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## Research Article

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# Environmental toxicant Zoxamide sorption, degradation and *Punica granatum*-based activated carbon-mediated removal from soils

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## Abstract

An intricate pesticide study is essential to assess its interaction with soil and environment. Fungicide Zoxamide has been examined for adsorption-desorption and degradation behaviour. Adsorption and desorption behaviour of Zoxamide on soil samples from geographically different regions of Pakistan utilizing batch equilibrium method was assessed. Degradation of Zoxamide was performed by hydrolysis, soil degradation and photodegradation. Degradation samples were extracted with dichloromethane and analysed at regular time intervals. The adsorption distribution coefficient values ranged from  $0.9303 \mu\text{g ml}^{-1}$  to  $45.7 \mu\text{g ml}^{-1}$  with  $R^2$  value lying from 0.84-1. The variable sorption values can be associated with the diverse physicochemical properties.  $\Delta G$  ranged from  $-9.3$  to  $-11.39$  KJ/mol, which indicates weak Van der Waal forces for interaction. Linear and Freundlich models were used for calculating sorption rate of the fungicide. The desorption values increased in following order: S2 < S9 < S6 < S5 < S7 < S3 < S4 < S2 < S8 < S1 < S10. The highest percentage of degradation was observed through hydrolysis (99.7%) and photodegradation (99%). Activated carbon prepared from *Punica granatum* peel was used for the removal of Zoxamide from soils for environmental remediation. Concentration dependent studies displayed the concentration of 7.5 mg/L showed highest removal percentage of 96%. Zoxamide displayed an overall varying fate in the environment, which can be attributable to the type and geological nature of soils.

**Keywords:** adsorption; desorption; hydrolysis; degradation; photo-degradation

## 1. Introduction

Pesticides are agrochemicals or biological agents such as viruses, bacteria etc. that exterminate or debilitate pests (Baker 2020). Pesticides have become a constitutional part of our modernistic lifestyle, which are used to safeguard agribusiness and agroecology as well as to eliminate the pests transfusing infectious diseases (Silva et al. 2019). It has been calculated that globally approximately \$38 billion are spent on pesticides per annum (Germany 2012). The repeated use of pesticides for agriculture leads to the soil accumulation problem (Iftikhar et al. 2018; Neuwirthová et al. 2019). The pesticides fate is determined by the several factors including soil properties or flora fauna, due to which they encounter a variegation of degradation and adsorption/desorption phenomenon (Naeem et al. 2020; Gul and Ahmad 2020; Hussain 2009). The accumulated pesticides in soil is effected by its microbial content, enzymatic and biochemical processes (Egbe et al. 2021). Pesticides that outstretch to the soil surface can modify the diversity and biomass of soil's microorganisms (Gul and Ahmad 2018). This alternation in microbial species eventually leads to the soil ecosystem disruption and loss of soil fertility. Various studies have been performed, which feature the deleterious impacts of pesticides on soil flora and fauna (Arora et al. 2019; Sofo 2012). Furthermore, extrinsic applications of pesticides could also affect the function of beneficial species of bacteria, fungi and algae in soil by influencing their growth, colonization and metabolic activities etc. (Debenest 2010; Tien 2012). When a pesticide enters the environment several events occur, some of which are advantageous (Kanmani 2017). For instant, leaching of some herbicides into the root can control diseases in more excellent way. Contrary to it, releasing pesticides into the environment can be damaging, as not all the chemical reaches the site of target. For example, due to runoff pesticides can be removed from the target area. Many processes affect the fate of pesticides in the environment. These processes include adsorption, desorption, degradation, runoff, vitalization and leaching (Chiari 2017).

Zoxamide (3,5-Dichloro-*N*-(3-chloro-1-ethyl-1-methyl-2-oxopropyl)-4-methylbenzamide), a chemical derivative of benzamide, possesses an anti-fungicidal effect for oomycetes, which cause diseases in different vegetables. Zoxamide has low acute toxicity of category IV. Carcinogenic studies have proved that Zoxamide is not carcinogenic in humans (Malandrakis 2011). Toxicity of Zoxamide for aquatic organisms range from moderate to highly toxic. The major routes of dissipation for Zoxamide are hydrolysis and photodegradation. Zoxamide may remain in the environment for days to months due to its immobile nature (Rekanović et al. 2012).

Pesticides are abated via various means; chemical, biological and physical. One efficient remediation mode is removal by activated carbon, also known as activated charcoal (AC). It is as low volume porous form of carbon (Xu et al. 2019). It has relatively more surface area than normal carbon. It is a very strong and reliable adsorbent. Activated carbons can be manufactured from various organic materials like, coconut shell, peat, hard and soft wood, coal, olive pits among others (Liang et al. 2020).

Current research focuses on the determination and analysis of fungicide, Zoxamide in various soil samples to predict its nature and effect in environment. Multiple experiments will direct towards elucidating its fate, adumbrating any pesticide-induced toxicity in the environment. Furthermore, greener route for pesticide removal from soil has also been adopted by synthesizing biomass based (*Punica granatum*-derived) activated carbon and utilizing it for environmental remediation.

## **2. Materials and methods**

Pesticide Zoxamide, 99% pure analytical grade ethanol, anhydrous Na<sub>2</sub>SO<sub>4</sub>, NaCl and CaCl<sub>2</sub> was utilized in the experimental work. Solvent, dichloromethane was used as a solvent for extraction. All experiments were carried with deionized water and analytical grade reagents.

### **2.1 Soil Sampling and processing**

Ten soil samples were collected from Pakistan; including, Mang, Tulamba, Dharyal Jalap, Sai, Gujranwala, Faisalabad, Dharaki, Janjal Khaetar, Mian Channu, Abdul Hakeem and Khyber Pakhtunkhwa (KPK) (Fig. 1). Random sampling was selected for sampling purpose. These samples were collected in the month of February 2019. Samples were obtained from the depth of 0-30 cm. Polythene bags were used for storing the samples and later transferred to laboratory for research purpose (Das et al. 2020).

Soil samples were air dried in the green house for two days followed by manually grinding and sieved via 2 mm mesh. The fine powdered samples were stored in sterilized petri dishes for sorption, degradation experiments and physicochemical analysis.

### **2.2 Physicochemical analysis**

Different physicochemical properties of soil were analysed. EC meter was used to evaluate the electrical conductivity of the samples. Soil and deionized water were mixed in the ratio of 1:5 to determine the pH. Octagonal sieve shaker was used to calculate the percentage of the soil texture i.e. sand, silt and clay. Walkley

and Black methodology was preferred to assess the organic matter content of soil. Acid digestion of soil samples were carried followed by analysis of heavy metals with the aid of atomic absorption spectrometry in the soil.

### **2.3 Batch sorption experiment of Zoxamide**

Batch equilibrium method was used for the adsorption experiment (Shariff 2012; Zhang et al. 2020). Stock solution of ten parts per million was prepared in deionized water as per protocol. Eight diluted solutions having concentration of 0 mg/L, 0.25 mg/L, 0.5 mg/L, 0.75 mg/L, 1 mg/L, 2.5 mg/L, 7.5 mg/L were set up. Ionic strength of soil was maintained by addition of 10 ml of 0.1 M NaCl solution in each dilution. 0.5 g of each sieved soil sample were added in falcon tubes followed by the addition of 10 mL of solution and kept in orbital shaker for 24 hours at 150 rpm. One blank and one control tube were also prepared. Samples were subjected to centrifugation for 10 to 15 minutes at 3000 rpm. Filtration was conducted through nylon filters and syringes and analysed on UV spectrophotometer. All experimentations were done in duplicates.

For desorption, 11 g of CaCl<sub>2</sub> was mixed with 1000 ml distilled water in a volumetric flask. The prepared solution was placed on magnetic stirrer for a few minutes and poured into the falcon tube containing soil left after adsorption. The falcon tubes were kept in the orbital shaker for 24 hours at 150 rpm. The samples were centrifuged for 10 -15 minutes at 3000 rpm and filtered with nylon filters and syringes and analysed by UV spectrophotometer (Naeem et al. 2020).

### **2.4 Degradation of Zoxamide**

#### **2.4.1 Hydrolysis**

1 g sieved soil was added in each flask along with 10 mL of stock solution. To avoid any microbial contamination, the flask was wrapped with parafilm tape. All the flasks were stored in the incubator at 27°C. Sampling was done on the intervals of 7 days. 10 mL of sample was taken out from each conical flask and added to a separating funnel. The sample was extracted with 5 mL dichloromethane, followed by adding anhydrous sodium sulphate to eliminate the remaining moisture. Hot plate was used to evaporate the extractant inside the fume-hood to get the required quantity and the extractant was stored in Eppendorf tube in refrigerator at -4 °C until further analysis by UV-Vis spectrophotometer and GC-MS (Gul and Ahmad 2018).

#### **2.4.2 Photolysis**

Previously prepared dilutions were used to perform photo-degradation of Zoxamide. Two batches were prepared for this experiment; one set comprised of light induced assortment and the second experimental set was carried

out in complete dark. Photolysis experiments were performed under direct sunlight from 12:00 pm onwards on a bright sunny day. Extraction was done at regular intervals and samples were analysed by UV-Vis spectrophotometer.

### **2.4.3 Soil based degradation**

For the evaluation of the inherent potential of soil for Zoxamide biodegradation, soil degradation was done. Soil degradation was observed in all the ten collected soils. Soil samples were kept in petri dishes and 10 ml stock solution was poured to each plate. To mimic the natural day/night conditions, petri dishes were placed in green house underneath natural temperature and light. Samples were extracted with dichloromethane and analysed by UV-Vis spectrophotometer (Naeem et al. 2020).

## **2.5 Synthesis of activated carbon**

For the preparation of activated carbon 2 kg of pomegranates were procured from local market in Rawalpindi, Pakistan. Activated carbon was synthesized by mean of 600 g of pomegranate peels. The peels were air dried for 15 days. When the peels were completely dried, they were converted into fine powder using electrical grinder. Equal quantity of concentrated  $H_2SO_4$ , was added to the powder for activation purpose with simultaneous stirring. Pomegranate peels soaked with  $H_2SO_4$ , were kept in fume hood for 24 hours to obtain a homogenized mixture. In order to attain neutral pH, washing was done with distilled water and soaked in 5%  $Na_2SO_4$  solution for 24 hours. 5% sodium bicarbonate solution was prepared by mixing 5 g of sodium bicarbonate in 100 mL distilled water. Soaking in  $Na_2SO_4$  solution was repeated until the achievement of neutral pH. The neutralized activated carbon was dried in oven for two hours at  $105^\circ C$ . Pomegranate activated carbon (PAC) was grinded and kept in an airtight bottle to avoid any moisture and contamination (Santhi et al. 2010).

### **2.5.1 Fourier Transform Infrared Spectroscopy (FTIR) for functional group characterization**

Analysis for determining the functional groups present in activated carbon and its raw materials was done using FTIR spectrometry. Functional groups were studied in the range of  $500$  to  $4000\text{ cm}^{-1}$  that act as an active site to attach pesticide using KBr pallets.

### **2.5.2 PAC driven removal of Zoxamide**

Two different dilutions of 5 mg/L and 7.5 mg/L were formulated from 10 mg/L stock solution. 0.5 g of sieved soil was added in centrifuged tubes along with 10 mL of each dilution and their absorbance was measured using UV-Vis spectrophotometer. 0.5 g of activated carbon was added to each centrifuged tube and left for 2 hours,

followed by checking the UV-Vis absorbance to measure the percentage of removal that had occurred due to activated carbon. The process was repeated after 2 hours.

## 2.6 Data analysis

For calculation of adsorption capacity of Zoxamide in ten distinct soils, Linear and Freundlich model was used.

Amount of Zoxamide absorbance  $\mu\text{g g}^{-1}$  in soil is given by following equation 1:

$$C_s = \frac{V}{m} \times C_b - C_a \quad (1)$$

Where  $C_s$  represents the concentration of pesticide absorbed, volume of solution is represented by  $v$ ,  $m$  is the amount of soil in grams,  $C_b$  is equilibrium concentration of Blank and  $C_a$  represents the equilibrium concentration of supernatant. From above equation values of linear isotherm can be written as equation 2

$$k_d = c_s/c_e \quad (2)$$

$K_d$  = linear sorption coefficient (ml/ $\mu\text{g}$ )

$C_e$  = concentration of Zoxamide at equilibrium ( $\mu\text{g ml}^{-1}$ )

Freundlich equation used was given by equation 3

$$C_s = K_f C_e^{1/n} \quad (3)$$

where  $C_s$  is the amount of pesticide absorbed,  $k_f$  and  $n$  are constant, and  $C_e$  is the equilibrium concentration. To determine equilibrium distribution constant, equation (4) can be used:

$$K_d(ads) = \frac{C_s}{C_e}$$

where,  $K_d$  is the distribution constant in  $\mu\text{g ml}^{-1}$ ,  $C_e$  is the equilibrium concentration, and

$C_s$  is the amount of pesticide adsorbed.  $K_{foc}$  which is Freundlich constant normalized to organic matter is given by equation (5)

$$K_{foc} = \frac{K_f}{\%C} \times 100 \quad (5)$$

$K_{OM}$  is given by equation (6):

$$K_{OM} = \frac{K_d}{\%C} \times 100 \quad (6)$$

$K_{OC}$  is given by equation (7):

$$K_{OC} = \frac{K_d}{\%C} \times 100 \quad (7)$$

$\Delta G$  (Gibbs free energy for adsorption in  $\text{KJ mol}^{-1}$ ) is given by equation (8):

$$\Delta G = -RT \ln K_{OM} \quad (8)$$

Where, R is the universal gas constant, T is the temperature in Kelvin.

For the calculation of degradation half-life and percentage of degradation was calculated. Following equation 9 was used for calculating the degradation percentage.

$$x = \frac{C_t}{C_o} \times 100 \quad (9)$$

Degradation at a specific time was calculated by equation 10.

$$D_t = x - 100 \quad (10)$$

Where,  $D_t$  is the percentage degradation of pesticide at a specific time, t,  $C_t$  is the concentration of pesticide at time, t,  $C_o$  is the concentration of pesticide at the beginning or zeroth time.

Calculation of each week's half-life was done by using following equation 11.

$$t_{1/2} = -\ln(C_t) \quad (11)$$

For calculating the total Half-life of each soil sample following equation 12 was used,

$$t_{1/2} = 0.693/k \quad (12)$$

Where, k is the rate constant obtained from the slope of the line.

### 3. Results and discussion

#### 3.1 Physiochemical Studies

Soils adsorptive potential can differ based on physical and chemical properties of soil and the pesticide. Table 1 displays the physiochemical properties of selected soil samples. The highest percentage of organic content was determined in Abdul Hakeem soil (0.50%) and lowest in Gujranwala (0.29%). The soil of Gujranwala was highly deficient in organic matter. Climate, soil texture and rainfall determine the electrical conductivity of soil. Rainfall is the most important factor in determination of soil's EC with high rainfall linked to low EC value. In the selected

soils, EC ranges from 1.04 to 16.39 ( $\text{Sm}^{-1}$ ). The highest EC value was observed in Tulumba due to less rainfall and the lowest EC value was of Sai due to more rainfall. pH ranged from 7.39 to 7.92. The percentage of sand ranged from 41% to 59%, percentage of silt ranged from 32% to 38% and percentage of clay ranged from 6% to 22%. Number of natural and anthropogenic processes lead to disposition of heavy metals in soil. In all samples it was scrutinized that the concentration of copper and chromium was above the permissible limits of WHO (10 mg/kg and 1.30 mg/kg respectively). Correspondingly, the nickel and lead concentrations were found exceeding the permissible limits in all samples (10 mg/kg and 2 mg/kg by WHO, respectively).

### 3.2 Adsorption isotherm

Zoxamide was investigated for sorption behaviour on ten different soil samples utilizing batch equilibrium method. Numerous adsorption parameters were investigated and recorded in Table 2. The adsorption distribution coefficient ranged from 0.9303 to 45.7  $\mu\text{g/ml}$  (Fig. 2). The highest  $K_d$  value was obtained in the soil sample S10 (Abdul Hakeem). Adsorption and mobility study of other fungicides conducted in Spain showed that the product of the adsorption distribution coefficient,  $K_d$ , showed good correlation with the soil organic content, suggesting that soil OC is the main controlling factor for adsorption (Peña et al. 2017). The high  $K_d$  value was observed in soil sample 10 due to the presence of high organic content i.e. 0.50%.  $R^2$  (Regression coefficient) for linear isotherm ranged 0.84-69.4 depicting the most excellent fitted response to linear adsorption. The adsorption experiment of another fungicide, Ethaboxam, displayed a proximity close to the adsorption rate of current study. The experiment was also conducted on Pakistan's soil (Ahmad 2018b).

'C' type isotherm curve was displayed by Zoxamide. The 'C' type curve graph was achieved in this study for the reason that by increasing concentration of Zoxamide, the adsorption value increases significantly. This curve portrayed that for all concentrations, there is a continuous accessibility of adsorption sites to fungicide. Assessment of mobility of fungicide, Zoxamide, was assessed based on  $K_{oc}$  values. To determine the leaching potential of pesticides into ground water, mobility index was used based on the  $K_{oc}$  value. Classification of pesticide was done based on  $K_{oc}$  values. Values of  $K_{oc}$  less than 50 depicts highest mobility whereas, values ranging from 150 to 500 shows the high mobility. In the current research,  $K_{oc}$  coefficient for Zoxamide ranged from 91.207 -168.35  $\mu\text{g ml}^{-1}$ . Additionally,  $K_{oc}$  depended upon the amount of organic matter present in soil. Higher organic matter will increase the  $K_{oc}$  value and increasing retention time in soil surface thus decreasing the rate of leaching. S2 possessed low  $K_{oc}$  value (91.207  $\mu\text{g ml}^{-1}$ ), depicting highest mobility. Highest  $K_{oc}$  value was observed in sample

10 displaying least mobility. Zoxamide displayed fluctuating mobility in soil because of varying physicochemical properties. Adsorption order was found according to the values of  $K_d$  for Zoxamide, which was as follows,

S10>S7>S9>S8>S4>S1>S3>S6>S5>S2.....  $K_d$  ( $\mu\text{g/mL}$ )

The assessment of adsorption for fungicide, Zoxamide, was also done based on the thermodynamic parameter.  $\Delta G$  (Gibbs free energy) values showed that all values were  $< -40$  KJ/mol, which indicated exothermic and physisorption interaction of pesticide and soil. In the current study, the value of  $\Delta G$  ranged from  $-9.3$  to  $-11.39$  KJ/mol, indicating that the weak Van der Waal forces were responsible for interaction.

### 3.2.1 Comparative Freundlich isotherms of Zoxamide in selected soil samples

Freundlich adsorption distribution coefficient ( $K_f$ ) ranged from 1.77 to 10  $\mu\text{g/ml}$ . Freundlich adsorption rate and presence of organic content are directly linked to each other, with the increase in organic matter the value of  $K_f$  increases. In current study, highest  $K_f$  value was observed in sample 1 and the lowest value was observed in S5. Value of  $K_f$  increased with the decrease in pH value. Some variations in adsorption may be due to other physiochemical properties. For Freundlich adsorption,  $R^2$  values were between 0.86 and 1. Result of adsorption is in a significant relation with linear isotherm model.

In the current study, it was noted that the adsorption rate depends on physiochemical properties of the soil. S10 displayed a very high linear adsorption rate (45.7  $\mu\text{g/ml}$ ). The reason for the highest adsorption was due to its lowest pH (7.39) and highest percentage of organic matter (0.50%), which facilitated further binding of pesticide with soil, consequently, increased the adsorption rate (Naeem et al. 2020). The effect of pH and organic matter content on adsorption can also be seen in S2 where the linear adsorption rate was lowest, due to the presence of lowest concentration of organic matter (0.29%) and highest pH (7.79). Due to variation in soil pH, the stability of soil particles is disturbed, which hindered the binding of soil with pesticide. Textural analysis showed that S10, possessed high adsorption rate, with high clay content (20%). Contrastingly, the sample 2 had lowest clay content (11%).

It was also observed in the current study that electrical conductivity and rate of adsorption had an inverse relation, that is with the increase in EC value the rate of adsorption decreases and vice versa. This point was justified by the results of soil samples 10 and 2 that have the EC 1.02  $\mu\text{S/cm}$  and 16.39  $\mu\text{S/cm}$  respectively.

### 3.3 Desorption Isotherm

C-type desorption isotherm was observed for all the soil samples as well. Desorption is the reverse of the adsorption phenomena (Fig. 2). High pH will enhance the rate of desorption i.e. in more alkaline soil, the desorption process will occur at high speed.  $K_{d(des)}$  value ranged from 549.51 to 11344.2  $\mu\text{g/ml}$ . Soil 10 showed the lowest desorption (549.51  $\mu\text{g/ml}$ ) and the highest rate of desorption was observed in the sample 2 (11344.2  $\mu\text{g/ml}$ ). The reason behind this trend was the presence of high organic matter and clay content, low pH and higher EC, which decreases the rate of desorption. Moreover, the desorption values increased in the following order:

S2 < S9 < S6 < S5 < S7 < S3 < S4 < S2 < S8 < S1 < S10

Linear and Freundlich models were used for calculating the rate of desorption of the fungicide Zoxamide because they were found to be the best fitted models. In the current experimental data, the  $R^2$  values for linear model varied from 0.88 to 0.99. The  $R^2$  of Freundlich model were in the range from 0.76 to 0.98.

### 3.3.1 Hysteresis phenomena

The ratio between  $n_{(des)}$  and  $n_{(ads)}$  is known as the apparent hysteresis, which indicated the irreversibility of adsorption in the soil samples. The hysteresis coefficient for current study indicated quick sorption in soil. The highest value of hysteresis coefficient was observed in sample 6. Desorption hysteresis can be related to the immobilization of pesticides in the soil, which are the result of irreversible chemical bond. Hysteresis coefficient in the current study ranged from 1.6 to 29.4

### 3.4 Statistical analysis

Statistical analysis of all the soil samples was done for the evaluation of their physicochemical properties including pH, and OC and  $K_d$  values. (Table 3). For the analysis of relationship of physicochemical properties of soil samples with  $K_d$  was done in Minitab 19. From the residual plots, it is revealed that normal minimum square norms were being confronted. Maintaining them indicates that the ordinary least squares regression results in unbiased coefficient estimates with the minimum variance (Fig. 3).

### 3.5 Degradation of Zoxamide

#### 3.5.1 Hydrolysis

Hydrolysis followed the first order kinetics (Fig. 4). The rate of hydrolysis in current study ranged from 96.99 to 99.75% (Table 4). The highest degradation percentage was observed in the soil sample S5 due to high

concentration of clay particles present in it, which enabled more binding of pesticide to the soil. On the other hand, the lowest degradation was in S9 due to the presence of highest percentage (51%) of sand in that sample.

Rate constant ( $k$ ) of hydrolysis varied from 0.08 to 0.172. Half-life ( $t_{1/2}$ ) was highest in sample 5 (8.66 days) and lowest was observed in S4 (3.78 days). Relating to their physicochemical properties, lowest organic matter was present in S5 (Gujranwala), along with highest pH, low organic matter and high pH can result in longer half-life. Furthermore, presence of heavy metal can hinder the rate of pesticide hydrolysis in soil.

The reason for high degradation percentage lies in the fact that a constant temperature of 30°C was provided to the hydrolysis assembly in the current research that acts as favourable factor for accelerating the rate of hydrolytic degradation. This constant temperature was maintained by placing the soil samples in incubator.

Factors influencing the rate of hydrolysis are presence of sand, clay particles and the concentration organic matter. The presence of organic matter has the most impact on the degradation due to hydrolysis. Organic matter can be categorized into two categories, living and non-living particles. In the category of living particle, fungi, bacteria and algae are included and non-living particles are the amino acids, fatty acids and proteins. The organic polymers form collides in soil resulting in the decrease of hydrolytic degradation. The clay minerals can enhance the binding of pesticide with soil particles, ensuring different reactions such as hydrolysis, elimination, oxidation reduction reactions.

### **3.5.2 Photodegradation**

Photochemical degradation of Zoxamide followed the first order kinetics. Experimental result showed varying readings for the photolytic degradation in sunlight. The rate of degradation was negligible for the dark batch. In the current study, highest photodegradation rate constant ( $k$ ), 0.3612, and lowest Half-life ( $t_{1/2}$ ), 1.918 days, was observed in concentration 0.75 mg/L. Concentrations 0.5 mg/L displayed the lowest photodegradation rate constant and highest half-life ( $t_{1/2}$ ), 0.076 and 9.11 days, respectively. Concentrations 0.5 mg/L exhibited the lowest percentage degradation to be 96.8% while concentration 0.75 mg/L had the highest percentage degradation to be 99.9% (Fig. 5, Table 4).

### **3.5.3 Soil degradation of Zoxamide**

For the current study, the degradation percentage ranged from 15.36% to 99.5%. Highest percentage was observed in sample 1 and lowest percentage was observed in sample seven. The rate constant  $k$  ranges from 0.002 to

0.1912. The highest value was observed in S4 (Fig. 6). Furthermore, the values of half-life and  $R^2$  ranged from 1.14 to 27.05 days and 0.6921 to 0.982, respectively.

### **3.6 PAC removal of Zoxamide**

#### **3.6.1 FTIR characterization of activated carbon**

FTIR employed for characterization was within range of 500 to 4000  $\text{cm}^{-1}$ . After the activation process, C-Br stretch was observed at 669.32  $\text{cm}^{-1}$ . At 802.41  $\text{cm}^{-1}$  C-Cl stretch with medium strength was observed. Strong C-N stretch was reduced to a medium stretch at a peak of 1261.49  $\text{cm}^{-1}$ . Strong stretch of N-H at peak 1624.12  $\text{cm}^{-1}$ , C=O at peak 1735.99  $\text{cm}^{-1}$  were not observed after the activation process. Two medium O-H stretches at peaks 2341.66  $\text{cm}^{-1}$  and 2360.95  $\text{cm}^{-1}$  were also seen (Fig. 7).

#### **3.6.2 Removal of Zoxamide by PAC**

Pesticides removal was performed on ten soils with two different concentrations, 5 mg/L and 7.5 mg/L. For this purpose, analysis was done for absorbance before and after adding activated carbon. Results were analysed following 2 and 4 hours and graphs were plotted for absorbance versus time (Fig. 8). After four hours, in 5 mg/L concentration maximum removal was from S3, 95.27%. The percentage of removal ranged from 76.64 to 95.27% (Table 5). The decreasing rate of removal percentage was as follows:

S3> S10> S7> S5> S2> S9> S1> S8> S6> S4

At concentration 7.5 mg/L, maximum removal was done in the sample 10 (96.165%). The removal percentage ranged from 80.21% to 96.16%, minimum removal was from the soil of S2 (80.21%). Moreover, the trend found in accordance to the removal percentage was as follows:

S10> S7> S9> S3> S5> S1> S8> S6> S2> S4

On comparing percent removal of Zoxamide from soils in both concentrations, it was observed that pesticide removal possessed direct relation with concentration. At lower concentration, removal is low. In the present study, this trend was observed in the S10, S9, and S1, in 5 mg/L concentration where removal was 94.2, 84.6 and 83%, respectively, while in 7 mg/L their removal was 96, 91 and 86.7%, respectively. At lower concentration, there is less availability of molecules to get adsorbed on the surface of activated carbon, due to which the rate of removal decreases.

## **4. Conclusion**

Soils obtained from various areas were analysed for sorption and degradation of Zoxamide followed by its removal by biologically synthesized activated carbon from *Punica granatum* peels. Adsorption of Zoxamide is directly related to clay content, organic matter and total organic carbon content of soil. Soil samples possessing high organic matter exhibited high  $K_d$  and  $K_f$  values, hence displayed a high potential for adsorption of pesticide. Textural properties were found to highly influence the adsorption capabilities of soil. Activated carbon prepared from the peels of pomegranate was used for the removal of fungicide Zoxamide from the soil. This method is environment friendly and less costly. For the degradation of fungicide Zoxamide various processes including hydrolysis, soil degradation and photodegradation were performed. The highest percentage of degradation was observed through hydrolysis (99.7%) and photodegradation (99.7%). Evaluation of the effects of pesticides need to be done under different laws like National Environmental Policy Act. Grass-root level approach should be used for bringing relief from pesticide problems.

Conflict of interest: Authors declare no potential conflict of interest

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Figure captions

**Fig. 1** Map of soil samples for pesticide studies

**Fig 2** Comparative sorption graphs (A) Linear adsorption (B) Freundlich adsorption (C) Linear desorption (D) Freundlich desorption

**Fig. 3** ANOVA residual plots for adsorption distribution coefficient  $K_d$

**Fig. 4** First order reaction kinetics isotherms for Zoxamide hydrolysis on ten soils

**Fig. 5** Photodegradation of Zoxamide in various concentrations

**Fig. 6** Degradation of Zoxamide in various soil samples

**Fig. 7** FTIR characterization of *Punica granatum* derived activated carbon

**Fig. 8** Removal of Zoxamide by activated carbon

**Table 1.** Soil physiochemical analysis

Sr.no	Samples	EC (Sm <sup>-1</sup> )	pH	OM %	Texture	Sand %	Silt %	Clay %	Lead mg/L	Chromium mg/L	Copper mg/L	Nickel mg/L
1	Mang	1.42	7.59	0.38	Loam	45	37	18	2.956	0.417	24.51	22.4641
2	Tulamba	16.3	7.79	0.29	Loam	49	38	11	6.666	0.573	18.76	17.9923
3	Dharyal Jalap	2.54	7.63	0.30	Loam	42	41	17	23.41	0.261	14.85	15.3975
4	Sai	1.04	7.58	0.46	Loam	45	36	19	3.103	0.231	22.91	30.2595
5	Gujranwala	2.73	7.61	0.41	Loam	50	38	12	25.28	0.250	47.78	12.3224
6	Faisalabad	10.7	7.92	0.40	Sandy Loam	45	38	17	2.303	0.192	18.95	14.9061
7	Dharaki	5.64	7.77	0.30	Loam	50	38	12	1.848	0.230	11.88	13.8848
8	Janjal Khaetar	1.32	7.40	0.35	Loam	43	39	18	12.90	1.967	14.19	18.086
9	Mian Channu	2.27	7.46	0.43	Loam	51	36	13	16.43	0.584	24.81	13.3769
10	Abdul Hakeem	1.02	7.39	0.50	Loam	49	39	20	3.975	0.243	16.16	16.3626

**Table 2.** Sorption data for Zoxamide concentration

S. no	Adsorption parameters							Desorption parameters								
	$K_d$ ( $\mu\text{g/ml}$ )	$R^2$	$K_{om}$ ( $\mu\text{g/ml}$ )	$\Delta G$ ( $\text{KJ/mol}$ )	$K_{oc}$ ( $\mu\text{g/ml}$ )	$K_f$ ( $\mu\text{g/ml}$ )	$R^2$	$K_{foc}$ ( $\mu\text{g/ml}$ )	$n_a$	$K_d(\text{des})$ ( $\mu\text{g/ml}$ )	$R^2$	H	$K_f$ (des)	$R^2$	nd	na
S1	1.29	1	73.86	-10.65	126.7	10	100	980.39	1	747.6	0.95	1.6	3.0	0.98	1.7	1
S2	0.93	0.69	53.16	-9.84	91.20	6.53	92	5934.3	0.37	11344	0.95	8.2	3.6	0.87	3.0	0.3
S3	21.0	0.86	66.91	-10.41	114.8	4.48	0.86	4360.7	0.37	1306.8	0.85	2.6	3.0	0.91	2.9	0.3
S4	1.61	0.89	92.34	-11.21	158.4	2.84	90.9	2043.5	0.39	1223.5	0.93	1.6	2.6	0.96	1.7	0.3
S5	1.01	0.84	58.16	-10.06	99.80	1.77	74	17353	0.32	3183.9	0.93	5.3	2.2	0.63	1.9	0.3
S6	1.13	0.86	64.70	-10.33	111.0	5.9	82.4	5852.9	0.36	4727.9	0.94	29	3.3	0.76	1.4	0.3
S7	37.0	0.99	97.61	-11.34	167.4	2.32	0.99	227.45	1.07	2380.6	0.98	5.8	3.9	0.75	2.2	1.0
S8	1.69	0.99	96.67	-11.32	165.8	2.35	99.5	209.80	1.05	840.70	0.98	1.7	3.6	0.30	1.9	1.0
S9	45.6	0.99	97.23	-11.34	166.8	2.36	99.6	231.37	1.07	9859.8	0.88	8.6	2.7	0.86	3.2	1.0
S10	45.7	0.99	98.12	-11.36	168.3	2.14	99.7	209.80	1.05	549.51	0.99	1.4	3.4	0.98	1.4	1.0

**Table 3.** MANOVA Tests for OM and pH

<b>OM</b>					
Criterion	Test Statistic	F	DF		<u>P</u>
			Num	Denom	
Wilks'	0.91365	0.662	1	7	0.443
Lawley- Hotelling	0.09451	0.662	1	7	0.443
Pillai's	0.08635	0.662	1	7	0.443
Roy's	0.09451				
<b>pH</b>					
Wilks'	0.80050	1.745	1	7	0.228
Lawley- Hotelling	0.24923	1.745	1	7	0.228
Pillai's	0.19950	1.745	1	7	0.228
Roy's	0.24923				

$$s = 1 \quad m = -0.5 \quad n = 2.5$$

**Table 4.** Degradation of Zoxamide by hydrolysis

Samples	Hydrolysis				Soil degradation			
	Percentage degradation	Half life	k	R <sup>2</sup>	Percentage degradation (%)	Half-life (days)	k	R <sup>2</sup>
S1	98.75	4.02	0.172	0.768	99.5	5.318	0.1303	0.815
S2	99.9	3.87	0.1719	0.864	98.4	5.33	0.1318	0.854
S3	99.33	5.09	0.136	0.821	98.1	17.325	0.040	0.6921
S4	99.74	3.78	0.183	0.861	79.28	3.62	0.1912	0.8903
S5	99.75	8.66	0.08	0.876	24.9	27.5	0.0252	0.9572
S6	98.78	7.37	0.094	0.826	39.37	4.50	0.1538	0.9071
S7	99.73	5.33	0.130	0.919	15.36	1.14	0.606	0.982
S8	99.59	8.45	0.082	0.867	39.5	5.36	0.1292	0.9043
S9	96.99	4.2	0.165	0.901	84.3	11.32	0.002	0.8226
S10	99.52	5.72	0.121	0.856	53.08	4.10	0.1689	0.9

Photodegradation			
No.	Concentrations	Photodegradation rate constant (k)	Half-life (t1/2) (days)
1	0	0.086	8.05
2	0.25	0.3569	1.941
3	0.5	0.076	9.11
4	0.75	0.3612	1.918
5	1	0.203	3.41
6	2.5	0.2771	2.50
7	5	0.107	6.47
8	7.5	0.2713	2.554

**Table 5.** Removal of 5 and 7.5 mg/L concentration of Zoxamide

Soil Samples	Percentage Removal (5 mg/L)	Percentage Removal (7.5 mg/L)
S1	83.44	86.70
S2	85.54	80.21
S3	95.27	91.07
S4	76.64	78.06
S5	86.92	90.09
S6	79.42	82.23
S7	90.21	93.25
S8	83.41	83.95
S9	84.602	91.25
S10	94.201	96.165

# Figures

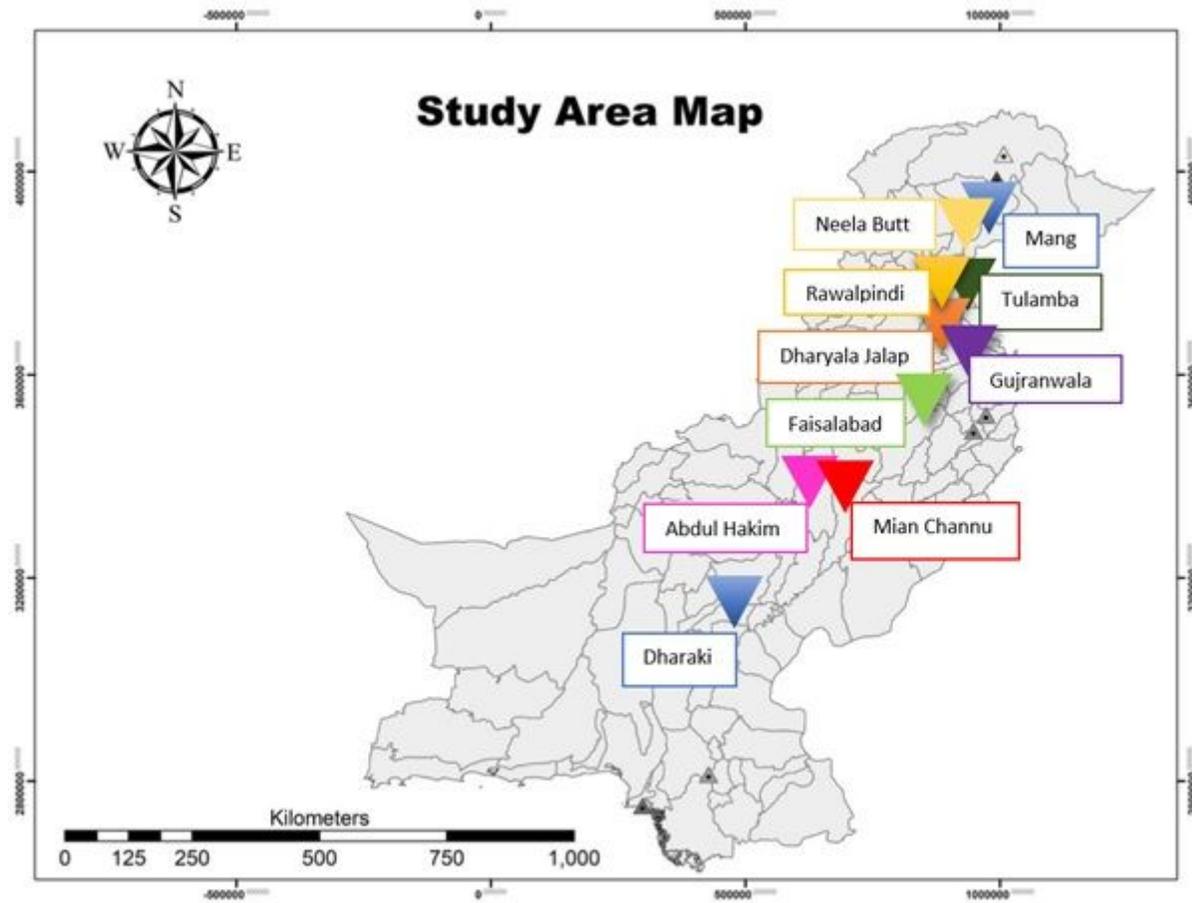


Figure 1

Map of soil samples for pesticide studies

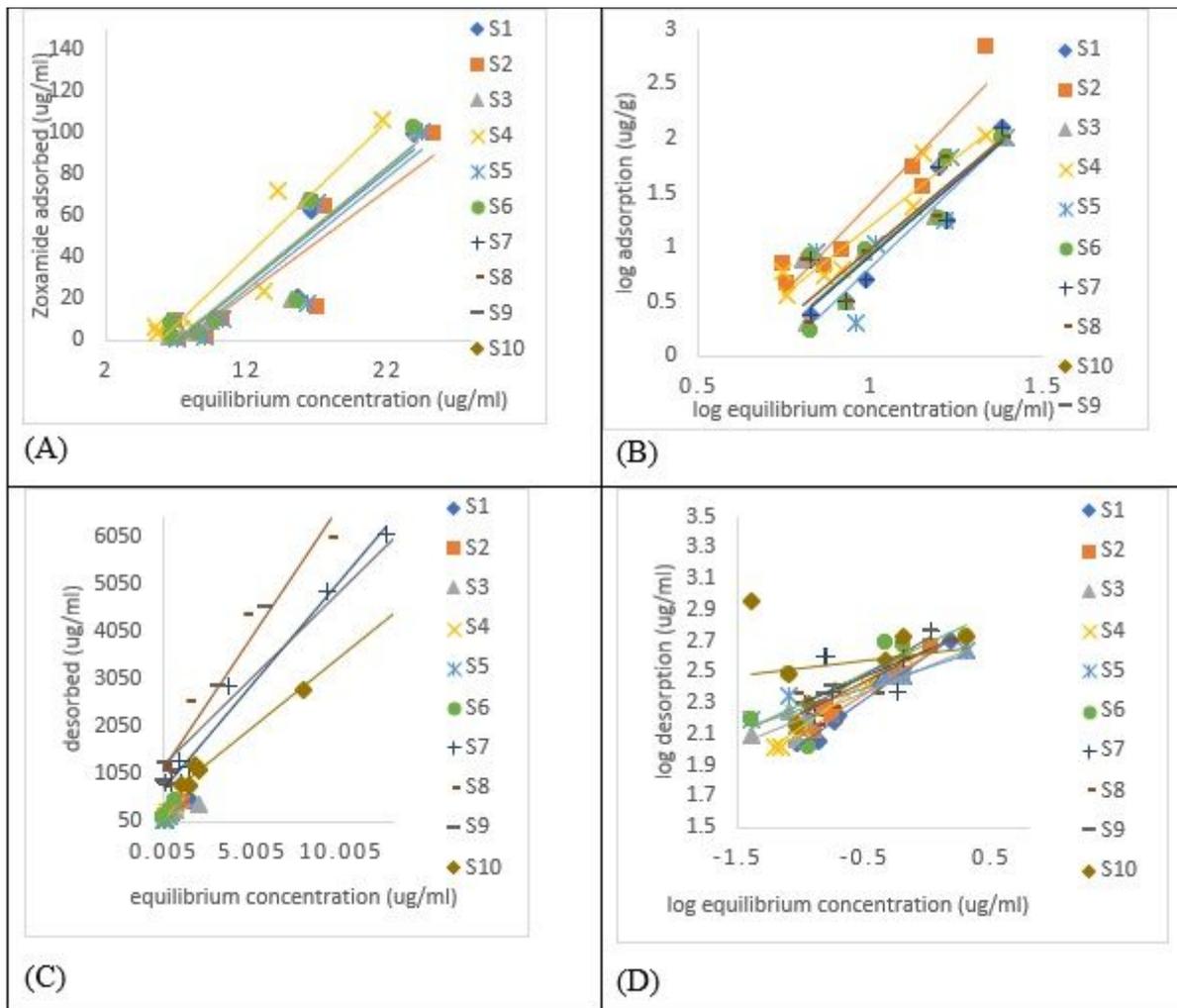


Figure 2

Comparative sorption graphs (A) Linear adsorption (B) Freundlich adsorption (C) Linear desorption (D) Freundlich desorption

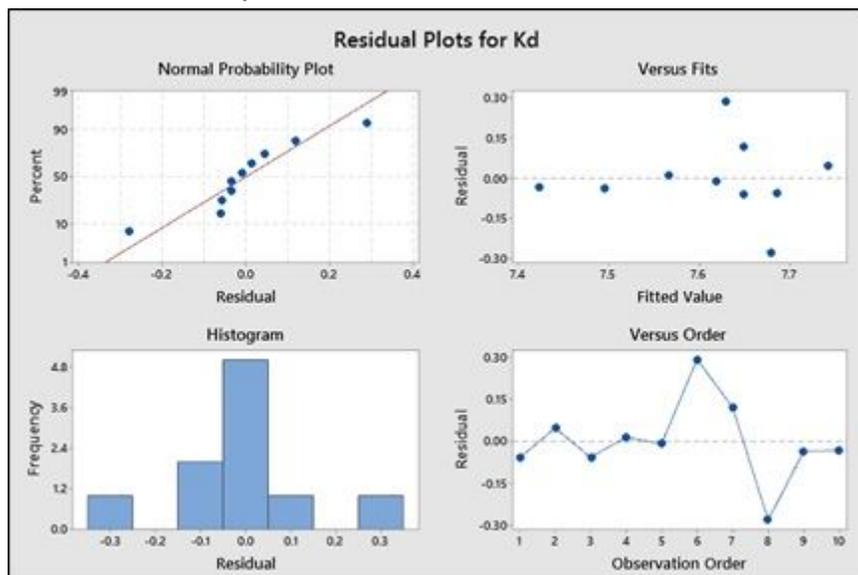


Figure 3

ANOVA residual plots for adsorption distribution coefficient  $K_d$

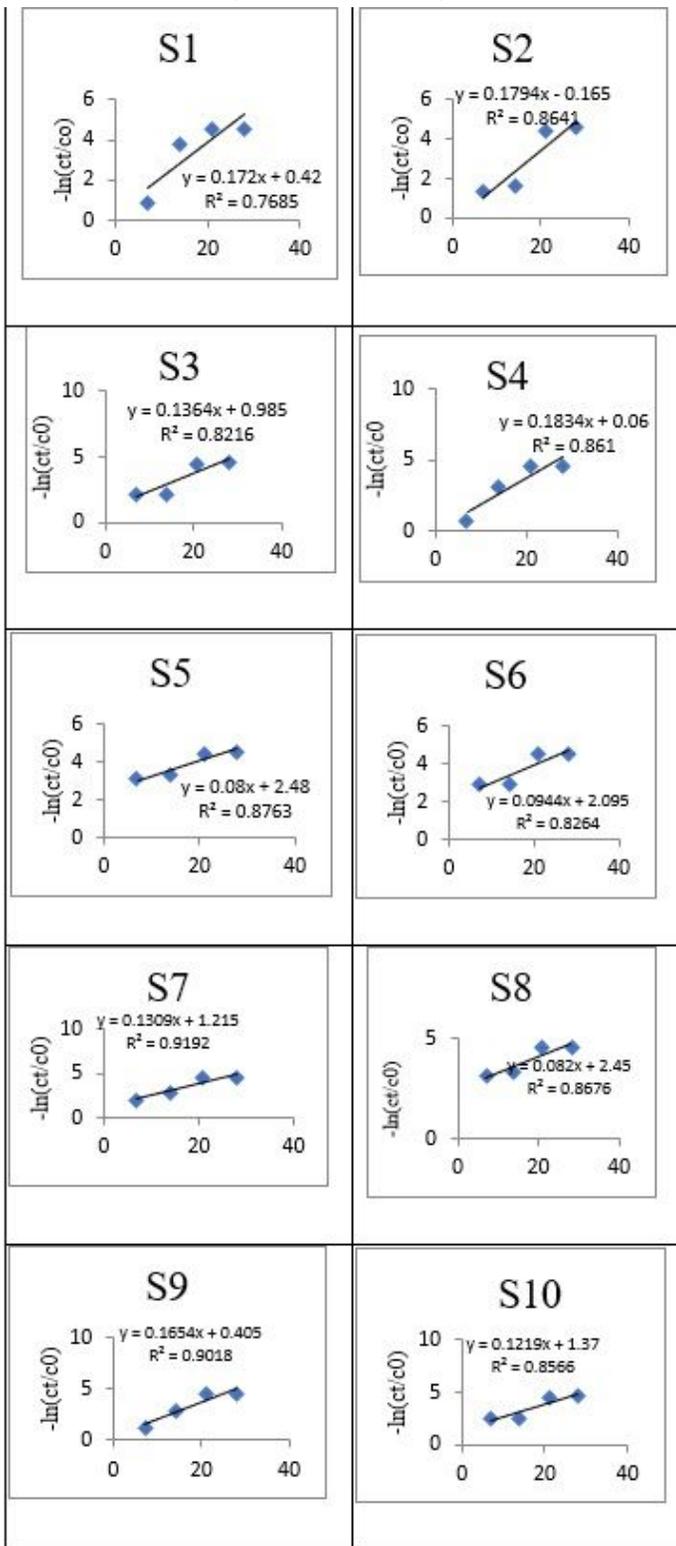
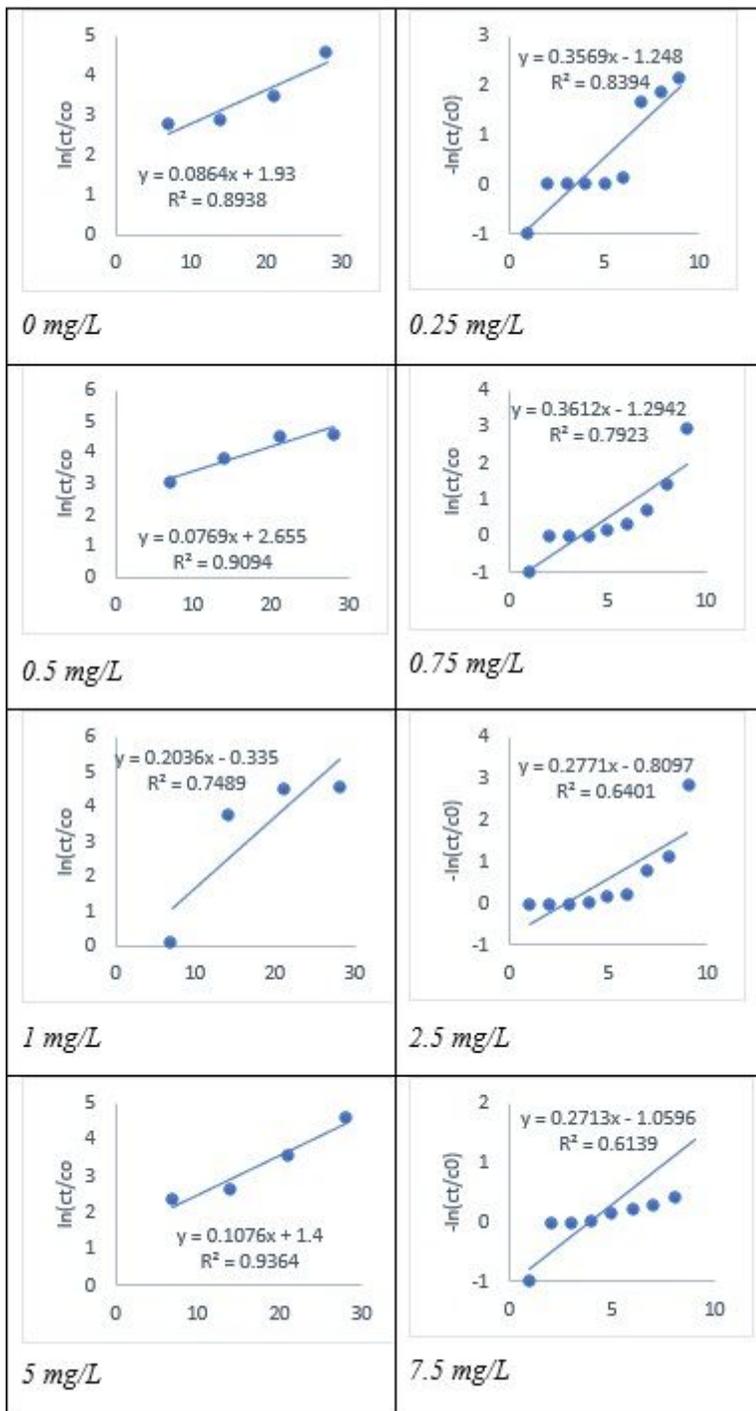


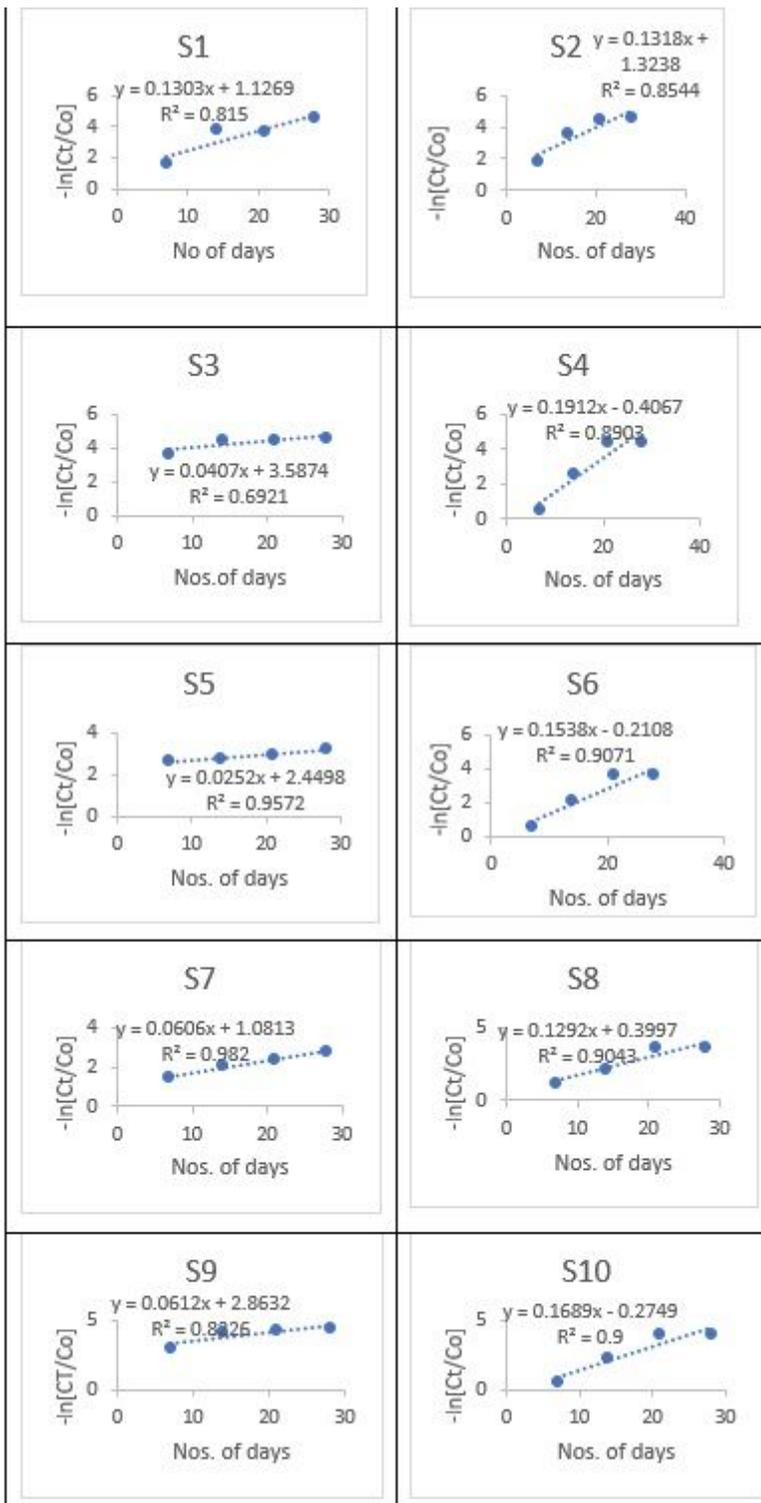
Figure 4

First order reaction kinetics isotherms for Zoxamide hydrolysis on ten soils



**Figure 5**

Photodegradation of Zoxamide in various concentrations



**Figure 6**

Degradation of Zoxamide in various soil samples

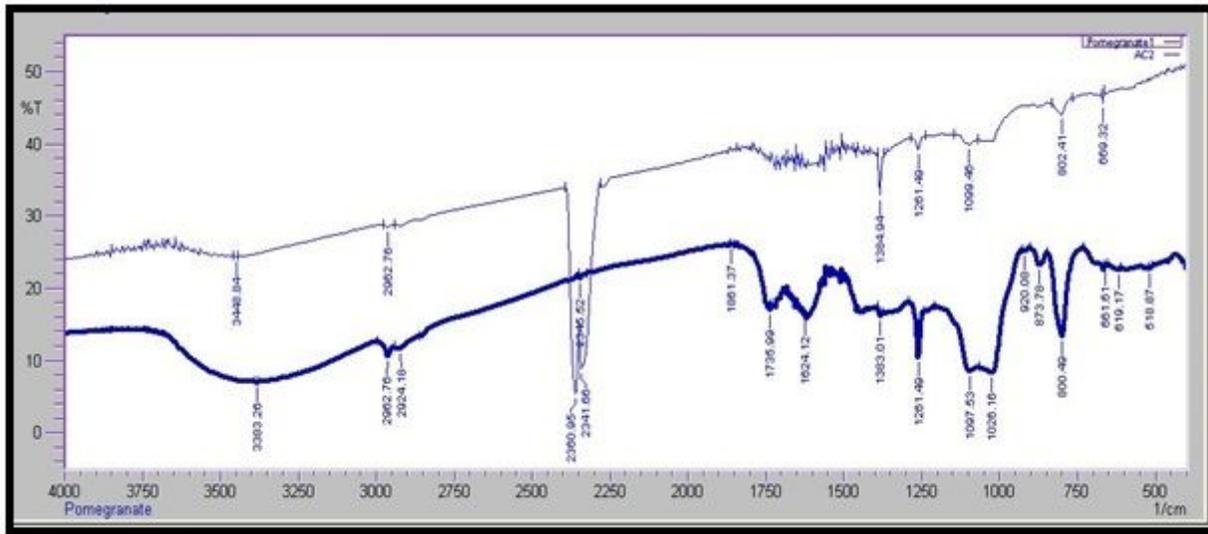


Figure 7

FTIR characterization of Punica granatum derived activated carbon

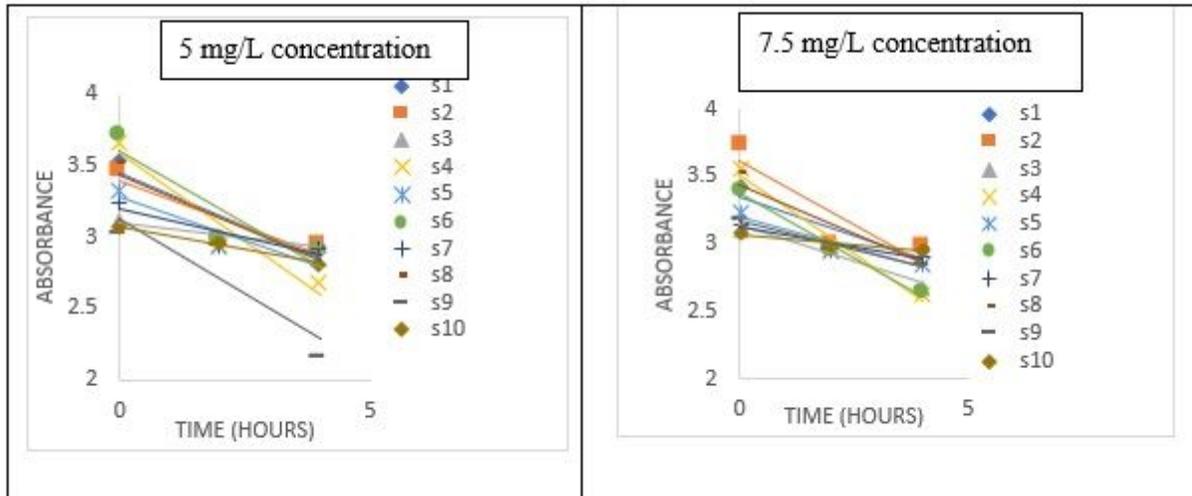


Figure 8

Removal of Zoxamide by activated carbon