

# Studies on the Adsorption of Heavy Metals in a Paint Industry Effluent Using Activated Maize Cob

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**Abstract**—This research work on the studies of adsorption of heavy metal in an effluent from a paint industry using chemically activated maize cob as adsorbent was aimed at removal of  $Pb^{2+}$  contaminants from Lead based paint effluent. The results of production, characterization and adsorption studies showed that activated maize cob with surface area of  $1195.12 \text{ m}^2/\text{g}$  and pore volume of  $1.28 \text{ cm}^3/\text{g}$  was achieved at  $500^\circ\text{C}$  and 90ml concentration by volume of phosphoric acid and zinc chloride as activating agents. It was observed that sample  $C_3$  using activating agents concentration by volume 50 – 120 ml at  $500^\circ\text{C}$  gave the optimum value for characteristic performance in adsorption of Pb ions from effluent. Langmuir isotherm model, pseudo- first order kinetic equations were fitted with generated data. The Langmuir and pseudo- first order model fitted favourably with a correlation coefficient of 0.98 and a rate constant of  $0.00104 \text{ mgg}^{-1}\text{min}^{-1}$ .

**Keywords**—adsorption; heavy metal; effluent; maize cob; activating agent

## INTRODUCTION

The release of heavy metals into the environment through industrial effluent is a major concern worldwide and removal of such pollutants has been of great concern during the last decades. Heavy metals can pose health hazards to man and aquatic lives

if their concentrations exceed the allowable limits. Concentrations of heavy metals below these limits have potentials for long term contamination, because heavy metals are known to be accumulative within biological systems [1].

Lead, cadmium and cobalt are particularly common heavy metals found in paint industrial wastewater. Lead contamination of the environment is primarily due to anthropogenic activities making it the most ubiquitous toxic metal in the environment. Lead readily accumulates in the humus-rich surface layer of the soil due to its complexity with organic matter and it was reported to be the least mobile heavy metal in soils under reducing or non-reducing conditions. It has been the most common heavy metal contaminant in

urban soil due to atmospheric depositions from automobile emissions and industries [2]. The release of industrial wastewater to the environment causes several adverse effects. This wastewater commonly contains Cd, Pb, Cu, Ni and Co. These heavy metals are not biodegradable and their presence in stream, lakes leads to bioaccumulations in living organisms, causing health problems in animals, plants and human beings [2].

Paint industries are among these industries that discharge effluents containing heavy metals. Paint components are pigments, solvents, blotters and auxiliary additives of which heavy metals are mainly used as pigment and blotters in paints. Several methods have been developed for the decontamination of municipal, industrial and wastewaters. Among different heavy metal removal methods are chemical precipitation, membrane filtration (reverse osmosis and electrodialysis), electrolytic processes, adsorption and biological sorption. Adsorption techniques for wastewater treatment have become more popular in recent years with regard to their efficiency in the removal of pollutants, especially heavy metal ions, color, odor and organic pollutants [3]; [4]. Adsorption has advantages over other methods for remediation of heavy metals from wastewater because its design is simple; it is sludge free and can be of low capital cost. Chemical precipitation, coagulation or flocculation and ion exchange are also techniques used for removal of heavy metal, but these techniques are expensive and have some disadvantages such as incomplete metal removal, high reagent and energy requirements and generation of toxic sludges or other wastewater products. Therefore due to these problems, research efforts have been directed to the production of alternative adsorbents, especially those which have metal binding capacities and are able to remove unwanted heavy metals from contaminated water at low cost using materials like zeolite, ash, rice husk, vermin-compost, maize cob, peat, volcanic stone for adsorption of heavy metal ions [5]. For this purpose, activated carbon was developed from maize cobs in adsorbing heavy metals from an industrial paint effluent (usually contains Pb, Co, Cr, and Cu). On the other hand, the kinetics of the process will enable one

to determine the time frame as well as throw light on the mechanism of adsorption process. According to [6], the study of adsorption dynamics describes the solute uptake rate and eventually the rate controlling step.

Therefore this study plans to investigate the effect of temperature and concentration of phosphoric acid on the rate of adsorption as well as test the Langmuir and pseudo-first order kinetic models. Maize is a major staple cereal in Nigeria and therefore produces large volume of waste. The cobs can therefore be used as potential source of adsorbent for removal of  $Pb^{2+}$  from paint industrial effluents. The cob has relatively high carbon content (cellulosic matter) compared to other agricultural wastes in the production of activated carbon [7]. Since conventional methods are expensive, the need to develop cheaper methods in a developing country like Nigeria becomes imperative.

### KINETICS OF ADSORPTION

The most commonly used kinetic models are those of Freundlich and Langmuir [8]. In this work, Langmuir Model was tested and given as,

$$q = \frac{q_m K_c C}{1 + K_c C} \quad (1)$$

Where  $q_m = q$  for a complete monolayer (g adsorbate/g sorbate)

$K_a =$  a coefficient ( $kg/m^3$  or  $g/cm^3$ )

Taking reciprocal and rearranging equation (1) gives:

$$\frac{1}{q} = \frac{1}{q_m} + \frac{1}{K_c q_m C} \quad (2)$$

A plot of  $\frac{1}{q}$  versus  $\frac{1}{C}$  gives a straight line of slope  $\frac{1}{K_c q_m}$  and an intercept of  $\frac{1}{q_m}$ . Equation (2) could be expressed in a standard format as given below:

$$\frac{C_e}{q_e} = \frac{1}{Q_0} + \frac{C_e}{Q_0} \quad (3)$$

Where  $C_e$  is the equilibrium concentration of sorbate ( $mg/liter$  or  $ppm$  or  $g/cm^3$  or  $mol/m^3$ ),  $q_e$  is the amount adsorbed at equilibrium ( $mgg^{-1}$ ) while  $Q_0$  and  $b$  are the Langmuir constants related to capacity ( $mgg^{-1}$ ) and energy respectively. A plot of  $\frac{C_e}{q_e}$  Versus  $C_e$  gives a straight line of slope  $\frac{1}{Q_0}$  and intercept of  $\frac{1}{Q_0}$ .

However, a pseudo-first order kinetic model as recommended by [6]; [9] is given as;

$$\frac{dq_t}{dt} = K_t (q_e - q_t) \quad (4)$$

where  $q_e$  and  $q_t$  are adsorption capacity terms at equilibrium and at time  $t$  respectively ( $mg/g$ ),  $K_t$  is the rate constant. Integrating equation (4) with the boundary conditions gives;

$$\log (q_e - q_t) = \log q_e - K \frac{t}{2.303} \quad (5)$$

A plot of  $\log (q_e - q_t)$  versus  $t$  is a linear relationship from where  $K$  and  $q_e$  can be determined respectively. In a similar manner the pseudo-second order model is expressed as;

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 \quad (6)$$

where  $K_2$  is the pseudo- second order rate constant of adsorption. The linearized form of equation (6) is;

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right) t \quad (7)$$

Again, a plot of  $\frac{t}{q_t}$  versus  $t$  will give a linear relationship with  $\frac{1}{q_e}$  and  $\frac{1}{K_2 q_e^2}$  as the slope and intercept respectively.

## MATERIALS AND METHODS

### Sample collection and preparation

Corn cobs were collected from farmers at Gidan Mangoro Minna, Niger state, Nigeria. The cobs were washed with pipe- born water and sun dried for two weeks. The Corn cobs were reduced into smaller particle sizes using mortar and pestle.



Plate 1: Maize cob feedstock

### Ash Content Determination

Two grams of Maize cob were placed into a porcelain crucible and transferred into a muffle furnace (Gallenkamp SG 93/008/990) set at a temperature of  $900^\circ C$ . The furnace was left on for 1 hour, after which the crucible and content was transferred into a desiccator and allowed to cool. The crucible and content was reweighed and weight noted.  $W_0$  is the dry weight of the sample (g) and  $W_{ash}$  is the constant weight after drying (g), then the % ash is given by [10].

$$Ash = \frac{100 W_{ash}}{W_0} \quad (8)$$

### Moisture Content Determination

Two grams of Maize cob was also weighed and dried in an oven continuously. The drying was constantly re-weighed at 10 min time interval until a constant weight was obtained. The ratio of the change in weight to the original weight expressed in percentage gives the moisture content [11].

$$MC = \frac{W_0 - W_f}{W_0} \quad (9)$$

### Volatile Content Determination

Again two grams of the carbon sample were heated for about 850 °C for 10 min in a muffle furnace. The crucible and its content was retrieved and cooled in a desiccator. The difference in weight was recorded and the volatile content (VC) determined [11].

$$VC = \frac{W_0 - W_f}{W_0} \% \quad (10)$$

where,  $W_f$  = difference in weight (g)

$W_0$  = oven dry weight of 2 g of carbon.

### Carbon Yield Determination

The carbon yield of the dried weight  $W_0$  of carbon was determined according to [11].

$$Y = \frac{100W_f}{W_0} \quad (11)$$

where,  $W_f$  = weight of carbon retrieved from furnace (g).

$W_0$  = dried weight of the carbon sample (g).

### Fixed Carbon

By assuming that the sulphur content was negligible in all cases, the fixed carbon content (FC) is given by [11] as;

$$FC = \frac{Y - MC - VC - Aash}{Y} \% \quad (12)$$

### Preparation of 1.0 M phosphoric acid and zinc chloride solutions

100 ml of concentrated phosphoric acid was measured using a 100 ml measuring cylinder and introduced into 1000 ml (1L) measuring cylinder. This was topped to the 1000 ml mark with distilled water.

### Doping of feedstock

Weights of 30g, 50 g, 60 g and 80 g of the feedstock (corn cob) and 1M solution of phosphoric acid was carefully introduced separately into a 500ml beaker containing 1M solution  $H_3PO_4$  in the ratio 1:1.5, after which the content was stirred vigorously using a glass rod to give a homogeneous slurry mixture. The mixture was allowed to stand for 48 hours. After this time interval the feedstock is termed impregnated [12].

### Carbonization of Corn cobs

Again weights of 30 g, 50 g, 60 g and 80 g of the feedstock were mixed with varying amounts of phosphoric acid solution (concentration by percentage volume) ranging from 50 ml, 70 ml, 90 ml and 120 ml in the weight ratio of 1:1.5 in 500 ml beakers. The excess acid solution was removed by drying at 150 °C and the mixture transferred into heating mugs and placed in the muffle furnace. The samples were then carbonized for 60 min at temperatures of 400, 450, 500 and 550 °C respectively. After carbonization, the carbon was washed thoroughly to a pH of 7 to remove the excess acid. The activated carbon was however mixed with varying amounts of  $ZnCl_2$  solution in the

ratio 1:1, the slurry was then heated to temperature of 650 °C for 60mins to form the activated carbon with zinc chloride solution as activating agent. The final product was thoroughly washed with distilled water to remove the un-reacted  $ZnCl_2$ . The carbon contents of the activated carbon were characterized to check performance of the carbon product.

### Characterization of activated maize cob

#### Determination of pH Level

The activated carbon produced was washed several times with tap water firstly, then with distilled water and the pH of aqueous extract was determined using the pH meter until a pH of 7 was achieved.

#### Determination of Bulk Density

The density of activated carbon was found by filling activated carbon into a 10ml measuring cylinder and then weighed using the digital weighing balance. The weight noted as the bulk weight was then divided by the volume of the cylinder used. It provides the method for determining the packed density of a bed of activated carbon. It is calculated thus according to [13].

$$\text{Bulk density (B. d)} = \frac{W_{c_{actv}}}{100} \left( \frac{g}{ml} \right) \quad (13)$$

#### Determination of pore (void) volume

Two grams of the activated carbon was immersed in a 30 ml distilled water, whose weight was noted and boiled for 25 minutes to displace the air contained in the pores after which the sample was retrieved from the water and re-weighed. The sample was superficially dried on a filter paper. The increase in weight per unit mass of the sample divided by the density of water gave the pore volume [14].

#### Porosity

The porosity or void fraction  $P_o$  of the porous activated carbon was calculated based on the following equation.

$$P_o = P_b V_v \quad (14)$$

where,  $P_b$  is the bulk density,  $V_v$  is the void volume.

#### Determination of the surface area

Standard solution of methylene blue (MB) was prepared by dissolving 200 g of methylene blue in 250 ml of distilled water to produce 0.0025 M concentration of the methylene blue. 0.5 g of the activated carbon was introduced into the standard solutions and allowed for 12 hrs after which the activated carbon was filtered from the solution and the concentration was determined using a colorimeter. The difference between the initial and the final concentration of the equilibrium solutions gave the number of molecules ( $N_g$ ) which is the amount of methylene blue adsorbed onto the monolayer of the activated carbon. Thus, the expression used by [15] is;

$$\text{Surface area} = (3175.0305) \times N_g \quad (15)$$

Where, Ng is the number of molecules absorbed on the monolayer of activated carbon.

### Digestion of the paint effluent

Two mills of the paint effluent (glossy Lead based paint) was weighed and introduced into 50 ml beakers. 20 ml of digestion mixture (hypochloric acid mixture) was introduced into the beakers. The sample was digested for 1 hour at 175 °C and then filtered into a 100 ml standard volumetric flask with the Whatman No.1 qualitative circles 110mm filter paper. The filtrate was made up to the mark with distilled water and labeled accordingly.

### Determination of the adsorption capacity using the atomic adsorption spectrophotometer

Half a gram of prepared activated carbon was carefully weighed using the weighing balance and was added to 50 ml of the paint effluent already digested for the heavy metals to dissolve into solution in beakers. The mixture was shaken and allowed to stand for 24 hours, and then filtered using the Whatman filter papers.

Since the metal to be analyzed has a characteristic wave length that will be used to determine the adsorption of the metals, the sample was introduced into the flame; the metal present in the sample absorbed some of the light, thereby reducing the intensity of the light. The computerized equipment therefore converts the intensity of light into an absorbance term which is directly proportional to the concentration of the metal ions present in the sample determined from the standard calibration curve for various metals [12].

## RESULTS AND DISCUSSION

### Proximate Analysis

The Proximate Analysis result of maize cob determines the distribution of its elemental contents. It may be noted that the volatile matter present in maize cob, contributes maximally to its contents. The moisture content present in the sample can also be considered as water vapor when it is heated to high temperatures. Hence, about 34.30 % of the contents tend to leave the sample when heated, of which 29.30 % is volatile matter and 6.00 % is moisture content. The values from table 1 indicate that the ash content of the sample is 29.30 % and also the fixed carbon content of the sample is 78.30 %. This gives an overview about the properties and components of the precursor.

**Table 1:** Proximate Analysis of the Maize Cob

| Parameter        | Value % |
|------------------|---------|
| Volatile content | 29.30   |
| Moisture content | 6.00    |
| Ash content      | 29.30   |
| Carbon yield     | 29.24   |
| Fixed carbon     | 78.30   |

### Characterization

Tables 2 – 5 are the results obtained on characterization of the carbon produced from maize cob.

**Table 2:** Carbonization at 400°C for 1 Hr Holding Time with H<sub>3</sub>PO<sub>4</sub> by Volume, % Vol.

| Sample Conc. of Acid (% vol)      | A1 50ml | A2 70ml | A3 90ml | A4 120ml |
|-----------------------------------|---------|---------|---------|----------|
| Pore volume (cm <sup>3</sup> /g)  | 0.71    | 0.68    | 0.84    | 0.98     |
| Bulk density (g/cm <sup>3</sup> ) | 0.317   | 0.310   | 0.315   | 0.319    |
| Surface area (m <sup>2</sup> /g)  | 910.0   | 920.9   | 875.2   | 894.5    |
| Porosity                          | 0.230   | 0.210   | 0.260   | 0.31     |
| Particle size (µm)                | 0.70    | 0.70    | 0.70    | 0.70     |

**Table 3:** Carbonization at 450°C for 1 Hr Holding Time with H<sub>3</sub>PO<sub>4</sub> by Volume, % Vol.

| Sample Conc. of acid (% vol)      | B1 50ml | B2 70ml | B3 90ml | B4 120ml |
|-----------------------------------|---------|---------|---------|----------|
| Pore volume (cm <sup>3</sup> /g)  | 0.78    | 0.82    | 1.02    | 1.00     |
| Bulk density (g/cm <sup>3</sup> ) | 0.32    | 0.35    | 0.32    | 0.30     |
| Surface area (m <sup>2</sup> /g)  | 756.0   | 710.0   | 894.1   | 960.4    |
| Porosity                          | 0.250   | 0.270   | 0.320   | 0.302    |
| Particle size (µm)                | 0.70    | 0.70    | 0.70    | 0.7      |

**Table 4:** Carbonization at 500°C for 1 Hr Holding Time with H<sub>3</sub>PO<sub>4</sub> by Volume, % Vol.

| Sample Conc. of acid (% vol)      | C1 50ml | C2 70ml | C3 90ml | C4 120ml |
|-----------------------------------|---------|---------|---------|----------|
| Pore volume (cm <sup>3</sup> /g)  | 1.102   | 1.140   | 1.280   | 1.230    |
| Bulk density (g/cm <sup>3</sup> ) | 0.430   | 0.410   | 0.412   | 0.931    |
| Surface area (m <sup>2</sup> /g)  | 987.3   | 1083.0  | 1195.1  | 1143.5   |
| Porosity                          | 0.480   | 0.470   | 0.530   | 0.480    |
| Particle size (µm)                | 0.70    | 0.70    | 0.70    | 0.7      |



**Table 5:** Carbonization at 550°C for 1 Hr Holding Time with H<sub>3</sub>PO<sub>4</sub> by Volume, % Vol.

| Sample Conc. of acid (% vol)      | C1 50ml | C2 70ml | C3 90ml | C4 120ml |
|-----------------------------------|---------|---------|---------|----------|
| Pore volume (cm <sup>3</sup> /g)  | 0.810   | 0.951   | 1.120   | 1.020    |
| Bulk density (g/cm <sup>3</sup> ) | 0.319   | 0.326   | 0.334   | 0.339    |
| Surface area (m <sup>2</sup> /g)  | 602.31  | 896.2   | 1073.4  | 987.1    |
| Porosity                          | 0.27    | 0.31    | 0.37    | 0.35     |
| Particle size (µm)                | 0.70    | 0.70    | 0.70    | 0.7      |

### Pore Volume

From tables 2 – 5 it is observed that as the temperature of carbonization increased from 400 – 550°C, the pore volume increased and sharply reduces from 0.78 – 0.68 cm<sup>3</sup>/g as the concentration of acid increases. These values are within the ASTM range of 0.68 – 2.80 cm<sup>3</sup>/g as reported by Ekwuoha (2010) and Shah (2007). Concentration of H<sub>3</sub>PO<sub>4</sub> and ZnCl<sub>2</sub> chloride solutions with temperature are critical parameters that control the final pore in the carbon. However, activation with zinc chloride at 650 °C gave the best results with pore volume of 1.28 cm<sup>3</sup>/g. The primary reason for this observation is that the higher concentration leads to a better phosphorylation of the lignin and cellulose molecules present in the cobs as reported by [17]. Temperature higher than 500 °C causes the cross linkages between the phosphate esters which make them unstable. As a result, a drop is noticed in pore volume [17].

### Bulk Density

This is a useful property that defines the materials present in a given volume. Results in Tables 2 – 5 showed that the activated carbon produced based on temperature gave lower values from 0.317 – 0.311 cm<sup>3</sup>. Also from each table, as concentration by % vol. increased from 50 ml – 120 ml acid at a given temperature of carbonization, an increase in bulk density was recorded with the best value at 500°C. The result conforms to the standard of range 0.3 – 0.4 g/cm<sup>3</sup> as obtained by [14]. Therefore carbonization at 500 °C with 90 ml concentration of acid and zinc chloride gave optimum results and suitable capacity for adsorption.

### Porosity

At lower temperatures, the values of porosity were small but increased with increase in temperature from 0.21 – 0.53 while the effect of concentration of acid on porosity follows a similar trend. These values were seen to be lower than the values obtained by [16] and [14].

The increase in porosity by increase in concentration of activating acid was as a result of the

matrix expansion in the structure of the carbon [18]. However, this reduction from standard value (0.42-2.20) could be as a result of effect of parameters such as soaking time and rate of heating that were not studied. It should be noted that porosity is an indication of the atomic arrangement in adsorbent and the space between each atom in the adsorbent [19].

### Surface Area

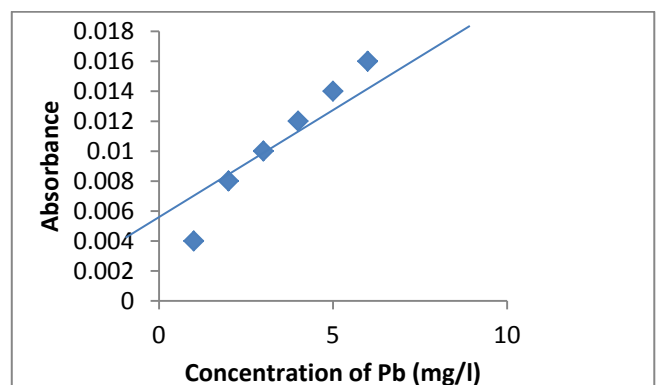
The final surface area in the carbon can be conditioned by the final heat treatment, temperature and % volume of acid used as shown from Tables 2 – 5. Surface area of 1195.12 m<sup>2</sup>/g was achieved at 500°C with 90 ml % volume concentration of acid and zinc chloride ratio at 1:1. On the other hand, an increase in temperature causes reduction in surface area. Upon treatment with zinc chloride, the surface area increased and also the pore volume. An area of 1195.12 m<sup>2</sup>/g was obtained with pore volume of 1.28 cm<sup>3</sup>/g. This result conforms with the standard of range

500 – 1500 m<sup>2</sup>/g reported by [14]. Similar values were obtained by [12] on Nano-porous carbon from corn cobs. It is of interest that these activating agents produced activated carbons of high surface areas and pore volume.

The reason for drop in surface area may be as a result of breakage of the cross linkages and phosphate esters, making the char or carbon less stable and increasing the loss of carbon in the form of CO, CO<sub>2</sub>, CH<sub>4</sub> gases. However zinc chloride improved the matrix of the carbon and the variation in concentration of acid has a stable linkage of phosphate ester and the aromatization of the aliphatic chains containing phosphate.

### Adsorption Capacity

The adsorption capacity studies were carried out using spectrophotometry and the absorbance readings showed proportionality to the concentration of the adsorbate which is in accordance with the Lambert- Beer law.



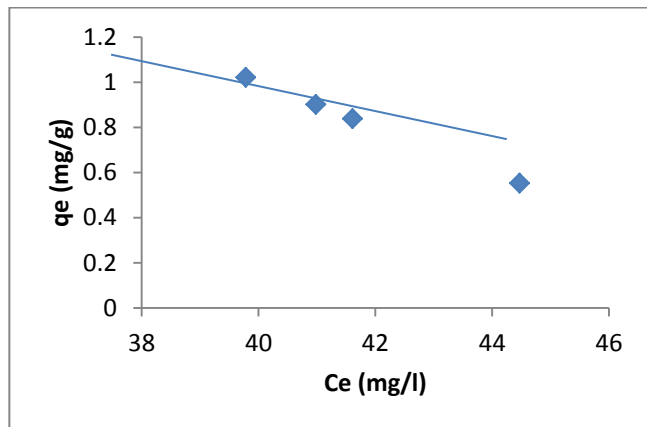
**Fig.1:** Standard Calibration Curve for Pb<sup>2+</sup>

Figure 1 shows the value of absorbance and standard calibration plot for Pb<sup>2+</sup>. From the plot, the equilibrium concentration were obtained with high amount of adsorption at 24 hours which gave 4.866

mg/g. the equilibrium concentration obtained was 1.34 mg/l from initial concentration of 50 mg/l.

### Equilibrium Studies

The amount of adsorbate ranged from 0.553 mg/g – 1.128 mg/g at 30 to 150 mins with equilibrium concentration between 39.78 mg/l and 44.47 mg/l respectively. Therefore, at 500 °C activation temperature and 90 ml % vol. of H<sub>2</sub>PO<sub>4</sub> and ZnCl<sub>2</sub> ratio of 1:1, the activated carbon produced has optimum adsorptive capacity. The results showed a rapid uptake of adsorbate molecules onto the surface of the adsorbent at the first 30 min, and then a slower uptake through to 120 min. The reason for this behaviour is that the adsorptive site becomes loaded as molecules adhere to the surface of the carbon structure. The values however greatly depend on the equilibrium concentration of the effluent with the adsorbent [20].

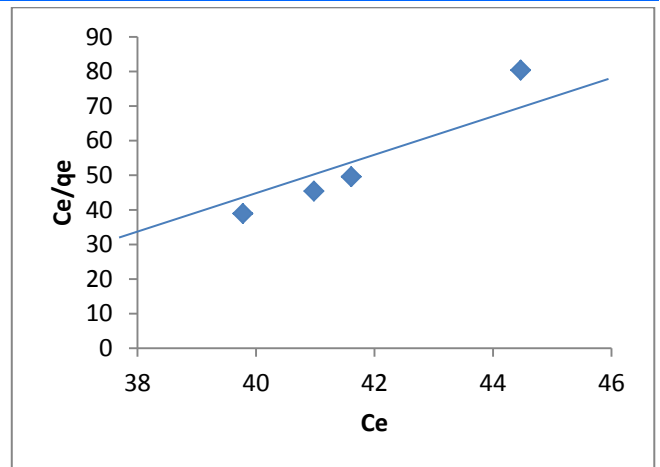


**Fig.2:** Equilibrium Curve for Pb<sup>2+</sup> Using Optimum Value Obtained

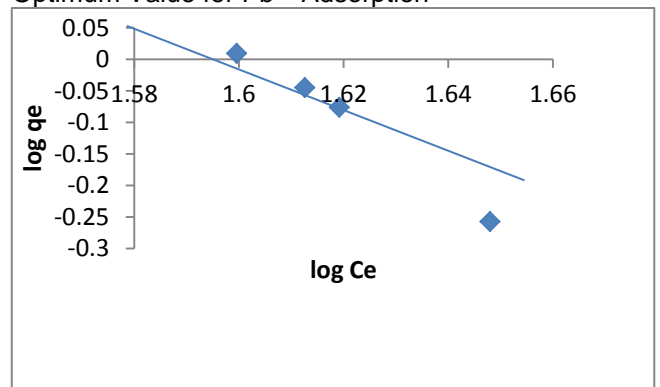
### Langmuir and Freundlich isotherms

The experimental data were fitted into Langmuir and Freundlich isotherm and represented in figures 3 and 4. The slope is the constant related to the energy of adsorption (l/mg) while the intercept K<sub>f</sub> another constant related to the overall solute adsorptivity (l/g) [21] and their values were obtained by a plot of Ce/qe versus Ce which are 9.145 l/g, 24.95 l/mg and -5.62, 0.051 for Langmuir and Freundlich plots respectively.

The correlation coefficient which is a dimensionless separation factor R<sub>L</sub> gave 0.98 and n < 1 for Freundlich model. The Langmuir plot fitted favorably well while on the other hand, the Freundlich plot did not fit favorably well with the isotherms because the value of n obtained from slope is less than unity. For Freundlich isotherm, a value of n > 1 represents a favorable condition following the works of Mckay and Ho (1998).

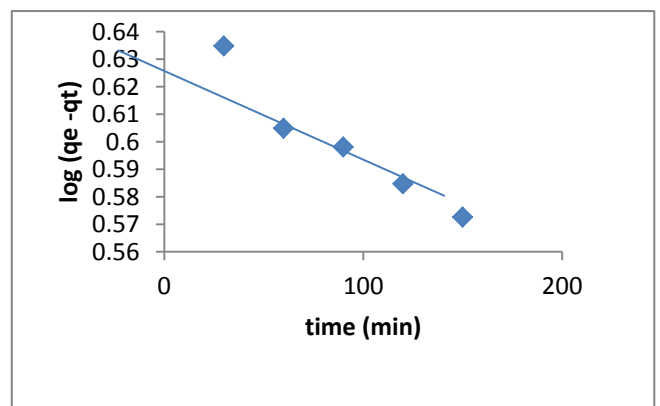


**Fig.3:** Langmuir Plot for Activated Carbon Using Optimum Value for Pb<sup>2+</sup> Adsorption

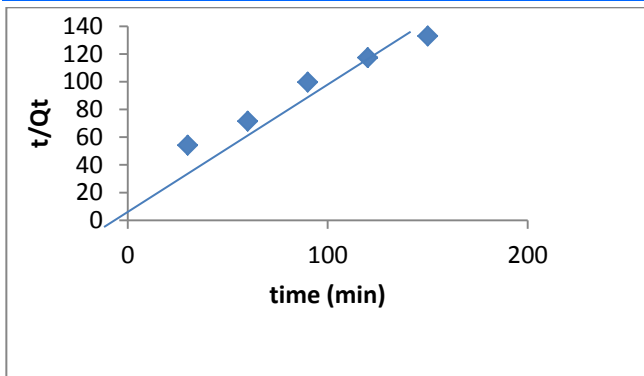


**Fig.4:** Freundlich Plot for Activated Carbon Using Optimum Value for Pb<sup>2+</sup> Adsorption Kinetic Studies

A pseudo-first order rate constant, k<sub>1</sub> and equilibrium uptake Q<sub>e</sub> were determined from the pseudo-first order plot of log (Q<sub>e</sub> – Q<sub>t</sub>) verses time figures 5 ad 6. The slope and intercept were -0.00048 and 0.642 respectively, while for the pseudo-second order kinetic model they were 0.678 and 30.12 respectively. From this finding, the pseudo-first order kinetic model favored the adsorption process with a regression correlation (r<sup>2</sup>) of 0.942 while the pseudo-second order kinetic regression gave 0.91. The correlation coefficient using pseudo-first order model is more than that of the second order model, therefore the adsorption of Pb<sup>2+</sup> ions is not suitable using the pseudo-second order plot.



**Fig.5:** Pseudo First Order Kinetic Adsorption Model from Optimum Value Obtained



**Fig 6:** Pseudo Second Order Kinetic Model for  $Pb^{2+}$  Adsorption from Optimum Value Obtained

On calculating the standard deviations, it was seen that the first order kinetic model was better than the second order model with values of 0.0065 and 0.073 respectively. Therefore the adsorption and kinetics of Pb ions could be well approximated adequately by the first order rather than the second order model.

### CONCLUSION

The carbon from corn cob is an effective adsorbent for removing heavy metals such as  $Pb^{2+}$  from paint effluent. However, from the above study, it can be concluded that activated carbon with pore volume of  $1.28 \text{ cm}^3/\text{g}$  and surface area of  $1195.12 \text{ m}^2/\text{g}$  can be produced from corn cobs. For phosphoric acid /  $ZnCl_2$  activation it is advantageous to soak the corn cobs at lower temperature because of the soft nature of the precursor. Also temperature of activation of  $450 - 500 \text{ }^\circ\text{C}$  and an acid concentration by volume of 70ml and 90ml is appropriate for getting high pore volume and surface area. In which case  $500 \text{ }^\circ\text{C}$  and 90 ml acid concentration gave optimum values.

The adsorptive capacity of the developed carbon depends on the activation process which has impacts on pore size, pore volume and surface area. An adsorption capacity of  $4.866 \text{ mg/g}$  was achieved with an acid concentration of  $50 \text{ mg/l}$ . From the isotherm plot, it was observed that Langmuir plot fitted the generated data with  $R_L$  of 0.98. A pseudo-first order kinetic model with a correction factor  $r^2$  of 0.942, and a rate constant of  $0.00104 \text{ mg g}^{-1} \text{ min}^{-1}$  and a standard deviation of 0.0065 were achieved as in contrast to second order model of 0.073. Therefore, a pseudo-first kinetic model is preferred to pseudo-second model for the kinetics of sorption for  $Pb^{2+}$  adsorption. The carbon with higher pore volume and surface area was found to be more effective in removing these heavy metal ions.

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