



REMOVAL OF Pb (II) FROM SYNTHETIC SOLUTION USING ACTIVATED CARBONS PRODUCED FROM AGRICULTURAL WASTES

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ABSTRACT

The potentials of activated carbons of ten agricultural wastes, as adsorbents for removal of Pb (II) were investigated using pure lead nitrate Pb(NO₃)₂ on a batch mode. The waste peels were sun-dried for 24 hours, grounded and sieved through 150 microns sieve. These were washed with distilled water, dried in an oven at 105°C. Chemical method was used in activation by soaking the charcoal in 100 ml 0.1 M KOH for 24 hours, then filtered, rinsed thoroughly with distilled water and carbonized in the furnace at 400°C for 3 hours. Batch treatment method was used to study adsorption capacity Q_e and percentage lead removal R under pH 2, 4, 10, 12; 100 mg/l lead ion concentration, 100 g adsorbent loading, at 25°C ± 1 and 20 minutes. The optimum pH for R% and Q_e is 10 at 100 mg/l concentration of lead waste water, for all the studied biosorbents, 100 g loading, except carrot peels and rice husk that recorded optimum pH of 4 for R% and Q_e (98.527%; 99.02 mg/g and 99.98%; 100.482 mg/g respectively). The highest R and Q_e is 99.988% and 100.488 mg/g for corn husk while the least is 98.527% and 99.02 mg/g for carrot peels. Langmuir (R² = 0.950 to 1.00) and Freundlich isotherms (R² = 0.924 to 0.975) were used for fitting the equilibrium data. The system pH, adsorbent loading, concentration of metal ion, and the activation reagent all affect the R% and Q_e. It is recommended that agricultural wastes be recycled to activated carbons for use in lead waste water treatments.

INTRODUCTION

Activated carbon also called activated charcoal is a form of carbon processed to have small, low-volume pores that increase the surface area available for adsorption of heavy metals or chemical reactions. There are two factors that should be considered when designing a good sorbent: (i) the adsorbent should be porous and with a reasonable surface area and (ii) adsorption rate should be high

with more preference given to chemisorption [1,2]. The activated carbons are useful in adsorption technology because of their large surface area and different surface functional groups such as carboxylic, carbonylic, phenolic, quinonic, lactonic and other groups which are bound to the graphite-like layer [3]. Biosorbents are used in the removal of toxic metals, for example lead. Galadima and Garba, [4] reported the lead pollution in Nigeria that claimed the lives of over five hundred children and left thousands of people with severe health problems. Lead contamination of water sources in Owerri locale has been reported by Ogueke *et al.* [5,6]. Both independently concluded that the water samples studied contained lead above safe levels.

There are many parameters that influence the sorption of metals using biosorbents one of which is pH. The pH of a medium, according to [7] is considered to be a key factor governing the process of metal adsorption from an aqueous solution. They observed that under highly acidic conditions, formation of links between metal ions and the active site is restricted by excessive protonation of the active sites which ultimately results in lower adsorption. The solution pH influences the dissociation state of the adsorbents, ionic state of functional groups and species of metals [8,7]. The effect of pH on solution chemistry of the target metal includes hydrolysis, complexation by organic and/or inorganic ligands and redox potentials [9,7]. At elevated pH values according to [7], adsorption is reduced due to high precipitation, ion exchange and aqueous metal hydroxide formation. Memon *et al.* [10] observed that under basic condition, the binding sites may not activate as in acidic medium. Demirbas *et al.* [11] reported that at slightly acidic conditions linked H^+ is released from the active sites allowing metals ions to be absorbed. However, when pH was further lowered, H_3O^+ ions begin to compete with metal ions for binding onto adsorbent sites resulting in poor adsorption capacity.

The use of biosorbent in metal removal is best studied using adsorption isotherms. The adsorption isotherm is the graphical representation showing the relationship between the amount adsorbed by a unit weight of adsorbent and the amount of adsorbate remaining in a test medium at equilibrium and it shows the distribution of adsorbable solute between the liquid and solid phase at various equilibrium concentration. Lima *et al.* [1] noted that a suitable isotherm is the one that can basically replicate the experimental data. The two most common are Langmuir and Freundlich isotherms. The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies with no transmigration of adsorbate in the plane surface. The Freundlich isotherm explains multilayer adsorption taking place on heterogeneous sites.

The recent search for low cost adsorbents channeled attention to agro-wastes. The agricultural wastes are low cost and can be gathered and converted to low cost activated carbons and to create industries, that will create wealth from these wastes, with the current global pandemic. Recycling industries can spring up from these available wastes, to boost the economy, market, employment for our teeming population. This current study was based on improving of their adsorption capacity given that their costs is kept low; the recycling of these wastes so as to rid our environment of rubbish; the increased presence of lead pollutants in the northern Nigeria; to produce activated carbon that can be used to remove lead contaminants, by varying pH of a single concentration of lead pollution, of ten (10) agro-wastes under the same prevailing laboratory conditions; as existing literatures studied one or two biosorbents for lead removal and not ten under the same study.

METHODS

Collection and preparation of agro-waste

The wastes were collected food and fruit sellers in Owerri municipal, Imo state. The wastes were rinsed thoroughly with distilled water to remove adherent extraneous matter and then sun-dried for 24 h. It was grinded, sieved through 150 microns sieve, washed with distilled water and dried in an oven to a constant weight at a temperature of 105°C. The activation of the sample was achieved by soaking the charcoal in 100 ml of 0.1 M potassium hydroxide for 24 h. Thereafter was filtered using Whatman filter paper. The product was rinsed thoroughly with distilled water and dried for about 3 hr at 400°C in the furnace for final activation of the charcoal.

Preparation of synthetic lead stock solution

The $Pb(NO_3)_2$ (1.600 g) was measured and dissolved in 10 ml distilled water placed in a 1 L volumetric flask and the volume made up to 1000 ml with distilled water. This formed the stock solution. The working solution of 100 mg/l was prepared from this stock by dissolving 100 ml stock in 1 L distilled water. The chemicals potassium hydroxide, hydrochloric acid, sodium hydroxide, hydrochloric acid and lead (II) nitrate were of analytical grades.

Experimental procedure/Batch treatment method

The effect of pH was studied using a 100 ml of 100 mg/l concentration of the lead water solution. This was put in plastic bottles labeled pH 2, 4, 10 and 12. Then, 100 mg of the adsorbents (i.e. activated carbon) was introduced into each of labeled plastic bottles. The pH of the solutions was adjusted by drop wise addition of the 0.1 M sodium hydroxide and 0.1 M hydrochloric acid. The solution was shaken using a mechanical stirrer at 100 rpm to enhance the mixing process at room temperature. Then at the end of the mixing, the adsorbents were separated from the solution by filtration.

Metal analysis

The lead content of the solution was analyzed using the Atomic Absorption Spectrometer.

Efficiency calculation (Percentage removal of lead)

The equations employed in the calculations of percentage lead adsorption is

Percentage lead removal using mass balance equation $R\% = 100(Co - Ce)/Co$ Equation 1

Co – initial AAS reading of lead ion in 100 mg/l solution of waste water (100.5)

Ce = final AAs reading of lead ion in solution which is the equilibrium lead concentration.

Calculation of metal uptake (adsorption capacity)

The equation employed in the calculation of adsorption capacity is

Adsorption capacity Q_e (mg/g) = $(Co - Ce)V/M$ Equation 2

M = 100 mg, Co – initial AAS reading of lead concentration in 100 mg/l solutions (100.5),

Ce = final AAs reading of lead metal in solution,

V = 100 ml,

Q_e = The amount of adsorbate adsorbed per unit amount of adsorbent.

Adsorption isotherm study

Langmuir isotherm model

The equation employed in the calculation of Langmuir isotherm

$Ce/Q_e = 1/qmK_L + Ce/qm$ Equation 3.

Rewriting the equation to fit the linear equation $y = mx + c$

$Ce/Q_e = Ce/qm + 1/qmK_L$

C_e = equilibrium concentration, qm (mg/g) = maximum sorption capacity, K_L = coefficient of determination or adsorption coefficient and relates to the energy of adsorption. qm (mg/g) and K_L are Langmuir constants/linear isotherm parameters.

Freundlich isotherm model

The equation employed in the calculation of Freundlich isotherms are given below:

$Q_e = K_F (C_e)^{1/n}$ Equation 4.

K_F is the adsorption capacity and is temperature dependent constants, $1/n$ is dimensionless depicting adsorption intensity (both are Freundlich constants).

Separation factor

The equation employed in the calculation of separation factor are given below:

$R_L = 1 / (1 + K_L C_1)$ Equation 5

where K_L is the Langmuir constant and C_1 is the initial concentration (100.5).

RESULTS

Percentage metal removal and adsorption capacity

The equilibrium concentrations recorded after each experiment with each biosorbent is recorded in Table 1. These values were used to calculate the percentage metal removal and adsorption capacity using equations 1 and 2 above.

Table 1: The initial and equilibrium concentrations of activated carbons from ten agricultural wastes at 100 mg/l metal concentration

pH	Co	Ce (BP)	Ce (CC)	Ce (CH)	Ce (CP)	Ce (GS)	Ce (OP)	Ce (PIP)	Ce (POP)	Ce (RH)	Ce (SCB)
2	100.5	0.033	0.071	0.017	152.9	0.075	1.78	127.4	0.088	0.048	0.047
4	100.5	0.104	0.063	0.32	1.48	0.089	13.43	7.49	0.121	0.018	0.21
10	100.5	0.028	0.059	0.012	1.87	0.067	0.22	0.59	0.071	0.053	0.014
12	100.5	1.35	0.069	0.041	3.38	0.093	3.71	2.53	0.093	0.086	0.52

Key: BP = Banana peel, CC = Corn cob, CH = Corn husk, CP = Carrot peel, GS = Groundnut shell, OP = Orange peel, PIP = Pineapple peel, POP = Potato peel, RH = Rice husk, SCB = Sugarcane bagasse, Co – initial AAS reading of lead concentration in 100 ml, Ce = final AAs reading of lead concentration in solution which is the equilibrium lead concentration

Activation of biosorbents, Percentage metal removal (R%) and adsorption capacity (Qe)

The activation method contributed to the high values of R% and Q_e recorded. These biosorbents subjected to the above treatments recorded varied percentage metal removal (R%) and adsorption capacity (Q_e) values. Banana peels recorded the highest R% and Q_e at pH 10 (99.972%; 100.47 mg/g) (Fig 1). Corn cob recorded highest at pH 10 (99.941%; 100.441 mg/g) (Fig 2). Corn husk recorded its highest at pH 10 (99.988%; 100.488 mg/g) (Fig 3). Groundnut shells (99.933%; 100.433 mg/g) (Fig 5), Orange peels (99.781%; 100.28 mg/g) (Fig 6), Pineapple peels (99.41%; 99.91 mg/g) (Fig 7), Potato peels (99.929%; 100.429 mg/g) (Fig 8) and Sugarcane bagasse (99.986%; 100.486 mg/g) (Fig 10) all recorded highest R% and Q_e values at pH 10. Carrot peels (98.527; 99.02 mg/g) (Fig 4) and Rice husk (99.98; 100.482 mg/g) (Fig 9) recorded their highest R% and Q_e values at pH 4. The highest R% and Q_e values was recorded by

Corn husk (99.988%; 100.488 mg/g) while the least values were recorded by Carrot peels 98.527%; 99.02 mg/g). From the results of this study it shows that there is a relationship between percentage metal removal and adsorption capacity, as one quantity increases the other increases thus.

Effect of pH on percentage metal removal and adsorption capacity

The effect of pH on percentage lead removal (R%) and adsorption capacity (Qe mg/g) using Banana peels showed that R% and Qe were initially highest at high acidic pH 2 (99.967%; 100.46 mg/g), then dropped drastically at pH 12 (98.65%; 99.15 mg/g). This means that R% and Qe decreased with increasing pH (Fig 1). The optimum pH for R% and Qe is pH 10 (99.941%; 100.441 mg/g) using Corn cob. There was a gradual increase in R% and Qe from acidic pH 2 (99.929%; 100.429 mg/g) to alkaline pH 10, the optimum pH (99.941%; 100.441 mg/g), thereafter a sharp drop in R% and Qe at pH 12 (99.931%; 100.431 mg/g) (Fig 2). The result using Corn husk showed that R% and Qe were initially high at high acidic pH 2 (99.983%; 100.483 mg/g), this dropped at pH 4 (99.681%; 100.18 mg/g), increased rapidly again at pH 10 and dropped at highest alkaline pH 12 (99.959%; 100.459 mg/g). The result shows that highest adsorption capacity (100.488 mg/g) and percentage lead removal (99.988%) occurred at optimum pH 10 (Fig 3). The R% and Qe recorded using Carrot peels were very low at high acidic pH 2 (-52.139%; -52.4 mg/g) but increased at slight acidity pH 4 (98.527%; 99.02 mg/g) which is the recorded optimum pH. This trend after, decreased at pH 12 (96.636%; 97.12 mg/g) (Fig 4). The Groundnut shell R% and Qe values were high at the initial acidic pH 2 (99.925%; 100.425 mg/g), this dropped at pH 4 (99.911%; 100.411 mg/g) and increased at optimum alkaline pH 10 (99.933%; 100.433 mg/g), finally dropped at pH 12 (99.907%; 100.407 mg/g) (Fig 5). The R% and Qe values for Orange peels were initially high at highest acidic pH 2 (98.229%; 98.72 mg/g), then dropped at pH 4 (86.637%; 87.07 mg/g), thereafter increased (99.781%; 100.28 mg/g) at alkaline pH 10, the optimum pH. The R% and Qe finally dropped at pH 12 (96.3%; 96.79 mg/g) (Fig 6). The use of the biosorbent Pineapple peels recorded very lowest R% and Qe at initial acidic pH 2 (-26.766%; -26.9 mg/g). This increased at pH 10 (99.41%; 99.91 mg/g), which happened to be the optimum pH. The R% and Qe finally dropped at pH 12 (97.774%; 97.97 mg/g) (Fig 7). There was a drop in R% and Qe from the initial acidic pH 2 (99.912%; 100.412 mg/g) to pH 4 (99.879%; 100.379 mg/g) using Potato peels as biosorbent. The R% and Qe increased at pH 10, the optimum alkaline pH (99.929%; 100.429 mg/g); then decreased at pH 12 (99.907%; 100.407 mg/g) (Fig 8). The R% and Qe, for Rice husk, increased from initial acidic pH 2 (99.95%; 100.452 mg/g) to pH 4, which was the optimum pH (99.98%; 100.482 mg/g). This dropped at pH 12 (99.914%; 100.414 mg/g) (Fig 9). There was a drop in R% and Qe from the initial pH 2 (99.953%; 100.453 mg/g) when Sugarcane bagasse was used. This increased at alkaline pH 10, the optimum pH (99.986%; 100.486 mg/g). The R% and Qe finally dropped at pH 12 (99.482%; 99.98 mg/g) (Fig 10).

Isothermal studies

Langmuir isotherm

The sorption capacity (q_m , mg/g) is the measure of the maximum sorption capacity which corresponds to complete monolayer coverage. The application of Langmuir isotherm to the system yielded maximum adsorption capacity of lead (111.11 mg/g; Table 2) using the adsorbent Potato peels. The other biosorbents Banana peels, Corn cob, Corn husk, Rice husk and Sugarcane bagasse recorded 100 mg/g; while the least maximum adsorption capacity shown on Langmuir isotherm is Pineapple peels which showed 26.32 mg/g, (Table 2). The adsorption coefficient (K_L) of Langmuir isotherm which is related to the apparent energy of sorption for lead ion is found to be highest in Corn husk (12,500 L/mg) than the other biosorbents studied (Table 2). Langmuir isotherm recorded highest values of R^2 ranging from 0.950-1.00. Banana peels, Corn cob, Corn husk, Groundnut shells, Potato peels, Rice husk, and Sugarcane bagasse recorded the highest value of 1.00 respectively (Table 2; Fig 11, 12; 13; 15; 18; 19; 20) while Carrot peels (0.999; Table 2; Fig 14), Orange peels (0.999; Table 2; Fig 16) and Pineapple peels (0.996; Table 2; Fig 17).

Freundlich isotherm

Freundlich isotherm yielded maximum adsorption capacity of lead for Carrot peels (207.65 mg/g; Table 3); followed by Pineapple peels (158.064 mg/g) then Rice husk (100.28 mg/g); Corn cob and Groundnut shells (100.183 respectively); Corn husk (100.083 mg/g). Potato peels recorded the least value of 7.98 mg/g. The adsorption coefficient or intensity ($1/n$) of Freundlich theorem showed negative values for all biosorbents studied (Table 3). Freundlich isotherm which describes multilayer adsorption taking place on heterogenous sites showed that the R^2 values are high for Banana peels (0.924; Table 3); Corn husk (0.919; Table 3); Carrot peels (0.947; Table 3); Groundnut shells (0.969; Table 3) and Rice husk (0.938; Table 3). The maximum adsorption capacity recorded for Langmuir isotherm is potato peels; the least is carrot. Carrot is best fitted in Freundlich isotherm because of the high R^2 value it recorded and Potato peels recorded the least value for Freundlich isotherm. This result may be that potato fitted better in Langmuir isotherm suitable for the monolayer adsorption. If the recorded R^2 values be higher that isotherm theory is fitted better than the other isotherm. The results from the two isothermal studies showed that the data recorded are best fitted on Langmuir model than Freundlich model with highest values of R^2 as given by Equations 3 and 4.

Table 2: Langmuir isotherm parameters

Activated carbon	q m(mg/g)	K _L (L/mg)	R ²	R _L
Banana Peel	100	-5000	1.00	1.1x10 ⁻³
Corn Cob	100.00	∞	1.00	-
Corn Husk	100.00	12,500	1.00	7.9x10 ⁻⁷
Carrot Peel	-52.63	- 0.288	0.999	-0.035
Groundnut Shell	100.00	∞	1.00	-
Orange Peel	90.91	- 5.5	0.999	-0.002
Pineapple Peel	26.32	0.2235	0.996	4.3x10 ⁻²
Potato Peel	111.11	1000	1.00	9.9x10 ⁻⁶
Rice Husk	100.00	∞	1.00	-
Sugarcane Bagasse	100.00	- 5000	1.00	-1.9x10 ⁻⁶

Table 3: Freundlich isotherm parameters

Activated carbon	K _F (mg/l)	1/n	R ²
Banana Peel	99.286	-0.003	0.924
Corn Cob	100.183	0	0.793
Corn Husk	100.083	-0.001	0.919
Carrot Peel	207.65	-1.043	0.975
Groundnut Shell	100.183	0	0.947
Orange Peel	97.807	-0.031	0.720
Pineapple Peel	158.064	-0.899	0.800
Potato Peel	7.98	-1.004	0.718
Rice Husk	100.28	0	0.938
Sugarcane Bagasse	99.983	-0.001	0.836

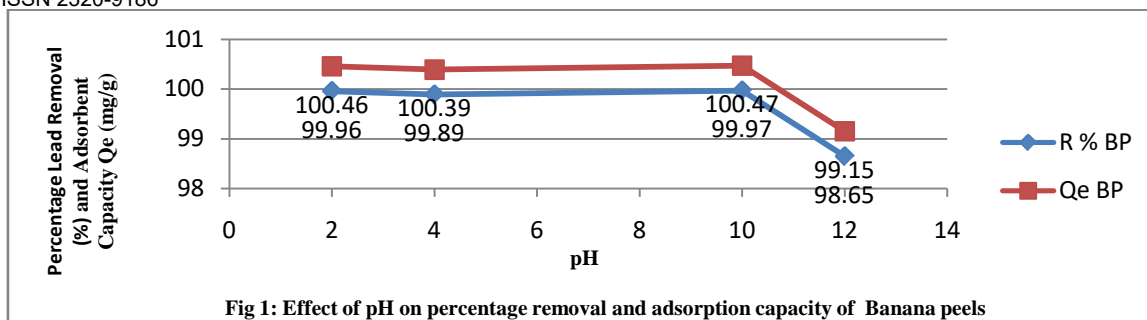


Fig 1: Effect of pH on percentage removal and adsorption capacity of Banana peels

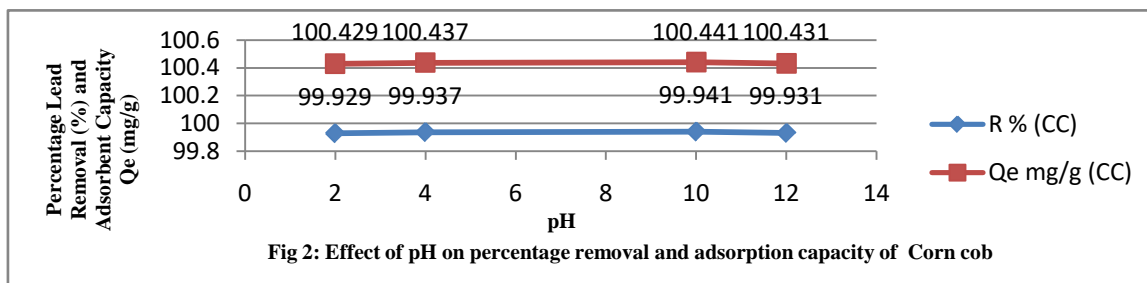


Fig 2: Effect of pH on percentage removal and adsorption capacity of Corn cob

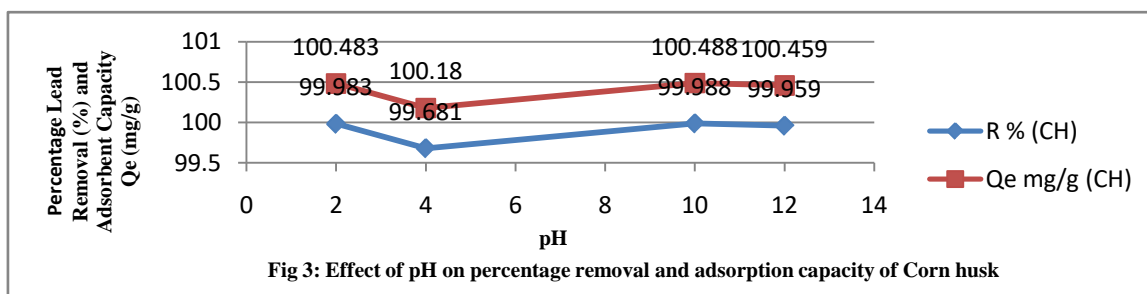


Fig 3: Effect of pH on percentage removal and adsorption capacity of Corn husk

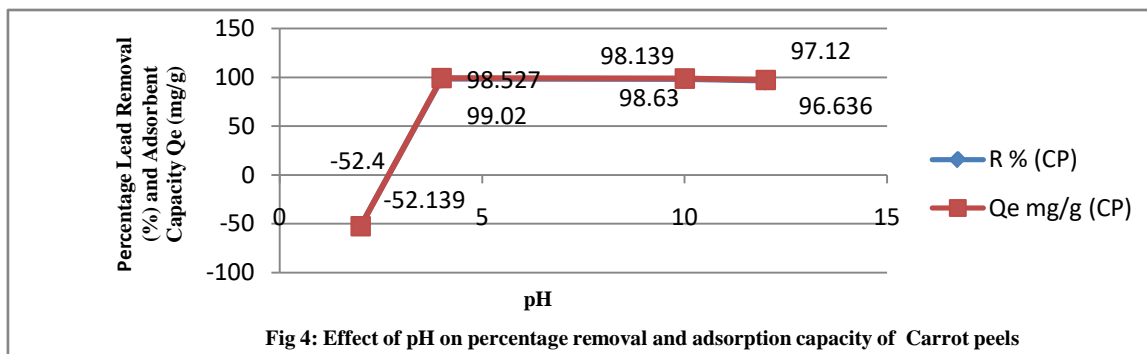


Fig 4: Effect of pH on percentage removal and adsorption capacity of Carrot peels

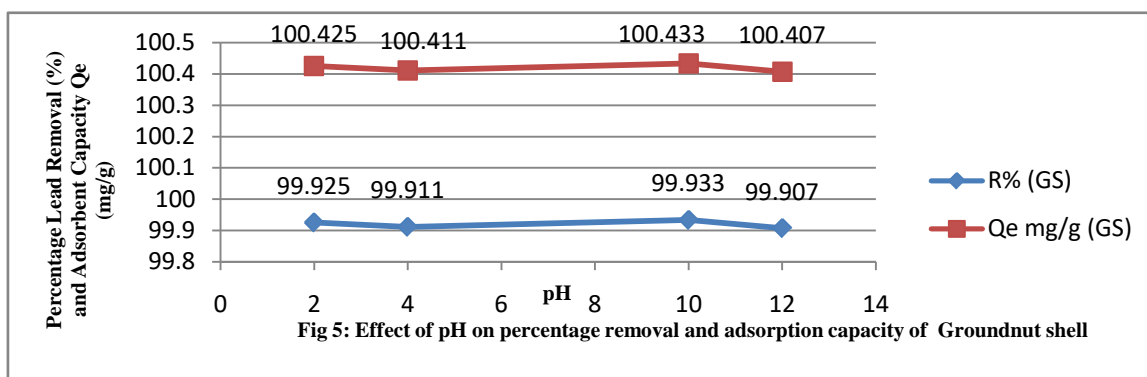
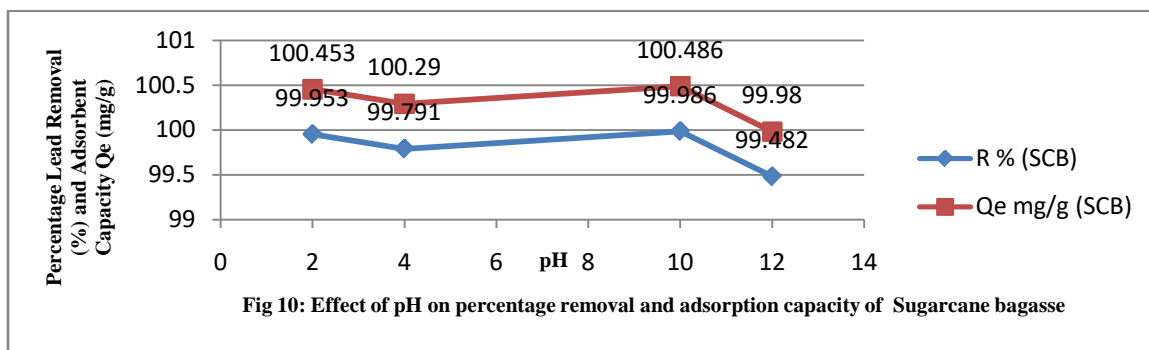
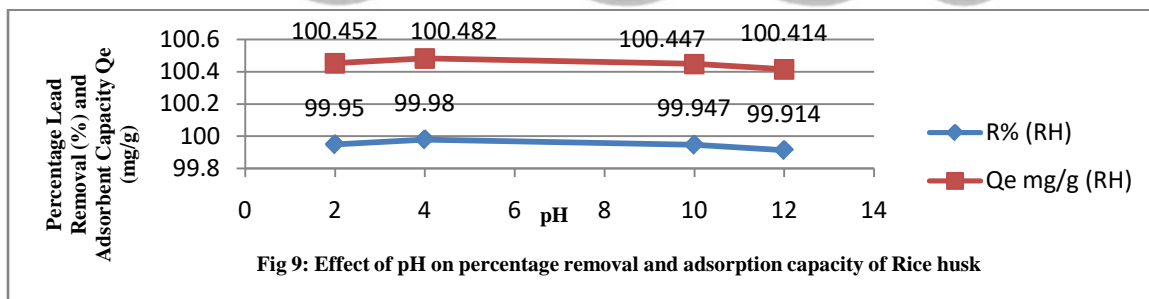
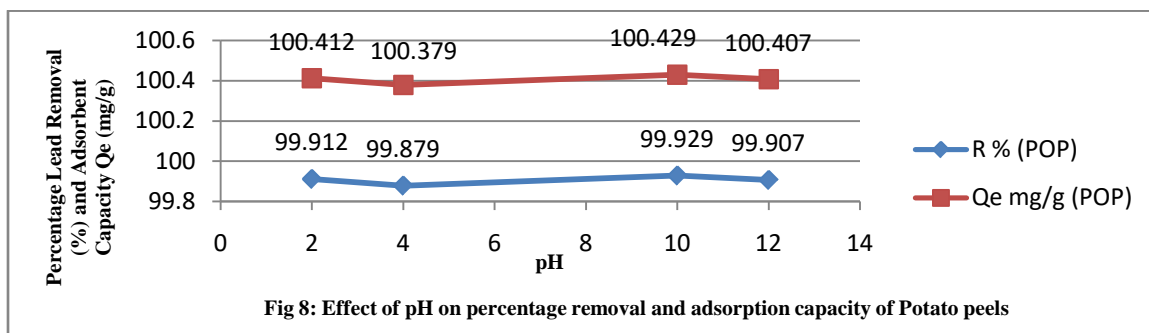
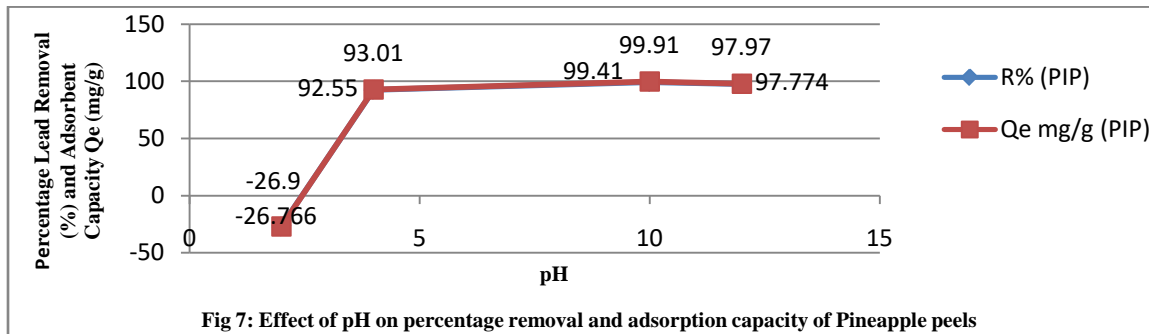
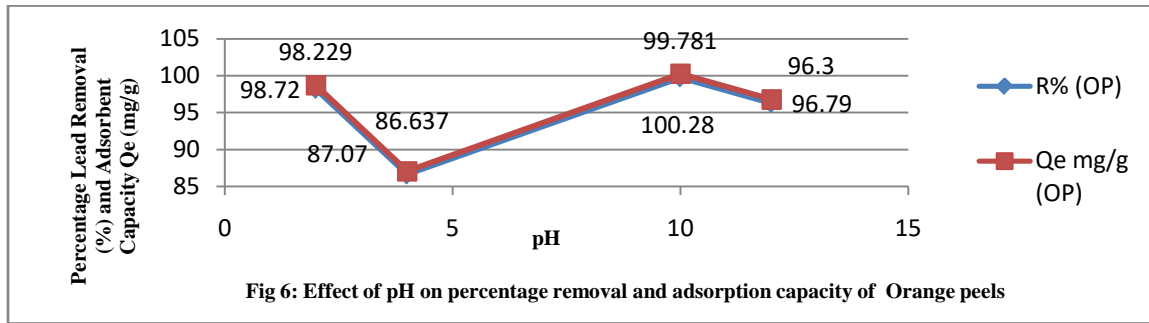


Fig 5: Effect of pH on percentage removal and adsorption capacity of Groundnut shell



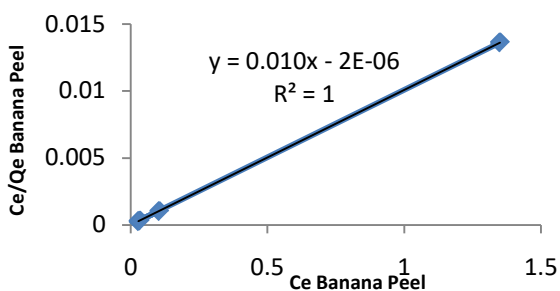


Fig 11: Langmuir Isotherm for adsorption of Lead on Banana peel

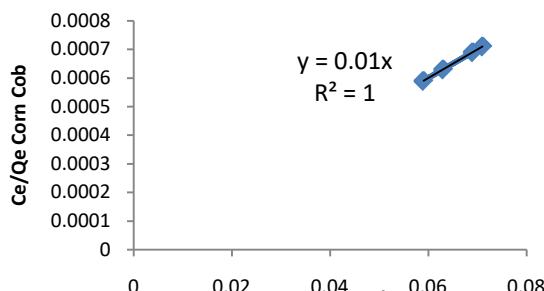


Fig 12: Langmuir Isotherm for adsorption of Lead on Corn cob

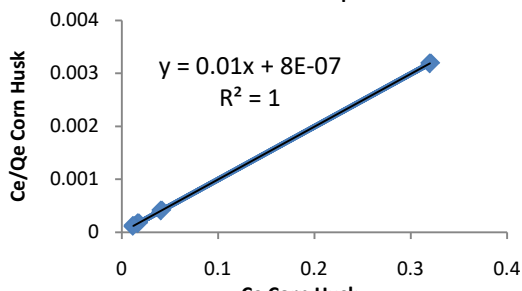


Fig 13: Specific sorption capacity versus equilibrium concentration for Corn Cob

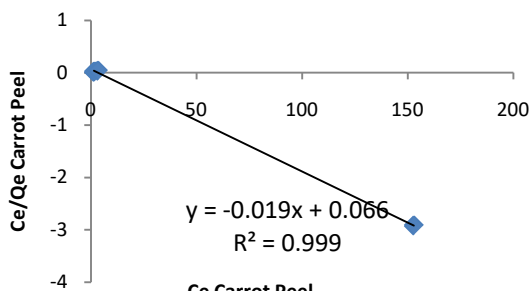


Fig 14: Specific sorption capacity versus equilibrium concentration for Carrot Peel

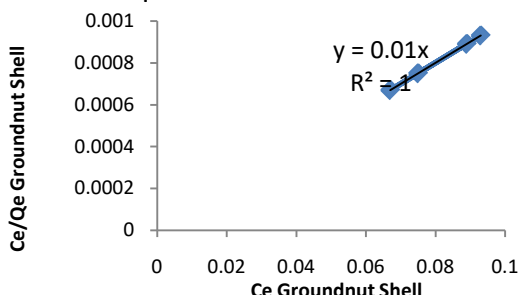


Fig 15: Langmuir Isotherm for adsorption of Lead on Groundnut shell

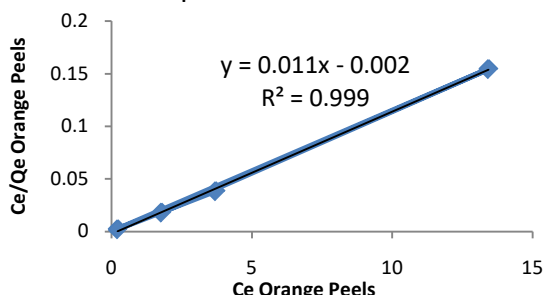


Fig 16: Langmuir Isotherm for adsorption of Lead on Orange peels

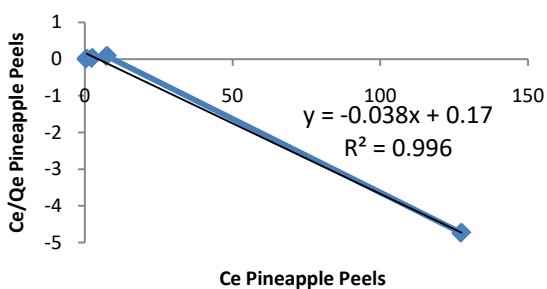


Fig 17: Langmuir Isotherm for adsorption of Lead on Pineapple peels

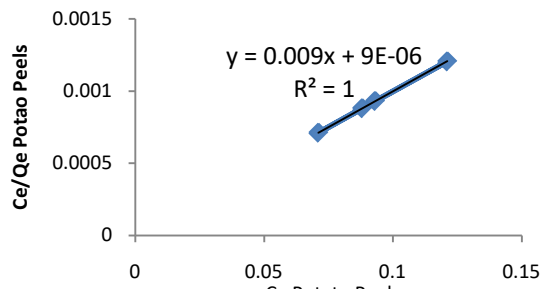


Fig 18: Langmuir Isotherm for adsorption of Lead on Potato peels

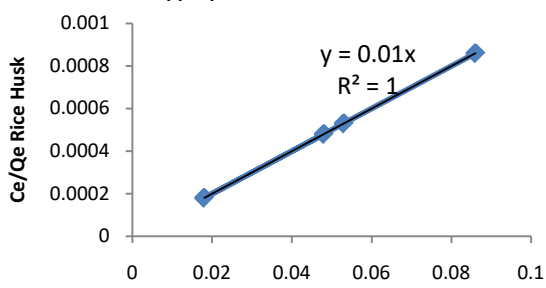


Fig 19: Langmuir Isotherm for adsorption of Lead on Rice husk

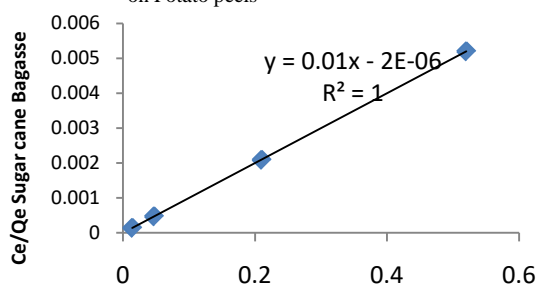


Fig 20: Langmuir Isotherm for adsorption of Lead on Sugarcane bagasse

DISCUSSION

Activation of biosorbents, Percentage lead removal (R%) and adsorption capacity (Qe)

This study recorded high values of R% ranging from 98.525% pH 4 (carrot peels) to 99.988 % pH 10 (corn husk) and high values of Qe ranging from 99.02 mg/g (carrot peels) to 100.488 mg/g (corn husk). The differences observed in the R% and Qe values may be attributed to the different surface areas of the biosorbents according to [3]. The percentage removal of lead as cited in Jain, [12] reported that orange peels removed 96% lead at optimum pH 6 and Banana peels removed 74% lead at optimum pH 7.

El-Azazy *et al.* [2] reported the % removal of Pb(II) recorded 77.34% using potato peels waste. They contributed that the superior capability of burnt potato peels is as a result of its surface characterization influenced by the thermal activation which they said is essential for enhancing the porosity and hence the adsorption process. They also contributed that burning process of agricultural wastes, results in increasing their carbon content, due to the destruction of cellulose and organic materials. The formation of carbonyl, ether, ketones and carboxylic functional groups and the disappearance of hydroxyl group, this they added also would explain the improved capability of burnt potato peels to remove heavy metals. They showed that the percentage of carbon in burnt potato peels, is 74.76%. On the other hand, oxygen content decreased to 16.65% in burnt potato peels. This was because most oxygen functional groups were eliminated by burning of potato peels and converted to mainly carbon which is responsible for the high adsorption efficiency for Pb(II). They contributed that the porosity of prepared adsorbent is an important variable that impacts the performance of the adsorption process. They added that pore size distribution, is another important feature that exemplifies the physical heterogeneity of the burnt agro-wastes adsorbents. The result of our study is in line with their conclusions, the activation temperature at 400°C of the ten agro-wastes, improved the percentage lead removal (98.525% carrot peels to 99.988 % corn husk) and adsorption capacity 207.65 mg/g carrot peels, 158.064 mg/g pineapple peels, 111.11 mg/g potato peels and 100 mg/g banana peels. The activation in KOH equally improved the R% and Qe.

Ahmad *et al.* [13] recorded maximum lead removal of 28.55 mg/g at pH 4 using pineapple peels. They observed that the biosorption of metal ions onto the pineapple fruit peel may be due to the electrostatic attraction/chelation between positively charged Pb(II) and negatively charged carboxylate ($-\text{COO}^-$), and hydroxyl (OH^-) ligands as the carboxylic/hydroxyl groups are deprotonated at pH over 3–4. Their analysis is in line with our study, the treatment of pineapple peels with the reagents and dried in furnace improved the adsorption potential of the pineapple. Their result however is in the same range (28.55 mg/g) to the maximum adsorption capacity recorded for Langmuir isotherm (26.32 mg/g) in this current study.

Ahile *et al.* [14] in their study on removal of Pb^{2+} using rice husk as an adsorbent recorded percentage removal efficiency of 92.44 %. The researchers equally subjected the rice husk to high temperature drying and chemical activation to yield biosorbent with the high % lead removal 99.44%. We also recorded very high % lead removal of 99.98% using rice husk. Kyzas *et al.* [15] prepared activated carbon of potato peels this method recorded maximum adsorption capacity of 171 mg/g for Pb^{2+} . We also recorded maximum Pb^{2+} adsorption of 111.11 mg/g in this current study using potato peels. Agwaramgbo *et al.* [14] worked on lead removal with corn and palm nut husks which percent lead removed was 92%. In this current study we recorded 99.988% of Pb^{2+} removal using corn husk. Salihi *et al.* [17] removed lead using sugarcane bagasse which recorded a maximum uptake capacity of 23.4 mg/g at optimum pH 5.0 while in this current study we used 100 mg/L Pb^{2+} solution and 100 g sugarcane bagasse loading to record adsorption capacity of 100.486 mg/g at pH 10.

Effect of pH on percentage metal removal and adsorption capacity

The study showed these five biosorbents (banana peels, corn husk, groundnut shells, orange peels, and potato peels) recorded a sharp drop in R% and Qe at pH 4 whereas corn cob, carrot peels, pineapple peels, rice husk and sugarcane bagasse recorded the reverse, sharp increase in R% and Qe, at pH 4. There was a decrease in the R% and Qe at high alkaline pH 12 for all the biosorbents studied. This observation could be because all the binding sites on the biosorbents have been occupied by the lead ions at pH 4 and pH 10 with no Pb^{2+} left in solution for further uptake. The biosorbents all recorded optimum pH of 10 for R% and Qe, with the exceptions of Rice husk and Carrot peels which showed optimum pH of 4 for R% and Qe. The reason could be that between slightly acidic pH 4 and high alkaline pH 10, the H^+ ions concentration is less available for competition with the Pb^{2+} ions in solution, and as a result more of the Pb^{2+} ions were adsorbed onto the activated biosorbents used in this study. The result of this current study is in agreement with the findings of Agbozu and Emoruwa, [18] who implied that the susceptibility of the system pH changes may be attributed to ions in solutions and the adsorbent used. They also inferred that the lower or acidic the pH the more H^+ ions competing with the metal ions for adsorption sites thus reducing their adsorption. They also added that the higher or alkaline pH, the less the H^+ ions competing with metal ions for adsorption sites, thus increasing their adsorption. The decrease in percentage metal removal with increased pH, according to [19] may be due to the decrease in electrostatic force of attraction between the sorbent and the sorbate ion. They added that at lower pH ranges due to high electrostatic force of attraction the percentage metal removal is high. The result of this study is in agreement with their findings for all the sorbates used, with the exception of pineapple peels and carrot peels, that recorded low percentage metal removal and adsorption capacity at pH 2. According to [19] at very low pH values the surface of the sorbents would be surrounded by hydronium ions, H_3O^+ (Oxonium ion) which enhances metal interaction with the binding sites of the adsorbent by greater attractive forces. Ekpete *et al.* [19] also added that the decrease in adsorption at high pH values may be due to the competitiveness of Oxyanion of the metal and OH^- in the bulk. The results of our study is in line with their findings, as the pH

increased, the overall surface charge on the adsorbents became negative with more OH⁻ ions, and percentage metal removal and adsorption capacity, decreased. Ekpete *et al.* [19] concluded that a sharp decrease from pH 3 to pH 8 may be due to occupation of the adsorption sites by anionic species (OH⁻) which retards the approach of metals ions further towards the sorbent surface. According to [14] the adsorption of lead using rice husk was found to strongly depend on pH of the solution. It was found that the optimum pH for Pb²⁺ ions adsorption was about 10, an alkaline pH. At lower pH, there was an excessive protonation of the active sites at rice husk surface and which often prevents the formation of links between Pb²⁺ ions and the active site. At moderate pH values of between 6-8, linked H⁺ is released from the active sites on the adsorbent, therefore the adsorbed amount of Pb ions increases.

Isothermal studies

Bibaj *et al.* [3] carried out a detailed equilibrium analysis using Langmuir isotherm, Freundlich isotherm and Langmuir-Freundlich isotherm for the fitting of equilibrium data. The adsorption of their test metal on to the activated banana peels fitted the three isotherm theories analyzed. According to [15] commercial activated carbons have high adsorption capacities (>200 mg/g) but with demanding synthesis steps and high cost; adsorption materials of medium adsorption (50-200 mg/g) but with simple synthesis routes and really low costs is the category of these activated carbon from waste materials. This current study is in line with the second category of activated carbons with adsorption capacity between 50 mg/g and 200 mg/g. The Freundlich isotherm in our study however recorded the highest adsorption capacity of 207.65 mg/L using the carrot peels as opposed to Langmuir theorem that recorded 52.63 mg/g for the same carrot peels. The Langmuir adsorption isotherm have been used by many researchers [8,12,20,21,22] for banana peels. The work cited in [12] for banana peels at pH 3, showed maximum adsorption capacity of 0.02 mol/g for Pb²⁺. Mohammad *et al.* [23] studied the use of orange peels to remove Pb²⁺ from aqueous solutions, this followed Langmuir and Freundlich isotherms. Arunakumara *et al.* [7] reported that banana peels is capable of adsorbing 7.97 mg/g of Pb²⁺ from aqueous solution also they reported maximum lead removal of 91.74 mg/g for Banana peels; According to [14] the adsorption of lead using rice husk was found to be the best fit on the Langmuir isotherm. According to Ahmad, *et al.* [13] the equilibrium biosorption data fit better with Langmuir equation than Freundlich isotherm for lead removal using pineapple peels. According to [17] Langmuir isotherm model satisfactorily described the adsorption of Pb²⁺ onto sugarcane bagasse. The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies with no transmigration of adsorbate in the plane surface [24]. Once a site is filled, no further sorption can take place at that site. This indicates that the surface reaches a saturation point where the maximum adsorption of the surface will be achieved. The value of "n" in Freundlich isotherm according to [24] indicates the degree of nonlinearity between solution concentration and adsorption as follows: if n = 1, then adsorption is linear; if n < 1, then adsorption is a chemical process; if n > 1, then adsorption is a physical process. The situation n > 1 is most common and may be due to a distribution of surface sites or any factor that causes a decrease in adsorbent-adsorbate interaction with increasing surface density and the values of within the range of 1–10 represent good adsorption. In our current study the values of n are < 1 showed the adsorptions are chemical process on to all the biosorbents.

Separation factor R_L

The essential features of Langmuir adsorption isotherm parameter (Table 2) can be used to predict the affinity between the sorbate and sorbents using a dimensionless constant called separation factor or equilibrium parameter, which is expressed by [24]. The value of R_L = 0 indicated the type of Langmuir isotherm to be irreversible, linear R_L = 1, unfavorable R_L > 1, or favorable 0 < R_L < 1. The values between 0 and 1 indicate favorable adsorption. In our present investigation the R_L calculated (Table 2) showed values indicating favorability for lead adsorption onto BP = 0.0011 (favorable), CH = 7.96 x 10⁻⁷ (favorable), PIP = 0.043 (favorable), POP = 9.9 x 10⁻⁶ (favorable), while the others showed negative values for R_L: CP = -0.035, OP = -0.002 and SCB = -1.9 x 10⁻⁶.

Conclusion

The agricultural wastes products that are generated can be recycled to value added products like biosorbents. This method of waste recycling can reduce the indiscriminate dumping and defacing of the environment. We found out that pH affects the percentage lead removal (R%) and adsorption capacity (Q_e). The process of activation of the carbons is very important for it enhances the surface area of the biosorbents for maximum adsorption. The highest percentage lead removal adsorption capacity recorded is corn husk while the least is for carrot peels. The other biosorbents studied all recorded high R% and Q_e, this may be due to the process of synthesis. Langmuir and Freundlich isotherms were used for fitting the equilibrium data. The best fit is shown by very high values of R² recorded for Langmuir isotherm than Freundlich isotherm. In conclusion the system pH, adsorbent loading, concentration of metal ion, the surface density, the pore volume, the activation reagent and activation temperature all affect the R% metal removal efficiency and adsorption capacity, Q_e.

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