

EFFECT OF BIOCHAR AMENDMENT AND AGEING ON SORPTION AND DISSIPATION OF TETRACYCLINE'S IN SOILS

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ABSTRACT

This study pertains to investigate the effects of biochar an environmental friendly soil amendment used to enhance the soil fertility on the sorption dissipation and mobility of three tetracycline antibiotics, viz., chlortetracycline (CTC), oxytetracycline (OTC) and tetracycline (TC) on six agricultural field soil samples collected from different parts of India. The results of the study revealed that with the increase in TCs concentration the sorption of TCs increased in both the bulk soils and biochar amended soils denoting that process of TCs sorption is influenced by the soil properties mainly organic carbon and

CEC. The sorption of TCs was significantly increased in presence of biochar which might be attributed to availability of sorption sites on biochar and the presence of micro pores in biochar. However, the sorption retards in aged biochar amended soils which might be due to covering of micro pores by organic and inorganic substances and oxidation of functional groups on the biochar surface. The adsorptive capacity of soils was in order soil No. $3 > 5 > 2 > 4 > 1 > 6$. The adsorption capacity was significantly positively correlated with the amount of biochar amended. The interaction between TCs and biochar might occur via multiple bonding mechanisms including ionic bond between negative charged organic matter and positively charged TCs and/or hydrogen bonds in between TCs and organic matter. The sorption data of un- amended and biochar amended soils were best fitted in Freundlich adsorption equation and the adsorption isotherms were of 'L' type. The TCs dissipation in all the substrates followed the first order rate equation and DT_{50} ranged in between 34.3 to 58.7 d. Soils amended with biochar enhanced the stability of TCs and reduced their mobility. The concentration of TCs below 10 cm after 91 days of application in biochar amended soils was 70% lesser than un-amended soil. The dissipation in soil environment was slow, indicating that these compounds may persist in soils.

KEYWORDS: Antibiotics, compost, DT₅₀, organic carbon, soils.

INTRODUCTION

Antibiotics particularly tetracyclines are among the most common medications used for human and veterinary treatments. Veterinary antibiotics are used in large amounts for therapeutic and prophylactic purposes as well as growth promoters.^[1,2] The tetracycline's {Tetracycline (TC), Oxytetracycline (OTC) and chlortetracycline (CTC)} are broad spectrum antibiotics widely used in animal production. As tetracycline's and other antibiotics administered in humans and animals undergo minimal or no metabolism and are excreted in urine and manure in an either unaltered or as metabolites, a large number of antibiotics have been detected in soil, animal manure, sediment, ground and sewage water samples. These antibiotics are released in the terrestrial environment via the application of animal manure and bio solids containing excreted antibiotics to agricultural land as fertilizer.^[3,4] Antibiotics can also be introduced to the agricultural land through irrigation with sewage waste water.^[5,6] The fate of pharmaceuticals in the environment is not different from that of other organic chemicals such as pesticides.^[7] Knowledge of persistence pollutants and their sorption behavior is crucial for the evaluation of the leaching. The sorption of tetracycline is influenced by soil pH, organic matter and metal ions.^[8]

As biochar has environmental benefits it is a acceptable soil amendment. Biochar amendment can alter soil properties such as sorption, degradation and leaching of different chemicals. Biochar is a carbon rich bio product that is produced from feedstock through the process of pyrolysis which is stable carbonaceous substance with high porosity, big surface area. Addition of biochar in soils boost soil fertility and improve soil quality by changing the pH, increasing water holding capacity, enhancing the cation Exchange Capacity (CEC), nutrient availability and microbial population.^[9-11] The high specific surface area and CEC of biochar as compared to soil reduces leaching of nutrients.^[12,13]

The main objective of the present study was to investigate the effects of biochar and aged biochar amended six soils differing significantly in organic matter (OM) and other physical and chemical properties on the sorption, dissipation and leaching of tetracycline. The results of this study will be helpful for understanding the impact of biochar amendment on sorption, dissipation and leaching of tetracycline.

MATERIALS AND METHODS

Six types of surface soils (0-25 cm depth), which had never been applied with tetracycline were collected from different parts of India. These soils were air dried, crushed and grounded to pass through <70 mesh sieve, then stored at 4°C before use. The physicochemical properties of these soils are given in Table 1.

Preparation and ageing of soil - Biochar Mixtures

The biochar used was prepared from paddy straw by the methods as described by Reddy.^[14] The characteristics of the biochar are given in Table 2. Soil mixtures were prepared by mixing soil with sieved biochar (< 2mm) at a rate of 1, 2 and 5% biochar per unit soil dry weight. Biochar ageing was performed by amending soils with 2% of biochar. These mixtures were incubated in darkness at room temperature for 4 months. The moisture content was adjusted to 60% of water holding capacity and monitored and adjusted weekly by addition of deionized water.

Sorption isotherms

Sorption experiments were conducted by placing 5 g of air dried soils and soil-biochar mixtures in large number of glass stoppered tubes and adding various amounts of tetracycline solution in methanol (0-15 ml of 20 µg ml⁻¹) and making upto 25 ml with distilled water. The suspensions were shaken for 30 h at 25±2°C (Preliminary studies indicated that equilibrium was attained < 27 h). When equilibrium was attained the suspensions were centrifuged at 13,000 rpm for 15 min. The amount of tetracyclines in supernatants was estimated.

Analysis of tetracyclines

The concentration of TC, OTC and CTC in soil extracts were analyzed by HPLC using an Agilent 1100 system with an octadecylsilan column (50mmx4mmx3µm, AQ-YMC), TC, OTC and CTC were analyzed simultaneously.^[15] A gradient elution was carried out over 20 min with 0.1% formic acid in acetonitrile (Solvent A) and 0.1% formic acid in water (Solvent B). The initial percent of Solvent A was 5%, which was then increased to 30% from 0 to 7 min and remained at 30% from 7 to 8.5 min. The percentage of Solvent A was returned to 5% from 8.5 to 10 min and remained at 5% from 10 to 12 min. The flow rate was maintained 0.70 mL min⁻¹ throughout the analysis and simultaneous detection of TC, OTC and CTC was performed at 360 nm. Retention times of OTC, CTC and TC were 6.4, 17.3 and 9.6 min. respectively. The minimum limit of detection was 0.5µg kg⁻¹ soil.

Degradation and movement studies

For persistence and degradation studies 1 kg of soil and soil-biochar mixtures were incubated with 0, 5, 10, 20 and 50 $\mu\text{g g}^{-1}$ soils of tetracycline in methanol in several polypropylene pots separately at 60% of water retention capacity. Moisture was regularly maintained based on the difference in between two consecutive days. Samples were incubated at room temperature. The residues were monitored at the time interval of 0 (4 h), 7, 14, 21, 28, 35, 42, 49, 56, 63, 70, 77, 84 and 91 days after incubation followed by residue analysis.

Mobility studies

The mobility studies were conducted in 60 x 12 cm PVC pipes. The lower end of pipes was sealed with polythene and cotton cloth. The pipes were filled with 10 kg of each soil and soil-biochar mixtures. 200 mg of tetracycline in methanol (20 $\mu\text{g g}^{-1}$ soils) were applied separately in all the pipes at 60% of water retention capacity. Soil samples were collected using a steel soil sampler at the depth of 0-15 and 15-30 cm after 0, 7, 14, 21, 28, 35, 42, 49 days of application and at the depth of 0-15, 15-30, 30-45, 45-60 cm after 56, 63, 70, 77 and 91 days of application followed by residue analysis.

All the chemicals used were of analytical grade and all the experiments were done in three replicates with suitable blanks.

RESULTS AND DISCUSSION

The adsorption isotherms, Freundlich and Langmuir were used to fit the sorption of TCs in the sorbents. The results showed that Freundlich relationship ($R^2 > 0.91$) can be best used to describe TCs adsorption results on soils and biochar amended soils. The linear form of this equation is $\log C = \log K + 1/n \log C_e$. Where C is the amount (mg kg^{-1}) of TCs adsorbed, C_e is the equilibrium concentration in solution (mg L^{-1}), K ($\text{mg}^{-1}/\text{nL}^1/\text{nkg}^{-1}$) is the Freundlich adsorption coefficient and $1/n$ is a describer of isotherm curvature. The values of $1/n$ were less than unity indicating a L' type of isotherm. The values of K and $1/n$ (Table 3) followed the order CTC > OTC > TC. The values of K and $1/n$ were higher in biochar amended soils than un-amended soils and followed the order 5% biochar > 2% biochar > 2% aged biochar > 1% biochar > un-amended soil. The data of Table 3 also denote that sorption of TCs on different soils were in the order soil 3 > 5 > 2 > 4 > 1 > 6. The enhancement in TCs sorption in biochar amended soils may be availability of sorption sites on biochar and the presence of micro pores in biochar.^[16,17] Data of Fig 1 and Table 3 also denote that sorption capacity of aged biochar decreases with time. The values of K for 2% aged biochar were approx. 14%

lower than 2% fresh biochar amended soils. The decrease in sorption of studied antibiotics in aged biochar amended soils might be due to covering of micropores by organic and inorganic substances and oxidation of functional groups on the biochar surface.^[18]

The sorption isotherms (Fig. 1) showed that the quantity of TCs adsorbed on all matrices increased with increasing TC concentration in equilibrium solution. The slope of the isotherm steadily decreases with the rise in solute concentration as vacant sites become less accessible with the progressive covering of the surface. The curvilinear isotherm suggests that the number of available sites for the adsorption become a limiting factor. The sorption isotherms were convex or 'L' type^[19] (Fig.1). These kinds of isotherm arise because of minimum competition of solvent for sites on the adsorbing surface. The adsorption was in the order CTC > OTC > TC. The adsorption of all the three antibiotics followed the order soil 3 > 5 > 2 > 4 > 1 > 6 supporting the hypothesis that clay content, CEC and organic matter plays an important role in sorption of antibiotics. The sorption isotherms for biochar amended soils (Fig. 1) were non-linear and similar to those un-amended soils. When biochar is added in soils the sorption of TCs was increased significantly as addition of biochar in soils increases the organic carbon content and CEC of soils by increasing available sorption sites on biochar and the presence of micro pores in biochar. The more the biochar was added more the sorption of TCs was observed and sorption followed the order 5% biochar > 2% biochar > 2% aged biochar > 1% biochar > un-amended soil. This increase could be related to the sorption of organic matter to the soil by increasing the sorption sites available for adsorption as organic matter enhanced carboxyl and phenolic groups that may interact with polar groups of TCs. The interaction between TCs and organic matter occur via multiple bonding mechanisms including ionic bond between negative charged organic matter and positively charged TCs and/or hydrogen bonds in between TCs and organic matter.^[20] The decrease in sorption of studied TCs in aged biochar amended soils might be due to covering of micropores by organic and inorganic substances and oxidation of functional groups on the biochar surface.^[18]

Preliminary studies denoted that the dissipation of TCs on studied samples followed the first order reaction, as all the regression lines generated have a coefficient of determination (R^2) more than 0.92.

The Equation (1) describes the dissipation kinetics and equation (2) is used to calculate dissipation half-lives.

$$C_t = C_0 \times e^{-(kt)} \dots (1) \quad DT_{50} = 0.693/k \dots (2)$$

Where C_0 and C_t are the concentration of analytes at time 0 and time t (days) and k is the first order rate constant determined as the slope value from test substance dissipation curves.

The time taken for dissipation of 50% (DT_{50}) of the CTC in all the treatments were 36.1 to 58.7 d (Table 4) which were longer than OTC (35-55 d), which were longer than TC (34.3-53.3 d), denoting that CTC was more stable in the soils and soil biochar mixture followed by OTC and TC. An examination of data of Table 4 showed that the rate of degradation followed the soil order $S_6 > S_1 > S_4 > S_2 > S_5 > S_3$ indicating thereby a role of soil organic matter, CEC and clay content.^[21,22] The rate of degradation was inverse the order of sorption. The DT_{50} increased with increase in amount of biochar. The dissipation in different compost amended soils was in the order 5% biochar < 2% biochar < 2% aged biochar < 1% aged biochar < un-amended which might be significantly correlated with soil organic carbon and CEC which in turn enhance the sorption of TCs.^[23] The difference in dissipation times of different antibiotics on same substrates may be due to their characteristics and the nature of substrate.

Mobility Studies

Results of mobility studies denote that the TCs in all the studied biochar un-amended soils did not leach below 30 cm. The concentration of studied tetracyclines below 15 cm after 91 days of application in un-amended soils was 20-38% of the initial amount of TCs applied. With the amendment of biochar into the soil, leaching of antibiotics in soil columns retards which may be due to enhanced sorption. The concentration of TCs below 10 cm after 91 days of application in biochar amended soils was 10-23% of the initial amount of tetracycline's applied. The leaching of the studied antibiotics in the aged biochar amended soils was more than fresh biochar amended soils. These results confirm the results that ageing of biochar in soil environment decreases the sorption capacity of biochar. Similar results are also reported by other researchers on pesticide sorption.^[24,25] Data of Fig 2 also showed that the leaching of tetracycline's was in the order soil $S_6 > S_1 > S_4 > S_2 > S_5 > S_3$ (Fig. 2). The amount of TCs leaching below 15 cm depth showed a strong inverse relationship to sorption and soil organic matter.

Table 1: Selected Physical and Chemical properties of the soils used.

| Soil | Location | Organic Carbon(g kg ⁻¹) | Clay % | Sand % | Silt % | pH (1:2.5) | CEC (cmol (p+) kg ⁻¹) |
|----------------|-----------|-------------------------------------|--------|--------|--------|------------|-----------------------------------|
| S ₁ | Bangalore | 1.34 | 20.2 | 30.8 | 49 | 6.3 | 6.7 |
| S ₂ | Aligarh | 1.68 | 13.0 | 39 | 48.0 | 8.9 | 11.2 |
| S ₃ | Kota | 3.30 | 45.2 | 10.6 | 44.2 | 7.1 | 31.8 |
| S ₄ | Jhansi | 1.32 | 27.2 | 48.2 | 24.6 | 7.6 | 16.5 |
| S ₅ | Doiawala | 2.50 | 20.2 | 25.4 | 54.4 | 5.8 | 20.4 |
| S ₆ | Ludhiana | 0.84 | 30.0 | 32.5 | 37.5 | 8.1 | 15.8 |

Table 2: Selected Physical and Chemical properties of the biochar used in this study.

| pH (1:2.5) | Specific surface area (m ² /g) | Bulk density (g/mL) | Ash content (% w/w) | Total Pore volume (mL/g) | Micro Pore volume (mL/g) | CEC (cmol (p+) kg ⁻¹) | Total Organic Carbon (%) | Total Nitrogen (%) | Total Phosphorous (%) | Exchangeable Acidity (m mol/kg) |
|------------|---|---------------------|---------------------|--------------------------|--------------------------|-----------------------------------|--------------------------|--------------------|-----------------------|---------------------------------|
| 9.14 | 11.84. | 0.484 | 21.24 | 0.044 | 0.006 | 9.1 | 51.2 | 0.88 | 0.22 | 21 |

Table 3: Freundlich parameters for tetracycline antibiotics (CTC, OTC and TC) adsorption in unamended and biochar- amended soils.

| Properties | Soils | | | | | | | | | | | | | | | | | |
|----------------------|----------------|-------|----------------|----------------|-------|----------------|----------------|-------|----------------|----------------|-------|----------------|----------------|-------|----------------|----------------|-------|----------------|
| | S ₁ | | | S ₂ | | | S ₃ | | | S ₄ | | | S ₅ | | | S ₆ | | |
| | CTC | | | | | | | | | | | | | | | | | |
| | K | 1/n | R ² | K _f | 1/n | R ² | K _f | 1/n | R ² | K _f | 1/n | R ² | K _f | 1/n | R ² | K _f | 1/n | R ² |
| Fresh soil | 9.61 | 0.915 | 0.932 | 11.86 | 0.882 | 0.924 | 13.82 | 0.858 | 0.920 | 10.79 | 0.898 | 0.912 | 12.64 | 0.866 | 0.922 | 8.48 | 0.922 | 0.918 |
| Soil+1% Biochar | 13.49 | 0.878 | 0.912 | 15.94 | 0.866 | 0.908 | 17.26 | 0.838 | 0.914 | 14.12 | 0.872 | 0.908 | 16.16 | 0.844 | 0.916 | 11.34 | 0.886 | 0.936 |
| Soil+2% Biochar | 16.24 | 0.866 | 0.918 | 18.27 | 0.854 | 0.924 | 20.85 | 0.826 | 0.946 | 17.84 | 0.860 | 0.926 | 19.22 | 0.832 | 0.932 | 14.54 | 0.874 | 0.924 |
| Soil+5% Biochar | 20.85 | 0.842 | 0.916 | 22.32 | 0.828 | 0.936 | 25.12 | 0.810 | 0.932 | 21.48 | 0.834 | 0.934 | 23.66 | 0.820 | 0.914 | 18.42 | 0.848 | 0.932 |
| Soil+2% Aged Biochar | 14.25 | 0.872 | 0.926 | 16.78 | 0.864 | 0.922 | 18.45 | 0.832 | 0.924 | 15.48 | 0.866 | 0.916 | 17.58 | 0.838 | 0.918 | 13.48 | 0.876 | 0.926 |

OTC

| | | | | | | | | | | | | | | | | | | |
|----------------------|-------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|-------------|--------------|--------------|--------------|--------------|--------------|-------------|--------------|--------------|
| Fresh soil | 9.12 | 0.910 | 0.924 | 10.36 | 0.874 | 0.934 | 12.16 | 0.852 | 0.916 | 9.79 | 0.892 | 0.920 | 11.88 | 0.860 | 0.948 | 8.08 | 0.914 | 0.916 |
| Soil+1% Biochar | 11.68 | 0.872 | 0.912 | 13.94 | 0.860 | 0.922 | 15.78 | 0.832 | 0.922 | 12.64 | 0.864 | 0.918 | 14.72 | 0.840 | 0.920 | 10.18 | 0.880 | 0.926 |
| Soil+2% Biochar | 13.84 | 0.860 | 0.940 | 15.88 | 0.848 | 0.918 | 18.18 | 0.826 | 0.934 | 14.72 | 0.852 | 0.912 | 16.84 | 0.822 | 0.912 | 12.66 | 0.866 | 0.942 |
| Soil+5% Biochar | 17.14 | 0.832 | 0.926 | 19.68 | 0.816 | 0.944 | 22.44 | 0.810 | 0.922 | 18.52 | 0.826 | 0.924 | 21.08 | 0.814 | 0.920 | 15.88 | 0.840 | 0.924 |
| Soil+2% Aged Biochar | 12.94 | 0.866 | 0.916 | 14.16 | 0.856 | 0.916 | 16.88 | 0.826 | 0.934 | 13.66 | 0.860 | 0.928 | 15.38 | 0.830 | 0.922 | 12.14 | 0.870 | 0.932 |

TC

| | | | | | | | | | | | | | | | | | | |
|----------------------|-------------|--------------|--------------|-------------|--------------|--------------|--------------|--------------|--------------|-------------|--------------|--------------|--------------|--------------|--------------|-------------|--------------|--------------|
| Fresh soil | 8.84 | 0.902 | 0.942 | 9.64 | 0.870 | 0.922 | 11.44 | 0.848 | 0.934 | 9.22 | 0.884 | 0.932 | 10.88 | 0.852 | 0.932 | 7.68 | 0.908 | 0.934 |
| Soil+1% Biochar | 10.42 | 0.866 | 0.926 | 11.84 | 0.852 | 0.936 | 14.84 | 0.824 | 0.928 | 11.08 | 0.860 | 0.924 | 13.14 | 0.834 | 0.920 | 9.82 | 0.872 | 0.920 |
| Soil+2% Biochar | 12.12 | 0.852 | 0.928 | 14.16 | 0.844 | 0.924 | 16.12 | 0.820 | 0.926 | 12.96 | 0.844 | 0.934 | 14.54 | 0.818 | 0.922 | 10.66 | 0.860 | 0.926 |
| Soil+5% Biochar | 15.18 | 0.824 | 0.920 | 17.44 | 0.812 | 0.932 | 20.76 | 0.804 | 0.918 | 16.48 | 0.820 | 0.918 | 19.14 | 0.810 | 0.924 | 13.64 | 0.834 | 0.916 |
| Soil+2% Aged Biochar | 11.66 | 0.860 | 0.928 | 12.96 | 0.850 | 0.916 | 15.14 | 0.822 | 0.920 | 12.34 | 0.852 | 0.920 | 13.96 | 0.822 | 0.916 | 11.06 | 0.860 | 0.924 |

Table 4: Average degradation rate constants, half-lives for tetracycline antibiotics (CTC, OTC and TC) in unamended and biochar-amended soils.

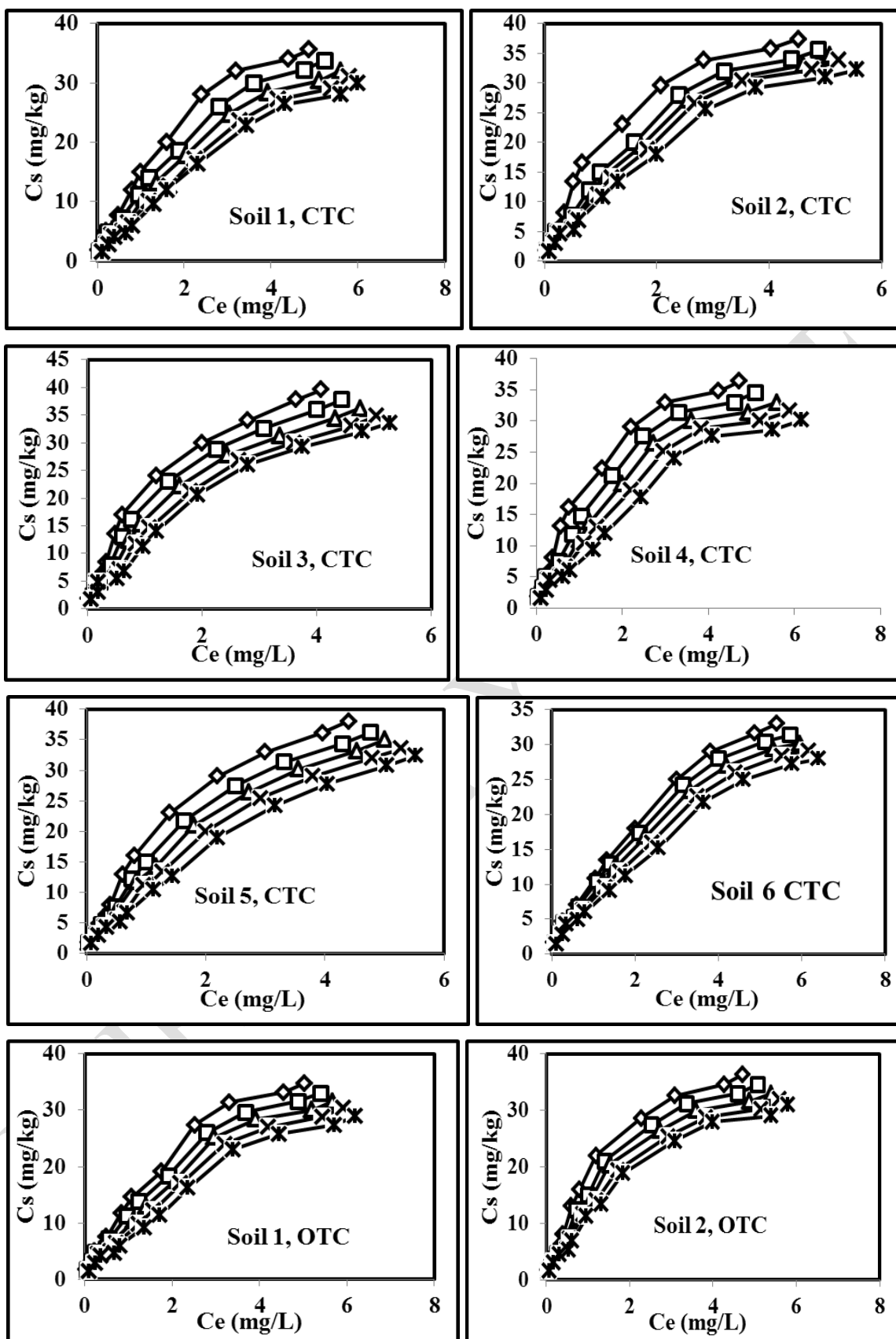
| Soil | Soils | | | | | | | | | | | | | | |
|------|--------------------------------------|------------------|----------------|--------------------------------------|------------------|----------------|--------------------------------------|------------------|----------------|--------------------------------------|------------------|----------------|--------------------------------------|------------------|----------------|
| | Fresh soil | | | Soil+1% Biochar | | | Soil+2% Biochar | | | Soil+5% Biochar | | | Soil+2% Aged Biochar | | |
| | CTC | | | | | | | | | | | | | | |
| | k (d ⁻¹)x10 ¹ | DT ₅₀ | R ² | k (d ⁻¹)x10 ¹ | DT ₅₀ | R ² | k (d ⁻¹)x10 ¹ | DT ₅₀ | R ² | k (d ⁻¹)x10 ¹ | DT ₅₀ | R ² | k (d ⁻¹)x10 ¹ | DT ₅₀ | R ² |
| S1 | 0.180±0.05 | 38.5±1.0 | 0.952 | 0.166±0.05 | 41.7±1.4 | 0.954 | 0.156±0.03 | 44.4±1.6 | 0.944 | 0.146±0.04 | 47.6±1.3 | 0.938 | 0.158±0.05 | 43.9±1.3 | 0.938 |
| S2 | 0.166±0.03 | 41.7±1.2 | 0.938 | 0.156±0.03 | 44.4±1.1 | 0.958 | 0.148±0.03 | 46.8±1.3 | 0.938 | 0.134±0.04 | 51.7±1.5 | 0.952 | 0.154±0.04 | 45±1.0 | 0.948 |
| S3 | 0.146±0.02 | 47.4±1.4 | 0.958 | 0.134±0.03 | 51.7±1.5 | 0.944 | 0.126±0.03 | 55±1.6 | 0.948 | 0.118±0.03 | 58.7±1.5 | 0.946 | 0.130±0.03 | 53.3±1.5 | 0.952 |
| S4 | 0.172±0.05 | 40.3±1.0 | 0.962 | 0.158±0.05 | 43.9±1.3 | 0.932 | 0.150±0.03 | 46.2±1.3 | 0.952 | 0.142±0.05 | 48.8±1.3 | 0.952 | 0.154±0.04 | 45±1.3 | 0.946 |
| S5 | 0.160±0.04 | 43.3±0.9 | 0.944 | 0.150±0.04 | 46.2±1.2 | 0.942 | 0.140±0.04 | 49.5±1.5 | 0.928 | 0.132±0.04 | 52.5±1.4 | 0.944 | 0.144±0.03 | 48.1±1.4 | 0.928 |
| S6 | 0.192±0.04 | 36.1±1.2 | 0.954 | 0.182±0.04 | 38.1±0.9 | 0.938 | 0.170±0.04 | 40.8±1.3 | 0.936 | 0.162±0.04 | 42.8±1.5 | 0.936 | 0.174±0.04 | 39.8±1.2 | 0.942 |

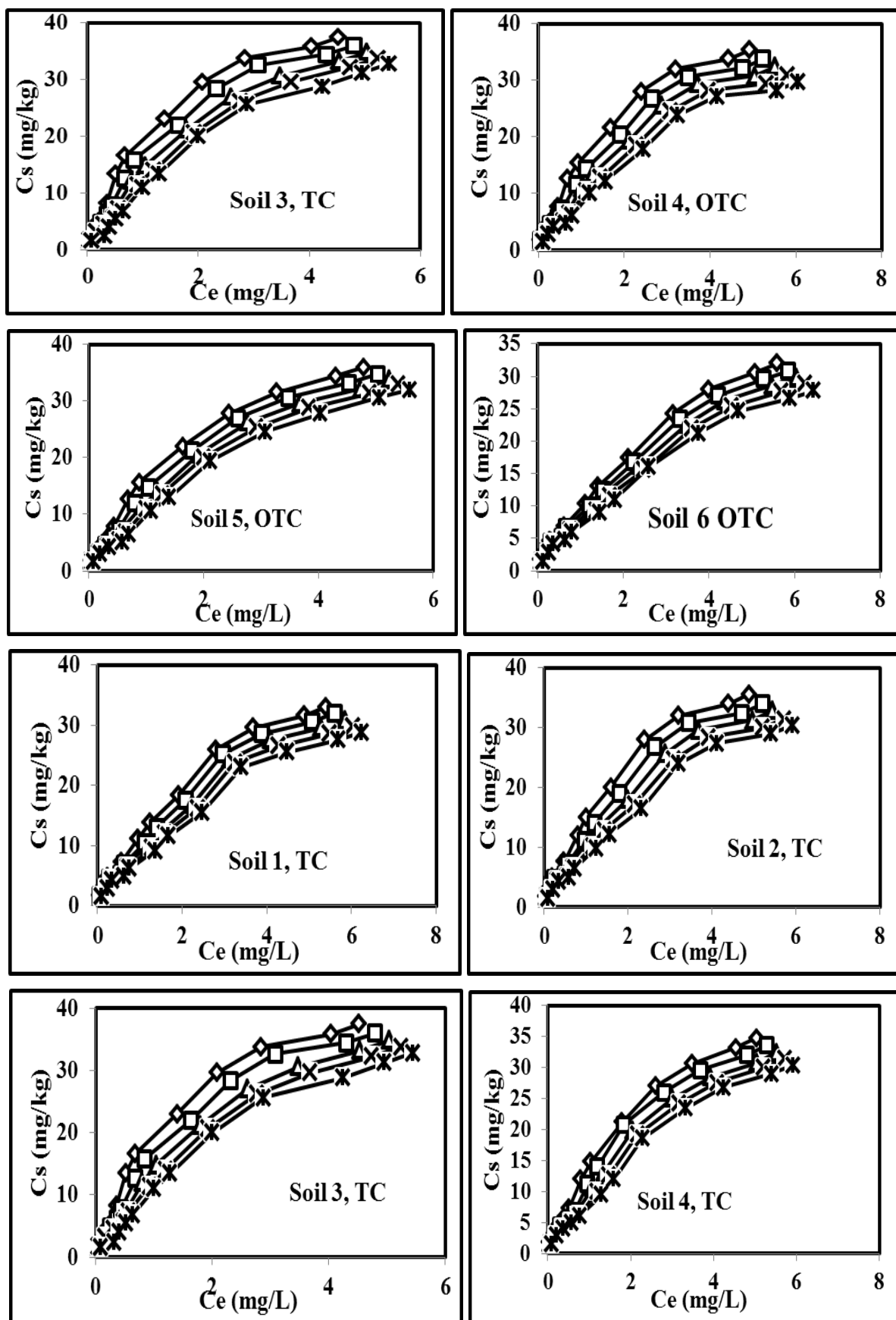
OTC

| | | | | | | | | | | | | | | | |
|----|------------|----------|-------|------------|----------|-------|------------|----------|-------|------------|----------|-------|------------|----------|-------|
| S1 | 0.184±0.04 | 37.7±1.2 | 0.936 | 0.172±0.04 | 40.3±1.0 | 0.934 | 0.162±0.03 | 42.8±1.3 | 0.944 | 0.152±0.04 | 45.6±1.2 | 0.936 | 0.166±0.04 | 41.7±1.4 | 0.936 |
| S2 | 0.170±0.05 | 40.8±1.1 | 0.946 | 0.162±0.04 | 42.8±1.2 | 0.952 | 0.156±0.03 | 44.4±1.5 | 0.948 | 0.142±0.04 | 48.8±1.4 | 0.944 | 0.160±0.04 | 43.3±1.3 | 0.952 |
| S3 | 0.152±0.05 | 45.6±1.3 | 0.954 | 0.142±0.03 | 48.8±1.3 | 0.948 | 0.132±0.03 | 52.5±1.6 | 0.934 | 0.126±0.03 | 55±1.6 | 0.948 | 0.134±0.03 | 51.7±1.3 | 0.948 |
| S4 | 0.176±0.05 | 39.4±1.3 | 0.932 | 0.166±0.05 | 41.7±1.2 | 0.936 | 0.158±0.03 | 43.9±1.1 | 0.946 | 0.148±0.05 | 46.8±1.3 | 0.938 | 0.160±0.05 | 43.3±1.4 | 0.944 |
| S5 | 0.164±0.03 | 42.2±1.1 | 0.942 | 0.154±0.04 | 45±1.3 | 0.940 | 0.146±0.04 | 47.5±1.2 | 0.952 | 0.138±0.04 | 50.2±1.4 | 0.942 | 0.150±0.04 | 46.2±1.5 | 0.948 |
| S6 | 0.198±0.04 | 35±0.9 | 0.926 | 0.188±0.05 | 36.9±1.3 | 0.950 | 0.178±0.04 | 38.9±1.2 | 0.960 | 0.166±0.04 | 41.2±1.4 | 0.936 | 0.182±0.04 | 38.1±1.2 | 0.936 |

TC

| | | | | | | | | | | | | | | | |
|----|------------|----------|-------|------------|----------|-------|------------|----------|-------|------------|----------|-------|------------|----------|-------|
| S1 | 0.188±0.04 | 36.9±1.0 | 0.946 | 0.174±0.04 | 39.8±1.2 | 0.936 | 0.166±0.03 | 41.7±1.3 | 0.948 | 0.158±0.03 | 43.9±1.4 | 0.954 | 0.170±0.04 | 40.8±1.3 | 0.944 |
| S2 | 0.176±0.05 | 39.4±1.1 | 0.958 | 0.166±0.04 | 41.7±1.4 | 0.948 | 0.160±0.03 | 43.3±1.1 | 0.942 | 0.150±0.04 | 46.2±1.2 | 0.936 | 0.162±0.04 | 42.8±1.4 | 0.956 |
| S3 | 0.154±0.04 | 45±1.2 | 0.954 | 0.146±0.03 | 47.5±1.3 | 0.948 | 0.138±0.03 | 50.2±1.4 | 0.948 | 0.130±0.03 | 53.3±1.3 | 0.946 | 0.140±0.03 | 49.5±1.3 | 0.952 |
| S4 | 0.180±0.05 | 38.5±1.2 | 0.942 | 0.170±0.04 | 40.8±1.1 | 0.942 | 0.160±0.03 | 43.3±1.5 | 0.936 | 0.154±0.05 | 45±1.4 | 0.938 | 0.166±0.05 | 41.7±1.2 | 0.944 |
| S5 | 0.166±0.04 | 41.7±1.2 | 0.936 | 0.160±0.04 | 43.3±1.3 | 0.954 | 0.152±0.04 | 45.6±1.3 | 0.952 | 0.146±0.04 | 47.5±1.5 | 0.952 | 0.154±0.04 | 45±1.3 | 0.936 |
| S6 | 0.202±0.04 | 34.3±1.0 | 0.964 | 0.192±0.04 | 36.1±1.1 | 0.946 | 0.184±0.04 | 37.7±1.2 | 0.944 | 0.176±0.04 | 39.4±1.5 | 0.942 | 0.188±0.04 | 37±1.2 | 0.946 |





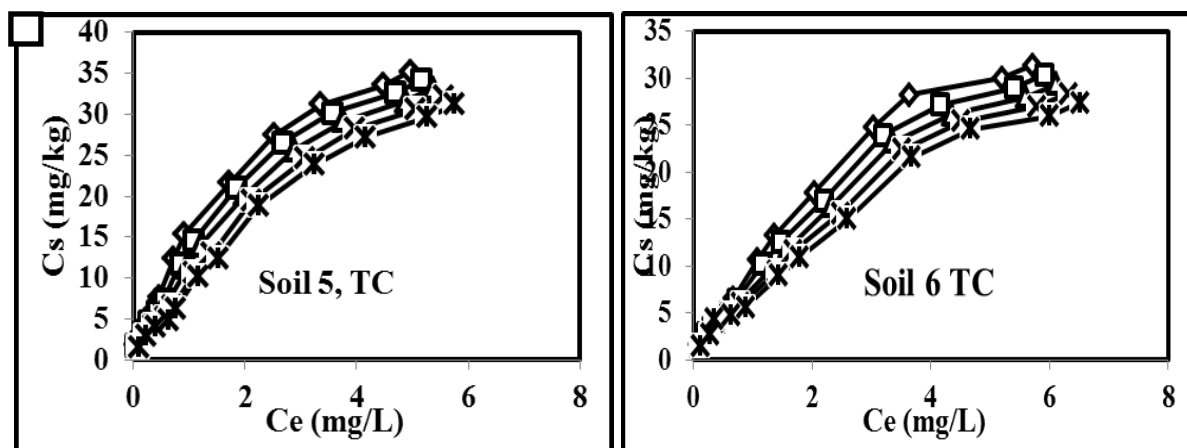
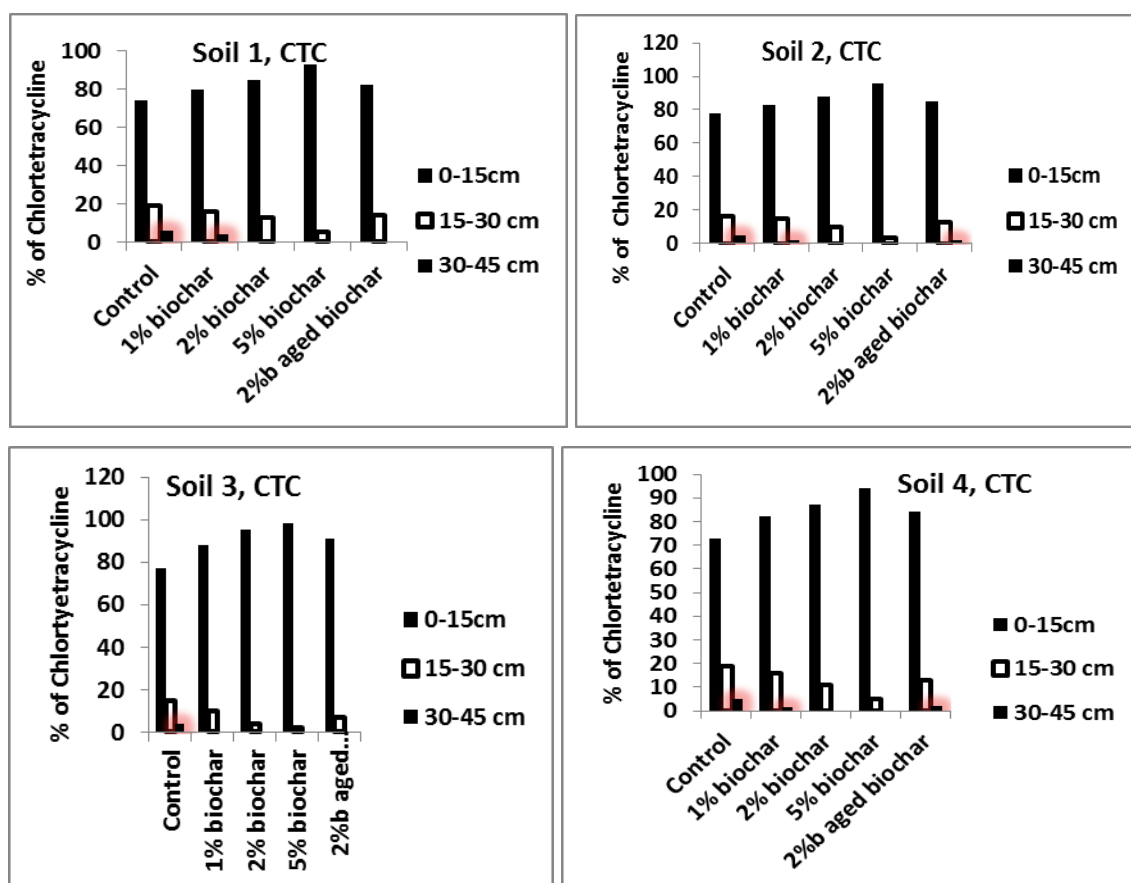
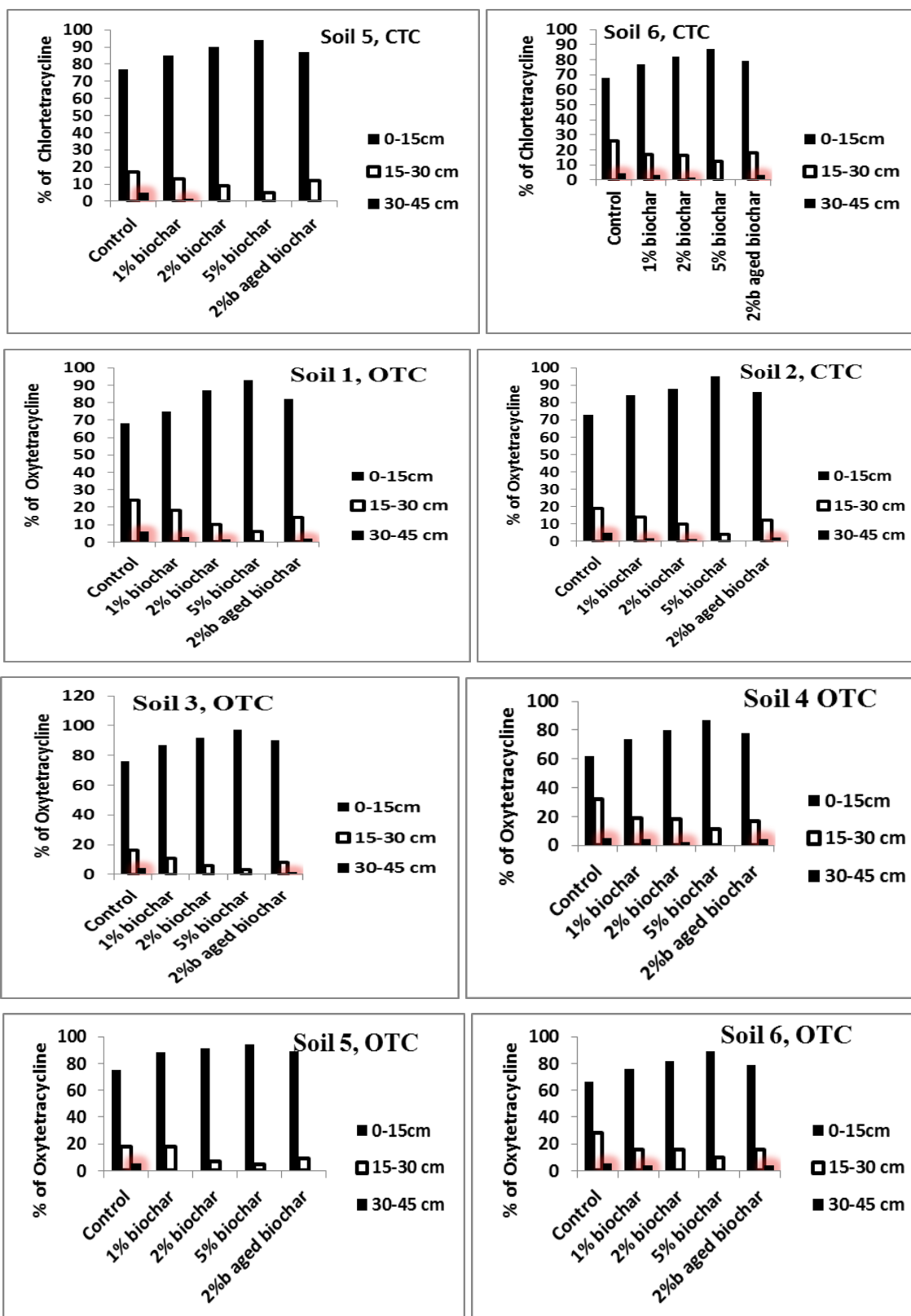


Fig. 1: Adsorption isotherms of Tetracycline's (CTC, OTC and TC) adsorption on six soils in \square 5% biochar amended, \diamond , 2% biochar amended, \triangle 1% biochar amended, (X) 2% aged biochar amended and (*) fresh soils.





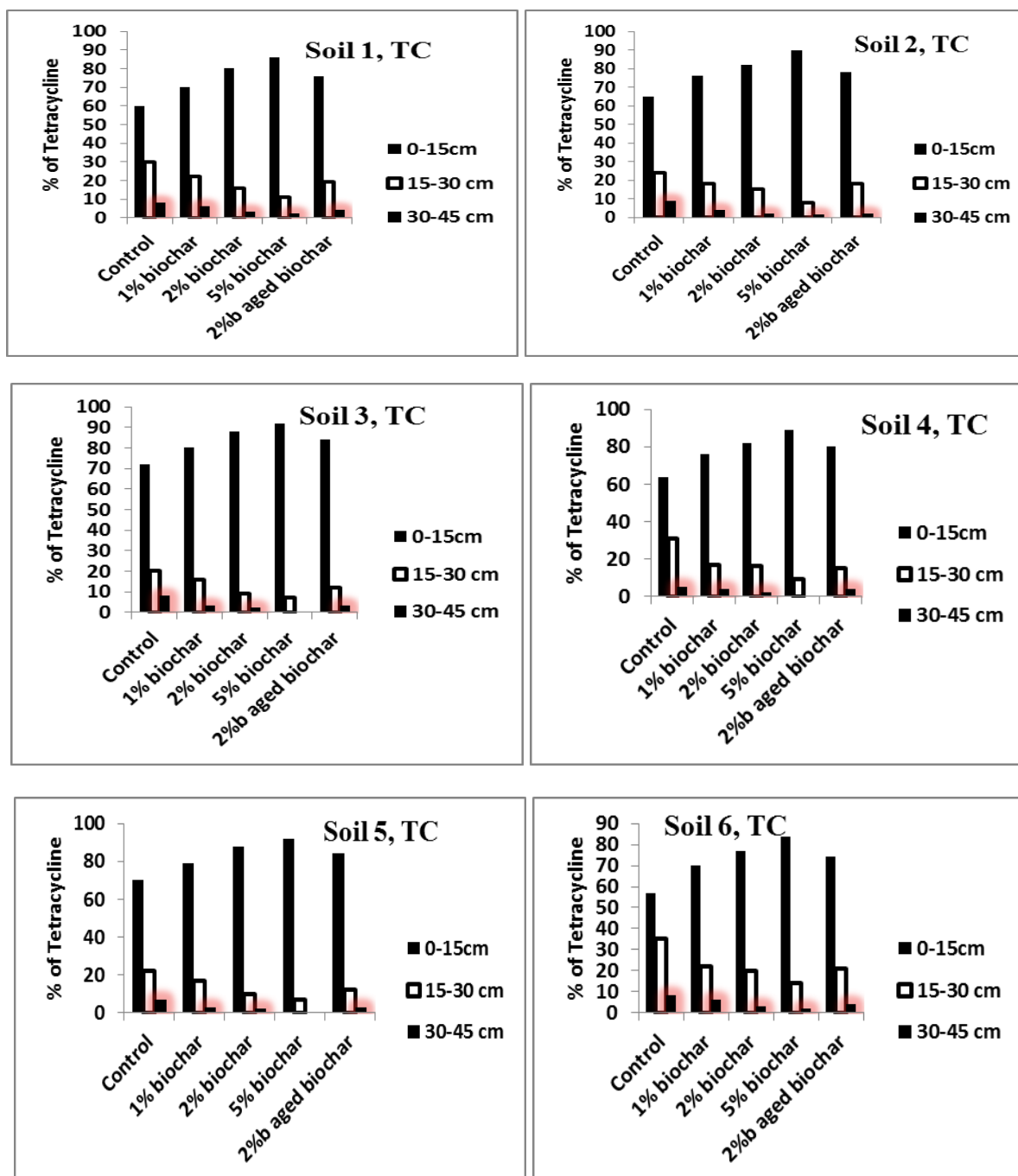


Fig. 2: Distribution of Tetracycline's (CTC, OTC and TC) at different depths in Biochar amended and unamended soils.

CONCLUSIONS

The batch sorption studies of this work demonstrate that the sorption behaviour of TCs in soils is caused by interactions of soils and antibiotics which are related to soil and antibiotics properties. The results of this study also showed that soil amended with biochar enhance the sorption of TCs, reduce their dissipation, mobility and decrease the environmental risk. However the sorption onto the aged biochar amended soils decreases. The dissipation of TCs

in the soil environment was slow denoting that these compounds persist in soils for a longer period.

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