based on the dried weight). Ash contents of the PCCS were 3.13 % (3.37 % based on the dried weight), and 0.52 % (0.56 % based on the dried weight) at 550°C and 1200°C respectively. Ogunjobi and Labunmi (2013) stated that yellow corncobs contained 9.80 % ash content and 3.81 % moisture, while white corn cobs had 9.77% ash and 6.43 % moisture contents. These results revealed that composition of corncobs is a function of the type of corncobs and locations. Results of water and acid solubilities were 4.53 % (5.42 % of dried weight) and 13.00 % (13.61 % of dried weight) respectively. Mineral composition of the PCCS indicated that one gram of PCCS contained 131.00 mg of Fe as Fe^{2+}per gram of PCCS (13.10%), 1.70 mg calcium as Ca^{2+} (0.17%) and 0.010 mg Al as Al^{3+} (0.001%). Zinc and Nickel contents were 0.01 mg /g each with neither lead ion nor cadmium ion present. Wanitwattanarumlug *et al.(*2012) reported that corn cob contained Cellulose 41.27 %, Hemicellulose 46.00 % and Lignin 7.40 %. Okoronkwo *et al.* (2016) reported that corncobs ash contains 47.78 % SiO_3, 9.40 % Al_2O_3, 8.31 % Fe_2O_3, 16.70 % CaO, 7.80 % MgO, 2.70 % Mn_2O_3, 5.42 % K_2O and 1.89 % Na_2O. These results indicate that PCCS ash was made up alkali metals (as K_2O and Na_2O), alkali earth metals, other metals and silicates. It has been reported that some salts (calcium, iron and aluminum salts) undergo displacement reaction in aqueous medium as follows:

$$Al^{3+} + 3H_2O \rightarrow \frac{3}{2}H_2 + Al(OH)_3 \quad (21a)$$

$$Al^{3+} + 2H_2O \rightarrow \frac{3}{2}H_2 + AlO(OH) \quad (21b)$$

$$Al^{3+} + \frac{3}{2}H_2O \rightarrow \frac{3}{2}H_2 + \frac{1}{2}Al_2(O)_3 \quad (21c)$$

$$Fe^{2+} + 2H_2O \rightarrow H_2 + Fe(OH)_2 \quad (21d)$$

$$Ca^{2+} + 2H_2O \rightarrow H_2 + Ca(OH)_2 \quad (21e)$$

$$Mg^{2+} + 2H_2O \rightarrow H_2 + Mg(OH)_2 \quad (21f)$$

$$Mn^{2+} + 2H_2O \rightarrow H_2 + Mn(OH)_2 \quad (21g)$$

$$2K^{+} + 2H_2O \rightarrow H_2 + 2K(OH) \quad (21h)$$

$$2Na^{+} + 2H_2O \rightarrow H_2 + 2Na(OH) \quad (21i)$$

The first reaction (21a) forms the aluminum hydroxide bayerite ($Al(OH)_3$) and hydrogen, the second reaction (21b) forms the aluminum hydroxide boehmite (AlO(OH)) and hydrogen, and the third reaction (21c) forms aluminum oxide and hydrogen. All these reactions are thermodynamically favorable from room temperature past the melting point of aluminum (660^0C). All are also highly exothermic. From room temperature to 280^0C, $Al(OH)_3$ is the most stable product, while from 280-480^0 C, AlO(OH) is most stable. Above 480 ^{0}C, Al_2O_3 is the most stable product. This result shows that the PCCS underwent the reaction in equation (22) with lead ion, which can reduce the pH and the end product reacted with lead ion to precipitate the pollutant.

$$Ca(OH)_2 + Pb^{2+} \rightarrow Ca^{2+} + Pb(OH)_2 \quad (22a)$$

$$Fe(OH)_2 + Pb^{2+} \rightarrow Fe^{2+} + Pb(OH)_2 \quad (22b)$$

$$2Al(OH)_3 + 3Pb^{2+} \rightarrow 2Al^{3+} + 3Pb(OH)_2 \quad (22c)$$

$$Mg(OH)_2 + Pb^{2+} \rightarrow Mg^{2+} + Pb(OH)_2 \quad (22d)$$

$$Mn(OH)_2 + Pb^{2+} \rightarrow Mn^{2+} + Pb(OH)_2 \quad (22e)$$

$$2Na(OH) + 2Pb^{2+} \rightarrow 2Na^{+} + Pb(OH)_2 \quad (22f)$$

These equations revealed the reaction PCCS underwent with Pb^{2+}, which reduced the pH of the treated solution and the end product reacted with Pb^{2+} to precipitate the pollutant. Literature such as Wanitwattanarumlug *et al.(*2012), Amoko *et al.(*2015), Okoronkwo *et al.* (2016) and Arellano *et al.* (2016) show effects of selected factors and reagents on micrograph structure of the PCCS. These figures from literature (Wanitwattanarumlug *et al*,.2012, Amoko *et al.*, 2015, Okoronkwo *et al.*, 2016 and Arellano *et al.*,

2016) revealed that the potassium hydroxide pre-treatment with microwave on corncobs was an effective technique for improving enzymatic hydrolysis accessibility. The optimum conditions for PCCS were found to be 2 % of KOH at 120 °C for a duration of 25 minutes which could increase in surface area by 45.67% and the cellulose crystallinity index of the material up to 57.28 %. Figure 2 presents the micrograph structures of the PCCS as obtained from Literature. These figures (SEM) revealed that there are pores on raw, modified and treated PCCS, which indicate that PCCS is a good adsorbent at various stages.

Figure 3 (a and b) presents adsorption kinetics of lead onto the adsorbent. From the figure it can be seen that adsorption of lead by the adsorbent increases with time. This observation agrees with the literature on adsorption of lead by various adsorbents. From the figure, it was evident that the adsorption processes of Pb^{2+} onto the adsorbent followed two steps. The first step was linear portion followed the boundary layer diffusion followed by another linear portion which represents the intra particle diffusion. This shows that the adsorption processes were not only by intraparticle diffusion but the film diffusion also played a role in the observed processes. Adsorption kinetics are important ingredients in environmental pollution control. In order to investigate in detail of the mechanism of adsorption rate for the adsorption of Pb^{2+} onto the adsorbents, the constants were determined using MES, graphical and least square methods for the pseudo second kinetic order, Elovich and intraparticle models. Table 1 shows the values of pseudo second order pseudo second order, Elovich and Intraparticle kinetics models. The pseudo second order kinetics model's parameters (k_2 and q_e) for each of the methods. k_2 and q_e were in the range of 0.006 to 22.455 and 0.044 to 59.880, 0.001 to 18.153 and 0.091 to 59.880, and -0.002 to 18.151 and 0.089 to 59.878 for graphical, least square and MES methods respectively. The lowest k_2 (- 0.002) came from Microsoft Excel Solver method and the highest value of k_2 came from least square and graphical methods. Also, the lowest q_e (0.044) came from graphical method. The highest value of q_e came from the Microsoft Excel Solver method. These results indicated that the values of k_2 and q_e are functions of the adsorbates, adsorbents and methods used. In the case of Elovich and intrapaticle kinetics models, their constants follow the same pattern as pseudo second kinetics model. For intra-particle model, the values for C revealed the idea on the thickness of the boundary layer. The values of C were found to be less than zero (0) in almost all the cases (including raw water samples), which indicated that the mode of adsorption and transport are affected by more than one process.

Table 2 presents statistical evaluation of the three methods. The table revealed that the overall lowest AIC (-36.39), and the highest MSC (7.46) came from MES method. The next to MES method was least square method while graphical was the methods with the highest overall AIC and the lowest MSC. The observations indicate that the order of accuracy of the methods was in Microsoft Excel Solver > Least Squared > Graphical method based on the value of MSC. Tables 3 to 7 present statistical evaluation of effects of the selected factors on the performance adsorption of lead ion onto PCCS.

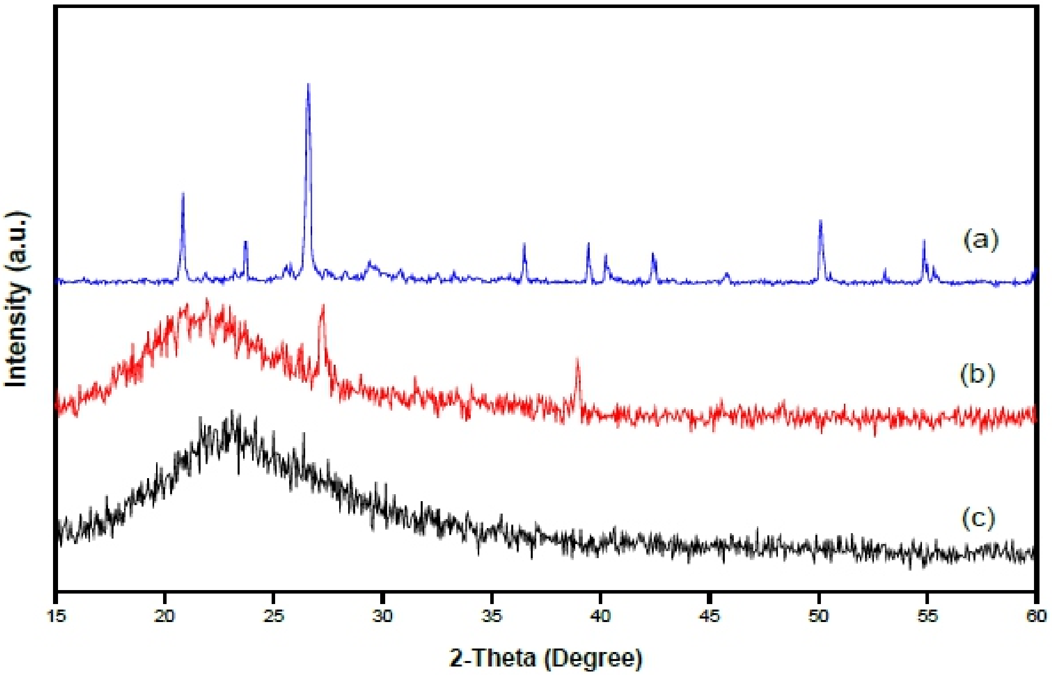
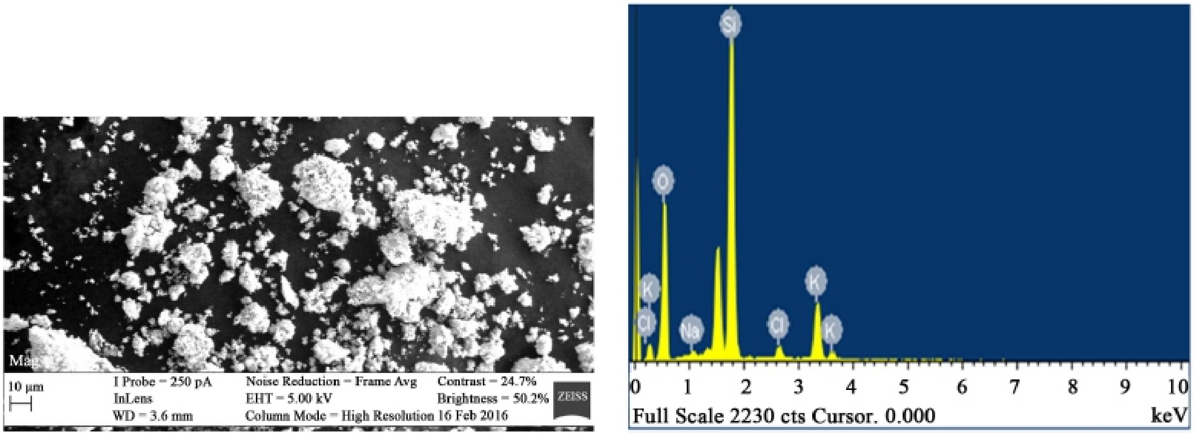
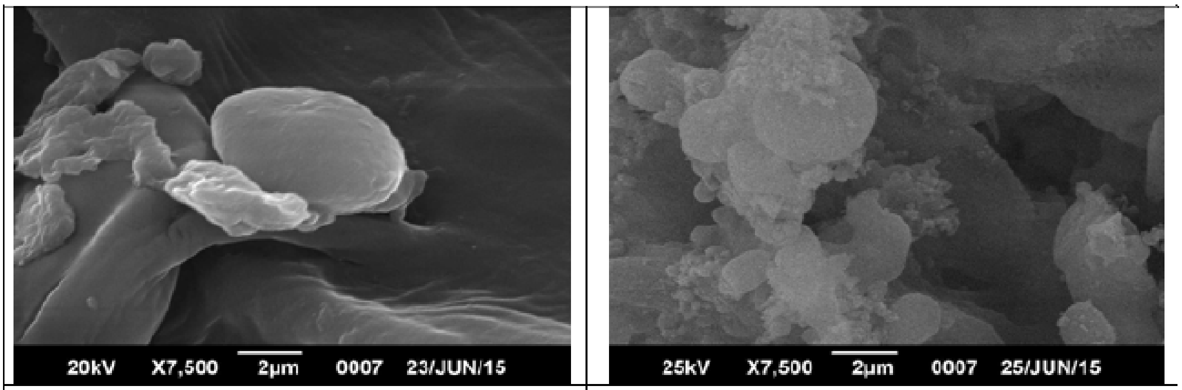


Figure 2a. XRD pattern of (a) Corn con ash; (b) extracted silica and (c) Nano silica (Source: Okoronkwo *et al*. 2016)

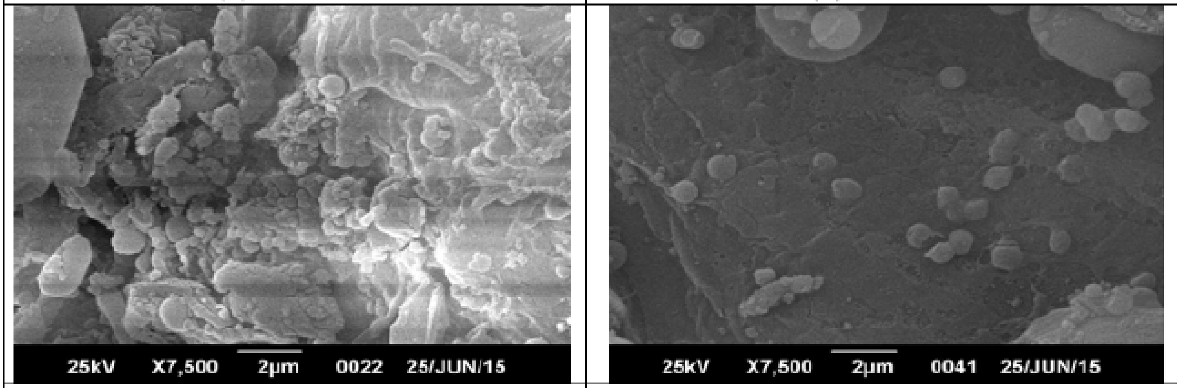


(a) (b)

Figure 2b. SEM image of (a) Nano-structured silica and (b) EDS spectrum (Source: Okoronkwo *et al.* 2016)

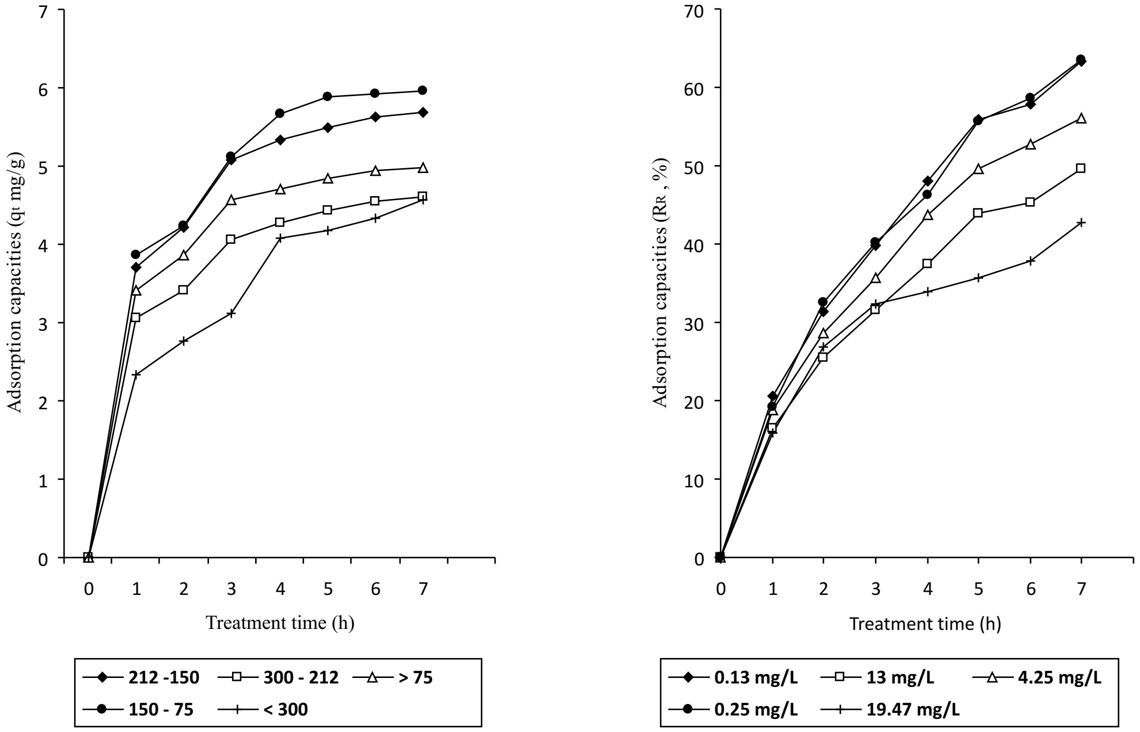


(a) Biomass raw **(b) HTC -180 °C**



(c) HTC – 250 °C **(d) HTC – 350 °C**

Figure 2c: Micrographs obtained for biomass (a) hydrothermal carbonization (HTC) products at, (b) 180 °C, , (c) 250 °C and (d) 350 °C(Source: Arellano *et al.* 2016)



(a) (b)

Figure 3: Adsorption capacities and kinetics of lead ion unto the PCCS at pH of 7.2 and at room temperature (a) Adsorption capacities (mg/g) at various particle sizes (x 10^{-6}m) with respect to time; (b) Adsorption capacities (%) at various initial concentration of Pb^{2+} with respect to time

Table 1: Constants in the kinetics models

Medium/ Factor	Factor	Pseudo Second Order Kinetics						Elovich						Intra Particle					
		Graphical		Least Square		MES		Graphical		Least Square		MES		Graphical		Least Square		MES	
		qe	k_2	qe	k_2	qe	k_2	α	β	α	β	α	β	k	C	k	C	k	C
Raw Water	0.05 mg/l	0.105	3.696	0.119	2.606	0.117	2.604	0.076	36.630	0.076	36.640	0.076	36.640	1.738	1.933	1.738	1.932	1.738	1.932
	0.053 mg/l	0.105	3.902	0.123	2.547	0.121	2.545	0.078	35.587	0.078	35.622	0.078	35.622	2.492	0.175	2.009	0.960	2.009	0.960
	0.055 mg/l	0.113	3.415	0.122	2.764	0.12	2.762	0.082	35.336	0.082	35.362	0.082	35.363	2.073	0.997	2.073	0.997	2.073	0.997
	0.060 mg/l	0.092	6.392	0.091	6.664	0.089	6.662	0.103	44.643	0.103	44.690	0.103	44.691	1.962	1.358	1.962	1.358	1.962	1.358
Initial Concentration of Pb^{2+}	13.01	11.351	0.006	12.330	0.005	12.328	0.003	1.976	0.852	1.976	0.852	1.976	0.852	86.547	-64.693	86.547	-64.693	86.547	-64.693
	0.13	0.044	22.455	0.047	18.153	0.045	18.151	0.080	93.458	0.080	93.356	0.080	93.361	37.808	18.830	37.808	18.830	37.808	18.830
	19.47	9.050	0.033	9.579	0.028	9.577	0.026	5.494	0.473	5.494	0.473	5.494	0.473	54.608	-21.711	54.608	-21.711	54.608	-21.711
	0.25	0.092	6.370	0.091	6.704	0.089	6.702	0.103	44.843	0.103	44.914	0.103	44.915	40.727	6.421	40.727	6.421	44.249	0.694
Particle size of the adsorbent	0.3mm	14.124	0.010	14.124	0.010	14.122	0.008	4.690	0.423	4.690	0.423	4.690	0.423	67.639	-45.110	67.639	-45.110	67.639	-45.109
	0.212 mm	59.880	0.000	59.880	0.000	59.878	-0.002	3.663	0.423	3.663	0.423	3.663	0.423	55.584	-32.493	55.584	-32.493	55.583	-32.492
	0.15mm	10.482	0.019	10.482	0.019	10.48	0.017	4.603	0.483	4.603	0.483	4.603	0.483	63.325	-44.415	63.325	-44.415	63.324	-44.415
	0.075 mm	10.627	0.020	10.627	0.020	10.625	0.018	4.944	0.461	4.946	0.461	4.946	0.461	68.003	-48.564	68.003	-48.564	68.003	-48.563
Initial pH of the solution	3	5.013	0.060	5.013	0.060	5.011	0.058	3.124	0.887	3.124	0.887	3.124	0.887	27.157	-6.726	27.157	-6.726	27.157	-6.725
	4.47	13.793	0.010	13.793	0.010	13.791	0.008	4.723	0.425	4.723	0.425	4.723	0.425	54.608	-21.711	54.608	-21.711	54.607	-21.710
	7.58	3.460	0.112	4.184	0.077	4.182	0.075	2.781	1.064	2.781	1.064	2.781	1.064	24.813	-7.209	24.813	-7.209	24.812	-7.208
	11.74	4.073	0.084	4.073	0.084	4.071	0.082	2.812	1.060	2.812	1.060	2.812	1.060	23.204	-5.802	23.204	-5.801	23.204	-5.801
Mass of the adsorbent	1.0 gram	10.977	0.018	10.975	0.018	10.973	0.016	4.717	0.446	4.717	0.446	4.717	0.446	54.608	-21.711	54.608	-21.711	54.607	-21.710
	0.5 gram	27.100	0.004	27.100	0.004	27.098	0.002	6.909	0.247	6.908	0.247	6.909	0.247	41.931	-26.590	41.931	-26.590	41.931	-26.589
	0.3 gram	22.026	0.008	22.026	0.008	22.024	0.006	9.021	0.227	9.021	0.227	9.021	0.227	26.069	-10.382	26.069	-10.382	26.069	-10.382

Table 2: Statistical Evaluation of the methods

Medium/ Factor	Factor	Pseudo Second Order Kinetics						Elovich						Intra Particle					
		Graphical		Least Square		MES		Graphical		Least Square		MES		Graphical		Least Square		MES	
		AIC	MSC	AIC	MSC	AIC	MSC	AIC	MSC	AIC	MSC	AIC	MSC	AIC	MSC	AIC	MSC	AIC	MSC
Raw Water	0.05 mg/l	13.24	3.78	10.57	4.44	10.55	4.45	-42.68	4.46	-42.69	4.46	-42.69	4.46	-5.01	5.13	-12.02	5.13	-12.02	5.13
	0.053 mg/l	13.49	3.65	9.40	4.68	9.38	4.69	-43.09	4.62	-43.10	4.62	-43.10	4.62	-1.94	3.55	-22.71	7.76	-22.71	7.76
	0.055 mg/l	9.02	6.02	6.57	6.64	6.55	6.65	-45.47	6.23	-45.48	6.23	-45.48	6.23	-6.14	5.72	-14.27	5.72	-14.27	7.04
	0.060 mg/l	9.37	5.97	9.29	5.99	9.27	6.00	-43.83	5.80	-43.83	5.80	-43.83	5.80	-4.72	5.01	-11.43	5.01	-11.43	6.49
Initial Concentration of Pb^{2+}	13.01	-26.00	6.17	-27.55	6.55	-27.57	6.56	-12.13	4.18	-12.13	4.18	-12.13	4.18	13.26	2.92	24.52	2.92	24.52	2.92
	0.13	12.44	5.49	8.10	6.58	8.08	6.59	-51.38	5.13	-51.38	5.13	-51.38	5.13	9.04	3.96	16.08	3.96	16.08	3.96
	19.47	-18.61	4.28	-18.77	4.32	-18.79	4.33	-5.28	4.84	-5.28	4.84	-5.28	4.84	11.07	3.23	20.15	3.23	20.15	4.20
	0.25	8.79	6.12	8.65	6.15	8.63	6.16	-44.34	5.92	-44.35	5.93	-44.35	5.93	9.82	3.55	17.65	3.55	18.19	4.68
Particle size of the adsorbent	0.3mm	-26.06	4.73	-26.06	4.73	-26.08	4.74	-7.87	4.56	-7.87	4.56	-7.87	4.56	12.93	2.65	23.86	2.65	23.86	2.65
	0.212 mm	-36.37	7.45	-36.37	7.45	-36.39	7.46	-4.58	3.67	-4.58	3.67	-4.58	3.67	8.49	4.45	14.98	4.45	14.98	4.45
	0.15mm	-28.24	6.98	-28.24	6.98	-28.26	6.99	-11.74	6.17	-11.74	6.17	-11.74	6.17	10.47	3.68	18.94	3.68	18.94	4.35
	0.075 mm	-26.29	6.40	-26.29	6.40	-26.31	6.41	-12.39	6.43	-12.39	6.43	-12.39	6.43	11.44	3.35	20.88	3.35	20.88	3.98
Initial pH of the solution	3	-20.43	4.73	-20.43	4.73	-20.45	4.74	-12.97	4.47	-12.97	4.47	-12.97	4.47	0.67	7.07	-0.65	7.07	-0.65	7.07
	4.47	-24.31	4.30	-24.31	4.30	-24.33	4.31	-8.52	4.72	-8.52	4.72	-8.52	4.72	11.07	3.23	20.15	3.23	20.15	3.23
	7.58	-7.39	3.17	-13.54	4.71	-13.56	4.72	-10.26	4.39	-10.26	4.39	-10.26	4.39	7.50	3.48	13.01	3.48	13.01	4.27
	11.74	-16.19	5.34	-16.19	5.34	-16.21	5.35	-12.68	5.03	-12.68	5.03	-12.68	5.03	7.47	3.39	12.94	3.39	12.94	4.21
Mass of the adsorbent	1.0 gram	-21.25	2.80	-15.36	5.41	-15.38	5.42	-19.20	6.64	-19.20	6.64	-19.20	6.64	24.67	3.24	24.67	3.24	24.69	3.23
	0.5 gram	-37.98	5.03	-12.61	6.39	-12.63	6.40	-2.32	4.34	-2.32	4.34	-2.32	4.34	27.27	2.16	27.27	2.16	27.27	2.16
	0.3 gram	-34.52	4.21	-4.29	4.95	-4.31	4.96	0.59	3.97	0.59	3.97	0.59	3.97	2.00	3.16	2.00	3.16	20.00	2.72
Sum		-257.27	96.61	-217.42	106.73	-217.44	106.74	-390.15	95.56	-390.17	95.57	-390.17	95.57	149.36	72.93	196.02	77.14	214.57	84.52
Average		-13.54	5.08	-11.44	5.62	-11.46	5.63	-20.53	5.03	-20.54	5.03	-20.54	5.03	7.86	3.84	10.32	4.06	11.29	4.45

Table 3: Result of statistical analysis of effect of adsorbent mass and adsorption period on performance

Source of Variation	*Sum of Squares*	*Degree of freedom*	*Mean Square*	*F-value*	*P-value*	*F crit*
Between Mass of Adsorbent	0.238	2	0.119	38.100	0.0004	5.143
Adsorption Period	0.091	3	0.030	9.696	0.0102	4.757
Error	0.019	6	0.003			
Total	0.347	11				

Table 4: Result of statistical analysis of effect of pH and adsorption period on performance

Source of Variation	*Sum of Squares*	*Degree of freedom*	*Mean Square*	*F-value*	*P-value*	*F crit*
Within pH	1.561	3	0.520	26.949	0.00001	3.490
pH and Time	1.059	4	0.265	13.706	0.00020	3.259
Error	0.232	12	0.019			
Total	2.852	19				

Table 5: Result of statistical analysis of effect of particle size of PCCS and adsorption period on performance

Source of Variation	*Sum of Squares*	*Degree of freedom*	*Mean Square*	*F-value*	*P-value*	*F crit*
Within Initial Concentration of Lead	28421.151	3	9473.717	32.460	4.867 x 10^{-06}	3.490
Initial concentration and Adsorption Time	2854.696	4	713.674	2.445	0.1033	3.259
Error	3502.263	12	291.855			
Total	34778.109	19				

Table 6: Result of statistical analysis of effect of initial concentration of lead ion and adsorption period on performance

Source of Variation	*Sum of Squares*	*Degree of freedom*	*Mean Square*	*F-value*	*P-value*	*F crit*
Within Particle size of PCC	0.075	3	0.025	10.262	0.0029	3.863
Particle size of PCCS and Adsorption time	0.097	3	0.032	13.157	0.0012	3.863
Error	0.022	9	0.002			
Total	0.194	15				

Table 7 Result of statistical analysis of applicability of adsorption performance on water quality

Source of Variation	*Sum of Squares*	*Degree of freedom*	*Mean Square*	*F-value*	*P-value*	*F crit*
Raw Water Samples	30.465	3	10.155	2.839	0.0827	3.490
Raw water and Adsorption Time	3804.649	4	951.162	265.904	1.337 x 10^{-11}	3.259
Error	42.925	12	3.577			
Total	3878.040	19				

Statistical evaluations of effects of the factors on performance of adsorption using analysis of variance (ANOVA) revealed that mass of adsorbent ($F_{2,6}$ = 38.10, p = 0.0004), adsorption period (treatment time, $F_{2,6}$ = 38.10, p = 0.0004), pH ($F_{3,126}$ = 26.949, p = 0.0004), interaction of pH and treatment time ($F_{4,6}$ = 13.706, p = 0.0002), interaction of particle size and treatment time ($F_{3,9}$ = 13.157, p = 0.0012) and initial concentration ($F_{3,12}$ = 32.460, p = 0.0029) were significant factors and interaction that had effects on performance of Pb^{2+} adsorption onto PCCS in synthetic wastewaters at 95 % confidence level. On typical raw water, the water sample (concentration of the pollutant, pH, temperature and other factors, $F_{3,12} = 2.839$, $p = 0.0827$), interaction of raw water and adsorption time ($F_{4,12} = 265.904$, $p = 1.337 \times 10^{-11}$) were significant factor and interaction that influence adsorption of the pollutant at 90 % confidence level.

CONCLUSION

This study investigated adsorption capacities of Pb^{2+} onto absorbents, and utilization of graphical, least square and MES methods for pseudo second order, Elovich and Intraparticle kinetics models as well as evaluation of the methods statistically. The study concluded that

a. the adsorption processes of Pb^{2+} onto the adsorbents followed two steps ,

b. mode of adsorption and transport are affected by more than one process,

c. the order of accuracy of the methods was in Microsoft Excel Solver > Least Squared > Graphical method based on the value of MSC and AIC,

d. mass of adsorbent ($F_{2,6} = 38.10$, $p = 0.0004$), adsorption period (treatment time, $F_{2,6} = 38.10$, $p = 0.0004$), pH ($F_{3,126} = 26.949$, $p = 0.0004$), interaction of pH and treatment time ($F_{4,6} = 13.706$, $p = 0.0002$), interaction of particle size and treatment time ($F_{3,9} = 13.157$, $p = 0.0012$) and initial concentration ($F_{3,12} = 32.460$, $p = 0.0029$) were significant factors that had effects on performance of Pb^{2+} adsorption onto PCCS in synthetic wastewaters at 95 % confidence level, and

e. the water sample (concentration of the pollutant, pH, temperature and other factors, $F_{3,12} = 2.839$, $p = 0.0827$), interaction of raw water and adsorption time ($F_{4,12} = 265.904$, $p = 1.337 \times 10^{-11}$) were significant factor and interaction that influence adsorption of the pollutant at 90 % confidence level

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