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Pseudo second order kinetics model of adsorption of Pb^{2+} onto powdered corn cobs: comparison of linear regression methods

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Research Paper

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This study reports adsorption kinetics of lead (Pb^{2+}) removal from aqueous solution by powdered corn cobs and comparison of linear regression methods for solving linearized pseudo second order kinetics model. The corn cobs were collected, washed with distilled water, air dried, pulverized, sieved into different particle sizes and stored. The properties of the powdered corn cobs (PCC) were determined. The PCC was used to remove Pb^{2+} from aqueous solution on single and multi-component systems. Adsorption kinetics of Pb^{2+} onto PCC and linearised regression methods of pseudo second order were studied using experimental data and evaluated statistically using total error, model of selection criterion and coefficient of determination. The study revealed that the PCC contains calcium, aluminum, and iron as its major components. Adsorption capacities for Pb^{2+} onto the PCC were 63.43 % and 45.83 % for mono-component and multi components synthetic wastewaters. Statistical evaluation revealed that the order of accuracy of the methods was in graphical greater than (>) elimination > Microsoft excel solver > iteration > least squares method based on the value of MSC. It was concluded that Microsoft excel solver is the best method of solving linear pseudo second order kinetics model based on lowest error.

Key words: Adsorption, powdered corn cobs, heavy metal removal, synthetic wastewaters, adsorption kinetics parameters.

INTRODUCTION

Adsorption processes are proved to be effective methods for the treatment of wastewaters. Activated carbon, agricultural wastes, synthetic resins, activated alumina and natural adsorbents are the most commonly used adsorbents for the removal of metallic ions from its aqueous solution (Fehintola et al., 2015). Simulations of batch adsorption kinetics models are necessary for design of industrial adsorption column (Kumar, 2006). Adsorption kinetics models the rate of chemical reaction occurs and also on the factors affecting the reaction rate. The nature of adsorption processes depend on physical or chemical characteristics of the adsorbent systems as well as on the environmental conditions. One of the most commonly used adsorption kinetics models is pseudo second-order kinetic model, which can be expressed as follows:

$$q_t = \frac{k_2 (q_e)^2 t}{1 + k_2 (q_e) t} \quad (1)$$

Where; q_t is the adsorption capacity at time t (mg/g), q_e

is equilibrium solid-phase concentration of sorbate (mg/mg); t is the time and k_2 *is* the rate constant of pseudo second-order adsorption.

More on adsorption can be found in literature such as (Ho ,2007; Ismail et al., 2009; Adie et al., 2010; Olarinoye et al., 2012; Oke et al., 2014; Umukoro et al., 2014, Fehintola et al., 2015).

Pseudo second-order kinetics model was found to explain the kinetics of the most of adsorption systems very well for the entire range of adsorption period. The model was found to show a better fit towards the adsorption of heavy metals, dyes onto adsorbent materials of organic nature and inorganic nature (Kumar, 2006). However linearized pseudo second-order regressions proposed by many researchers are without methods of parameters determination. The least-squares method with linearly transformed kinetics equations has been applied to confirm experimental data (kinetics) using coefficients of determination (Ho, 2014; Gusani et al., 2014). These reason and many other factors called for statistical evaluation of various methods of solving linear regression methods to ascertain their accuracy, reliability, good fitting and predictability to prevent engineering failure of adsorption reactors. With advancement in computer software, solving linear equations should not be a major issue or problem. Literature such as Bowman (1962); Loveday (1980); Stroud (1990) stated that linear equations can be solved using statistical and mathematical methods. Some of the methods are Gaussian elimination, Gauss-Jordian elimination, Matrix, least squared and iteration (numerical) methods. Previous studies on Microsoft excel Solver or similar package in solving non-linear regression equations include Barati, (2013) and Bhattacharjya, (2010) used solver for groundwater flow; Gay and Middleton, (1971) developed solutions for pipe network, Jewell, (2001) and Huddleston et al. (2004) used excel sheet for pipe network analysis; Canakci, (2007) used solver for pile foundation design while Tay et al. (2014) used solver for solving non-linear equation. This shows that literature on solving linear regressions with these methods is rare. In this study an extensive analysis of linear pseudo second-order regressions was made using the experimental kinetic data of adsorption of lead onto powdered corn cobs (PCC). Also, comparisons with methods of estimating the pseudo second-order kinetic parameters from linear regression equations were made.

MATERIALS AND METHODS

Corn cobs were collected from faculty of agricultural farm in the Obafemi Awolowo University, Ile-Ife, Nigeria. These corn cobs were washed with distilled water, air-dried, ground into powder and classified into 75 µm (PCC_1), 150 µm (PCC_2), 212 µm (PCC_3) and 300 µm (PCC_4) using British Standard (BS) sieve. The classified powdered corn cobs (PCC) were stored in desiccators. Physical and chemical properties of the powdered corn cob were determined using standard methods.

Moisture content determination

A well mixed sample of PCC was evaporated in weighed dishes to a constant weight in an oven at 105oC (APHA, 1998). The decrease in the weight of the PCC represents the moisture content (Mc) defined by Oke et al. (2014); Fehintola et al. (2015) as:

$$M_c(\%) = 100\left(\frac{W_1 - W_2}{W_1}\right) \quad (2)$$

where, M_c is moisture contents; W_1 and W_2 are initial and final weights of PCC after oven drying at 105ºC.

Volatile solid and ash content determination

Known masses of dried samples used for moisture content determination were placed in crucibles and transferred into a muffle furnace. The furnace was heated to 550oC for 2 h (APHA, 1998). The samples were cooled in desiccators and the final weights were measured. Volatile solid and ash content of PCC were calculated as follows (APHA, 1998; Oke et al., 2014; Fehintola et al., 2015):

$$VS\ (\%) = 100\left(\frac{W_2 - W_3}{W_2}\right) \quad (3)$$

where, W_3 is the final weight of the PCC after 2 h burnt in the furnace at 550ºC and VS is the volatile solid of the PCC.

$$Ash\ (\%) = 100\left(\frac{W_3}{W_1}\right) \quad (4)$$

where, Ash is the ash content of the PCC.

Water and acid solubilities determination

Known dried masses (5 gram) of the samples were separately soaked in 300 mL of distilled water and in 300 mL of 0.25 M of HCl for 24 h. The samples were filtered using pre-dried and weighed filter papers (Whatman number 1). The samples and the filter papers were dried in the oven at 105° C for 24 h, cooled in desiccators to balance the temperature and the final weights were measured. Water (Ws) and acid solubilities (As) of PCC were calculated as follows (APHA, 1998; Oke et al.,

2014; Fehintola et al., 2015):

$$W_s\ (\%) = 100\left(\frac{W_2 - W_4}{W_2}\right) \quad (5)$$

$$A_S\ (\%) = 100\left(\frac{W_2 - W_5}{W_2}\right) \quad (6)$$

where, W_S is water soluble of the PCC; AS is acid soluble of the PCC; W_4 and W_5 are dry weights of the PCC after soaked in water and acid respectively.

Metal concentrations determination

Known mass (1.0 g) of the PCC was digested using nitric acid digestion method and chemical components of the adsorbent were determined using APHA (1998) method. Total metal concentrations (Mcc) were determined using spectormetry method. Metal concentrations were computed following Oke et al. (2014) expression as:

$$M_{cc}\ (mg\ /\ L) = \left(\frac{A * B}{W_1}\right) \quad (7)$$

where, B is dilution factor of the solution; A is the concentration of the metals obtained in the solution (mg/L) and M_{cc} is actual metal concentration in the solution of the PCC.

Adsorption capacities of powdered corn cobs (PCC) were examined on synthetic wastewaters prepared by dissolving known masses of Pb^{2+} [1.598 g of $Pb(NO_3)_2$ in 100 ml of distilled water and was made up to 1000 ml mark with distilled water). Known masses of the adsorbent were added into beakers containing 300 ml of a known concentration of the pollutants.

The mixtures were stirred at 60 revolutions per minutes (rpm) for 3 min and allowed to stand for 18 h (a time at which equilibrium concentration have been reached). The supernatants were filtered through a filter paper Whatman Number 40 to remove suspended solids and to prevent interference of turbidity.

Concentrations of Pb^{2+} n the filtrates were determined using Atomic Absorption Spectrophotometer method (APHA, 1998).

In multi component synthetic wastewaters 1.598 g of $Pb(NO_3)_2$, 1.735 g of nickel chloride and 2.74 g of $Cd(NO_3)_2$. $4H_2O$ were dissolved in 100 ml of distilled water and was made up to 1000 ml mark with distilled water.

The procedures for the treatment of mono component wastewaters were repeated for raw water collected and for multi-component synthetic wastewater prepared. The amount of solute removed (adsorbed) at equilibrium and at any time were computed using equations (8) and (9) respectively.

$$q_e = \frac{(C_0 - C_e)}{M}V \quad (8)$$

$$q_t = \frac{(C_0 - C_t)}{M}V \quad (9)$$

where, q_e is the equilibrium solid-phase concentration of sorbate (mg/mg); C_0 is the initial concentration of metal in the solution (mg/l); C_e is the experimental concentration in the solution at equilibrium (mg/l); C_t is the experimental concentration in the solution at time t (mg/l); q_t is the adsorption capacity at time t (mg/g); V is the volume of solution (0.3L) and M is the mass of the adsorbent added (g)

The laboratory analysis of heavy metal concentrations in both synthetic wastewaters and raw water were carried out as specified in APHA (1998) method using the Alpha 4 Atomic Absorption Spectrophotometer (AAS) (Chem Techn Analytical) at the Central Science Laboratory, Obafemi Awolowo University, Ile-Ife, Nigeria. The adsorption capacities of the adsorbent were analyzed through the use of graphical, Microsoft excel solver, least squares, iteration and elimination methods. These accuracies of the methods in predicting pseudo second order kinetic model were evaluated statistically using total errors, coefficient of determination (CD) and model of selection criterion (MSC).

RESULTS AND DISCUSSION

Results from this study are discussed in categories as follows: properties of the PCC, ion exchange model, kinetics of lead adsorption onto PCC, kinetics model's parameters and statistical evaluation of the methods.

Properties of the Powdered Corn Cobs

Result of the digestion indicated that 1 g of PCC contained magnesium, iron, aluminium, zinc, nickel and calcium without cadmium and lead (Table 1). These compositions (presence coagulants such as aluminium and iron) make the material a good adsorbent. Micrographs of the adsorbent has been presented in previous studies and other literature such as (Ismail et al., 2009; Wanitwattanarumlug et al., 2012; Linna et al.,2013; Jun et al.,2014). Figures 1, 2 and 3 present micrograph of the corn cobs. It is well known that pore size distribution affects the kinetic properties of porous material and indicates the structural heterogeneity of porous materials. SEM analysis shows the structure of the adsorbent (Figures 1, 2 and 3).

It was observed from the figures that raw corn cobs gave cross-interconnected pores spongy like. It was also observed from the figures that different treatments caused noticeable changes in the structure of the waste material. Wet corn cobs are the composted corn cobs,

Table 1. some of the physical and chemical properties of PCC.

	Physical			Chemical										
Properties	Ash content (%)	Volatile (%)	Moisture content (%)	Magnesium (mg/g)	Aluminium (mg/g)	Solubility in water (%)	Solubility in 0.25 M HCl (%)	Calcium (mg/g)	Iron (mg/g)	Zinc (mg/g)	Cadmium (mg/g)	Chromium (mg/g)	Nickel (mg/g)	Lead (mg/g)
Average	2.331	86.889	10.78	54.4	0.01	0.52	4.56	1.7	131	0.01	0.02	0	0.01	0
Standard deviation	0.061	1.007	0.278	0.3	0.001	0.034	0.98	0.1	2.4	0.001	0.001	0	0.001	0
Coefficient of variation (%)	2.617	1.159	2.578	0.551	10	6.558	21.491	5.882	1.832	10	5	0	10	0

which were covered by fungal hyphae. Dried corn cobs are the pyrolysed corn cobs of which the external surfaces contained smooth, open pores of different sizes. Furthermore, the pyrolysed corn cobs contained larger and more regular pores. The external surface of pyrolysed corn cobs also had isodiametric, nearly circular cells with well-defined lumens arranged in a pattern that resembled a honeycomb. These indicated that treatments of corn cobs had effects on the micrograph structures. It is well known that corn cob contains calcium in form of CaO. It has been postulated that in the presence of water, inorganic salts undergo displacement reactions as indicated in equations 10- 13. This shows that the PCC underwent reactions in equations 10-15 with selected heavy metal ions, which can reduce the pH and the end product reacted with metallic ions to precipitate the pollutant (King'ori, 2011; Than et al., 2012; Nyankson et al., 2013; Oke et al., 2014).

$$CaO + H_2O \longrightarrow Ca(OH)_2 \quad (10)$$

$$H_2O + CO_2 + Ca(OH)_2 + X^{2+} \rightarrow H_2O + CO_2 + Ca^{2+} + X(OH)_2 \quad (11)$$

$$Al^{3+} + 3H_2O + \frac{3}{2}X[NO_3]_2 \rightarrow Al[NO_3]_3 + \frac{3}{2}X(OH)_2 + 3H^+ \quad (12)$$

$$Fe^{2+} + 2H_2O + X[NO_3]_2 \rightarrow Fe[NO_3]_2 + X(OH)_2 + 2H^+ \quad (13)$$

By expressing the mass of PCC in terms of Mg^{2+}, Fe^{2+}, Ca^{2+} and Al^{3+} contents 0.237 mole of Mg^{2+}; 0. 0.0425 mole of Ca^{2+}, 0.247 mole of Fe2+ and 3.70 x 10-5 mole of Al3+ could be found in one hundred (100) grams of the PCC. Literature such as Kin et al. (1995); Shuhadah et al. (2008); Siti and Supri (2009) provide more on Scanning Electron Microscopy microstructure. The microstructure of the PCC particle revealed that the size (Figures 1 to 3) and shape of the particles vary and PCC consists of porous irregular shaped particles.

Ion exchange model

PCC contains 86.889 % volatile solids (Table 1, Supri et al., 2012), which indicated that powdered corn cobs were partially cellulose-based adsorbents, which contain polar functional groups that can be involved in chemical bonding. The organic compounds could be responsible for the cation exchange capacity of the PCC. Thus, the PCC and Pb2+ reactions may be represented in two ways (Randal et al., 2013; Jun et al., 2014):

$$2PCCc^- + X^{2+} \quad XPCCc_2 \quad (14)$$

$$2HPCCc + X^{2+} \quad XPCCc_2 + 2H^+ \quad (15)$$

where, PCCc– and H PCCc– are the polar sites on the PCC surface and X is the pollutant. Literature (Kohler et al., 2007; Oke et al., 2014) reported that removal of heavy metals such as lead, nickel and cadmium in the presence of Ca2+ can be represented as:

$$yCa^{2+} + zPb^{2+} + CaCO_3 \rightarrow Pb_xCa_{(1-x)}CO_3 + (y+x)Ca^{2+} + (z-x)Pb^{2+} \quad (16)$$

In addition, Makshoof et al. (2013); Abbas et al. (2013) reported that on the basis of theoretical consideration, the adsorption of divalent metal ions (M) onto two free binding sites (B) can be explained by the following expressions:

$$M + B \quad \leftrightarrow B_2M \quad (17)$$

It means that the adsorption rate would be proportional to the concentration of metal ions and the square of the number of free sites onto PCC. Also, Randal et al. (2013) reported that yield of cellulose of corn cob was 55 g or 27% of the total weight of the starting ground corn cob. The cellulose content of corn cobs is about 35% (Duguid et al., 2009) so this represents 77% of the theoretical yield. Compositional analysis was (by weight) 89% glucose, 9% xylose, 0.1% arabinose and 0.4% mannose. No galactose, glucuronic acid or lignin was detected. pH of the cellulose/water gels was 6.0–6.5. These indicate that PCC is a

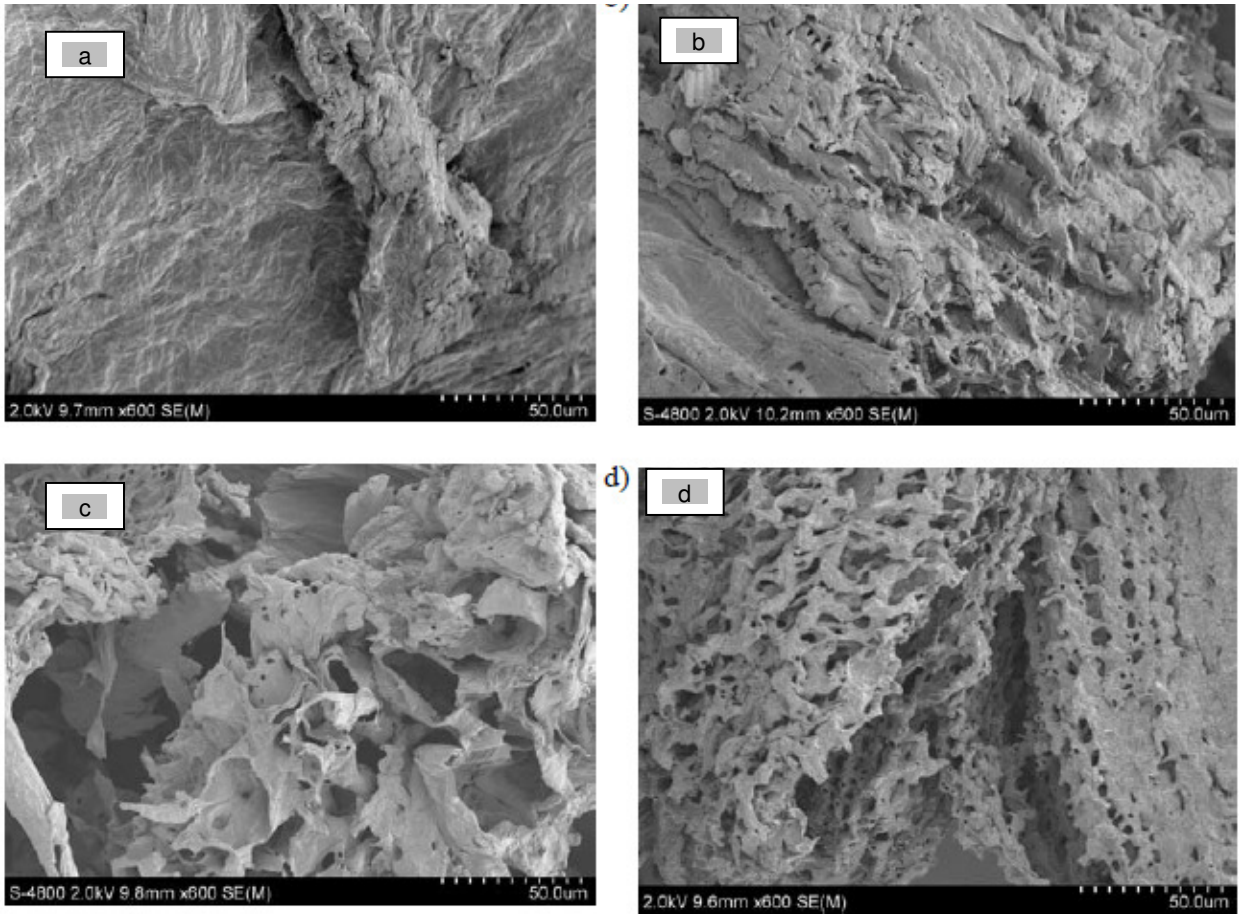

Figure 1. Scanning electron microscope images of corn cobs. (a) Raw corn cobs without treatment; (b) Corn cobs after pretreatment with 0.75% KOH at 60℃ for 25 min; (c) Corn cobs after pretreatment with 0.75% KOH at 120℃ for 25 min; (d) Corn cobs after pretreatment with 2% KOH at 120℃ for 25 min. (Source: Wanitwattanarumlug et al., 2012.

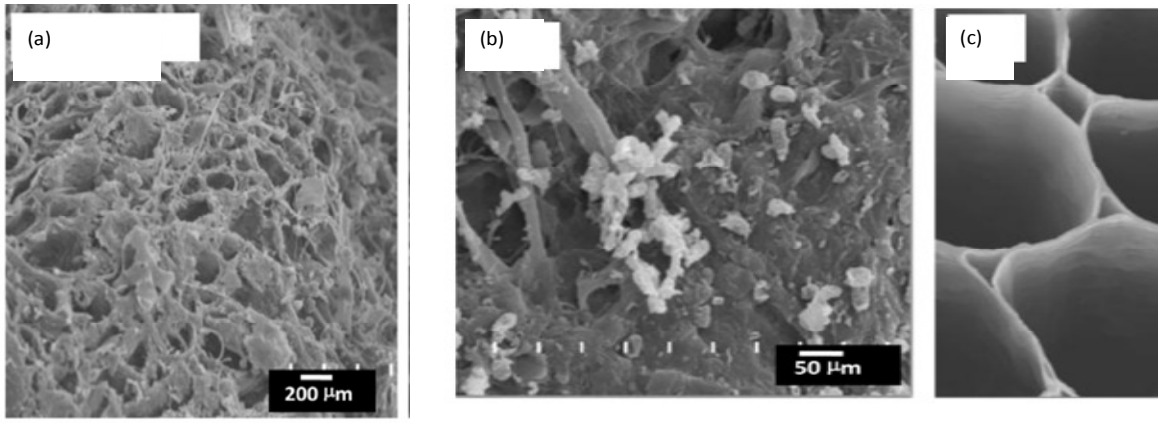

Figure 2. Scanning Electron Microscopy (SEM) Micrograph of Corn Cobs (a) SEM Micrograph (x 200) of untreated corn cobs; (b) SEM micrographs (x 1000) of the external surface of composted corn cobs; and (c) SEM Micrograph (x 1000) of pyrolysed corn cobs.(Source: Linna et al., 2013).

unique cell surface with various functional groups, providing the potential for adsorption of metal species. Detailed information on functional groups in PCC can be found in Randal et al. (2013). Reactions between the

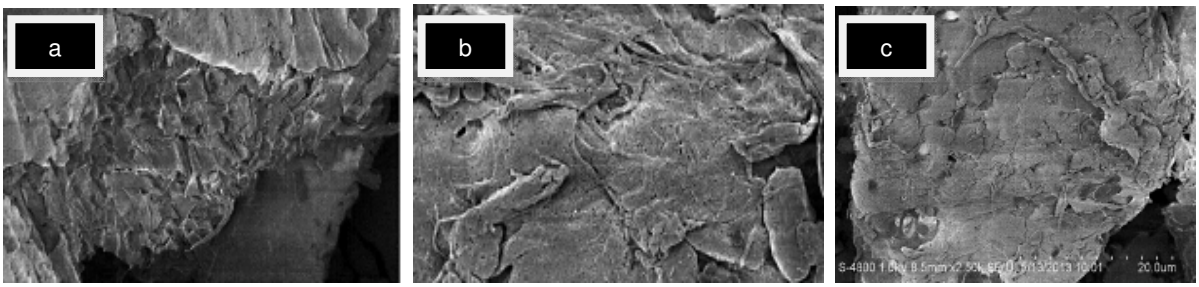

Figure 3. Scanning Electron Microscopy images at various magnifications for untreated and extruded corncobs.(Source: Jun et al., 2014). (A) untreated corncobs with no xylose removal, (B) extruded corncobs with 7% xylose removal and (C) extruded corncobs with 80% xylose removal.

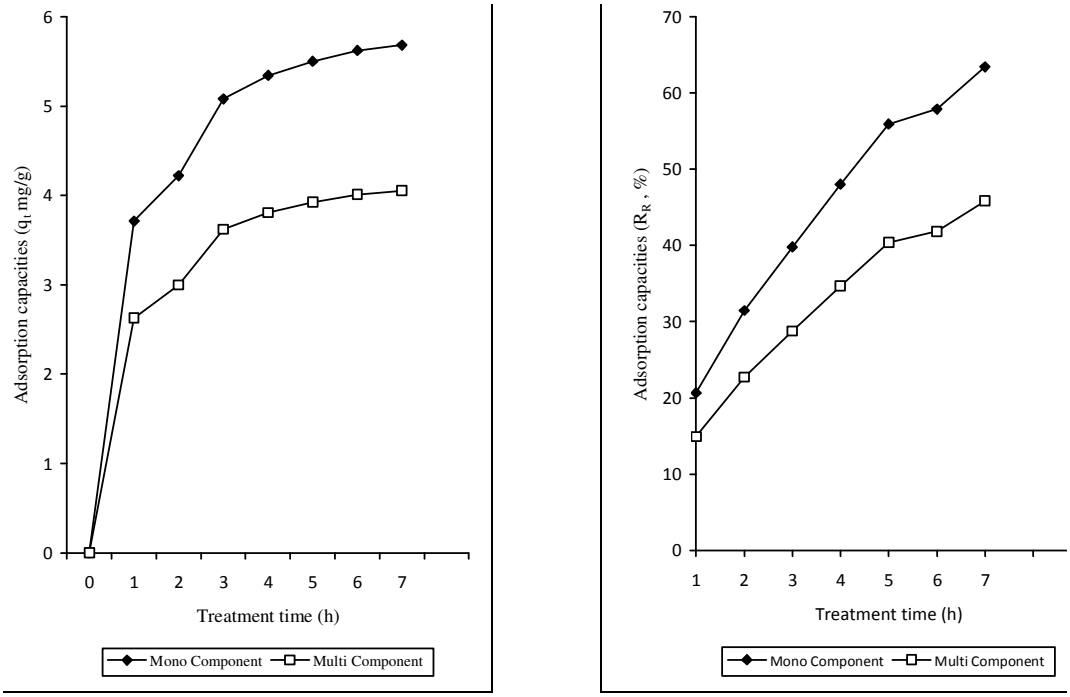

Figure 4. Adsorption capacities and kinetics of lead ion unto the selected agricultural waste (PCC).(a) Non-linear plot (b) Non linear plot of Adsorption of lead onto the adsorbent (intra-particle).

functional groups and the pollutants can be expressed as follows:

$$-----CONH---+Pb^{2+}\rightarrow Pb-----CONH---Pb \quad (18)$$

From the equations above, it can be explained that higher values of hydrogen concentration will lower the formation of $XPCCc_2$. This indicated that increasing pH value will not favour X^{2+} adsorption. Also, decreasing the pH either through addition of hydroxyl ions (OH^-) or otherwise will increase adsorption of X^{2+}. This phenomenon can be attributed to more charges, disassociation of more anions which will attract X^{2+}, higher attraction forces and formation of $X(OH)_2$ which will be precipitated or fill the pores. These observations agree with Jalili et al. (2008) on adsorption of palladium and platinum onto egg shell membrane, quality and ultra structure of egg shell studied and documented by Krystianiak et al. (2005) and morphology properties (Liu *et al.,* 2004).

Adsorption of Lead onto PCC and Pseudo Seconds Order Kinetics Model's Parameters

Adsorption kinetics is an important ingredient in

Table 2. Kinetics parameters for adsorption of Pb2+ onto selected adsorbents.

Linearized Equation	Parameters	Least Squared	Microsoft excel solver	Elimination	Graphical	Iteration
Linear regression A	K_2	0.02859	0.02855	0.02859	0.02861	0.02860
$\left(\frac{t}{q_t}\right) = \frac{1}{k_2(q_e)^2} + \frac{1}{q_e}t$	q_e	3.0665	3.0668	3.0668	3.0665	3.0668
Linear regression B	K_2	0.06449	0.06088	0.06028	0.06019	0.06028
$\left(\frac{1}{q_t}\right) = \frac{1}{k_2(q_e)^2}\left(\frac{1}{t}\right) + \frac{1}{q_e}$	q_e	2.1763	2.2401	2.2401	2.2422	2.2401
Linear regression C	K_2	0.04258	0.04873	0.04783	0.04784	0.04783
$q_t = q_e - \frac{1}{k_2(q_e)}\left(\frac{q_t}{t}\right)$	q_e	2.6007	2.4763	2.4763	2.4760	2.4763
Linear regression D	K_2	0.03193	0.03593	0.03193	0.03157	0.03584
$\left(\frac{q_t}{t}\right) = k_2(q_e)^2 - k_2(q_e)q_t$	q_e	2.8404	2.7938	2.9323	2.9462	2.7932
Linear regression E	K_2	0.05934	0.06068	0.05760	0.05720	0.05970
$\left(\frac{1}{t}\right) = -k_2(q_e) + k_2(q_e)^2\frac{1}{q_t}$	q_e	2.2544	2.2495	2.2838	2.2901	2.2492

environmental pollution control. Figure 4a 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 literature on adsorption of lead by various adsorbents. Table 2 shows the values of pseudo second order kinetics model's parameters (K_2 and q_e) for each of the linear equations. K_2 and q_e were in the range of 0.02855 to 0.06449 and 2.1763 to 3.0668 respectively. The lowest K_2 (0.02855) came from linear regression A solved with Microsoft excel Solver method and the highest value of K_2 came from equation B and solved with least squares method. Also, the lowest q_e (2.1763) came from linear regression B solved with least squares method and the highest value of q_e (3.0668) came from equation A solved with Microsoft excel Solver method. These results indicated the values of K_2 and q_e are functions of the linear equations and methods used. The different values of kinetics parameters by these linear regression methods, a theoretical pseudo second-order model was found to represent well the experimental kinetic data of lead onto PCC based on a linear regression A pseudo second order kinetic expression. However a linear regression B pseudo second-order expression very poorly represents the kinetic data of lead onto PCC. In addition a linear regression A pseudo second order expression predicts reasonably the K_2 and q_e values theoretically for all the methods (Table 3). These indicated that linear regression equation and least squares method assumes that the scatter of points around a line follows a Gaussian distribution and that the standard deviation is the same at every value of X. These assumptions are rarely true after transforming the experimental data and some cases these transformations alter the relation between Y and X. Furthermore, in linear regression A pseudo second-order expression, the adsorption kinetics of lead onto PCC uptake process was found to fit the kinetic trend for the entire adsorption period. The linear regression A pseudo second-order expression represents well the multi-step adsorption processes that include initial rapid phase and the later slower phase which proceeds towards saturation, while in the same experimental kinetic data in linear regression B pseudo second-order expression produced lower K_2 and q_e values. These results were in agreement with observations made in literature such as Kumar, 2006; Ho, 2006; Ho, 2014).

Statistical evaluation of the equilibrium isotherm models

Three different statistical expressions were used to evaluate the performance of the model estimations or to

Table 3. Statistical Evaluation of the Linear Regression Methods.

Statistical Methods	Evaluation technique	Least Squared	Microsoft excel solver	Elimination	Graphical	Iteration
Linear regression A $\left(\frac{t}{q_t}\right) = \frac{1}{k_2(q_e)^2} + \frac{1}{q_e}t$	MSC	4.1929	4.1933	4.1930	4.1925	4.1927
	CD	0.9849	0.9849	0.9849	0.9849	0.9849
	Total error	0.0104	0.0104	0.0104	0.0104	0.0104
Linear regression B $\left(\frac{1}{q_t}\right) = \frac{1}{k_2(q_e)^2}\left(\frac{1}{t}\right) + \frac{1}{q_e}$	MSC	3.0362	3.2051	3.1583	3.1651	3.1583
	CD	0.9522	0.9595	0.9576	0.9595	0.9576
	Total error	0.0332	0.0280	0.0294	0.0292	0.0294
Linear regression C $q_t = q_e - \frac{1}{k_2(q_e)}\left(\frac{q_t}{t}\right)$	MSC	3.7385	3.6002	3.5712	3.5702	3.5713
	CD	0.9762	0.9727	0.9719	0.9719	0.9719
	Total error	0.0164	0.0189	0.0194	0.0195	0.0194
Linear regression D $\left(\frac{q_t}{t}\right) = k_2(q_e)^2 - k_2(q_e)q_t$	MSC	3.3364	3.9539	4.0822	4.0942	3.9523
	CD	0.9649	0.9808	0.9831	0.9833	0.9808
	Total error	0.0246	0.0133	0.0117	0.0115	0.0133
Linear regression E $\left(\frac{1}{t}\right) = -k_2(q_e) + k_2(q_e)^2\frac{1}{q_t}$	MSC	3.1809	3.2473	3.2366	3.2460	3.1741
	CD	0.9586	0.9612	0.9608	0.9612	0.9583
	Total error	0.0287	0.0269	0.0272	0.0269	0.0289
Overall Average	MSC	3.49698	3.63996	3.64826	3.6536	3.60974
	CD	0.967	0.972	0.972	0.972	0.971
	Total error	0.0227	0.0195	0.0196	0.0195	0.0203

compare the model estimate values with the observed values. These statistical expressions are total error, coefficient of determination (CD) and model of selection criterion (MSC). Total error (Err2) can be computed using equation (19) as follows:

$$Err^2 = \sum_{i=1}^{n}\left(Y_{obsi} - Y_{cali}\right)^2 \quad (19)$$

Where; Yobsi is observed concentration and Ycali is calculated concentration

Table 3 shows the values of total error for each of the methods. The total errors are in the range of 0.0104 to 0.03322. The least total error (0.0104) was from linear regression A solved with Microsoft excel solver method and the highest error (0.03322) come from linear regression B solved with least squares method. The other linear regression expressions were within the range. CD can be expressed as follows:

$$CD = \frac{\sum_{i=1}^{n}\left(Y_{obsi} - \overline{Y}_{cali}\right)^2 - \sum_{i=1}^{n}\left(Y_{obsi} - Y_{cali}\right)^2}{\sum_{i=1}^{n}\left(Y_{obsi} - \overline{Y}_{cali}\right)^2} \quad (20)$$

where, $\overline{Y}_{obsi}$ is the average of observed flow and $\overline{Y}_{cali}$ is the average of calculated flow.

The CD values ranged from 0.9522 to 0.9849 (Table 3). The least CD value (0.9522) from linear regression B solved with least squares method and the highest value (0.9849) came from linear regression A solved with Microsoft excel solver. MSC can be computed using equation (21) as follows:

$$MSC = \ln\frac{\sum_{i=1}^{n}\left(Y_{obsi} - \overline{Y}_{obsi}\right)^2}{\sum_{i=1}^{n}\left(Y_{obsi} - Y_{cali}\right)^2} - \frac{2p}{n} \quad (21)$$

where; p is number of parameters and n is number of samples.

Values of MSC were in the range of 3.0362 to 4.1933 (Table 3). The lowest value of MSC (3.0362) was from linear regression B solved with least squares method and the highest value (4.933) was from linear regression A solved with Microsoft excel solver. The table revealed that the theory behind the linear pseudo second-order

model was getting valid for a linear regression A pseudo second-order expression solved with Microsoft excel solver and the theory of linear pseudo second-order kinetics and the adsorption theory was found of getting violated by linear regression B pseudo second-order expression for the same experimental data of lead onto PCC. These two observations based on linear regression A and linear regression B expressions suggest that the linear method just verify the hypothesis of linear regression instead of verifying the theory of adsorption kinetics. The observation also shows that the order of accuracy of the methods was in graphical greater than (>) elimination > Microsoft excel solver > iteration > least squares method based on the value of MSC; Microsoft excel solver > elimination > graphical > iteration > least squares based on CD and Microsoft excel solver equal to graphical > elimination > iteration > least squares based on error value.

CONCLUSION

This study investigated adsorption capacities of Pb^{2+} onto PCC. It was concluded based on the study that

a) linear pseudo second-order kinetics and the adsorption theory was found of getting violated by linear regression B pseudo second-order expression.
b) linear method just verify the hypothesis of linear regression instead of verifying the theory of adsorption kinetics.
c) The order of accuracy of the methods was in graphical greater than (>) elimination > Microsoft excel solver > iteration > least squares method based on the value of MSC.
d) Microsoft excel solver > elimination > graphical > iteration > least squares based on CD; and
e) Microsoft excel solver equal to graphical > elimination > iteration > least squares based on error value.

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