CHEMISTRY

SURFACE MODIFICATION OF CANARIUM OVATUM ENGL. (PILI) SHELL AS ADSORBENT OF LEAD (Pb^{2+}) FROM AQUEOUS SOLUTION

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Abstract. *This study was carried out to investigate the efficiency of raw pili shell (RPS) and the surface modified pili shell using EDTA (EMPS) and oxalic acid (OMPS). A comparative study on the adsorption capacity of the adsorbents was performed against lead (Pb^{2+}) from aqueous solution.*

The adsorbents were characterized by FTIR, which showed higher peak of adsorption bands of carboxylic groups on the acid modified pili shells. Scanning electron microscope or SEM was also used to describe the surface morphology of the adsorbents. The linear form of Langmuir and Freundlich models were applied to represent adsorption data. The calculated equilibrium data of Pb (II) best fitted to Langmuir compare to Freundlich isotherm model with maximum adsorption capacity (qmax) of 27.03 mg/g and 45.45 mg/g using EMPS and OMPS, respectively. Kinetic sorption models were used to determine the adsorption mechanism and the kinetic data of all the adsorbents correlated (R^2 =1) well with the pseudo second order kinetic model. Among the three adsorbents, OMPS shown higher percent removal of lead compared to RPS and EMPS. The large adsorption capacity rate indicated that chemically modified pili shell in present study has great potential to be used as a cost-effective adsorbent for the removal of lead ions from the water.

Keywords: *adsorption, surface modification, heavy metal, isotherm modelling, kinetic modelling.*

Introduction. Heavy metal water pollution has been a major concern worldwide. It is a matter of concern as it causes various health problems that may lead to diseases and disorders in the human population through food chain. Heavy metals are toxic and have the tendency to bio-accumulate. It has been consistently desired that their levels be reduced in industrial and municipal effluents before ultimate repository in the ecosystem (Anwar et al. 2009). At trace level, metals like lead and zinc are necessary micronutrients but can be very deadly in higher concentration.

A wide variety of heavy metal species enters the aquatic compartment through atmospheric deposition, lixiviation of mining areas and cultivated fields, and industrial discharges, and these activities follow an upward curve in response to the world’s ever-growing population and its needs (Castro 2011).

Metals cannot be ‘degraded’ biochemically and are therefore harmful for human health if consumed more than required (for trace elements) or permissible, which is usually in the order of ppm or ppb. Sources of heavy metals in the environment can be both natural (in rocks and soils) or of anthropogenic origin. The main anthropogenic sources are industrial activities such as mining, coal combustion and waste disposal (Chaterjee 2011).

There are several advanced methods for the treatment of heavy metals-contaminated wastewater. Activated carbon is undoubtedly considered as universal adsorbent for effluent treatment and is commonly used for the removal of various pollutants from water. However, its widespread use in wastewater treatment is sometimes restricted due to its higher cost (Gonen 2012). The main techniques which have been utilized to reduce the heavy metal ion content of effluents include lime precipitation, ion exchange, adsorption into activated carbon, membrane processes, and electrolytic methods. All these methods are generally expensive and have significant disadvantages including incomplete metal removal, requirements for expensive equipment and monitoring systems, high reagent or energy requirements, or generation of toxic sludge or other waste products that require disposal (Thirumavalavan et al. 2010).

However, these methods are not widely used due to their high cost and low feasibility for small-scale industries (Lasheen 2012).

Studies show that fruits and their products can be a possible avenue for waste water treatment.

Most studies on the binding capacity of cationic metals have been oriented towards fruit peels. In addition, to author's knowledge, none of these include any adsorption experiments using surface modified Pili shells (*Canarium ovatum* Engl.). The aim of this research is to obtain significant theoretical results for the creation of novel adsorbent of metal ions and reuse of Pili shells (*Canarium ovatum* Engl.) waste through chemical modification (introduction of carboxylic functional group).

Results.

Surface Modification of Pili Shell.

Fourier transform infrared (FTIR) spectrophotometer was used to characterize the surface functional groups of the raw pili shells (RPS), EDTA Modified Pili Shells (EMPS) and Oxalic acid Modified Pili Shells (OMPS).

Raw Pili Shell. The FTIR spectrum of Raw Pili Shells (RPS) is shown in Figure 1. It can be observed that a number of adsorption peaks were displayed in the spectra implying that the nature of the material is complex. The broad absorption peaks at 3416 cm^{-1} are indicative of the existence of bonded hydroxyl groups on the surface of the pili shell. This band was associated with the vibrations of hydroxyl groups in cellulose and lignin.

The peak near 1424 cm^{-1} was also attributed to a stretch vibration of C-O from carboxyl groups. The strong C-O band at 1064 cm^{-1} also confirms the lignin structure of the pili shell. The wide O-H peak at 3380cm^{-1} indicates the –OH stretching vibrations. The peak located at 1050 cm^{-1} is due to C-H and C-O bonds. The raw pili shell (RPS) showed a C=O stretched at 1747 cm^{-1}. The C=O stretched is found to be the attracting group of the Pb ions in the solution.

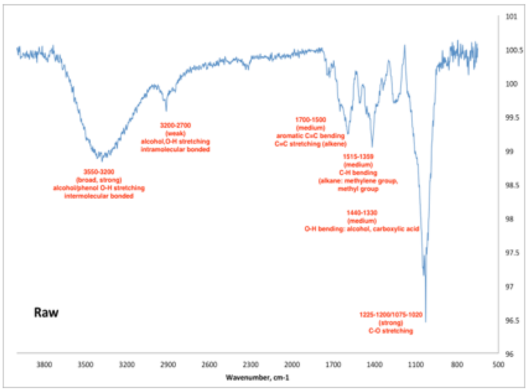


Figure 1 FTIR Result of Raw Pili Shell (RPS)

EDTA Modified Pili Shells.

Surface modification of raw pili shell was done using ethylenediaminetetraacetic acid (EDTA). The effect of EDTA modification is shown in Figure 2.

The wide O–H peak observed in both RPS and EMPS are due to the vibrational mode that being complicated by hydrogen bonding. The EMPS has shown a higher peak at 97.37cm^{-1} compared to the peak of RPS on the same band at 98.93 cm^{-1}. There is also an increase in the presence of O-H bending at peak of 97.52 cm^{-1} which implies presence of carboxylic acid from the medication.

In addition, it can be observed that after the modification of RPS by EDTA, there is an N-H stretch present near region of 3,310–3,500 cm^{-1}.

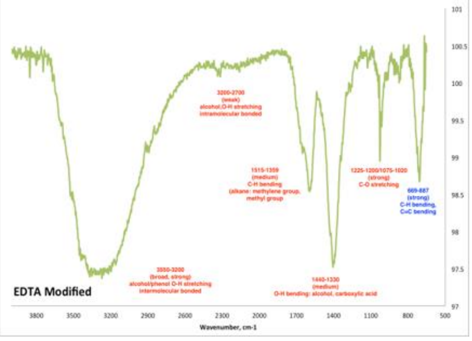


Figure 2 FTIR Result of EDTA Modified Pili Shell (EMPS)

Oxalic Acid Modified Pili Shells.

Raw pili shell was modified using oxalic acid (OMPS). Figure 3 shows the FTIR result after the surface modification of Pili shell. It can be observed that a presence of a medium to strong C=O stretching was found at 1735 to 1815 cm^{-1} with a peak recorded at 1725 cm^{-1}. The presence of C=O in the modified can be accounted to a higher adsorption of lead in the experiment compared to RPS and EMPS. Same with the surface of RPS, there is also a medium O-H bending observed 1330-1440cm^{-1} spectrum. The C=O and O-H may function as proton donors and deprotonated hydroxyl and carboxyl groups may be involved in coordination with cationic Pb^{2+} ions. The dissolved lead ions are positively charged and may be attracted by the anionic OMPS structure. This was also observed on the study of Thirumavalavan et al. using lemon peels and other fruit peels which clearly revealed that the carboxyl and hydroxyl groups content will influence the adsorption capacity, and the higher the content, the better the adsorption capacity.

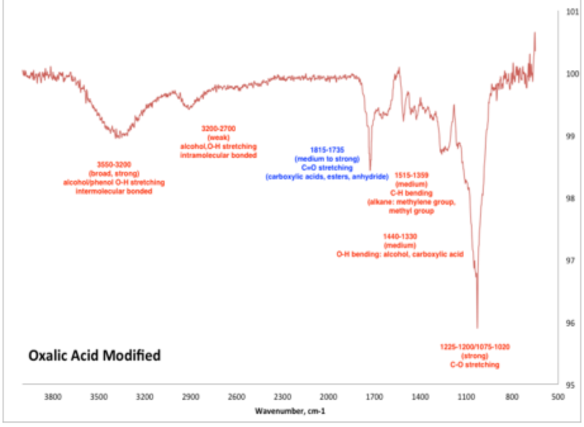


Figure 3 FTIR Result of Oxalic Acid Modified Pili Shell (OMPS)

Surface modification of raw pili shell (RPS) using oxalic acid result to appearance of a peak at 1729cm^{-1}. This appearance located between 1690-1760cm^{-1} confirms the presence of carboxylic group in the surface of raw pili shell. The carboxylic group may be accounted to the high adsorptivity of OMPS in the adsorption test of lead in aqueous solution.

The EDTA modified pili shell (EMPS) shown a very broad trough. The O-H bond can easily be recognized at 2500 - 3300 cm^{-1}. This O-H bond present in EMPS is the O-H bond of carboxylic acid that may explain better adsorption of the modified pili shell compared to the RPS.

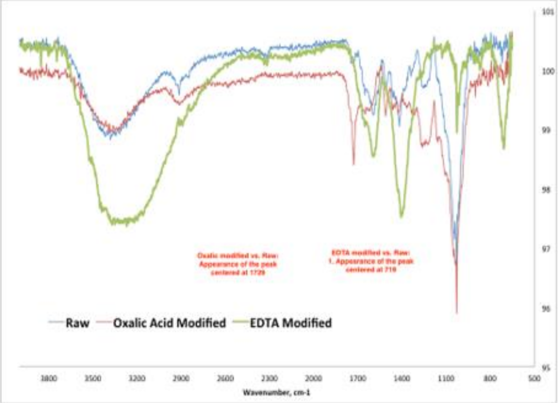


Figure 4 Comparison of the FTIR result of RPS, EMPS and OMPS

In addition to the characterization of the surface using FTIR, the surface structure of RPS, EMPS and OMPS was analyzed by scanning electron microscope (SEM). The scanning electron microscope enables the direct observation of the surface microstructures of the adsorbents.

The surface morphology of the raw pili shell (RPS) in Figure 5 revealed a smooth and compact with low porosity surface. The surface morphology of the samples as determined by scanning electron microscopy (SEM) show notable differences upon the modification of the surface using EDTA and oxalic acid as seen in Figure 6.

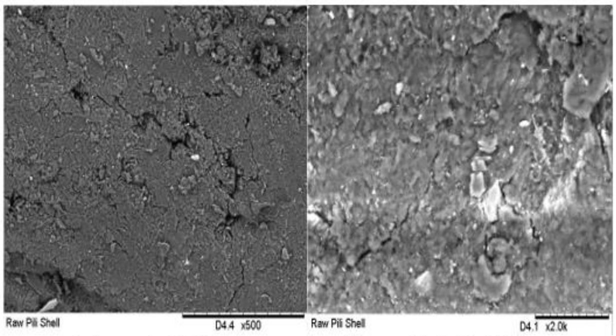


Figure 5 SEM micrographs of raw pili shell (RPS):
(A) x500 magnification (B) x2000 magnification

The modification of raw pili shell using EDTA resulted into fissures, narrow opening or cracks in the surface which represent some pore openings and cavities which may facilitate the solution flow into the pore and enhance the adsorption as shown in Figure 6a. In a higher magnification, Figure 6b revealed a spongy and more amorphous surface of the EMPS indicative of changes in surface area of the RPS. These irregular grooves and porous structure that might favor accessibility of Pb(II) to the adsorbent surface of EMPS.

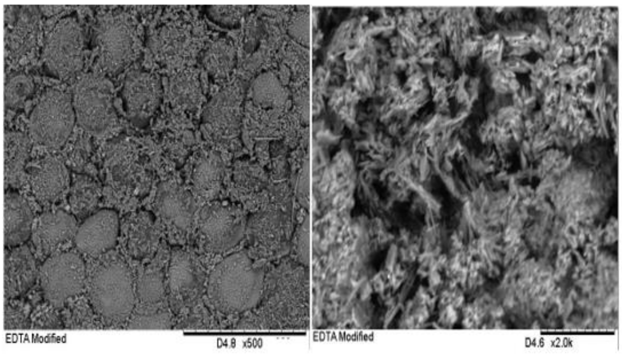


Figure 6 SEM micrographs of EDTA modified pili shell (EMPS):
(A) x500 magnification (B) x2000 magnification

Oxalic acid modified pili shell (OMPS) revealed the combination of small and large particle size, heterogeneous rough and porous surfaces with crater-like pores as shown in figure 7a. The surface of OMPS in figure 7b at higher magnification shows adsorbent surface is rough and porous, offering an easy access for metal ions diffusion inwards and being trapped

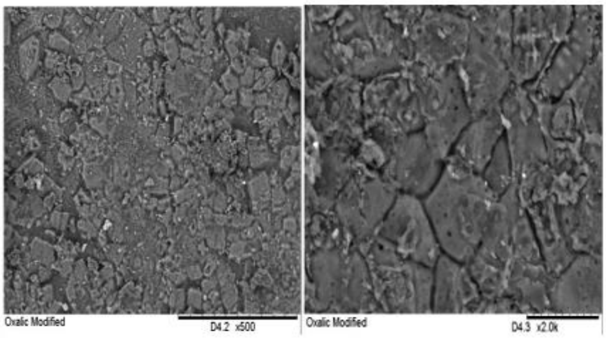


Figure 7 SEM micrographs of Oxalic modified pili shell (OMPS):
(A) x500 magnification (B) x2000 magnification

The particles having irregular shape and the surface exhibiting microrough texture are said to promote the adherence of toxic metal ions. More porous surfaces promote the adherence of lead (Annaduari et al. 2002).

Effect of pH of Pb in Aqueous Solution

Comparison of the effect of pH in the adsorption of RPS, EMPS and OMPS is shown in Figure 8. The highest adsorption of lead was observed using OMPS compared to EMPS and RPS. Although there is no significant variation in the amount of adsorbed lead from pH 1 to 9, it was observed that adsorption is greater in higher pH. This phenomenon was also observed by Annadurai *et al* (2002). using banana and orange peels in the adsorption of lead where adsorption decreases at lower pH and higher in increasing pH. At low value of pH, the competition would be between the proton and metal ions on the active binding sites. The protonation of active sites therefore prefers to reduce the metal sorption as explained by Abdulrazak (2016).

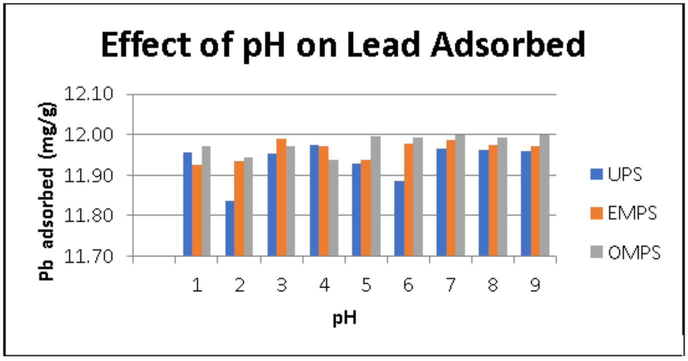


Figure 8 Effect of pH on Pb Adsorption

EMPS and RPS also exhibit the same adsorption property as OMPS. Using EMPS, it was observed that there is no significant variation in the amount of lead adsorbed from the solution. More so, the RPS also exhibits the same result. The amount of lead adsorbed by RPS has shown no significant variation from pH 1 to 9. Among all adsorption test using the three adsorbents, OMPS recorded the highest amount of adsorb lead at 12 mg/g.

Effect of Initial Metal Concentration on Pb Adsorption

The effect of initial metal concentration on the adsorption of lead was tested using the three adsorbents: RPS, EMPS and OMPS.

It can be observed that the result shows no significant variation on the amount of adsorbed lead from 100ppm to 500ppm concentration. However, 100% removal of lead was observed using OMPS at the lowest concentration of 100ppm and decreases gradually in higher concentration. EMPS also showed this phenomenon, as the percent removal of lead was recorded in the lowest concentration. This may be explained by the smaller number of available sites for adsorption as compared to metal ions present in solution. This was also observed in the study by Rajput (2015) using orange peels in the removal of lead.

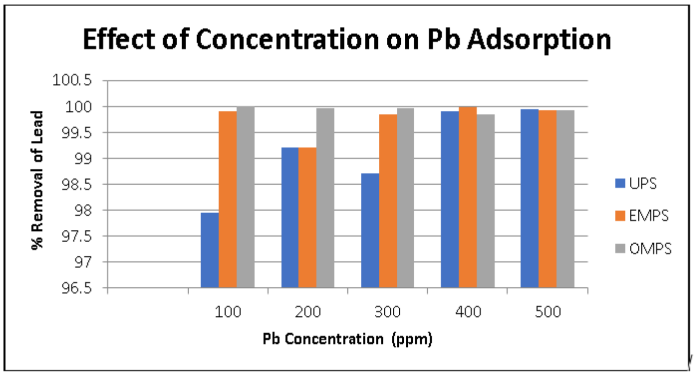


Figure 9 Effect of Initial Metal Concentration on Pb Adsorption

Effect of Adsorbent Size.

The effect of adsorbent size on lead adsorption was tested using the three adsorbents. Figure 10 shows that EMPS and OMPS recorded higher lead adsorption in smaller particles sizes using 40 and 60 mesh. Feng *et al.* (2004) observed that adsorption being a surface phenomenon, the smaller adsorption sizes offered comparatively larger surface area and hence higher adsorption occurs at equilibrium.

UPS on the other hand has higher adsorption on larger particle sizes. According to Charles and Odoemelam (2010) in their study on biosorption of Pb(II) and Cd(II) Ions from Aqueous Solution Crasstrotrea Gasar (Bivalve) Biomass, although one would expect that the smaller particle size should give a greater percentage removal because of the surface area, but as the particle size increased, the number of micro pores also increases. The increase in micro pores increases the number of the accessible sites, hence increases the percentage adsorbed.

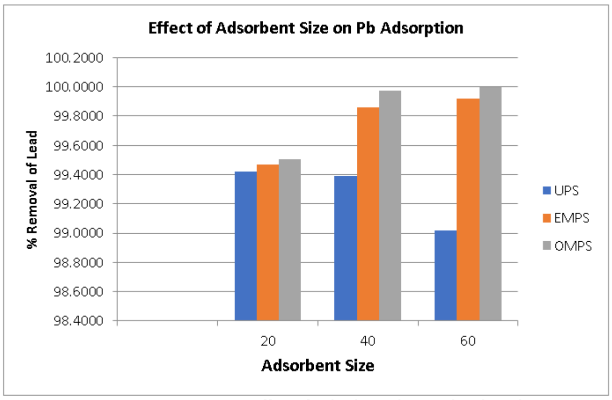


Figure 10 Effect of Adsorbent Size on Pb Adsorption

Effect of Adsorbent Dose.

As shown in Figure 11, the use of OMPS recorded higher adsorption in comparison with RPS and EMPS. More so, the lead adsorption of the three adsorbents in varying adsorbent dose showed no significant variation. Rajput (2015) concluded that it is apparent that the percent removal of heavy metals increases rapidly with increase in the dose of the adsorbents due to the greater availability of the exchangeable sites or surface area. Thus, these adsorption values of RPS, EMPS and OMPS may suggest that the adsorbents have abundant binding sites for lead in the solution.

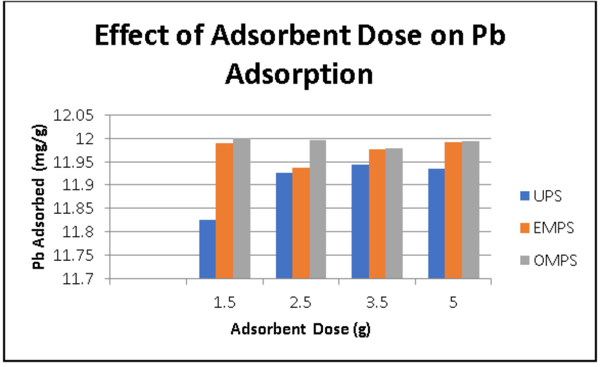


Figure 11 Effect of Adsorbent Dose on Pb Adsorption

Isotherm Modelling.

This study aims to provide an isotherm model using the three adsorbents as it is important to establish the most appropriate correlation for the equilibrium data. The Langmuir adsorption isotherm is a well-established model applied to different pollutants adsorption including heavy metals and widely use for the adsorption of different contaminants from a liquid solution.

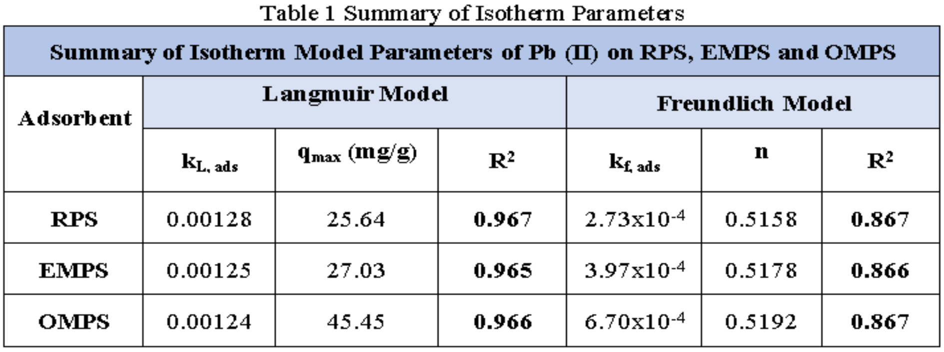
The data gathered from the adsorption of raw pili shell (RPS) were fitted to Langmuir and Freudlich Isotherm Model. It can be observed that the correlation coefficient is higher using Langmuir equation ($R^2 = 0.967$) compare to Freundlich equation ($R^2 = 0.867$) This implies that the RPS involves a dominant monolayer adsorption.

Data result of EDTA modified pili shell (EMPS) were also fitted to the Langmuir and Freundlich Isotherm. The result shows that the EMPS correlation coefficient fitting the Langmuir model ($R^2= 0.965$) and Freundlich model ($R^2= 0.866$) are both high. The first model fits the adsorption of EMPS as the Langmuir model recorded higher correlation coefficient value, this implies that adsorption on a surface of adsorbent is compatible in quality. Same observation was reported in the study of Chanmalee (2016) using nitric solution activated pomelo peel for adsorption of lead.

The OMPS also shows higher Langmuir model correlation value of $R^2= 0.967$ compare to Freundlich model correlation value of $R^2= 0.867$. It can also be observed that all three adsorbents recorded higher R^2 value fitting in the Langmuir isotherm model. Yan *et al.* (2014) concluded that the Langmuir isotherm model suggests that all sites within the adsorbent are energetically equivalent, the interaction between molecules adsorbed on neighboring sites can be negligible, and the adsorbent surface is saturated after monolayer adsorption.

Langmuir Isotherm and related parameters are shown in Table 1. OMPS reveals the highest maximum adsorption capacity, qm, for complete monolayer coverage. It can be clearly observed that all the R^2 (correlation coefficient) value of the three adsorbents are approaching to one ($R^2 > 0.9$) and clearly suggest that adsorption was a monolayer adsorption with assumptions that metal ions are chemically adsorbed at a fixed number of well-defined site and each site can hold only one ion.

Table 1 Summary of Isotherm Parameters



Summary of Isotherm Model Parameters of Pb (II) on RPS, EMPS and OMPS

Adsorbent	Langmuir Model			Freundlich Model		
	$k_{L,\ ads}$	q_{max} (mg/g)	R^2	$k_{f,\ ads}$	n	R^2
RPS	0.00128	25.64	**0.967**	$2.73x10^{-4}$	0.5158	**0.867**
EMPS	0.00125	27.03	**0.965**	$3.97x10^{-4}$	0.5178	**0.866**
OMPS	0.00124	45.45	**0.966**	$6.70x10^{-4}$	0.5192	**0.867**

Adsorption Kinetic Modeling.

The kinetic studies of lead adsorption on surface of raw pili shell (RPS), EDTA modified pili shell (EMPS) and oxalic modified pili shell (OMPS) were carried out using the pseudo first order and pseudo-second-order models on experimental data. The effects of initial lead concentrations were investigated to find the best fit kinetic model.

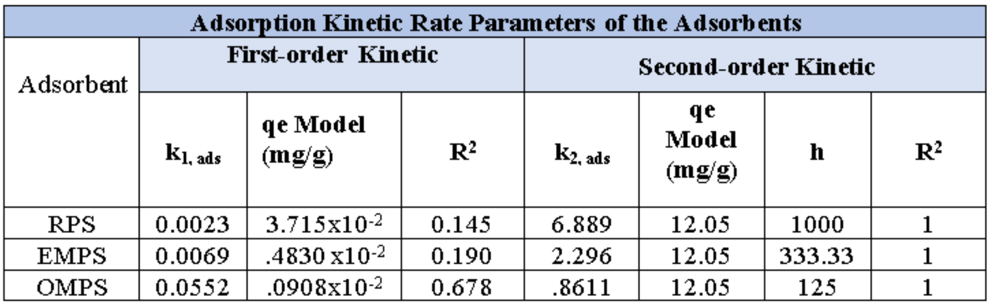
The kinetic constants and correlation coefficients of pseudo first-order kinetic model fail to give straight line with low correlation coefficient (R^2=0.145). Therefore, pseudo second-order kinetic model is preferred. The pseudo-second-order kinetic model was applied by plotting t/qt versus t, and this model gave high values of regression correlation coefficient (R^2=1). This implies that the mechanism of adsorption of Pb^{2+} ion on raw pili shell (RPS) follows the pseudo second-order kinetics indicating that the rate-limiting step was a chemical adsorption process between the metal ion and the adsorbent.

EMPS yields a low correlation coefficient (R= 0.190) for the Pseudo First-Order Lagergren Plot. The relationship between initial concentration and rate of adsorption will not be linear when pore diffusion limits the adsorption process. Same with the result of RPS in Pseudo First-Order Lagergren Plot, the EMPS yields a better fit on pseudo-second order kinetics with correlation coefficient of R^2=1. The plot of the linearized form (t/qt vs t) of the pseudo second order reaction of Pb (II) on adsorbent surface suggests that it relies on the assumption that chemisorption are rate limiting step.

Kinetic modelling of the OMPS was also fitted to pseudo first-order Lagergren model which yields to a correlation coefficient of R^2=0.678. According to Aderibigbe *et al.* (2017), the insufficiency of the first order model to fit the kinetics may be due to the limitations of the boundary layer controlling the adsorption. It was shown in Figure 4.22 that the date was best fitted into pseudo second-order Lagergren model that exhibits a far better degree on linearity R^2=1.

The pseudo-second-order kinetic model gave high values of regression correlation coefficient which implies that the mechanism of adsorption of Pb(II) ion on the OMPS follows the pseudo second-order kinetics. The same degree of linearity was also observed in the study of Aderibigbe *et al.* (2017) using citric acid modified plantain (Musa paradisiaca) peels in the adsorption of Pb 2+ in aqueous solution.

Table 2 Adsorption Kinetic Rate Parameters of the Adsorbent



Adsorption Kinetic Rate Parameters of the Adsorbents

Adsorbent	First-order Kinetic			Second-order Kinetic			
	$k_{1,\ ads}$	qe Model (mg/g)	R^2	$k_{2,\ ads}$	qe Model (mg/g)	h	R^2
RPS	0.0023	$3.715x10^{-2}$	0.145	6.889	12.05	1000	1
EMPS	0.0069	$.4830\ x10^{-2}$	0.190	2.296	12.05	333.33	1
OMPS	0.0552	$.0908x10^{-2}$	0.678	.8611	12.05	125	1

Where: qe(cal) = calculated equilibrium adsorption capacity(mg/g), k_1 = pseudo first order rate constant(L/min^{-1}), R^2 = correlation coefficient; k_2 = pseudo second order rate constant (g $mg^{-1}min^{-1}$), h = initial adsorption rate (mg/g min).

The adsorbents RPS, EMPS and OMPS all obtained a coefficient correlation value $R^2=1$ which implies that the pseudo-second order is the best sorption kinetic model for the adsorbents.

Conclusions. In this study, raw pili shell (RPS) was surface modified using ethylenediaminetetraacetic acid or EDTA (EMPS) and oxalic acid (OMPS) and used in adsorption test to determine their adsorption capacity.

The Fourier transform infrared (FTIR) spectrophotometer (FTIR- 2000, Perkin-Elmer, USA) analysis offers outstanding information on the nature of the functional groups present on the surface of the adsorbents.

FTIR confirms significant change in the surface of pili shell with the appearance of carboxylic group. New peaks were recorded in the OMPS significantly at $1729cm^{-1}$ implying the presence of carboxylic group that may be responsible for its adsorption profile. EMPS on the other hand shown a broad O-H group at $2500 – 3300cm^{-1}$ which means that the O-H detected is from a carboxylic acid. The presence of the carboxylic group in the surface of the pili shell may be accounted for its higher adsorption capacity compared to the raw pili shell.

The adsorbents were also subjected to scanning electron microscope (SEM) observe and compare the surface morphology before and after the surface modification of raw pili shell. It was observed that the EMPS and OMPS revealed a rough and more porous external surface in comparison with RPS. Even though all adsorbents exhibit good adsorption profile, the removal efficiency of EMPS and OMPS is higher in contrast to the raw pili shell. This implies that shapes and size of the particles in the adsorbent is an important factor in the exposure and availability of binding sites.

Batch experiments by varying conditions such as adsorbent dose, adsorbent size, initial concentration, pH, and contact time were conducted to provide an adsorption profile of lead in aqueous solution using RPS, EMPS and OMPS. Although, OMPS recorded higher percent removal in comparison with the other two adsorbents, result reveals that the three adsorbents exhibit a good adsorption capacity with minimal variation in the amount of adsorbed lead across different adsorbent size, pH, adsorbent dose and initial concentration.

Isotherm sorption and kinetic studies were conducted for the adsorption of Pb^{2+} ions from aqueous solution onto raw pili shell (RPS), EDTA modified pili shell (EMPS) and oxalic modified pili shell (OMPS). The equilibrium data have been analysed using Langmuir, Freundlich isotherms. The related correlation coefficients for each isotherm have been determined.

All the adsorbents best fitted in the Langmuir Isotherm model with correlation coefficient value approaching 1 ($R^2> 0.9$). This implies that RPS, EMPS and OMPS are following the Langmuir isotherm assumptions that metal ions are chemically adsorbed at a fixed number of well-defined sites and all sites are energetically equivalent.

The suitability of the pseudo second-order equations kinetic model for the sorption of Pb^{2+}ions onto RPS, EMPS and OMPS was also observed compared to pseudo-first. The pseudo second-order kinetic model agrees very well with the adsorption of Pb^{2+} ions onto the adsorbents. Thus, the type of adsorption is chemisorption based on the assumption that the rate-limiting step may be involving valency forces through sharing or exchange of electrons between the sorbent and sorbate.

These experimental studies on the three adsorbents would be helpful in developing a technology for the removal of lead ions from contaminated bodies of water. It may be concluded that raw pili shell (RPS), EDTA modified pili shell (EMPS) and oxalic acid modified pili shell (OMPS) may be used as a low-cost, natural and abundant source for the removal of Pb2+ ions from the wastewater.

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