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***RESEARCH ARTICLE***

**ADSORPTION OF AMMONIA ONTO ACTIVATED CARBON PREPARED FROM RICE STRAW.**

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***Key words:-***
Adsorption isotherm; ammonia ; rice straw; modeling.

***Abstract***

Many techniques were proposed for removal of ammonia as hazardous pollutant. Adsorption of ammonia from aqueous solutions onto activated carbon (prepared from rice straw as agricultural waste by calcination then activation with sodium hydroxide) was studied in batch reactor. Comparison of linear least-squares and trial-and-error non-linear methods of widely used isotherms (Langmuir, Freundlich, and Redlich-Peterson) was examined.

Results manifest that adsorption rate increases with temperature for calcination and activation. Maximum adsorption capacity of prepared activated carbon is96.4 $mg.g^{-1}$. Langmuir and Freundlich models provide a good fitting of data, with $R^2$ range 0.7:0.98.Non-linear Freundlich model is the best representation.



## Introduction:-

Different governments adopted new regulations in order to control pollutant emissions. Among them, ammonia is considered an important health hazard because it is poisonous if inhaled in great quantities (breathing levels above 50-100 ppm) while it can cause eyes, throat and nose irritation in lesser concentrations. Actual ammonia emissions are generated mainly from the fertilizer manufacture industry, coke manufacture, fossil fuel combustion, livestock and poultry management, and refrigeration methods. Among all these sources, fertilizers production accounts for about 90%of total ammonia emissions (Gonçalves et al.,2011).

Many techniques have been proposed in the literature for the removal of $NH_3$ in industrial effluents. These include absorption by solution, reaction with other gases, ion exchange using polymeric resins, separation using membranes, thermal treatment, catalytic decomposition and adsorption by porous solids which are economically convenient for high concentration pollutants (Pez et al.,1988; Blonigen, et al., 2003;Blonigenet al.,2005;Yunlong et al.,2015;Jared et al., 2016 ).

Some of these techniques (e.g. thermal combustion) are they become economically unviable for diluted waste streams. For these special cases adsorption on porous solids (e.g. activated carbons, zeolites, and so on) can be an excellent approach (Huang et al.,2008; Kim, and Park,2007; Le Leuch, and Bandosz, 2007; Park and Jin,2005;Petit and Bandosz, 2009; Zawadzki et al.,2003; Bernal, et al., 1993; Bandosz and Petit,2009; Grant et al.,2012).

Among the different porous solids described in the literature, activated carbons exhibit certain advantages such as a high “apparent” surface area, a highly developed porous structure in order to adapt it for a special application, in addition to its simplicity and economy in configuration and operation.

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Ammonia removal has been also described in the literature for metal-modified (Fe, Co, Cr, Mo and W) activated carbons (Le Leuch et al.,2007; Petit, and Bandosz,2009;. Bandosz, and Petit, 2009).

Le Leuch and Bandosz at 2007 reported that activated carbons with supported metals on the surface can be used for the removal of ammonia pollution and their capacity depends on the nature of the metal deposit and its acidity.
Activated carbons usually exhibit non-polar surfaces adsorb polar compounds (e.g. $NH_3$), and the amount and the nature of the oxygen surface groups present on the carbon surface, i.e. acidic groups, are responsible for the total amount adsorbed of a basic molecule such as ammonia (Kim and Park, 2007).

Rice is the world's second largest cereal crop after wheat, however, it produces large amounts of crop residues. Only about 20% of rice straw was used for purposes such as ethanol, paper, fertilizers and fodders and the remaining amount is either removed from the field, in situ burned, piled or spread in the field, incorporated in the soil, or used as mulch for the following crop. In Egypt, burning of rice straw causes air pollution called the "Black Cloud". Rice straw is unique relative to other cereal straws in being high in silica and lignin (Emtenan et al.,2012 )

It has been reported that it is in appropriate to use the coefficient of determination of a linear regression analysis for comparing the best-fitting solution of different isotherms. As linear regression has produced very different outcomes so non-linear method may be a better way to obtain the parameters (Yuh-Shan, 2006; Xunjun,2015)

In this study, adsorption of ammonia on activated carbon (prepared from rice straw as agricultural waste) from aqueous solutions has been studied in a batch reactor and a comparison of the linear least-squares method and a trial-and-error non-linear method of three widely used isotherms (the Langmuir, Freundlich, and Redlich-Peterson) were examined.

## Materials:-

Nessler reagent, Ammonium chloride ($NH_4Cl$), Sodium hydroxide (NaOH96%) and Hydrochloric acid (HCl - 36%)were purchased from (El-Nasr pharmaceutical chemicals, co).

**Adsorbent:**
In the present work the rice straw was used as adsorbent and collected from the byproduct of rice industry.

**Adsorbate:**
The adsorbate used in this study was a synthesized solution from ammonium chloride using distilled water as a solvent to prepare different concentrations of ammonia solution ranging from 10 to 350 mg/l.

The ammonia solution was prepared by the standard Nesslerization method ("APHA; 1989).In this method we add two droplets of Rochelle salt solution until the ammonium solution becomes clear. Then 1 ml of Nessler reagent is added to the ammonium chloride solution to obtain a yellow colored ammonia solution.

**Apparatus:**
The prepared concentrations of ammonia were measured using a spectrophotometer (shimadzu, inc. Kyoto, Japan model UV-1601).
Drying furnace (Tecnomedia Italy) and a shaker (Julabolabortech GMBH-7633 steel batch/west Germany) were used.

**Experimental:-**
All experiments were carried out at room temperature (25±2$^{o}$C) unless otherwise stated in the study of thermodynamic properties of the adsorption process.

Two series of batch experiments were performed to study adsorption isotherm in agitated glass bottles of 50 ml. The first was to investigate the ammonia adsorption on rice straw from aqueous solutions at different calcination temperatures 400$^{\circ}$C and 700$^{\circ}$C compared to raw rice straw and the second used calcinated rice straw treated with sodium hydroxide at different temperatures 25,40,50,and 60$^{\circ}$C.

Preliminary experiments using fixed amounts of adsorbent (0.1 g) were added to the bottles containing adsorbate of the same concentrations, shacked in a reciprocating shaker and centrifuged to remove the adsorbent showed that such equilibrium was established within about 3h contact time (Figure (1)).

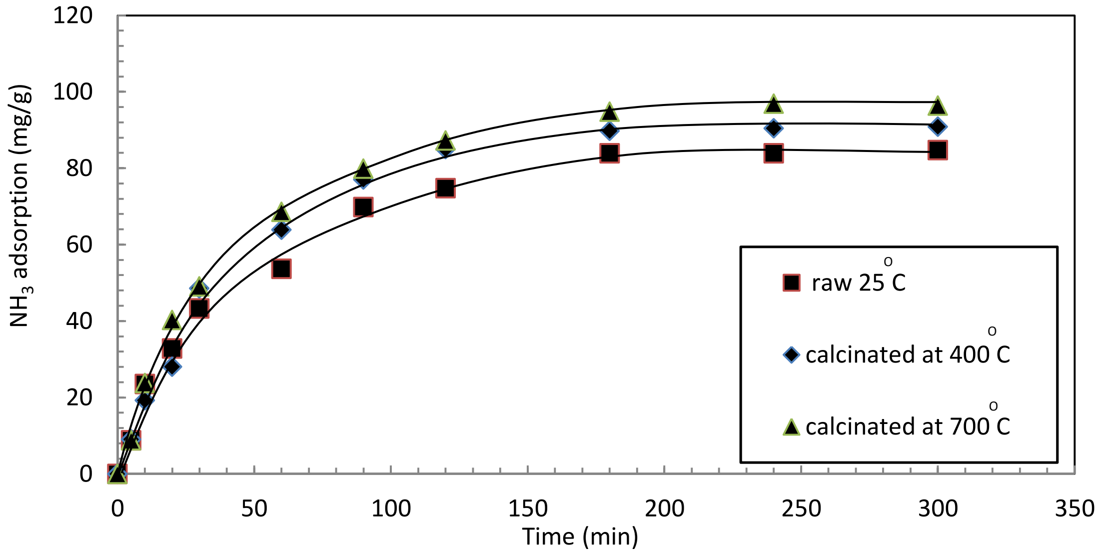


**Fig.1:-** Effect of temperature on equilibrium time for ammonia adsorption using rice straw.

Ammonia adsorption q ($mg.g^{-1}$) was calculated by using the following equation:

$$q = \frac{(C_o - C_t) x \ V \ x \ 17 \ x \ 1000}{m} \quad (1)$$

Where m is the mass of rice straw (g), $C_o$ is the initial ammonia concentration and $C_t$ is the ammonia concentration (mol. $L^{-1}$) at time t, 17 is the molecular weight of ammonia, and V is the volume of aqueous ammonia solution (L).

## Results and Discussions:-

4.1.Effect of rice straw calcination temperature on ammonia adsorption

Experiments were carried out using the same initial ammonia concentrationsfrom10 to 350($mg.dm^{-3}$), rice straw dose of 0.1(g) to investigate the effect of calcination temperature on ammonia adsorption.

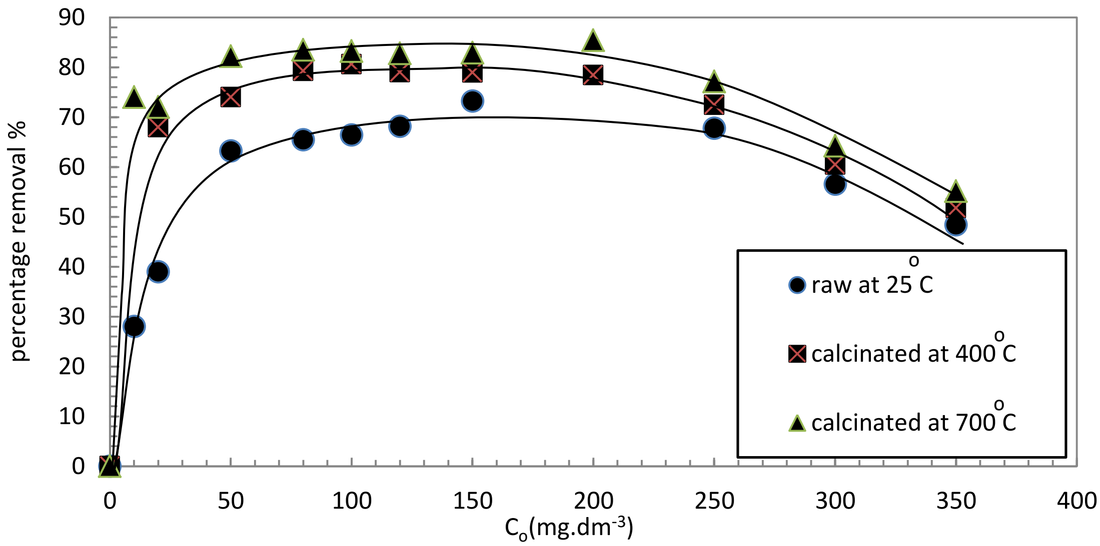


**Fig.2:-** Percentage removal of ammonia by adsorption onto raw and calcinated rice straw at different temperatures.

The results shown in Figure (2) depicts that the rate of uptake of ammonia is rapid in the beginning and that over 80, and 70 of ultimate adsorption are completed within 60 min for the 700 and 400°C calcination temperature, respectively compared to 60% for the raw rice straw at room temperature.

Figure (3) also demonstrates that ammonia adsorption increases with calcination temperature. After 60(min) operation, the ammonia adsorption increases from 84for raw rice straw to 90.6 and 98(mg.g$^{-1}$) as the temperature of calcination of rice straw reached 400 and 700°C, respectively. The increase in uptake with rise in temperature of calcination is due to the fact that the reaction rate between ammonia and the surface oxygen functional groups on the calcinated rice straw increases with temperature.

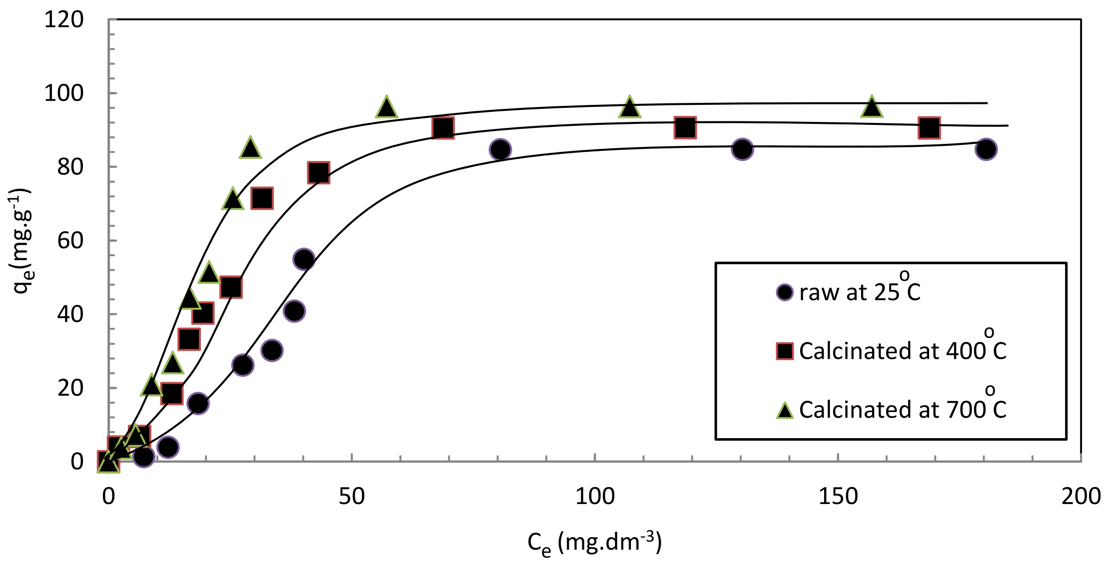


**Fig.3:-**Experimental isotherm of ammonia onto raw and calcinated rice straw at different temperatures.

Furthermore, the diffusivity of adsorbate through the external laminar layer into the micropores of the adsorbent also increases with temperature as diffusion is an endothermic process.

Also it can be suggested that some water molecules (bonded by strong hydrogen bonds with surface groups located at entrances to pores) can desorb from rice straw calcination temperature increases, which results in more pores open to $NH_3$.

4.2. Effect of treatment of calcinated rice straw with sodium hydroxide at different temperatures on ammonia adsorption.

The explanation can be expressed as follows:
Firstly, the mass-transfer between the liquid bulk and the surface of rice straw increases with the temperature in the aqueous solution. Secondly, the diffusivity of ammonia also increases with temperature. Thirdly, the ammonia on the surface of rice straw in equilibrium with the ammonia in the solution may increase with its temperature in the solution.

In Figure (5), it is very clear that with increase in temperature the actual number of active sites or adsorption sites per gram of adsorbent increase proportionately with adsorbate uptake.
This can be attributed to increased total adsorbent surface area due to availability of more adsorption sites.

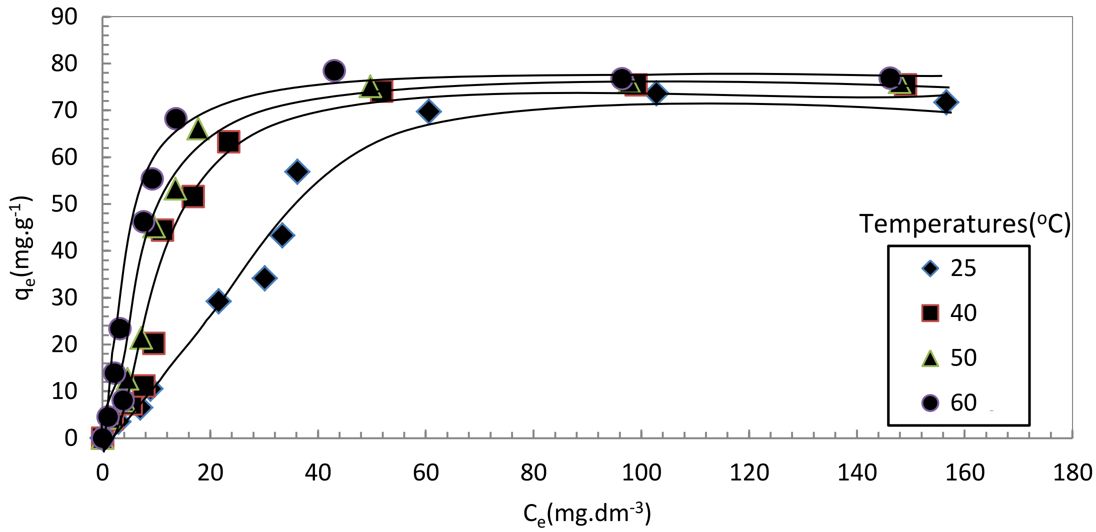


**Fig.4:-** Adsorption isotherm of ammonia onto prepared activated carbon at different temperatures.

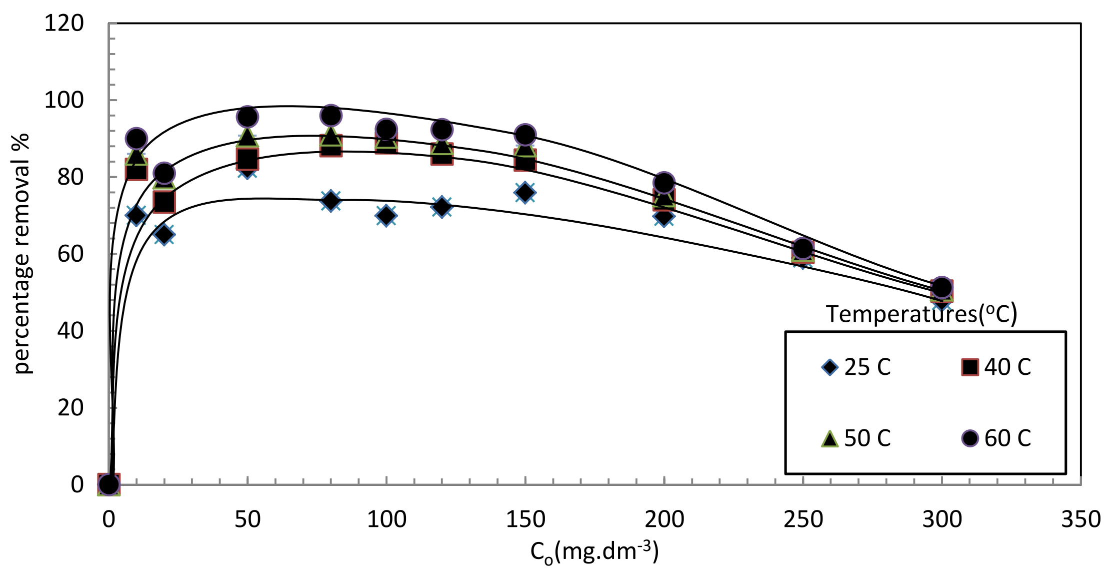


**Fig.5:-**Percentage removal of adsorption of ammonia onto prepared activated carbon at differenttemperatures.

4.3. Adsorption Isotherm Models
4.3.1. Langmuir Isotherm

Langmuir equation is based on a theoretical model and assumes that the maximum adsorption corresponds to a monolayer saturated with adsorbate molecules on the adsorbent surface that is energetically homogeneous (Langmuir,1916). Langmuir isotherm constants are calculated from the following linearized form:

$$C_e/q_e = 1/ KL + (a_L/K_L)*C_e \quad (2)$$

where $a_L$ and $K_L$are Langmuir constants determined from the slope $(a_L/K_L)$and intercept $(1/ K_L)$of the plot, where $(K_L/a_L)$ and $a_L$are indicative of maximum adsorption capacity (mg.g$^{-1}$) of adsorbent and energy of adsorption, respectively, while $C_e$ is the remaining concentration of adsorbate after equilibrium (mg.dm$^{-3}$) and $q_e$ is the amount adsorbed at equilibrium (mg.g$^{-1}$).

From the data shown in Tables(1) and (2), Langmuir isotherm curves can be given by plotting $C_e/q_e$ against $C_e$ (Figures(6) and (7)).

**Table 1:-** Langmuir constants for the adsorption of ammonia onto rice straw calcinated at different temperatures.

| **Rice straw (ammonia Conc. C0=0-200 mg.dm$^{-3}$)** | **slope** | **intercept** | **$K_{L1}$** | **$a_{L1}$** | **$r^2$** | **$K_L/a_L$** |
|---|---|---|---|---|---|---|
| raw | -0.1196 | 5.1869 | 0.1928 | -0.023 | 0.8749 | -8.3826 |
| calcinated at 400 | -0.018 | 0.9366 | 1.068 | -0.019 | 0.713 | -56.2105 |
| calcinated at 700 | -0.0145 | 0.7071 | 1.414 | -0.0205 | 0.694 | -68.9756 |
| **Rice straw (ammonia Conc. C0 =200-350 mg.dm$^{-3}$)** | **slope** | **intercept** | **$K_{L2}$** | **$a_{L2}$** | **$r^2$** | **$K_L/a_L$** |
| raw | 0.0102 | 0.2316 | 4.18 | 0.044 | 0.9813 | 95.2272 |
| calcinated at 400 | 0.0104 | 0.088 | 11.36 | 0.118 | 0.9979 | 96.2711 |
| calcinated at 700 | 0.0102 | 0.0268 | 37.31 | 0.381 | 0.9993 | 97.9265 |

**Table 2:-** Langmuir constants for the adsorption of ammonia onto prepared activated carbon at different temperatures.

| **Temperature (ammonia conc.=0:100 mg.dm$^{-3}$)** | **slope** | **intercept** | **$K_{L1}$** | **$a_{L1}$** | **$r^2$** | **$k_L/a_L$** |
|---|---|---|---|---|---|---|
| 25 | 0.068 | 0.8926 | 1.1203 | 0.0761 | 0.9433 | 14.7058 |
| 40 | 0.0572 | 1.0555 | 0.9474 | 0.0541 | 0.773 | 17.4825 |
| 50 | 0.0437 | 0.6343 | 1.5765 | 0.0688 | 0.8507 | 22.8833 |
| 60 | 0.0396 | 0.2564 | 3.9001 | 0.1544 | 0.9514 | 5.25253 |
| **Temperature (ammonia conc.=100:300mg.dm$^{-3}$)** | **slope** | **intercept** | **$K_{L2}$** | **$a_{L2}$** | **$r^2$** | **$k_L/a_L$** |
| 25 | 0.0127 | 0.0394 | 25.3807 | 0.3223 | 0.999 | 78.7401 |
| 40 | 0.0126 | 0.0651 | 15.3609 | 0.1935 | 0.9989 | 79.3651 |
| 50 | 0.011 | 0.2579 | 3.8774 | 0.0426 | 0.9746 | 90.9091 |
| 60 | 0.0104 | 0.4645 | 2.1528 | 0.0223 | 0.969 | 96.1538 |

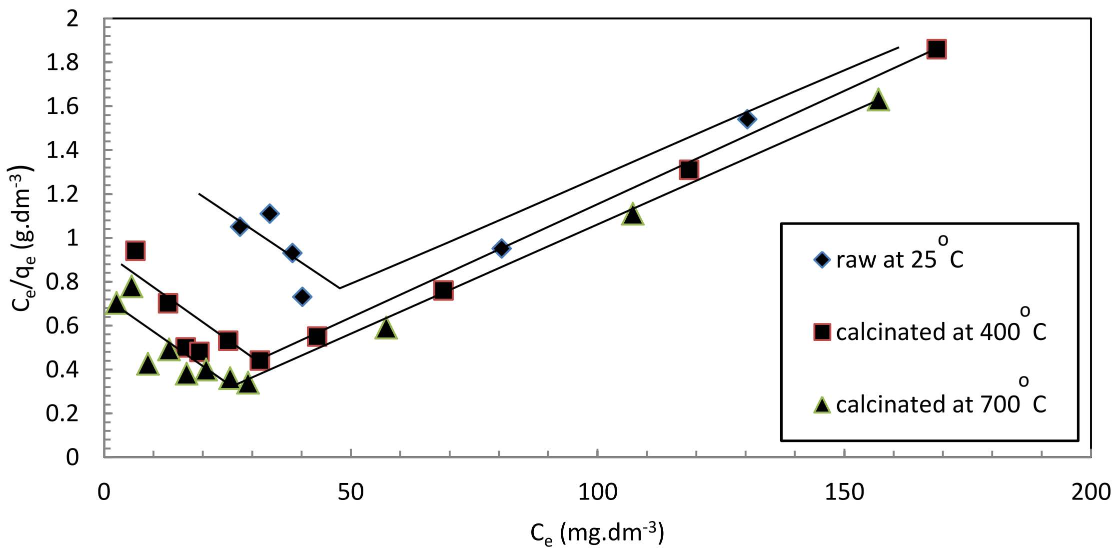


**Fig.6:-**Langmuir plots for the adsorption of ammonia onto rice straw calcinated at different temperatures.

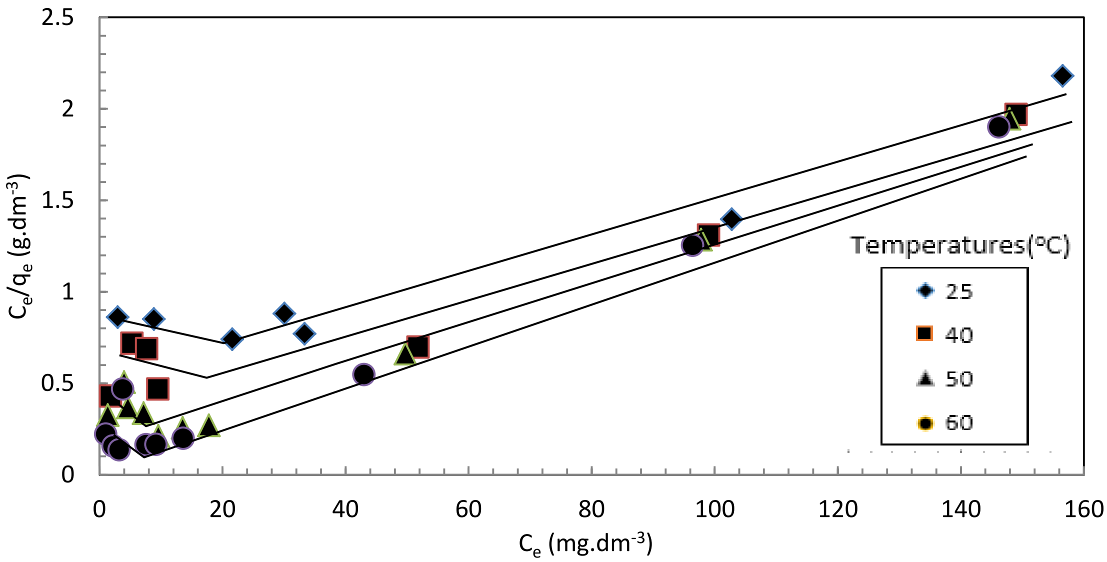


**Fig.7:-**Langmuir plots for adsorption of ammonia onto prepared activated carbon at different temperatures.

“S”type of adsorption isotherm is sigmoidal-shaped and thus has got a point of inflection. It is always a result of at least two opposite mechanisms. Compared to the “L” and “H” isotherms, the “S”class occurs less frequently (Dana et al., 2014).

Figure (6) demonstrates that the adsorption isotherm is in good agreement with the Langmuir adsorption equation however it has S-shape type of isotherm so the Langmuir plot is better represented by two consecutive straight lines. The highest value of 97.93(mg.g$^{-1}$)is obtained for ($K_L/a_L$) and a value of 0.38 is obtained for $a_L$ (correlation coefficient 0.99) for the adsorption of ammonia onto rice straw calcinated at 700$^{\circ}$C in the ammonia initial concentration range of (150-350) (mg.dm$^{-3}$).

The Langmuir plots in Figure (7) are represented by two consecutive straight lines with good correlation coefficients between 0.77 and 0.99. The highest value of maximum adsorption capacity in the ammonia initial concentration range of (10-80(mg.dm$^{-3}$)) 25.25 (mg.g$^{-1}$) is obtained with (correlation coefficient 0.95) for the adsorption of ammonia onto rice straw treated with NaOH at 60$^{\circ}$C.
However, for the ammonia initial concentration range (100-300(mg.dm$^{-3}$)), the highest adsorption capacity is 96.15 (mg.g$^{-1}$) obtained for the adsorption of ammonia onto rice straw treated with NaOH at 25$^{\circ}$C.

The Langmuir constant, $a_L$ is related with the affinity of the adsorbent for the adsorbate. Low values of $a_L$suggest a high affinity of rice straw for the ammonia.

4.3.2. Freundlich Isotherm
Freundlich isotherm assumes that the uptakes of adsorbate occur on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with an increase in concentration (Freundlich, 1906).

The Freundlich isotherm is expressed as:

$$q_e = K_F * C_e^{(1/n)} \quad (3)$$

where $K_F$ and n are constants of Freundlich isotherm incorporating adsorption capacity (mg.g$^{-1}$) and intensity, while $C_e$ and qe are the remaining concentrations of adsorbate after equilibrium (mg.dm$^{-3}$) and the amount adsorbed at equilibrium (mg.g$^{-1}$), respectively. Taking logarithm from the Eq. (3), a linearized form of Freundlich isotherm can be represented as follow:

$$\log q_e = \log K_F + (1/n) \log C_e \quad (4)$$

A Freundlich isotherm curve for the adsorption of ammonia on rice straw calcinated at different temperatures can be given by plotting log($q_e$) against log($C_e$) (Figure (8)and (9)). It can be noticed that the plots can be better fitted by two consecutive lines, this is in correspondence with the S-isotherm shape.

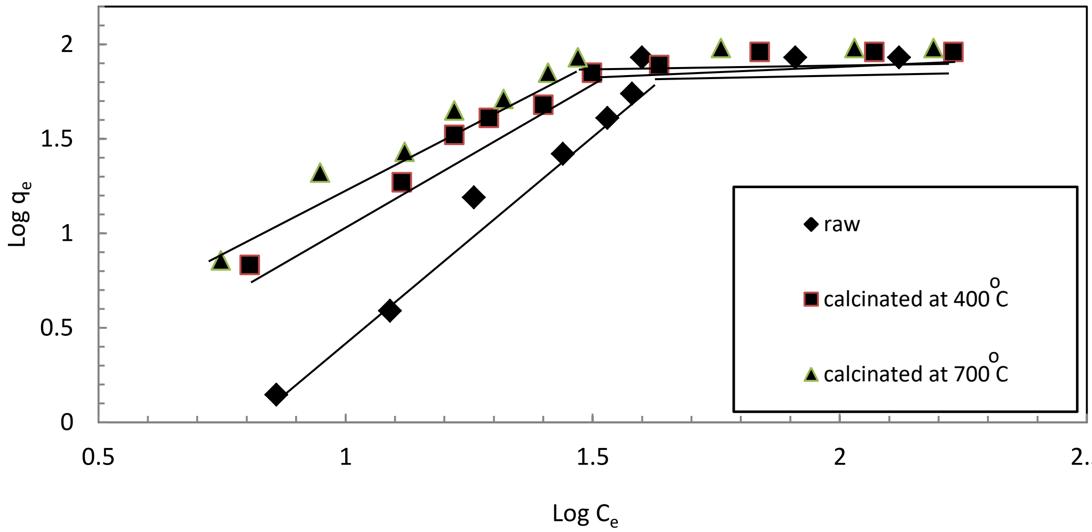


**Fig .8:-**Freundlich plots for adsorption of ammonia onto raw and calcinated rice straw at different temperatures.

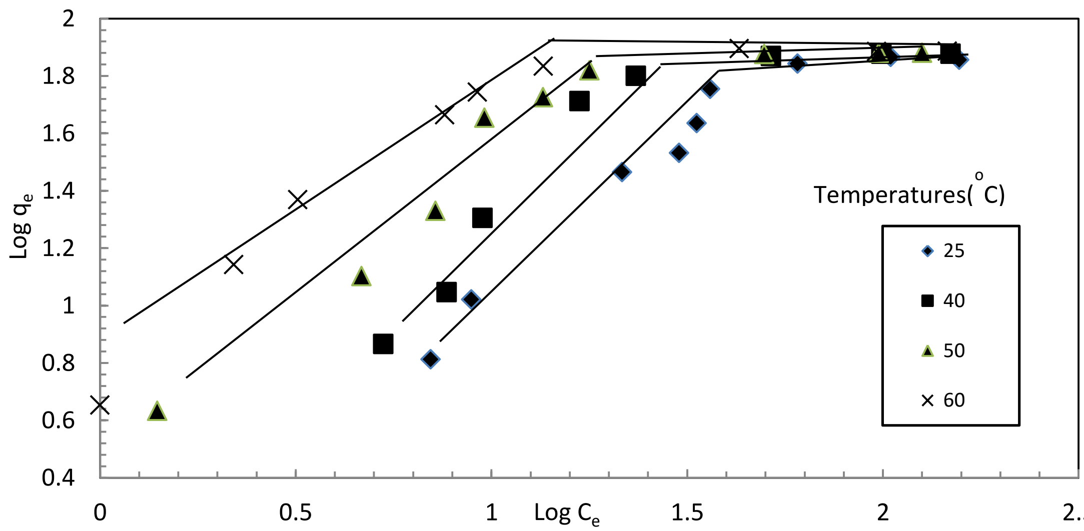


**Fig.9:-** Freundlich plots for adsorption of ammonia onto prepared activated carbon at different temperatures**.**

From the data shown in Table (3), the Freundlich isotherm constants give the highest value for adsorption at calcination temperature 700ºC.

However, for the adsorption of ammonia onto prepared activated carbon at different temperatures, the high values of $K_F$ showed a high feasibility of adsorption and n (intensity of adsorption) values between 1 and 7.4 represent a favorable adsorption. So adsorption is favorable in the ammonia initial concentration range (200-350) (mg.dm$^{-3}$) (Table (4)).

**Table 3:-** Freundlich constants for the adsorption of ammonia onto rice straw calcinated at different temperatures.

| **Rice straw (ammonia Conc. C0 =0-200 $mg.dm^{-3}$)** | **$K_{F1}$** | **$n_1$** | **$r^2$** |
|---|---|---|---|
| Raw | 0.018 | 0.451 | 0.985 |
| Calcinated at 400 $^oC$ | 1.415 | 0.918 | 0.944 |
| Calcinated at 700$^oC$ | 0.946 | 0.752 | 0.984 |
| **Rice straw (ammonia Conc.=(200-350 $mg.dm^{-3}$)** | **$K_{F2}$** | **$n_2$** | **$r^2$** |
| Raw | 20.96 | 3.522 | 0.75 |
| Calcinated at 400 $^oC$ | 44.19 | 6.653 | 0.778 |
| Calcinated at 700$^oC$ | 70.08 | 7.457 | 0.685 |

**Table 4:-**Freundlich constants for the adsorption of ammonia onto prepared activated carbon at different temperatures.

| **Temperature($^oC$) (ammonia Conc. C0 =10-100 $mg.dm^{-3}$)** | **$k_{F1}$** | **$n_1$** | **$r^2$** |
|---|---|---|---|
| 25 | 0.7096 | 0.844 | 0.9803 |
| 40 | 1.808 | 0.646 | 0.9754 |
| 50 | 2.662 | 0.878 | 0.9528 |
| 60 | 5.128 | 0.868 | 0.9738 |
| **Temperature($^oC$) (ammonia Conc. C0 =100-300 $mg.dm^{-3}$)** | **$k_{F2}$** | **$n_2$** | **$r^2$** |
| 25 | 34.25 | 6.394 | 0.7217 |
| 40 | 36.22 | 6.301 | 0.7858 |
| 50 | 40.37 | 6.882 | 0.7117 |
| 60 | 41.33 | 7.407 | 0.7563 |

4.3.3. Redlich-Peterson isotherm

The Redlich-Peterson isotherm contains three parameters and is a hybrid of the Langmuir and Freundlich isotherms (Redlich and Peterson,1959). The numerator is from the Langmuir isotherm and has the benefit of approaching the Henry region at infinite dilution.

$$q_e= (K_{RP} * C_e)/(1 + B * C_e^a) \quad (5)$$

The Redlich-Peterson isotherm may be rearranged to a linear form.

$$\log [(K_{RP} *C_e/q_e)-1] = \log B + a_{RP} \log C_e \quad (6)$$

It has three isotherm constants namely $K_{RP}$, β and $a_{RP}$ ($0 < a_{RP} <1$) which characterize the isotherm. Its limiting behavior is summarized as follows:

When $a_{RP}$ = 1, the Langmuir form results. On the other hand when ($K_{RP}$ and $a_{RP}$ )are much greater than unity, the Freundlich isotherm results. And when a = 0, the Henry's law results.

The three isotherm constants were determined by using trial and errors method to obtain the best value of $K_{RP}$ which yields the maximum value of the coefficient of determination,$r^2$using the solver add in the Microsoft excel sheet.

Table (5) represents the Redlich-Peterson constants for the adsorption of ammonia onto rice straw calcinated at different temperatures. However the best values of constants gave very low correlation coefficients $r^2$ between 0.3 and 0.7 so we cannot take this form in our consideration.

**Table 5:-** Redlich-Peterson constants for the adsorption of ammonia onto rice straw calcinated at different temperatures.

| Temp.(°C) | B | $A_{RP}$ | $r^2$ | $K_{RP}$ |
|---|---|---|---|---|
| 25 | 0.0317 | 0.6117 | 0.3227 | 1.2 |
| 400 | 1.04 | 0.2667 | 0.304 | 5.11 |
| 700 | 0.233 | 0.639 | 0.686 | 6 |

4.4. Selection of optimum adsorption isotherm

The analysis of the isotherm data is important to develop an equation which accurately represents the results and which could be used for design purposes. The most common isotherms applied in solid/liquid system are the theoretical equilibrium isotherm, Langmuir (Langmuir,1916),the best known and most often used isotherm for the sorption of a solute from a liquid solution; the Freundlich (Freundlich,1906), the earliest known relationship describing the adsorption equation and the Redlich–Peterson (Redlich and Peterson, 1959),the earlier presented, containing three parameters isotherm.

**Linear Method:-**

Linear regression was frequently used to determine the most fitted model throughout the years and the method of least squares has been frequently used for finding the parameters of the models. However, transformations of non-linear isotherm equations to linear forms implicitly alter their error structure (Jared et al., 2016).

In recent years, several error analysis methods, such as the coefficient of determination, the sum of the errors squared, a hybrid error function, Marquardt's percent standard deviation, the average relative error and the sum of absolute errors, have been used to determine the best-fitting isotherm (Ratkowsky,1990;Ho YS., et al., 2002;Allen et al.,2003;Zvezdelina et al.,2013;Srivastava and Syed ,2011;Foo and Hameed, 2010 ).

In addition to this, the better fit of model was checked by coefficient of determination ($r^2$), residual root mean square error (RMSE), and Chi square ($x^2$) values were evaluated through the following equations:

$$\mathrm{RMSE} = \sqrt{\frac{1}{N-p}\sum_{i=1}^{m}\left(q_{\exp} - q_{mod}\right)^2} \quad (7)$$

$$X^2 = \Sigma\left[(q_{exp}-q_{mod})^2/q_{mod}\right] \quad (8)$$

Where $q_{exp}$ is the experimental concentration of adsorbate on adsorbent, $q_{mod}$ is the calculated concentration of adsorbate on adsorbent obtained from model, N is the number of points in the experimental design, and p is the number of parameters to be determined.

The value of coefficient of determination, $r^2$, represents the percentage of the variability of the regression line between the predicted values and the actual values and may vary from 0 to 1; a perfect fit gives a coefficient of 1.

On the other hand, $x^2$ is basically the sum of the squares of the differences between the experimental data and the data obtained from the models divided by the corresponding data obtained from the models (Eq. (8)).

Smaller values of RMSE and $x^2$ and high values of correlation indicate a better fit of model (Srivastava and Syed, 2011) (Tables (6); and (7)).

Table (6) indicated that the theoretical Langmuir presentation gives the lowest values of the error tests; $x^2$ and RMSE and highest value of Correlation coefficient $r^2$ so it gives the best fit of isotherm data for the adsorption of ammonia onto rice straw calcinated at 700°C.

**Table 6:-** Isotherm constants of different isotherm models for the adsorption of ammonia onto rice straw calcinated at 700°C.(hint: the best numbers are highlighted).

| **Isotherm** | **$r^2$** | **$x^2$** | **RMSE** |
|---|---|---|---|
| Freundlich at $C_o$ (0-200 mg.dm$^{-3}$)<br>$K_F$ = 0.95 , n =0.75 | 0.98 | 21.58 | 16.49 |
| Freundlich at $C_o$ (200-350 mg.dm$^{-3}$)<br>$K_F$=70.08 ,n = 7.46 | 0.67 | | |
| Freundlich non linear<br>$K_F$ =13.8 ,n= 2.39 | 0.82 | 66.12 | 17.32 |
| Langmuir at $C_o$ (0-200 mg.dm$^{-3}$)<br>$K_L$=1.414 , $a_L$=-0.0205 | 0.69 | **4.83** | **4.11** |
| Langmuir at $C_o$ (200-350 mg.dm$^{-3}$)<br>$K_L$=37.31 ,aL= 0.381 | **0.99** | | |
| Langmuir non linear<br>$K_L$=4.53 ,$a_L$=0.036 | 0.82 | 33.32 | 12.27 |
| Redlich-Peterson<br>$K_{RP}$=6 , B=0.233, a=0.639 | 0.69 | 52.06 | 19.71 |
| Redlichpeterson non linear<br>$K_{RP}$=7, B=0.7, a=0.5 | 0.97 | 109.38 | 23 |

**Table 7:-** Isotherm constants of different isotherm models for the adsorption of ammonia onto rice straw activated with NaOH at 60°C.(hint:the best numbers are highlighted)

| **Isotherm** | **$r^2$** | **$X^2$** | **RMSE** |
|---|---|---|---|
| Freundlich at $C_o$(0-100 mg.dm$^{-3}$)<br>$K_F$ = 5.13, n =0.87 | **0.97** | **15.26** | **7.52** |
| Freundlich at $C_o$ (100-300 mg.dm$^{-3}$)<br>$K_F$ =41.33,n = 7.41 | 0.76 | | |
| Freundlich non linear<br>$K_F$ =20.77,n= 3.4 | 0.82 | 62.44 | 15.81 |
| Langmuir at $C_o$(10-100 mg.dm$^{-3}$)<br>$K_L$ =3.9,$a_L$ =0.154 | 0.95 | 320.81 | 25.86 |
| Langmuir at $C_o$(100-300 mg.dm$^{-3}$)<br>$K_L$=2.15,$a_L$ = 0.022 | 0.97 | | |
| Langmuir non linear<br>$K_L$=10.93,$a_L$=0.125 | 0.82 | 24.43 | 9.37 |
| Redlich-Peterson<br>$K_{RP}$=6.03,B=0.6$a_{RP}$=0.5 | 0.3 | 235.74 | 26.95 |
| Redlich-peterson nonlinear<br>$K_{RP}$=13.7,B=0.25, $a_{RP}$=0.9 | 0.56 | 31.41 | 11.74 |

However according to Table (7) for the adsorption of ammonia onto rice straw activated with NaOH at 60°C, the theoretical Freundlich presentation gives the lowest values of the error tests; $x^2$ and RMSE and highest value of Correlation coefficient $r^2$ so it gives the best fit of this isotherm data.

4.4.2.Non-linear Method

In the case of the non-linear method, a trial-and-error procedure, which is applicable to computer operation, was developed to determine the isotherm parameters using an optimization routine to maximize the coefficient of determination between the experimental data and isotherms in the solver add-in with Microsoft's spreadsheet, Microsoft Excel. The abilities of three widely used isotherms, the Freundlich, Langmuir, and Redlich-Peterson isotherms to model the equilibrium sorption data were examined (Foo and Hameed,2010).

From Figure (10) it seems that the best fit was obtained by Langmuir as compared with other isotherms because the Langmuir theoretical isotherm obtained from linear calculations and Langmuir model isotherm obtained from non-linear method were both closer to the experimental isotherm.

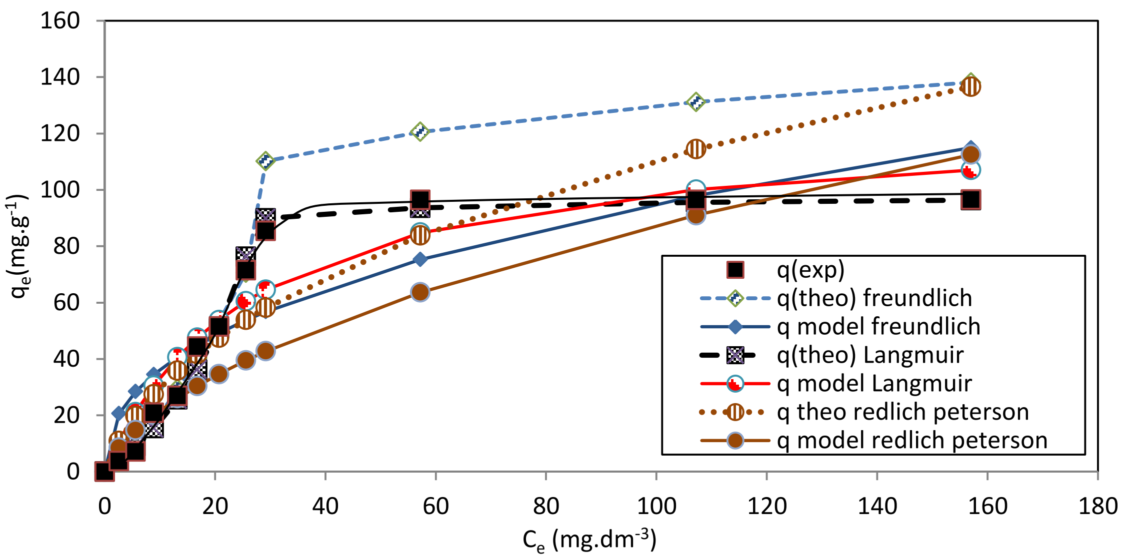


**Fig. 10:-** Plot of theoretical and non-linear isotherms for the adsorption of ammonia onto rice straw calcinated at 700ºC.

Also the Langmuir constants obtained by non linear method were closer to those obtained from theoretical linear calculations, (Table (6)).

So the predicted equations that can best fit this isotherm according to Langmuir theoretical calculations are:

$$q_e = \frac{1.41\ C_e}{1-0.021\ C_e} \tag{9}$$

For the initial ammonia concentration ranges [(10-200)( mg.dm$^{-3}$)].

$$q_e = \frac{37.31\ C_e}{1+0.38\ C_e} \tag{10}$$

For the initial ammonia concentration ranges (200-350(mg.dm$^{-3}$)).

And the predicted equation that can best fit this isotherm according to Langmuir non linear modelis:

$$q_e = \frac{4.53\ C_e}{1+0.036\ C_e} \tag{11}$$

`

This equation is applied for the initial ammonia concentration ranges (10-350(mg.dm$^{-3}$)).

Figure (11) shows the adsorption of ammonia onto rice straw activated with NaOH at 60°C, the best fit was obtained by the Freundlich theoretical isotherm obtained from linear calculations as it is the closest plot of the experimental data.

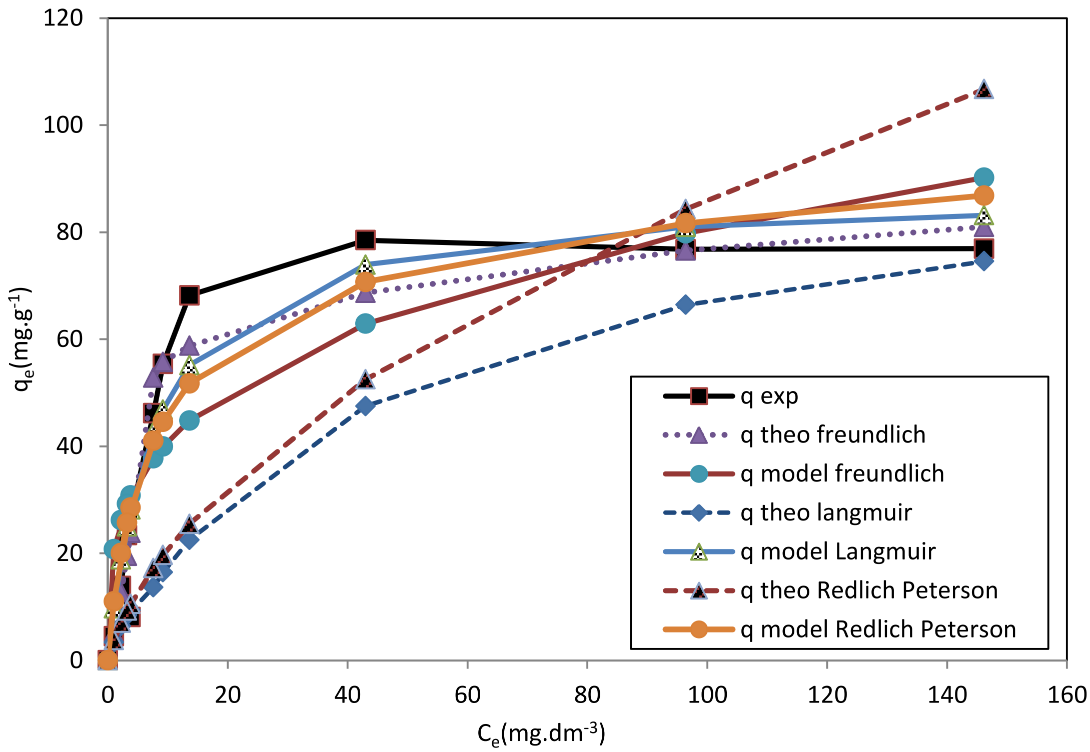


**Fig.11:-** Plot of theoretical and non-linear isotherms for the adsorption of ammonia onto rice straw activated with NaOH (prepared activated carbon) at 60°C.

So the predicted equations that can best fit this isotherm according to Freundlich theoretical calculations are:

$$q_e = 5.13\ C_e^{1/0.87} \qquad (12)$$

For the initial ammonia concentration ranges (0-100 (mg.dm$^{-3}$)).

$$q_e = 41.33\ C_e^{1/7.41} \qquad (13)$$

For the initial ammonia concentration ranges (100-300 (mg.dm$^{-3}$)).

And the predicted equation that can best fit this isotherm according to Freundlichnon linear modelis:

$$q_e = 20.77\ C_e^{3.4} \qquad (14)$$

4.5. Thermodynamic Parameters

Thermodynamic parameters, such as change infree energy (ΔG), enthalpy (ΔH), and entropy(ΔS) that describe ammonia uptake by rice straw can be estimated by considering the equilibrium constants under the several experimental conditions[30].Equilibrium constant for the adsorption reaction of ammonia on rice straw, $K_c$, is defined as follows:

$$K_c = \frac{C_{AE}}{C_e} = \frac{(C_o - C_o)}{C_e} = \frac{(C_o)}{C_e} - 1 \qquad (15)$$

Where $C_{AE}$ is the adsorbed amount of adsorbate at equilibrium, $C_o$ the initial concentration of adsorbate (mg/dm$^{-3}$), $C_e$ the equilibrium concentration of adsorbate (mg/dm$^{-3}$).

The change in the Gibbs free energy for a reaction is expressed as:

$$\Delta G^o = -RT \ln K_c \qquad (16)$$

Where R is the gas constant (8.314 J/mol.K) and T is temperature (K).

Moreover, using the relationship,

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (17)$$

ln$K_c$ can be expressed in Eq. (18).

$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (18)$$

Thus, if the equilibrium constants for an adsorption reaction at different temperatures are known, the standard enthalpy and entropic changes for adsorption can also be estimated from the slope and intercept of a linear plot of $\ln K_c$ versus 1/T (Figures (12; 13)).

$\Delta H^o$ and $\Delta S^o$ are obtained from the slope and intercept of van't Hoff plot of ln $K_C$ versus 1/T.

**Table 8:-** Thermodynamic parameters for the adsorption of ammonia onto rice straw calcinated at different temperatures.

| Temperature(°C) | T | $K_C$ | ΔH ($KJ.mol^{-1}$) | ΔS($J.K^{-1}.mol^{-1}$) | -ΔG($KJ.mol^{-1}$) |
|---|---|---|---|---|---|
| 25 | 298 | 0.639 | | | 3.98812 |
| 400 | 673 | 2.125 | 5.08 | 13.4 | 9.01312 |
| 700 | 973 | 2.57 | | | 13.03312 |

**Table 9:-** Thermodynamic parameters for the adsorption of ammonia onto prepared activated carbon at different temperatures.

| Temperature(°C) | T | $K_C$ | ΔH ($KJ.mol^{-1}$) | ΔS($J.K^{-1}.mol^{-1}$) | -ΔG($KJ.mol^{-1}$) |
|---|---|---|---|---|---|
| 25 | 298 | 1.857 | | | 22.21014 |
| 40 | 313 | 2.774 | 20.66 | 74.6 | 23.32914 |
| 50 | 323 | 3.951 | | | 24.07514 |
| 60 | 333 | 4.263 | | | 24.82114 |

In Tables (8; 9) A positive value of $\Delta H^o$ indicates that the adsorption process is endothermic in nature and negative values of $\Delta G^o$ how the spontaneous adsorption of ammonia on the rice straw. Positive $\Delta S^o$ shows the increased randomness of the solid/solution interface during the adsorption of ammonia on the rice straw.

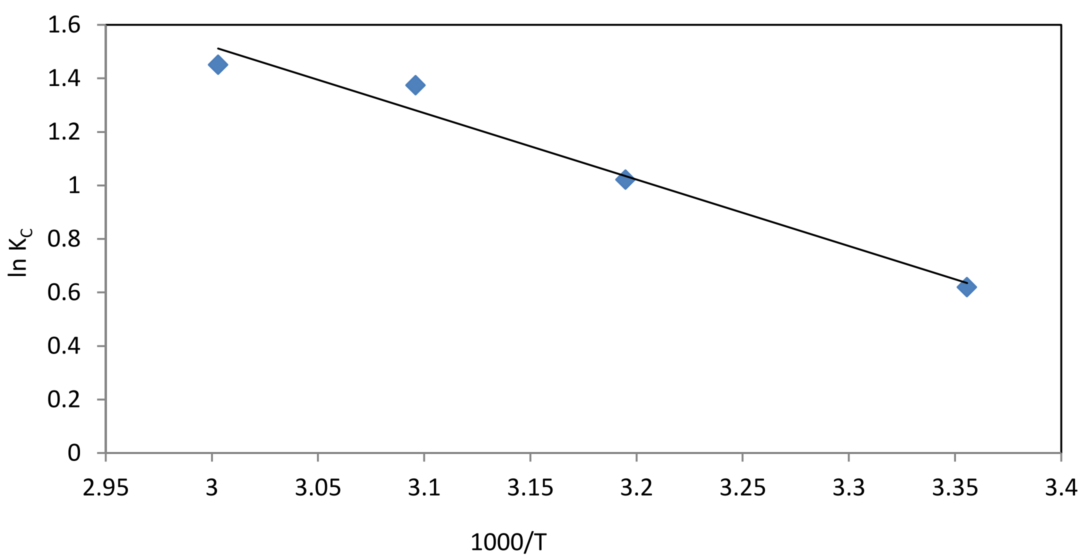


**Fig.12:-** Van't Hoff plot for the adsorption of ammonia onto rice straw calcinated at different temperatures at initial $NH_3$ concentration 20 ($mg.dm^{-3}$).

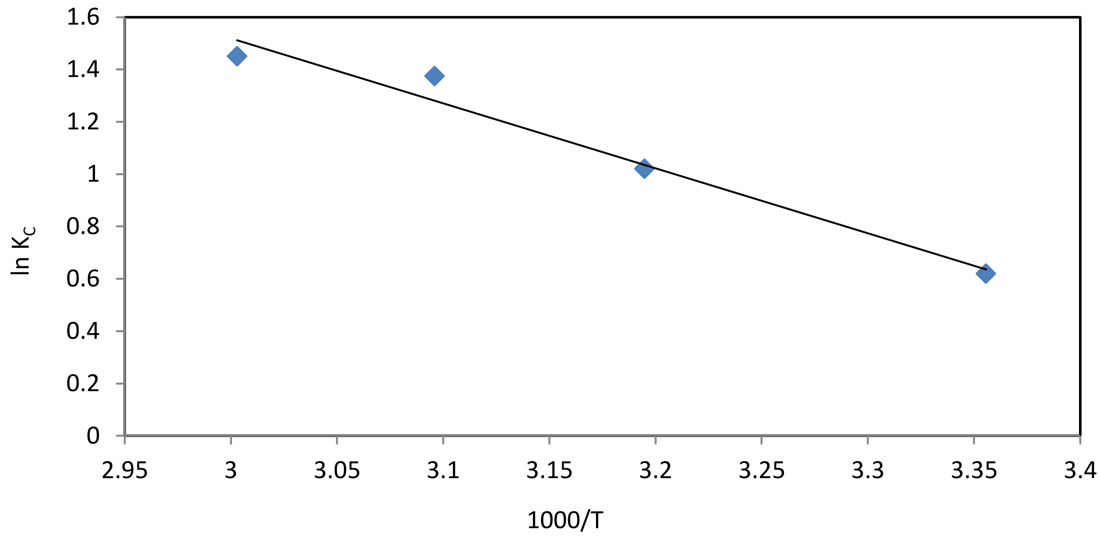


**Fig.13:-**Van't Hoff plot for the adsorption of ammonia onto prepared activated carbon at different temperatures at initial NH3 Concentration 20 mg/dm3.

## Conclusions:-

Adsorption of ammonia on rice straw from aqueous solutions has been studied. The following specific conclusions can be made from the experimental results:

1. Temperature is advantageous to the adsorption of ammonia on the rice with temperature. The adsorption isotherm follows the type S-shape.
2. The ammonia adsorption on rice straw increases with the temperature of calcination of rice straw in the aqueous solutions. The values of $q_e$ increased with an increase in temperature of calcinations from room temperature to700ºC.
3. The ammonia adsorption on rice straw treated with sodium hydroxide increases with the increase in temperature from 25 to 60ºC.
4. The Langmuir equilibrium isotherm model is found to provide a good fitting of the adsorption data especially in the ammonia initial concentration range of (200-350 (mg.dm$^{-3}$)) with $r^2$ of 0.99.
5. The maximum adsorption capacity obtained from the Langmuir equilibrium isotherm model is found to be 97.9(mg.g$^{-1}$) for the adsorption of ammonia onto rice straw calcinated at 700$^{\circ}$Cin the ammonia initial concentration range of (200-350(mg.dm$^{-3}$)). However it was 68.97(mg.g$^{-1}$) in the ammonia initial concentration range of (10-200 (mg.dm$^{-3}$)) at the same temperature.
6. For the activation of calcinated rice straw with NaOH at different temperatures the maximum adsorption capacity is found to be 25.25(mg.g$^{-1}$) at 60 $^{\circ}$C in the ammonia initial concentration range of (10-200(mg.dm$^{-3}$)) with $r^2$of 0.95. However it was 96.15(mg.g$^{-1}$) at 60$^{\circ}$Cin the ammonia initial concentration range of (200-350(mg.dm$^{-3}$)) with$r^2$ of 0.96 compared to 17.19 (mg.g$^{-1}$) maximum adsorption capacity of original activated carbon reported by Xiang et al.,(2008).
7. From the Freundlich isotherm, the highest values of $K_F$ and n were70.08 and 7.46, respectively obtained for the adsorption of ammonia onto rice straw calcinated at 700$^{\circ}$C proved its high favorability of adsorption in the ammonia initial concentration range (200-350(mg.dm$^{3}$)).
8. The highest values of $K_F$ and n were 5.13 and 0.87, respectively obtained for the adsorption of ammonia onto calcinated rice straw treated with NaOH at 60$^{\circ}$C in the ammonia initial concentration range (10-200(mg.dm$^{-3}$)). However they were 41.33 and 7.41, respectively obtained for the adsorption of ammonia onto rice straw treated with NaOH at 60$^{\circ}$C in the ammonia initial concentration range (200-350 (mg.dm$^{-3}$)) proved its high favorability of adsorption at this temperature.
9. Of all studied conditions the best one is the adsorption of ammonia onto rice straw calcinated at 700$^{\circ}$C as it gives the highest value of Freundlich constants and the maximum adsorption capacity according to Langmuir constants.

10. Thermodynamic parameters such as ΔGº, ΔHº, and ΔSº for adsorption reaction are estimated. A positive value of ΔHº indicates that the adsorption process is endothermic in nature and negative values of ΔGº show the spontaneous adsorption of ammonia on the rice straw. Positive ΔSº shows the increased randomness of the solid/solution interface during the adsorption of ammonia. The same result was reported by Xiang et al.[29] for the adsorption ammonia onto activated carbon.

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**Abbreviations:-**

1) ($NaOH$ ) : Sodium hydroxide
2) ($NH_4Cl$) : Ammonium chloride
3) ($HCl$) : Hydrochloric acid
4) $C_{e}$ : The remaining concentration of adsorbate after equilibrium (mg.dm$^{-3}$).
5) $C_o$ : The initial concentration of adsorbate(mg/dm$^{-3}$ ).
6) $C_t$ : The concentration at time t (mg/dm$^{-3}$).
7) $C_{AE}$ The adsorbed amount of adsorbate atequilibrium
8) $q_e$ : The amount adsorbed per gram of adsorbent at equilibrium (mg.g$^{-1}$).
9) $q_{theo}$: The theoretical amount adsorbed per gram of adsorbent obtained from linear models (mg.g$^{-1}$).
10) $q_{mod}$: The theoretical amount adsorbed per gram of adsorbent obtained from non linear models (mg.g$^{-1}$).
11) $a_L$: The indicative of maximum adsorption capacity (mg.g$^{-1}$) of adsorbentand energy of adsorption.
12) $K_L$: The Langmuir constants
13) $q_{exp}$: The experimental concentration of adsorbate on adsorbent (mg.g$^{-1}$).
14) $K_F$: The constant of Freundlich isotherm incorporating adsorption capacityand intensity(mg.g$^{-1}$).
15) $K_{RP}$: The Redlich-Peterson isotherm constant.
16) $\Delta G^o$ The change in the Gibbs free energy for a reaction(KJ.mol$^{-1}$).
17) $\Delta H^o$ The change in the enthalpy for a reaction(KJ.mol$^{-1}$)..
18) $\Delta S^o$ The change in the entropy for a reaction(KJ.mol$^{-1}$)..
19) $K_c$ Equilibrium constant for the adsorption reactionof ammonia on rice straw.