

## REMOVAL OF METRIBUZIN HERBICIDE FROM AQUEOUS SOLUTION USING CORN COB

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**Abstract:** Agricultural solid waste (corn cob) has been investigated as biosorbent for removal of metribuzin herbicide from aqueous solution. Parameters influencing extraction efficiency such as pH of the sample, contact time of sample with biosorbent, shaking time, temperature, heating time, sorbent dose were studied. Maximum sorption of metribuzin was found at pH 5.0. The sorption of metribuzin on corn cob was analyzed by Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherm models. Equilibrium data fitted well for Langmuir isotherm. Monolayer sorption capacity was found to be  $4.07 \text{ mg g}^{-1}$  using Langmuir isotherm. Freundlich empirical constants,  $K_F$  and  $n$  were  $1.23 \text{ mg g}^{-1}$  and  $2.05 \text{ L g}^{-1}$  respectively. Pseudo-first-order and pseudo-second-order models were used for kinetics study of sorption process. It was found that pseudo-second-order model has the best correlation value ( $r^2 = 0.9180$ ) among the kinetic models. Values of thermodynamic parameters such as change of free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) of sorption process indicated the process is endothermic and proceeded spontaneously.

**Keywords:** Metribuzin, Corn cob, Biosorption, Preconcentration, Isotherms, Thermodynamics.

### INTRODUCTION

Triazines have been used as selective herbicides in agriculture as pre-emergence or post-emergence herbicides for control of annual broadleaf weeds and annual grasses in a wide variety of crops around the world for 50 years. The triazines show their phototoxic effects by inhibiting Hill reaction during photosynthesis [1]. Many studies have shown triazine movement from the point of application to surface water [2]. Triazines are sometimes transported to surface waters, riparian zones or into non crop areas by flooding as free molecules and as molecules associated with DOC in surface runoff and on sediments [3-5]. Downward movement of triazines may occur from percolating water carrying them to lower soil depths. Within well-structured soils with abundant macropores, triazines have been reported to move to deeper depths than in non-structured soils with fewer pores. Increased permeability, percolation, and solute movement can result from increased porosity especially in no-tillage systems where there is pore connectivity at the soil surface. Triazines can move

to shallow groundwater by macropore flow in sandy soil if sufficient rainfall occurs shortly after they are applied [6]. Specific management practices influence triazine runoff and leaching, including fertilizer type, tillage crop residues, and previous crop history, as well as triazine application, formulation, and placement [7].

The *s*-triazinone class of herbicides includes metribuzin. In contrast to the *N*-alkyl groups of the *s*-triazine herbicides, this herbicide has a single *N*-amino group in the 4-position of the ring. Metribuzin absorbs UV light at wavelengths greater than 290 nm and thus are susceptible to degradation by direct photolysis [8]. Metribuzin is an asymmetric triazine herbicide with a short to moderate persistence, relatively high water solubility ( $1050 \text{ mgL}^{-1}$ ) and weak sorption. Magnitude of metribuzin sorption on surface soil was positively correlated to soil organic content and clay content; however, sorption was not completely reversible. In a degradation study conducted on two Mississippi flood plain soils, Mulbah *et al.* (2000) found that 73% of metribuzin degraded under aerobic condition [9].

The extraction of triazine group of herbicides and their enrichment from water samples has been done on different types of sorbents. Bamboo charcoal had been used as adsorbent for atrazine and simazine determination in environmental aqueous samples [10]. Jovan Lemic reported the use of organic zeolites for removal of atrazine from aqueous samples [11]. Atrazine removal from water had been studied by using two polycations pre-adsorbed on montmorillonite [12]. Sorption of the pesticides carbaryl, atrazine and parathion, with log  $K_{ow}$  being 1.59, 2.55 and 3.83 respectively was demonstrated using cold-pressed rapeseed (*Brassica napus*), moringa (*Moringa oleifera*) and soybean (*Glycine max*) [13]. Biosorption of the 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4-dichlorophenol (2,4-DCP), 4-chlorophenol (4-CP) and 2-chloro-ethylamino-6-isopropylamino-1,3,5 triazine (atrazine) has been studied on the mycelium of *Emericella nidulans* and *Penicillium miczynskii*, isolated from composted wheat straw and a soil respectively [14]. Castro *et al.* [15] combined the adsorption features of activated carbon and the oxidation properties of iron oxides in a composite to produce new materials for atrazine removal from aqueous medium.

In this present study, removal of metribuzin herbicide from aqueous samples was investigated using corn cob (inner part). Effects of physicochemical parameters such as adsorbent quantity, herbicide concentration, contact time and temperature were evaluated. The adsorption capacity of metribuzin was studied using the Freundlich, Langmuir, Temkin and D-R isotherms.

## **MATERIAL AND METHODS**

### *Instruments*

FTIR analysis of corn cob was done on spectrophotometer prestige 21 (shimadzu, Japan). A UV-Visible spectrophotometer (Unico 2100 United Products Instrument Inc., Dayton, NJ, USA) with 1 cm cell was used for all spectral measurements. A pH meter model pH-422 (wissenschaftlich-TechnischeWerkstätten, W. Germany) was used for pH measurements. Orbital shaker (OS-340, DigisystemLaboratory Instruments INC., China) was used for shaking purposes.

### *Reagents*

All chemicals used were of analytical grade or similar purity. Methanol was purchased from Merck (Darmstadt, Germany). Metribuzin standard was purchased from Dr Ehrenstorfer GmbH (Augsburg, Germany). Stock solution ( $1000 \mu\text{g mL}^{-1}$ ) of metribuzin herbicide was prepared by dissolving 0.1 g of standard herbicide in 100 mL methanol. Working standard of  $100 \mu\text{g mL}^{-1}$  and  $10 \mu\text{g mL}^{-1}$  solution were prepared by dilution of the stock solution with methanol.

### *Preparation of sorbent*

Corn cob (inner part) was dried, crushed, powdered and passed through  $350\mu\text{m}$  sieve. Powdered and uniform sized sample of corn cob (100 g) was stored in clean dry air tight glass bottle.

### *Sorption Procedure*

Adsorption studies for metribuzin herbicide were carried out using corn cob (0.1 g). Metribuzin solution was added with suitable amount of water. It was heated on water bath at  $100^\circ\text{C}$  for 3 min followed by equilibration time of 70 min with occasional shaking. Solution was filtered and the filtrate was diluted up to 100 mL with distilled water. Blank solution was prepared in the same way except for the addition of metribuzin solution. Absorbance of solution was measured at optimum  $\lambda$  of 300 nm. From absorbance of filtrate, amount of metribuzin adsorbed was determined spectrophotometrically.

## **RESULT AND DISCUSSION**

### *Specific surface area determination*

Analysis of surface area of corn cob was done using iodine adsorption method. The results of the surface area analyses are given in Table 1.

### ***FTIR analysis***

FTIR was used to study functional groups of different samples of corn cob. FTIR spectra of corn cob samples (unwashed) was recorded in the frequency range 400-4000  $\text{cm}^{-1}$  (Fig. 1). A peak 3336.85  $\text{cm}^{-1}$  is due to the N-H stretching of amides, peak 1600.92  $\text{cm}^{-1}$  is due to N-H deformation of primary aliphatic amines, peak 1506.41  $\text{cm}^{-1}$  is due to N-H  $\text{cm}^{-1}$  deformation of secondary aromatic amines, 1423.47  $\text{cm}^{-1}$  is due to  $\text{NO}_2$  deformation of nitro compounds, 1373.32  $\text{cm}^{-1}$  is due to O-H in-plane deformation of tertiary alcohols, 1242.16  $\text{cm}^{-1}$  and 1157.29  $\text{cm}^{-1}$  is due to C-O stretching of diaryl ethers, 1983.85  $\text{cm}^{-1}$  is due to R-O stretching of alkyl aryl ether, 993.34  $\text{cm}^{-1}$  is due to the C-H out-of-plane deformation of alkenes and 898.83  $\text{cm}^{-1}$  is due to C-H out-of-plane deformation of m-disubstituted aromatic compounds. It was observed that washing of corn cob with water, 1M  $\text{H}_2\text{SO}_4$ , and 1M HCl resulted in decreased peak intensity and surface area. Therefore sorption studies were carried out using unwashed corn cob as sorbent.

### ***Effect of pH on sorption of metribuzin on corn cob***

Metribuzin solution (4  $\mu\text{g mL}^{-1}$ ) was added to 0.1 g of corn cob followed by addition of 5 mL of Britton Robinson (B.R) buffer in the range of 2-7 pH respectively (Fig. 2). In one of the experiment sorption study was carried out without addition of B.R. buffer. All solutions were equilibrated for 40 min with occasional shaking. Solutions were filtered and the filtrate was diluted up to 100 mL with distilled water. Maximum Sorption was observed at pH 5. The pH of unbuffered solution was also 5.07. Therefore further studies were carried out without buffer addition.

### ***Effect of temperature on sorption of metribuzin on corn cob***

The effect of temperature was studied in the range of 40-100°C (Fig. 3). Metribuzin solution (4  $\mu\text{g mL}^{-1}$ ) was added to 0.1g of corn cob and was placed on water bath for 5 min followed by the equilibration time of 40 min at room temperature with occasional shaking. Solutions were filtered and the filtrate was diluted up to 100 mL with distilled water. A direct relation was observed between sorption capacity and temperature. 100% sorption was found at 100°C.

### ***The effect of contact time before heating on sorption of metribuzin on corn cob***

For optimization of the contact time before heating, solutions were equilibrated in the range of 30-80 min at room temperature (Fig. 4). Solutions were filtered and the filtrate was diluted up to 100 mL with distilled water. It was observed that sorption increased with increase in equilibration time up to 70 min.

### ***Kinetics of sorption of metribuzin on corn cob***

Kinetics of sorption of metribuzin on corn cob was studied using two common kinetic models, pseudo-first-order and pseudo-second-order. Pseudo-first-order and pseudo-second-order kinetic models plotted at 25 °C are shown in (Fig. 5 and 6) respectively. Rate constant was determined from the linear plot of time against  $\log (q_e - q_t)$ . The second-order rate constant  $K_2$  ( $\text{gmg}^{-1} \text{min}^{-1}$ ) was determined experimentally from the intercept and slope of plot time (t) against  $t/q_t$ . First order rate constant values  $K_1$ ,  $q_e$ ,  $R^2$  and second order rate constant values  $K_2$ ,  $q_e$ ,  $R^2$  are given in Table 2. It was observed that the correlation value of pseudo-second-order model is higher than the first order model. This suggests that the sorption might be controlled by second-order model.

***The effect of shaking time on sorption of metribuzin on corn cob***

Metribuzin solution ( $4 \mu\text{g mL}^{-1}$ ) was placed for 10 and 20 min on automatic shaker at a speed of 150 rpm. It was observed that with increase in shaking time there was decrease in the sorption phenomena.

***The effect of heating time on sorption of metribuzin on corn cob***

The temperature effect on the sorption of metribuzin on corn cob was studied at 100 °C for 1,2,3,4 and 5 min (Fig. 7). Corn cob (0.1 g) was added to  $4 \mu\text{g mL}^{-1}$  solution of metribuzin herbicide followed by equilibration time for 40 min at room temperature with occasional shaking. Solutions were filtered and the filtrate was diluted up to 100 mL with distilled water. Maximum sorption of metribuzin was found at 3 min heating. With further increase in heating time no pronounced increase in sorption was observed.

***The effect of contact time after heating on sorption of metribuzin on corn cob***

The contact time after heating was studied at 20, 30, 40, 50 and 60 min (Fig. 8). Metribuzin solution ( $4 \mu\text{g mL}^{-1}$ ) was added to 0.1 g of sorbent (corn cob). This solution was placed on a boiling water bath for 3 min followed by giving equilibration time in the range of 20-60 min respectively with occasional shaking. It was observed that there is no effect on sorption phenomena by giving contact time after heating.

***Study of sorption isotherm for sorption behavior of metribuzin on corn cob***

To observe sorption behavior of metribuzin on corn cob, Freundlich, Langmuir, Temkin and D-R sorption isotherm were examined for their ability to model the equilibrium sorption data. The data for these isotherms are given in Table 3. The Freundlich isotherm is used for non-ideal sorption on heterogeneous surfaces and is expressed by the following equation:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (1)$$

The logarithmic form of Freundlich equation is given as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (2)$$

Where  $K_F$  is the Freundlich adsorption isotherm constant ( $\text{mgg}^{-1}$ ),  $1/n$  ( $\text{gL}^{-1}$ ) is a measure of the sorption intensity and  $q_e$  is the amount of herbicide sorbed ( $\text{mgg}^{-1}$ ) and  $C_e$  is the equilibrium concentration of herbicide ( $\mu\text{gmL}^{-1}$ ).

The Langmuir isotherm is used for monolayer sorption on a homogeneous surface and expressed by the following equation:

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

In a linear form, it is expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L C_e}{K_L} \quad (4)$$

Where  $C_e$  is the equilibrium concentration ( $\mu\text{gmL}^{-1}$ ),  $q_e$  is the amount of solute sorbed per gram of sorbent;  $K_L$  and  $a_L$  are the Langmuir sorption isotherm constants and are related to the maximum capacity ( $\text{Lg}^{-1}$ ) and bonding strength ( $\text{Lmg}^{-1}$ ) respectively. The theoretical monolayer capacity is  $Q_0$  and is numerically equal to  $K_L/a_L$ .

Temkin and Pyzhev considered the effects of some indirect adsorbate/adsorbate interaction on adsorption isotherms and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The Temkin isotherm has been generally applied in the following form:

$$q_e = \frac{RT}{b} \ln A C_e \quad (5)$$

and can be linearized as:

$$q_e = B \ln A + B \ln C_e \quad (6)$$

where  $B = RT/b$ ,  $b$  is the Temkin constant related to heat of sorption ( $\text{J/mol}$ ),  $A$  is the Temkin isotherm constant ( $\text{L/g}$ ),  $R$  is the gas constant ( $8.314 \text{ J/mol K}$ ), and  $T$  is the absolute temperature ( $\text{K}$ ). The sorption data were analysed according to the linear form of the Temkin isotherm and the linear plots are shown in (Fig. 11). Examination of the data shows that the Temkin isotherm does not provide a close fit to the sorption data.

The equilibrium data were also applied to the D-R model to determine the type of sorption (physical or chemical). The linear form of D-R isotherm is presented as the following equation:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (7)$$

where  $q_e$  is the amount of herbicide sorbed onto per unit amount of corn cob ( $\text{molg}^{-1}$ ),  $q_m$  is the theoretical monolayer sorption capacity ( $\text{mol/g}$ ),  $\beta$  is the constant of the sorption energy

( $\text{mol}^2/\text{J}^2$ ), which is related to the average energy of sorption per mole of the adsorbate as it is transferred to the surface of the solid from infinity distance in the solution, and  $\varepsilon$  is Polanyi potential, which is described as:

$$\varepsilon = RT \ln \left( 1 + \frac{1}{c_e} \right) \quad (8)$$

Where T is the solution temperature (K) and R is the gas constant and is equal to 8.314 J/mol K. The value of mean sorption energy, E (kJ/mol), can be calculated from D-R parameter  $\beta$  as follows:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (9)$$

The value of mean sorption energy gives information about chemical and physical sorption. The E value ranges from 1 to 8 kJ/mol for physical sorption and from 8 to 16 kJ/mol for chemical sorption. Values of  $q_m$  and  $\beta$  are calculated from the intercept and slope of the plot by plotting  $\ln q_e$  versus  $\varepsilon^2$  (Fig. 12) and are listed in Table 3.

As seen in Table 3, the Langmuir isotherm fits quite well with the experimental data (correlation coefficient  $R^2 > 0.99$ ). This indicates that the Langmuir model was very suitable for describing the sorption equilibrium of metribuzin on corn cob. The Langmuir isotherm assumes monolayer sorption over a homogeneous corn cob biosorbent at 100 °C and the value was found to be 4.065  $\text{mgg}^{-1}$  for corn cob. The fact that the Langmuir isotherm fits the experimental data very well may be due to the homogeneous distribution of active sites on corn cob surface, since the Langmuir equation assumes that the surface is homogeneous. Compared with the correlation coefficient value of the linear plot of Langmuir isotherm, those of Freundlich model, Temkin model, and D-R model were found less satisfactory ( $R^2 < 0.98$ ). The value of Freundlich constant n larger than 1 points out the favorable sorption conditions. The E value ( $3.4 \times 10^{-4}$  kJ/mol) was found in the range of 0–8 kJ/mol, indicating that the type of sorption of metribuzin on corn cob is essentially physical. All sorption isotherms are shown in (Fig. 9-12) respectively.

#### ***Thermodynamics study of sorption of metribuzin on corn cob***

Study of thermodynamics of a system assumes that energy in an isolated system cannot be gained or lost when the entropy change is the driving force. Thermodynamics parameters were calculated for determination of sorption process. The change in energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) of sorption of metribuzin on corn cob were calculated by using the following equations.

$$K_D = \frac{q_e}{C_e}$$

$$\Delta G^\circ = -RT \ln K_D$$

$$\ln K_D = -\frac{G^\circ}{RT} = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

Where,

$K_D$  = distribution constant

$q_e$  = amount of metribuzin biosorbed at equilibrium

$C_e$  = equilibrium concentration

The values for  $K_D$ ,  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  were calculated. The positive value obtained for  $\Delta H^\circ$  indicated an endothermic sorption process. The endothermic sorption process could be due to increase in the rate of diffusion and mobility of metribuzin from external boundary layer into the internal pores of the biosorbent due to increase in temperature. The positive value of  $\Delta S^\circ$  showed the affinity of corn cob form etribuzin herbicide whereas the negative value of  $\Delta G^\circ$  showed the spontaneous sorption process (Table 4). The data for thermodynamics study is shown diagrammatically in (Fig.13).

## CONCLUSION

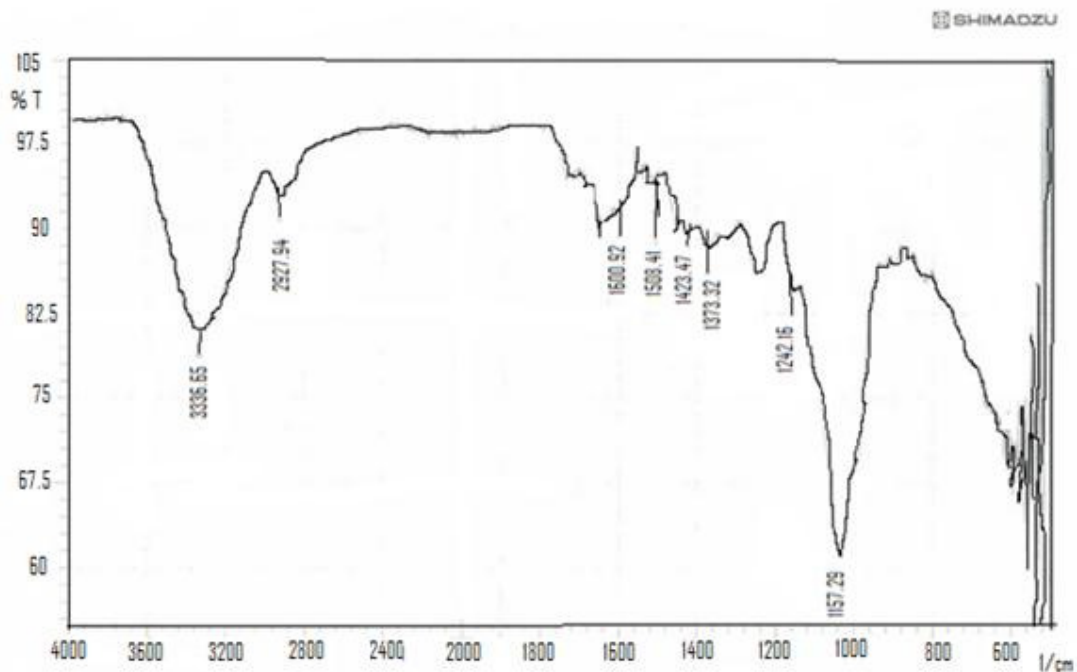
This work showed that corn cob (inner part) is not only economical but also effective for removal of metribuzin. Sorption studies using corn cob indicate that sorption of metribuzin is maximum at pH of its own solution i.e. 5.07 with 3 min heating time on boiling water bath and 70 min contact time at room temperature. The sorption data fitted well for Langmuir sorption isotherm. The kinetics of sorption phenomena was found to follow pseudo-second-order rate equation. Thermodynamics studies showed that sorption of metribuzin on corn cob were a spontaneous, endothermic process.

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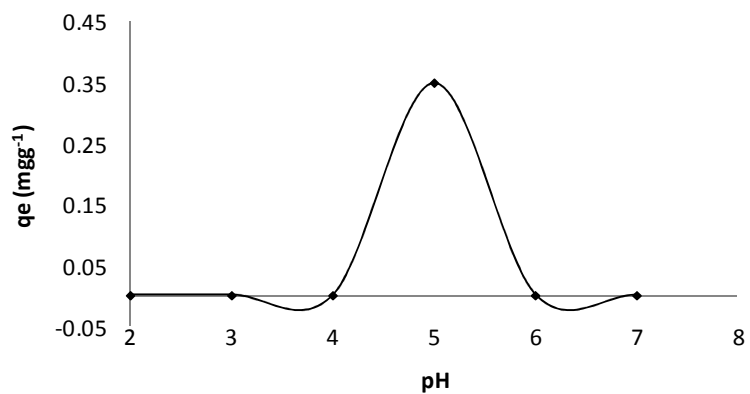
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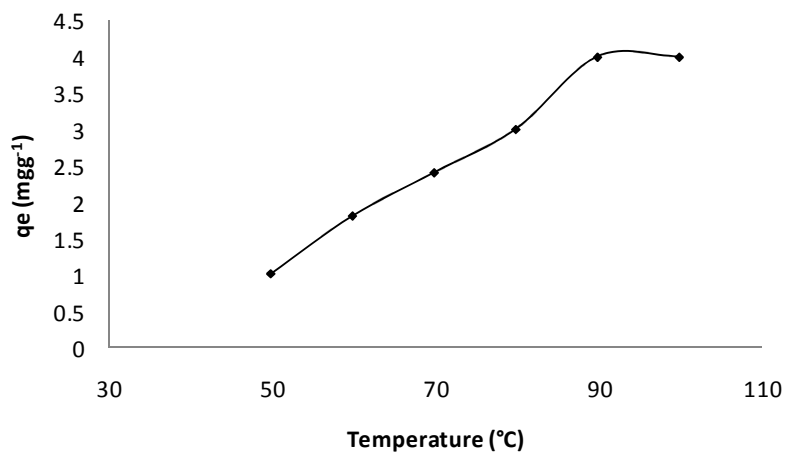
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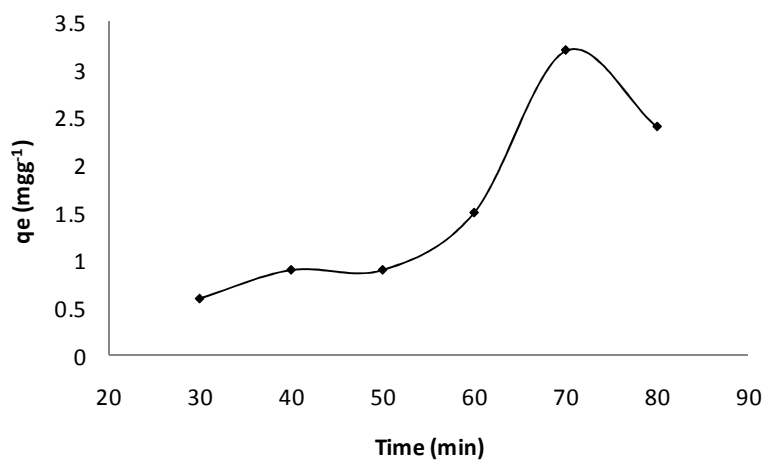
**Fig 1.** FTIR spectra of unwashed corn cob inner part.



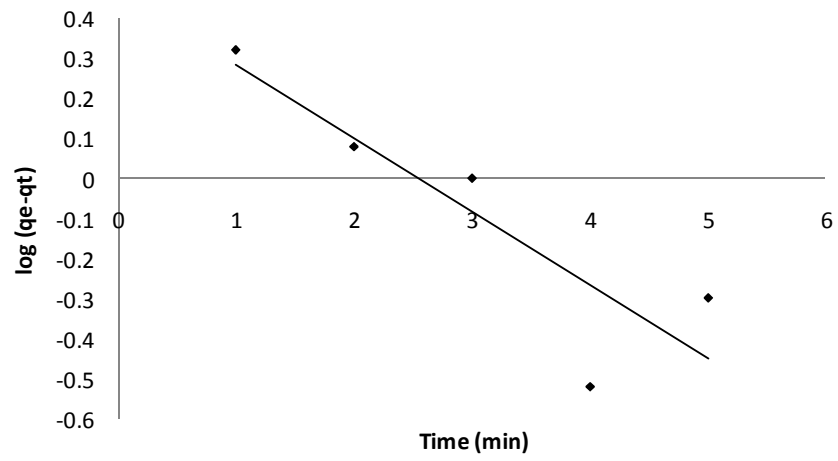
**Fig 2.** The effect of pH on sorption of metribuzin on corn cob.



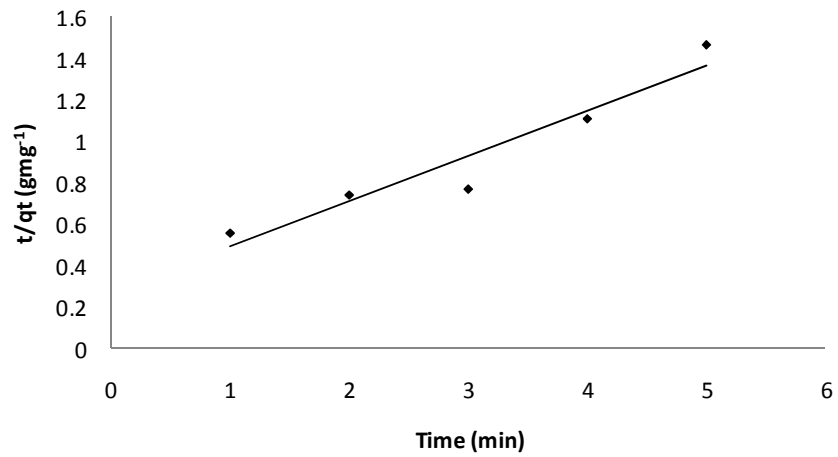
**Fig 3.** The effect of temperature on sorption of metribuzin on corn cob.



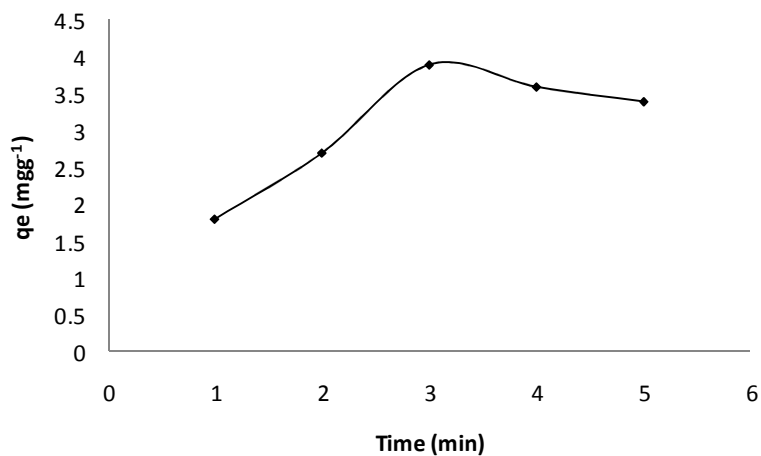
**Fig 4.** The effect of contact time before heating on sorption of metribuzin on corn cob.



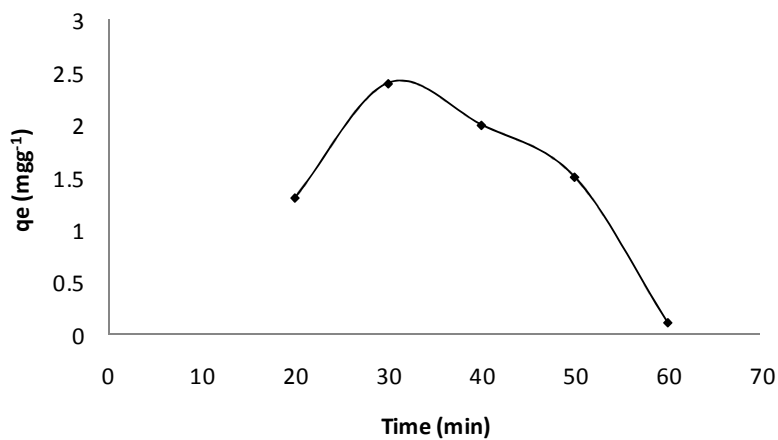
**Fig 5.** Pseudo-first-order kinetic model for sorption of metribuzin on corn cob.



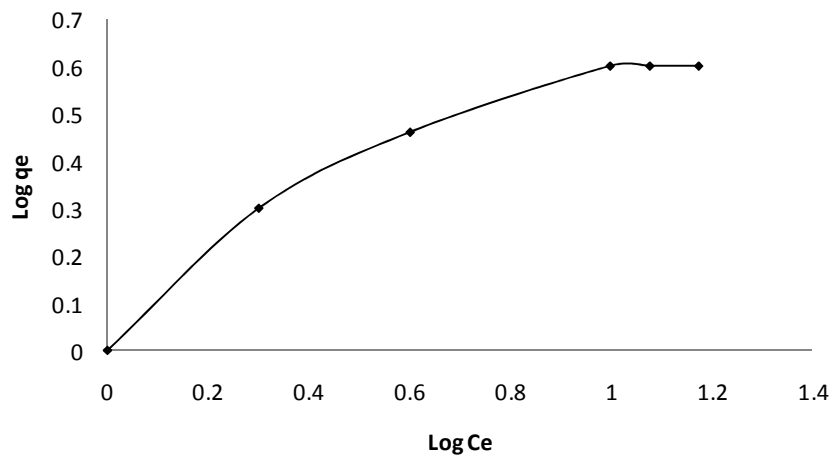
**Fig 6.** Pseudo-second-order kinetic model for sorption of metribuzin on corn cob.



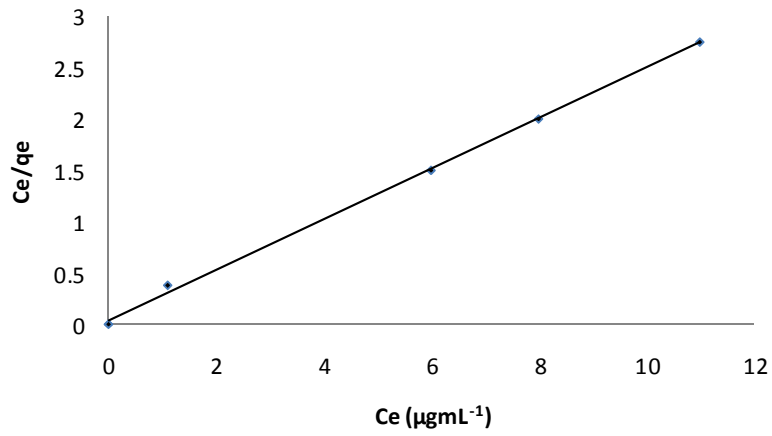
**Fig 7.** The effect of heating time on sorption of metribuzin on corn cob.



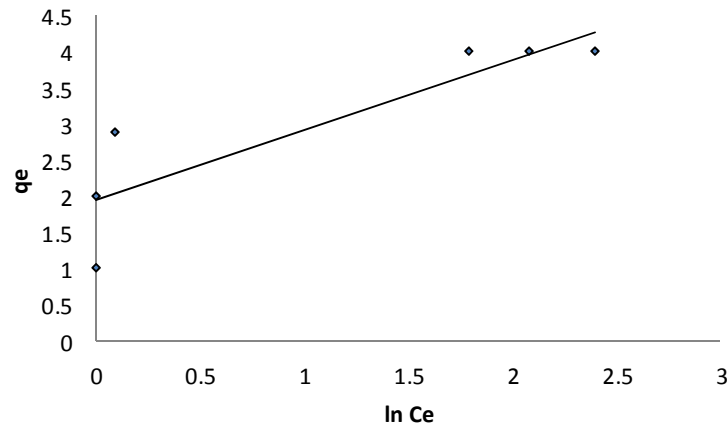
**Fig 8.** The effect of contact time after heating on sorption of metribuzin on corn cob.



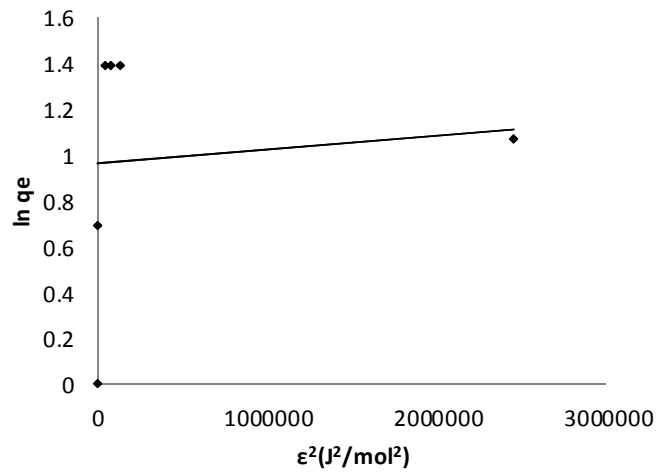
**Fig 9.** Freundlich sorption isotherm for sorption behavior of metribuzin on corn cob.



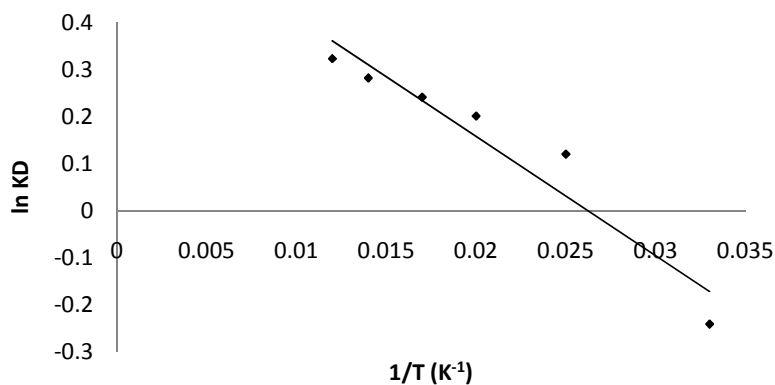
**Fig 10.** Langmuir sorption isotherm showing sorption behavior of metribuzin on corn cob.



**Fig 11.** Temkin sorption isotherm showing sorption behavior of metribuzin on corn cob.



**Fig 12.** D-R sorption isotherm showing sorption behavior of metribuzin on corn cob.



**Fig 13.** Plot of  $\ln K_D$  versus  $1/T$  for thermodynamic study of sorption of metribuzin on corn cob.

### Tables

**Table 1.** Surface area of corn cob (inner part) powder under different washing conditions

Sample	Particle size ( $\mu\text{m}$ )	Surface area ( $\text{m}^2\text{g}^{-1}$ )
Corn cob powder (unwashed)	350	3278.25
Corn cob powder HCl washed	350	888.30
Corn cob powder $\text{H}_2\text{SO}_4$ washed	350	244.04

**Table 2.** Kinetic parameters of metribuzin sorption on corn cob

Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
$K_1$ ( $\text{min}^{-1}$ )	$q_e$ ( $\text{mgg}^{-1}$ )	$R^2$	$K_2$ ( $\text{gmg}^{-1} \text{min}^{-1}$ )	$q_e$ ( $\text{mgg}^{-1}$ )	$R^2$
0.424	2.944	0.7790	0.18	4.54	0.9180

**Table 3.** Freundlich, Langmuir, Temkin and D-R isotherm model constants for the sorption of metribuzin on corn cob.

Isotherm	Parameter
Freundlich	
KF (m <sub>g</sub> g <sup>-1</sup> )	1.225
n (L <sub>g</sub> -1)	2.045
R <sup>2</sup>	0.921
Langmuir	
q <sub>max</sub> (m <sub>g</sub> g <sup>-1</sup> )	4.065
ac (Lm <sub>g</sub> <sup>-1</sup> )	8.200
R <sup>2</sup>	0.998
Temkin	
A (L <sub>g</sub> <sup>-1</sup> )	7.389
B	0.972
R <sup>2</sup>	0.7734
D-R	
B (mol <sup>2</sup> /J <sup>2</sup> )	6 x 10 <sup>-8</sup>
qm	2.6
E	3.4 x 10 <sup>-4</sup>
R <sup>2</sup>	0.012

**Table 4.** Thermodynamic parameters for sorption of metribuzin on corn cob

$\Delta G^\circ$ (K <sub>j</sub> mol <sup>-1</sup> )						$\Delta H^\circ$ (kJmol <sup>-1</sup> )	$\Delta S^\circ$ (kJK <sup>-1</sup> mol <sup>-1</sup> )
303K	313K	323K	333K	343K	353K		
607.54	-312.50	-538.99	-647.64	-803.80	-947.25	243.49	5.89