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Biosorption Efficacy of Biosorbents Prepared from Cocoa Leaves Used for Removal of Lead Polluted Wastewater at Birnin Gwari War Front, Kaduna State

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Abstract – The potential of Acid Treated (ATC) and Untreated Cocoa Leaves (UTC) biosorbents used for removal of Pb^{2+} from wastewater at warfront was studied using batch adsorption technique. Atomic Adsorption Spectroscopy (AAS) was used to ascertain the residual Pb^{2+} concentration after the adsorption process. The optimum operational experimental conditions: adsorbent dose, pH, initial Pb^{2+} concentration and contact time were obtained. It was found that the percentage sorption of Pb^{2+} increased with; higher adsorbent doses (0.8-1 g/25cm^3), increase in pH levels (7 - 9), increased Pb^{2+} concentration (between 150 – 200 mg/L) and increased contact time (150 - 180 minutes). The result showed that cocoa leaves have the potential to remove Pb^{2+} polluted wastewater at about 99.8% removal. The biosorbents were characterized using Fourier Transform Infrared Spectroscopy (FTIR). It showed the presence of O-H, O-CO-, N-N=O and -C-H are responsible for the adsorption of Pb^{2+} onto the biosorbents. The adsorption of Pb^{2+} onto ATC and UTC from wastewater at war front best fitted into Pseudo-Second Order Kinetic Model validated by the coefficient of regression R^2 values close to infinity. The equilibrium sorption data were fitted best into Freundlich isotherms with R^2 value for ATC is 0.5754 and UTC for 0.6441. The maximum monolayer coverage (Q_o) from Langmuir isotherm model was determined to be 117.65 mg/g for ATC and 53.35mg/g for UTC. The Freundlich Isotherm model showed the sorption intensity (n) of 0.348 for ATC and 0.1557 for UTC indicated favorable adsorption.

Keywords – Cocoa Leaves, Lead, Biosorption, wastewater, Kinetics, Isotherms.

I. INTRODUCTION

Water is a vital component for human life and human activities are very much connected to availability, accessibility of quality and portable water. Unfortunately, water is in limited supply, which even undergoes intense pollution. In the near future, availability of water could get worse as a consequence of climate change (Ajaelu and Dawodu, 2013). Some techniques which have been used in heavy metal removal from effluent include ion-exchange, chemical precipitation, electro dialysis, electrolytic extraction, reverse osmosis and cementation (Mohammed *et al.,* 2005) are expensive, cannot remove metals at low concentration (Bishnoi *et al*., 2004) and produce large volume of sludge (Srivastava and Goyal, 2010). Agricultural waste materials are usually composed of different components with varying functional groups like carboxyl, amino, alcohol and esters (Gupta and Ali, 2000). These groups have the ability to bind heavy metals by donating an electron pair for coordinate bonding to form complexes with the metal ions in solution or replacing hydrogen ions for metal ions in solution (Fomina and Gadd, 2014). Treatment of biomass for adsorption help to desorb inorganic and organic materials adsorbed during plant growth which may interfere with the metal ions during adsorption (Tichaona and

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Olindah, 2013) and also increases the capacity of the sorbent by cleaning up the surface, opening up pores and also chemically modifies the sorption sites (Mahamadi, and Chapeyama, 2011). Biosorption is the most recent environmentally friendly technique that is cost effective. It involves the use of natural waste (biomass) as an agent that attracts and adhere pollutants unto its surface (adsorbent) (Alfarra *et al.,* 2014). Although there are a number of reviews on the adsorption capacity of various biomasses considering the complexity of various factors that influence the process and highly efficient biosorbents that are cost effective need to be identified**.** Several wars have taken place where the war-front is the side of a river or even on water bodies. The fact that the bullet's head is about 90% lead, which makes it possible for the water body to be contaminated with the lead ions, coupled with the possibility of intentional contamination of the water with the metal by the opponent side. It's imperative to develop a simple, cost effective and efficient method of decontamination or purifying the water body in case the need for the usage of such water arises by the soldiers. Thus, the research is important and needed for application at war-front and other situations that need decontamination. This research is to evaluate the efficacy of biosorbent prepared from cocoa leaves for the removal of Pb^{2+} from contaminated water at warfront.

II. Materials And Methods

2.1 Samples collection

Cocoa leaves (*Theobroma cacao L*) were collected as composite sample made up of leaves obtained from many trees. The leaves were stored in air tight sacs, to avoid exposure to air and rotting. It was transported immediately and taken for identification. Water sample was collected from rivers located at Birnin Gwari warfront, Kaduna State.

2.2 Preparation of Adsorbate:

Stock solution of Pb^{2+} was prepared using standard method and serial dilution of the stock solution was made to obtain the working standard. The existing concentration of Pb^{2+} in the water sample was ascertained using AAS Spectroscopy and various known concentrations of the Pb^{2+} were spiked the water sample collected from the warfront. Analytical grade reagents were used throughout the work.

2.3 Adsorbent Preparation

The sample, cocoa leaves was pretreated as described by Tichaona and Olindah (2013). The plant leaves was washed with tap water, sun dried, grounded using a miller, sieved to obtain uniform particle size and oven dried at 105°C±0.1 to constant mass and stored in plastic container. The sample was divided into two, a part was modified using hydrochloric acid (0.1 mol dm^{-3}) and labeled as Acid Treated Cocoa (ATC) and the second was left unmodified, also labeled Unmodified Treated Cocoa (UTC). Cocoa powdered sample was modified using the procedure described by Ege and Doner (2013), where 10 g of the sample was mixed with 200 cm^3 of the 0.1M HCl solution for 72 hours at room temperature. At the end, the powdered sample was washed to obtain a pH of 7. After which it was oven dried at 60°C for three days and stored in a container for biosorption process.

2.4 Batch biosorption procedure

The biosorption process was carried out as described by Tijjani *et al*., (2011). 0.1 g of ATC and UTC samples each were mixed separately and water sample was spiked with 25 cm^3 of Pb^{2+} ion solution of initial concentration of 100 mg/L at room temperature. The mixture was shaken continuously on a shaker at 200 revolutions per minute (rpm), at varying time intervals. At the end of each contact time, the mixture was digested and filtered. The concentration of Pb^{2+} in the filtrate was determined using AAS (AAS-HP serial number MY14470001, model AA320N). The percent sorption of Pb^{2+} ions onto the biosorbents were calculated using the expression in equation 1:

$$\% \text{ Sorption} = \frac{C_0 - C_f}{C_0} \times 100 \ldots\ldots. (1)$$

The amount of Pb^{2+} ions adsorbed at equilibrium, q_e (mg/g) was calculated using equations 2

$$q_e = \frac{(C_o - C_e)}{m} V \ldots\ldots. (2)$$

Co = Initial concentration of Pb^{2+} before adsorption (mg L^{-1}), C_f = final concentration of Pb^{2+} after adsorption (mg/L); Ce = equilibrium concentration of Pb^{2+} (mg/L), m = mass of adsorbent (g), V = Volume of the Pb^{2+} solution (cm^3), q_e = amount of Pb^{2+} adsorbed at equilibrium per unit weight of the adsorbent (mg g^{-1});

2.5 Optimization of adsorption parameters

2.5.1 Effect of Biosorbent dosage on adsorption process

The adsorbent doses of ATC and UTC each were varied within the range of 0.1, 0.2, 0.4, 0.6, 0.8 and 1 g, which were mixed with 25 cm^3 of 100 mg/L of the Pb^{2+} solution. The mixture was agitated at 200 rpm at room temperature for a period of 60 minutes. The mixture was digested and filtered. The residual Pb^{2+} concentration was determined using AAS.

2.5.2 Effect of pH on adsorption process

The effect of pH on the adsorption of Pb^{2+} ions onto ATC and UTC biosorbent were investigated over a pH range of 3

to 9. Adjustments of pH were done using 0.1M HCl and 0.1M NaOH as required. The initial concentration 100 mg/L of Pb^{2+} was mixed and agitated with optimum biosorbents dose (0.8-1 g) for 60 minutes over a shaker at 200 rpm at room temperature. The mixture was digested and filtered. The concentration of the residual Pb^{2+} ion in the filtrate was determined using AAS.

2.5.3 Effect of adsorbate concentration on adsorption process

Varying the spiked initial concentrations of Pb^{2+} ion solution (5, 50, 100, 150 and 200) mg/L, 25 cm^3 of the solution was mixed with the biosorbents at optimum experimental conditions at 200 rpm for 60 minutes. The mixture was digested and filtered. The filtrate was taken for AAS analysis to determine the residual metal ion concentration.

2.5.4 Effect of contact time on adsorption process

The effect of contact time on the biosorption process was evaluated over a period of 30, 60, 120, 150 and 180 minutes at optimum experimental conditions. The mixture was digested and filtered. The filtrate was taken for AAS analysis to determine the residual Pb^{2+} concentration.

III. Results And Discussion

2.6 FTIR interpretation

The prominent vibration bands established for FTIR analysis of cocoa leaves are presented in Figure 1. The functional groups identified and their corresponding wave lengths include; O-H (3373 cm^{-1}), C-H_2 stretching (2922 cm^{-1}), -CH_3 (2855 cm^{-1}), O-CO- saturated acid anhydride (1736 cm^{-1}), N-N=O (1449 cm^{-1}), CH_3- symmetrical deformation (1375 cm^{-1}), S group of C=S (1162 cm^{-1}). Some of these functional groups participated in the adsorption process supporting a chemisorption mechanism (Dada *et al.,* 2015).

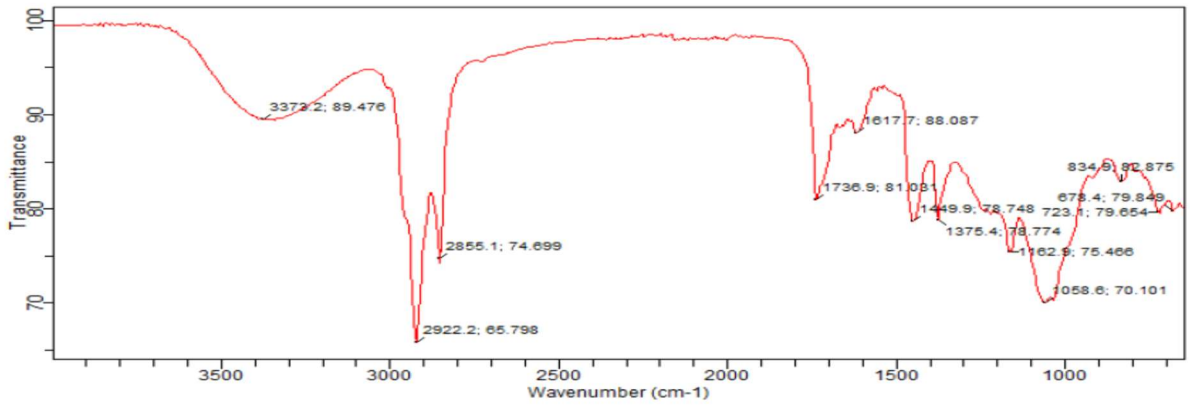

Figure 1. FTIR chart of biosorbent (Cocoa Leaves)

2.7 Effect of adsorption parameters

The effect of biosorbent dosage on Pb^{2+} removal from contaminated water at warfront using ATC and UTC is presented in figure 2. The percentage removal of Pb^{2+} was observed to increase from 99.9985 – 99.9990% for ATC and 99.9920 – 99.9968 % for UTC as the amount of biosorbent dose increased gradually from 0.1 – 1.0 g. The maximum biosorption was obtained at the biosorption dose of 1.00 g at 100 % for ATC and 0.8 g at 99.996 % for UTC removal which indicated that the optimum of the biosorbent was sufficient to adsorb maximum Pb^{2+} of 100 mg/L. Such increase could be due to the availability of vacant sites as biosorbent dose increased. The result is in conformity with previous studies on some biosorbents (Abdel-Chani and El-Chaghaby, 2009). Thereafter, the percentage removal of Pb^{2+} decreased for UTC with increase in biosorbent dose due to the biosorbent surface became saturated with the Pb^{2+}.

The amount of Pb^{2+} removed from contaminated water at warfront as a function of pH onto ATC and UTC is presented in Figure 3. The percentage removal of Pb^{2+} increased from 99.99 - 100 % for ATC and 99.41 - 99.72 % for UTC as the pH of the solution increased from 3-9. The increase was attributted to decrease competition between H^+ and the Pb^{2+} for the vacant sites which eventually lowers coulumbic repulsion of the Pb^{2+}. Decrease in percentage removal of Pb^{2+} from 99.72 – 99.68 % as pH increased is due to the formation

of soluble complexes of the Pb^{2+} which also compete for the active sites (Leyva *et al.,* 2009).

The concentration of Pb^{2+} adsorbed by ATC and UTC from contaminated water at warfront is presented in figure 4. The percentage removal increased progressively from 88.52 – 99.84 % for ATC and 61.74 - 99.44 % for UTC as Pb^{2+}concentration was increased from 5 – 200 mg/L. This is due to increased collision among the $Pb^{2+}$with the biosorbent surface and high rate of Pb^{2+} dispersion onto biosorbent surface (Wang *et al.,* 2013).

The effect of contact time on the removal Pb^{2+} from contaminated water at warfront by biosorbents is presented in figure 5. It was evident that percentage removal efficiency of Pb^{2+} increased slowly from 99.62 – 99.79 % for ATC and 98.71 - 99.84 % for UTC as contact time increased from 30.00 – 180.00 minutes. The result exhibited satisfactory sorption of Pb^{2+} attained within the first 150.00 min of contact time. Further increase in contact time led to no significant sorption of Pb^{2+}. Therefore, the contact time of 150.00 minutes was selected as the optimum contact time for ATC and UTC which was supported by Elhadi *et al.,* (2013). Increase in the first 150.00 minutes could be due to the availability of uncovered surface of the biosorbent.

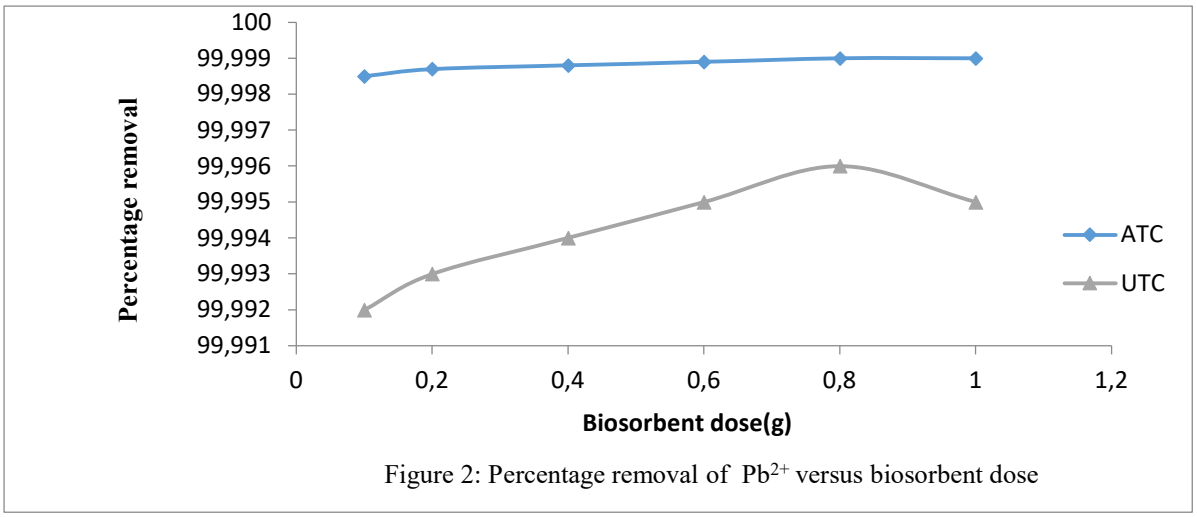

Figure 2: Percentage removal of Pb^{2+} versus biosorbent dose

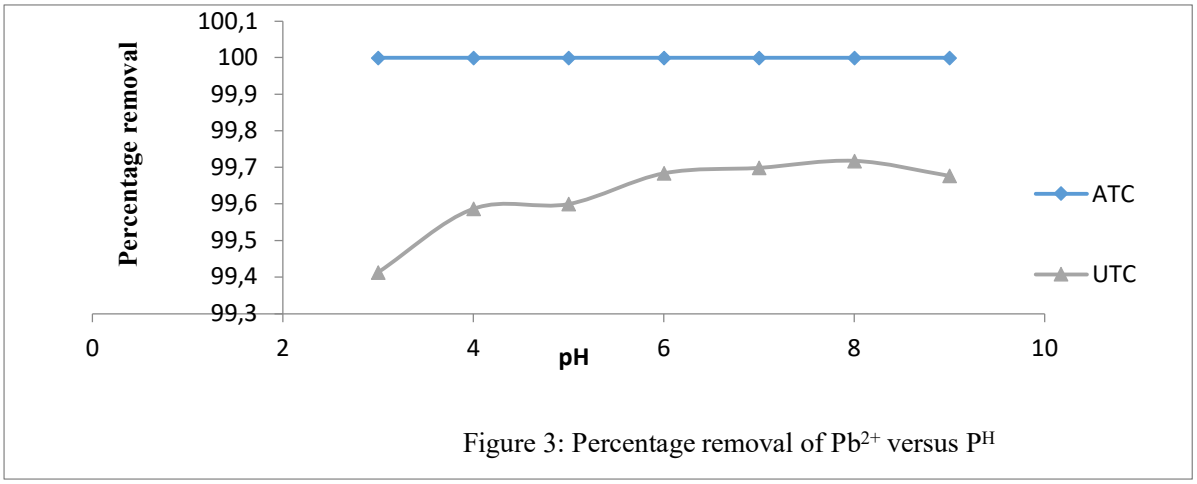

Figure 3: Percentage removal of Pb^{2+} versus P^{H}

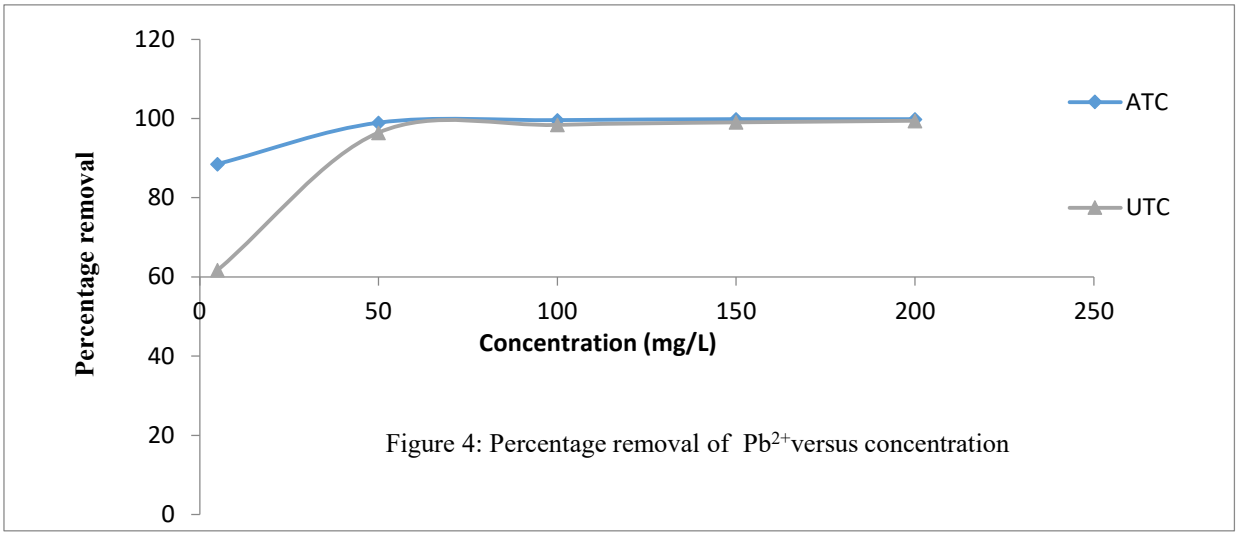

Figure 4: Percentage removal of Pb^{2+} versus concentration

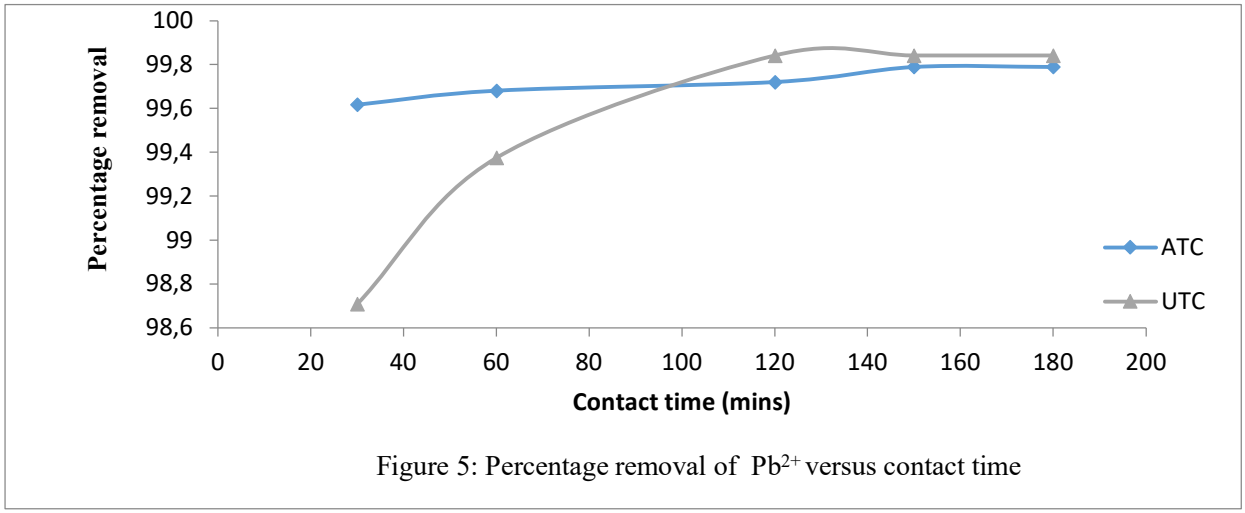

Figure 5: Percentage removal of Pb^{2+} versus contact time

2.8 Adsoption Kinetics

2.8.1 Pseudo First-order kinetics equation

It describes adsorption in solid-liquid systems according to the adsorption capacity of solids. It is assumed that one Pb^{2+} ion is adsorbed on one position of the adsorbent surface (Dada *et al.,* 2016). The linear equation of Pseudo first-order is shown in equation 3.

$$\log(q_e - q_t) = log q_e - \frac{k_1 t}{2.303} \quad \ldots\ldots\ldots\ldots (3)$$

k_1 and qe were determined from the slope and intercept of the linear plot of log (qe – qt) versus t. The correlation parameters obtained are presented in Table 1. The qe (2.23 mg/g for ATC and 2.177 mg/g for UTC biosorbents) values indicated that few amount of Pb^{2+} were adsorbed within a limited time k_1 (145.58 L/min for ATC and 158.33 L/min for UTC biosorbents) and the correlation of determination R^2 (0.8217 for ATC and 0.8833 for UTC biosorbents) suggested that biosorption of Pb^{2+} by biosorbent prepared from cocoa leaves partly fitted into Pseudo first order model due to fair correlation between $log\ (q_e - q_t)$ and t. (Tilaki *et al.,* 2004).

2.8.2 Pseudo second order kinetics model

It describes adsorption using chemisorption kinetics in liquid solutions (Dada *et al.,* 2016). The model assumes that one Pb^{2+} was adsorbed onto two vacant sites of the adsorbent surface. The linear expression is given in equation 4

$$t/q_t = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \ldots\ldots\ldots\ldots\ldots (4)$$

The constant k_2 was obtained from the slope of the linear plot of t/qt against t. Table 1 also showed the correlation parameters of Pseudo second order model of Pb^{2+} biosorption onto ATC and UTC biosorbents. The R^2 (1.00 for ATC and

1.00 for UTC biosorbents) values depicted that the adsorption of Pb^{2+} best fitted into pseudo second order model than pseudo first order model due to better correlation between $\frac{t}{q_t}$ and t.

2.8.3 Elovich model

The general explanation for this form of kinetics law involves that the active sites are heterogeneous in nature and therefore, exhibit different activation energies for chemisorption (Tilaki *et al.,* 2004). The linearized equation as presented in equation 5

$$q_t = \frac{1}{\beta} In(\alpha\beta) + \frac{1}{\beta} In\ t \ldots\ldots\ldots (5)$$

Where α is the initial adsorption rate ($mgg^{-1}.min$), β is desorption constant during any experiment. Both α and β were obtained from the slope and intercept of the plot of qt versus ln(t). The correlation parameters of Elovich model on Pb^{2+} adsorption onto ATC and UTC biosorbents are presented in Table 1. R^2 (0.2587 for ATC and 0.4574 for UTC biosorbents) values indicated that the adsorption of Pb^{2+} poorly fitted into Elovich model.

Table 1: Adsorption Kinetic Models' Parameters for the Sorption of Pb^{2+} onto ATC and UTC Biosorbents

Biosorbents	Kinetic Models		
	Pseudo first order	**Pseudo second order**	**Elovich model**
ATC	Q_e = 2.23 mg/g K_1= 145.58 min^{-1} R^2 = 0.8217	Qe = 0.015 mg/g K_2 = 23.64 g/mg/min R^2 =1	α= 4.25 g min^2/mg β=204.08 g min^2/mg R^2= 0.2587
UTC	Q_e = 2.177 mg/g K_1= 158.33min^{-1} R^2 = 0.88833	Qe = 0.0145 mg/g K_2 = 31.48 g/mg/min R^2 =1	α= 3.639 g min^2/mg β= 71.43 g min^2/mg R^2= 0.4574

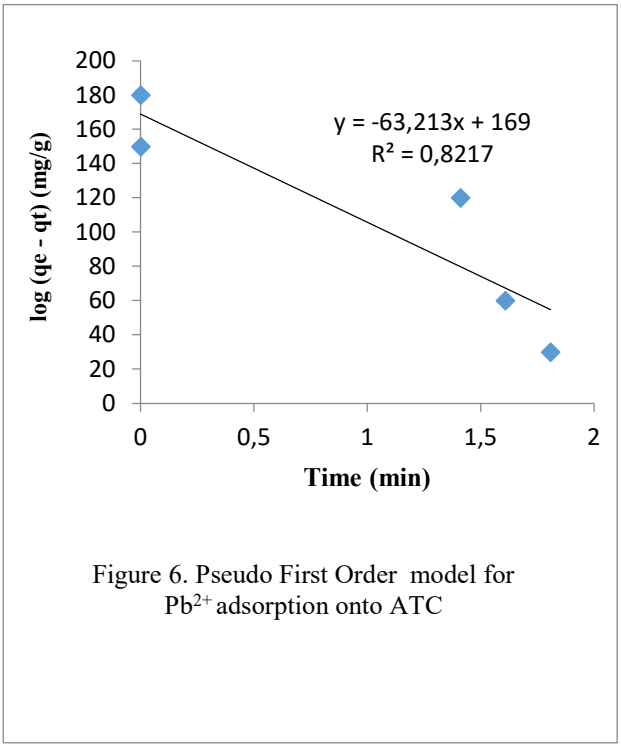

Figure 6. Pseudo First Order model for Pb^{2+} adsorption onto ATC

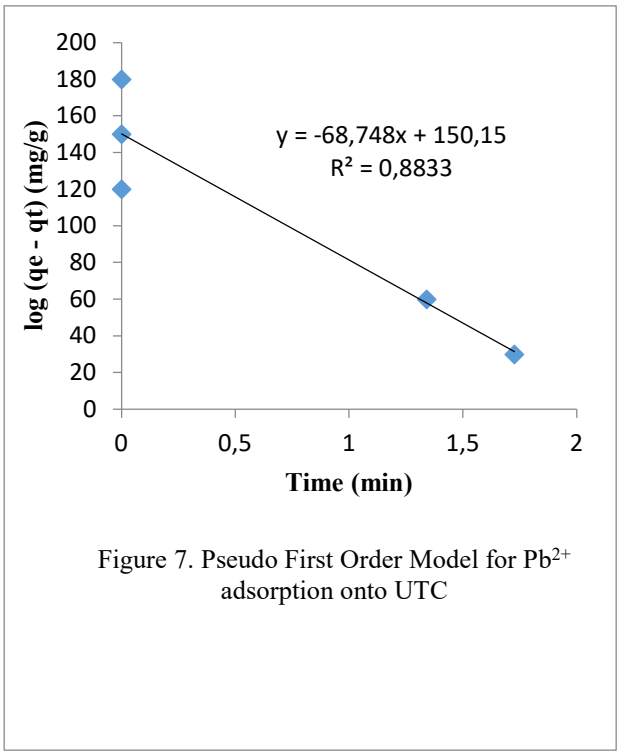

Figure 7. Pseudo First Order Model for Pb^{2+} adsorption onto UTC

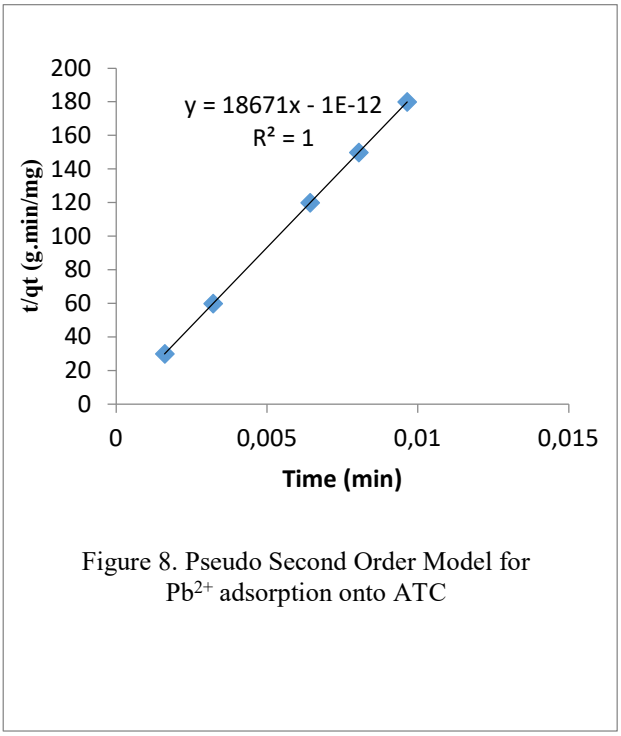

Figure 8. Pseudo Second Order Model for Pb^{2+} adsorption onto ATC

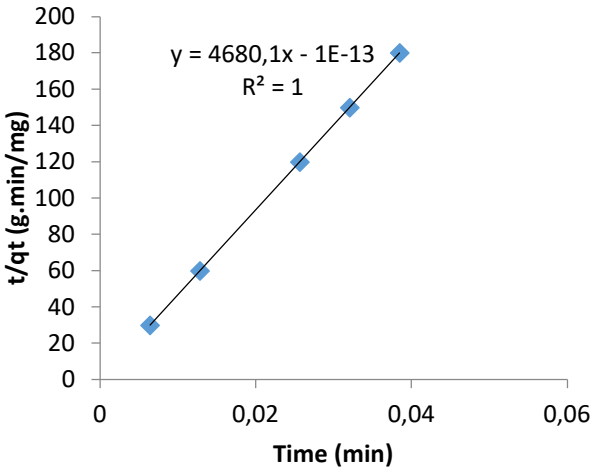

Figure 9. Pseudo Second Order Model for Pb^{2+} adsorption onto UTC

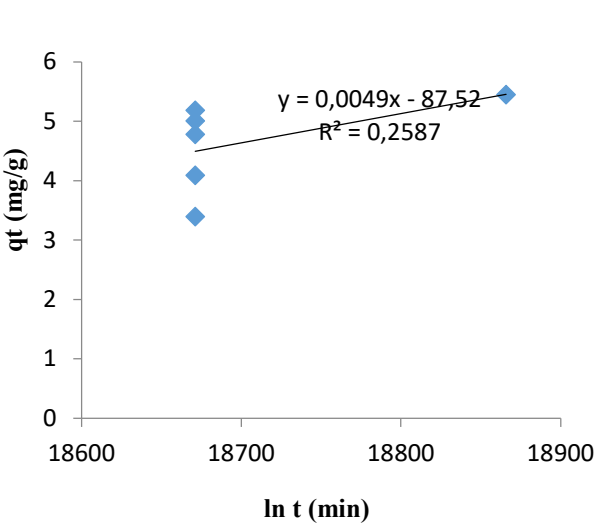

Figure 10. Elovich Model for Pb^{2+} adsorption onto ATC

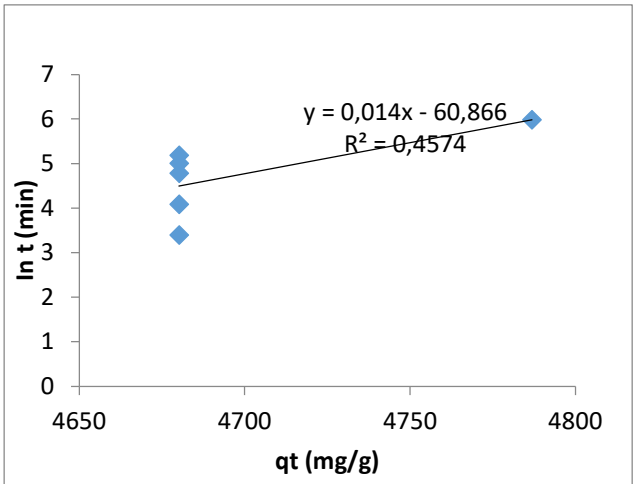

Figure 11. Elovich model for Pb^{2+} adsorption onto UTC

2.9 Adsorption Isotherm

The experimental equilibrium data obtained for the adsorption capacity (q_e) was used to plot the linear equation of the following adsorption models; Langmuir and Freundlich isotherms. The plot which best fits the experimental data (Ajaelu and Dawodu, 2013), having the highest R^2 value was used in explaining the adsorption processes (Febrianto *et al*., 2009).

2.9.1 Langmuir Isotherm

Assumes monolayer coverage with a second order reaction equilibrium model and that all adsorption sites are uniformly occupied. The linear equation is given in equation 6.

$$\frac{C_e}{q_e} = \frac{1}{q_{max}}.C_e + \frac{1}{K_L Q_{max}} \quad \ldots\ldots\ldots (6)$$

Table 2 showed the correlation parameter of Langmuir isotherm of Pb^{2+} biosorption onto ATC and UTC biosorbents. Q^o (117.65 mgg^{-1} and 54.35 mgg^{-1}) suggested that some heterogeneity in the surface or pores of biosorbent will play a role in large amount of Pb^{2+} removal in contaminated water at warfront. R_L values (0.0029 and 0.013) indicated that the biosorption of Pb^{2+} onto ATC and UTC was favourable and R^2 (0.4854 and 0.4426) value showed that the process of Pb^{2+} biosorption poorly fit into Langmuir isotherm due to poor correlation between $\frac{C_e}{q_e}$ and C_e.

2.9.2 Freundlich Isotherm

It assumes multi-layer adsorption of Pb^{2+}, that is having more one adsorbate in one pore. The linearized equation is presented in equation 7.

$$\log q_e = \log K_F + log\frac{1}{n}C_e \quad \ldots\ldots\ldots\ldots (7)$$

Table 2 also showed the Freundlich isotherm constants and correlation coefficient of Pb^{2+} biosorption onto ATC and UTC biosorbents. The 1/n (2.87 for ATC and 6.4 for UTC biosorbents) values indicate normal biosorption, which signified higher adsorption of Pb^{2+} unto ATC and UTC biosorbents, n (0.348 for ATC and 0.1557 for UTC biosorbents) values indicated favourable biosorption (since n<1) and R^2 (0.5754 for ATC and 0.6441 for UTC biosorbents) value indicated that sorption of Pb^{2+} onto ATC and UTC biosorbent fit into Freundlich isotherm better than Langmuir due to fair correlation between Inq_e and InC_e.

Table 2. Correlation Parameters of Langmuir and Freundlich Isotherms of Pb^{2+} adsorption onto ATC and UTC Biosorbents.

LANGMUIR ISOTHERM		FREUNDLICH ISOTHERM	
ATC	**UTC**	**ATC**	**UTC**
Q_o= 117.65(mgg^{-1}) K_L= 3.399(L/mg) R_L= 0.0029 R^2 = 0.4854	Q_o= 54.35(mgg^{-1}) K_L= 0.757(L/mg) R_L= 0.013 R^2 = 0.4426	K_f = 7.73 N = 0.348 R^2 = 0.5754	K_f = 82.459 N = 0.1557 R^2 = 0.6441

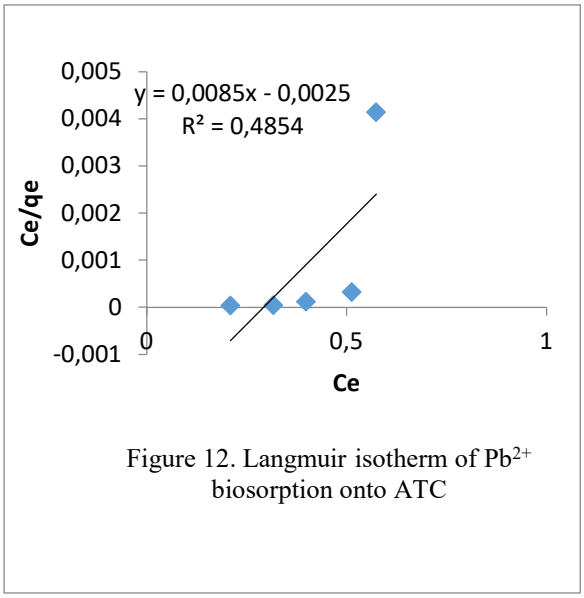

Figure 12. Langmuir isotherm of Pb^{2+} biosorption onto ATC

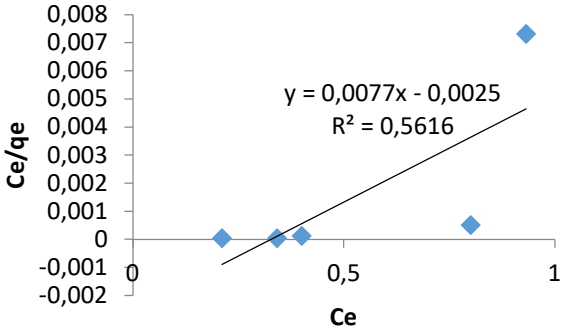

Figure 13. Langmuir isotherm of Pb^{2+} biosorption onto UTC

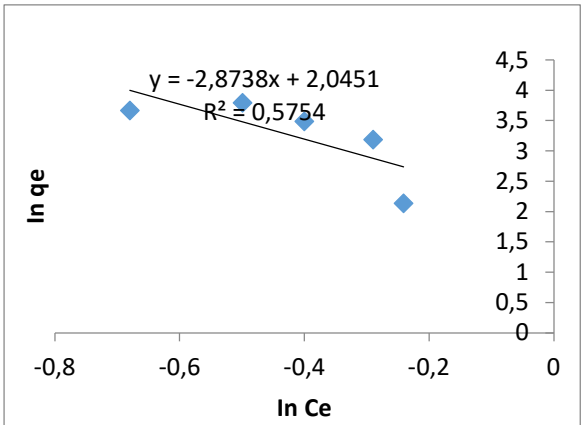

Figure 14. Freundlich isotherm of Pb^{2+} biosorption onto ATC

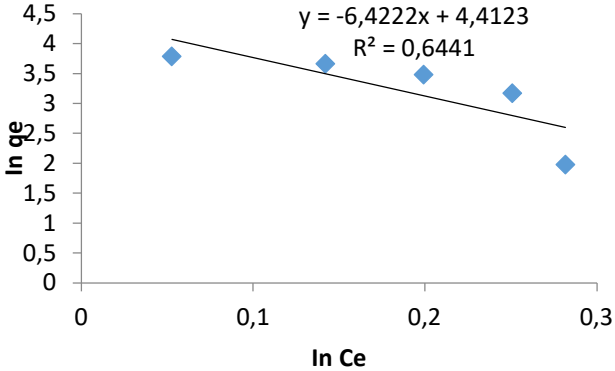

Figure 15. Freundlich isotherm of Pb^{2+} biosorption onto UTC

IV. Conclusion

This study revealed that biosorbents prepared from cocoa leaves have the potential of decontaminating Pb^{2+} from contaminated water sourced from warfront. The water sample was spiked with a known concentration of Pb^{2+} prior to experimental. The adsorption of Pb^{2+} onto Acid Treated Cocoa (ATC) and Untreated Cocoa (UTC) leaves depended on various operational parameters. It was inferred that the removal of Pb^{2+} from contaminated water increased as the biosorbent doses increased. Kinetics data were best described by pseudo second order, which is a chemisorption reaction. The equilibrium sorption data showed better correlation with the Freundlich isotherm therefore signifying the applicability of multilayer coverage of cocoa leaves which encompass the surface heterogeneity and exponential distribution of active sites. Cocoa leaves are therefore a potential and effective adsorbent for Pb^{2+} removal from wastewater at war front.

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LIST OF CAPTION FIGURE

Caption 1. FTIR chart of biosorbent (Cocoa Leaves)

FIGURES

Figure 2: Percentage removal of Pb^{2+} versus biosorbent dose

Figure 3: Percentage removal of Pb^{2+} versus P^{H}

Figure 4: Percentage removal of Pb^{2+} versus concentration

Figure 5: Percentage removal of Pb^{2+} versus contact time time

Figure 6: Pseudo first order model for Pb^{2+} adsorption onto ATC

Figure 7: Pseudo first order model for Pb^{2+} adsorption onto UTC

Figure 8: Pseudo second order model for Pb^{2+} adsorption onto ATC

Figure 9: Pseudo second order model for Pb^{2+} adsorption onto ATC

Figure 10: Elovich model for Pb^{2+} adsorption onto ATC

Figure 11: Elovich model for Pb^{2+} adsorption onto UTC

Figure 12. Langmuir isotherm of Pb^{2+} biosorption onto ATC

Figure 13. Langmuir isotherm of Pb^{2+} biosorption onto UTC

Figure 14. Freundlich isotherm of Pb^{2+} biosorption onto ATC

Figure 15. Freundlich isotherm of Pb^{2+} biosorption onto UTC

TABLES

Table 1: Adsorption Kinetic Models' Parameters for the Sorption of Pb^{2+} onto ATC and UTC Biosorbents.

Table 2. Correlation Parameters of Langmuir and Freundlich Isotherms of Pb^{2+} adsorption onto ATC and UTC Biosorbents.