Global NEST Journal, Vol 27, No 6, 07374

Adsorption-desorption of doxycycline using pyrophosphoric acid-modified biochar derived from sesame stalk

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Received: 14/02/2025, Accepted: 28/04/2025, Available online: 12/05/2025
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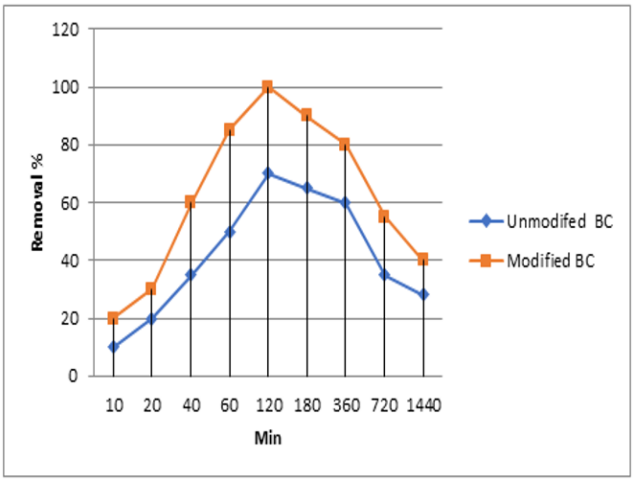
https://doi.org/10.30955/gnj.07374

Graphical abstract



Abstract

The knowledge of the adsorption-desorption behavior of doxycycline on pyrophosphoric acid modified biochar derived from sesame is limited. In this study, we examined the doxycycline sorption on pyrophosphoric acid modified-sesame stalk biochar. The isotherm and kinetic sorption data showed pyrophosphoric acid treatment enhanced the sorption of doxycycline on both modified and un-modified biochar; chemisorption including EDA (π-π electron-donor-acceptor) interaction, pore filling and H-bonding might be the primary mechanism. The maximum adsorption capacities for unmodified biochar were 87.6 mg g^{-1}, and 153.9mg g^{-1} for modified biochar. More than 90% of the adsorption capacity was retained after three successive adsorption-desorption cycles. Besides, the strong electrostatic attraction between biochars and doxycycline might largely explain the improved sorption capacity of doxycycline along with increasing pH from 5 to 9. The main responsible mechanisms for the sorption of doxycycline included surface complexation, H-bonding, EDA interactions, pore-filling effects. The results of the current study display that pyrophosphoric acid-modified biochar has potential applications as an efficient, recyclable adsorbent for the removal of antibiotics from wastewater for low-cost remediation.

Keywords: Sorption, doxycycline, chemisorptions, modification, adsorbent

1. Introduction

Doxycycline (CAS no. 564-25-0) is a broad-spectrum bacteriostatic agent (antibiotic) synthetically derived from a naturally occurring tetracycline produced by Streptomyces species bacteria known as oxytetracycline; it is a member of the tetracycline class of antibiotics (Yang *et al.* 2019). Doxycycline is one of the widely used tetracycline antibiotics in the world. The occurrence of antibiotics in the natural environment can induce serious risk to human health and ecosystems by causing growth of antibiotic-resistant bacteria, which can occur at low concentrations (Peng *et al.* 2025). In recent times, the wide presence of doxycycline in groundwater has attracted extensive attention (Peng *et al.* 2025; Wang *et al.* 2024). Thus, it is of great importance to develop highly efficient and low-cost methods to eliminate antibiotics from contaminated-water.

There are several ways to eliminate antibiotics -which are often persistent compounds- from waste-water, including bio-degradation, chemical oxidation, photo-degradation, and adsorption (Chen *et al.* 2024; Jin and Lei 2024). Among them, adsorption techniques have numerous advantages over other techniques, such as low energy consumption, high removal efficiency, environmental friendliness and easy operation (Zhang *et al.* 2025). Recently, biochars have been manufactured by carbonizing the feedstock and then utilized as adsorbents for antibiotics (Zhuo *et al.* 2023). Nonetheless, the adsorption capacities of unmodified biochars are usually low, and their limitations include low density, low surface area and small particle size. To enhance the adsorption capacity of biochar, several modification approaches, including chemical and physical activation techniques have been suggested and used on biochars (Yu *et al.* 2023). Most of the treatment methods could efficiently alter the physico-chemical properties of the biochar surface, i.e. increased density of functional groups, surface area, H/C, O/C ratios and altered porous structures (Lu *et al.* 2025; An *et al.* 2024).

Pyrophosphoric acid (aka diphosphoric acid, $[(HO)_2P(O)]_2O$) is a strong acid that can change physiochemical attributes of biochar. Therefore, pyrophosphoric acid was introduced in the current work to modify the biochar, with the purpose of increasing the doxycycline sorption capacity. In this work, sesame stalk biochar was manufactured via pyrolysis at 500°C. Then pyrophosphoric acid was applied to modify the produced biochar. The adsorption-desorption properties of doxycycline on both pyrophosphoric acid-modified and pristine biochar were examined. The main objectives of this study were to (1) assess the adsorption-desorption capacity of doxycycline on pyrophosphoric acid-modified and pristine biochar (2) elucidate the physiochemical changes before and after modification.

2. Materials and Methods

2.1. Materials and biochar production

Doxycycline hyclate (CAS no. 24390-14-5) was obtained from Asiatic chemical Karachi, Pakistan. Sesame stalk was taken from an agricultural farm in Faisalabad, Pakistan. Sesame stalks were air-dried and then used to produce the biochar by pyrolysis with a temperature at 500 oC for 4 h.

2.2. Modification of biochar

An aqueous solution of pyrophosphoric acid ($H_4P_2O_7$) was used for biochar modification for improving the sorption capability for the adsorption of doxycycline. Briefly, 15 g of biochar were soaked in 30 mL of 20% $H_4P_2O_7$ solution for 24 h at room temperature. Afterwards, the pyrophosphoric acid-modified biochar samples were washed with deionized (DI) water until the supernatant's pH was stable. Thereafter, the supernatant was discarded and biochar samples were dried in an oven.

2.3. Characterization of unmodified and modified biochar

The elemental composition was used to measure polarity indexes of biochar before and after modification. The H/C atomic ratios were used as a sign of aromaticity. Moreover, O/C ratios and polarity indexes (O + N)/C ratios were calculated to assess polarities of manufactured biochar. Ash contents of biochar were measured according to the ASTM (American Society for Testing and Materials) method D1762-84. Additionally, Brunauer-Emmett-Teller (BET) was used to measure the surface area.

2.4. Sorption experiments

2.4.1. Kinetics sorption

15mg modified and unmodified biochar was added to 40mL glass tubes comprising 30mL doxycycline solution with 80mg L^{-1} concentration. All glass tubes were placed in shakers and agitated at 200rpm at room temperature from 10 minutes to 1440 minutes. Each sample was measured in triplicate and also tubes comprising only 30mL doxycycline solution of the same concentration were used for noticing doxycycline loss during this experiment. At pre-determined times, glass tubes were extracted and centrifuged at 2800rpm for 25 minutes and then filtered via 0.45µm millipore membranes. Afterwards, the filtrate was measured via a spectrophotometer at 409 nm (Sun *et al.* 2021).

2.4.2. Sorption isotherms

Sorption isotherms for modified and unmodified biochars were measured at various initial concentration of doxycycline: 10, 20, 40, 60, 80, 100, 120, 150, 200, and $250mgL^{-1}$. To each 40mL glass tube, 5mg of modified and unmodified sesame adsorbent and 30mL of doxycycline solution with different concentration were added, followed by shaking at 250rpm at room temperature to reach apparent equilibrium based on kinetic sorption.

2.4.3. pH effect on sorption isotherms

The doxycycline solutions with different concentrations were adjusted to pH 5, 7, 9 via using 0.1M NaOH and HCl solution. Hereafter, isotherm sorption trials were performed at room temperature.

2.4.4. Data exploration

The adsorption capacity and removal efficiency (%) of doxycycline onto modified and un-modified biochar were calculated using Eq. 1 and 2:

$$q_e = (C_i - C_e) \times V / W \quad (1)$$

$$\%\,\text{removal doxycycline} = (C_i - C_e) / C_i \times 100 \quad (2)$$

Where q_e (mg/g) signifies the adsorbed volume of doxycycline through the adsorbent, and C_i and C_e are initial and equilibrium doxycycline concentrations (mg/L), respectively, while V represents the total amount (L) of the solution and W stands for the weight (g) of the adsorbent. The kinetics adsorption data was analyzed through pseudo-1^{st}-order and pseudo-2^{nd}-order reactions:

Pseudo-first-order:

$$q_t = q_e (1 - \exp(-K_1 t) \quad (3)$$

Pseudo-second-order:

$$q_t = qe_2 k_2 t / 1 + q * \exp(-K_2 t) \quad (4)$$

To examine the reaction behaviour between doxycycline and biochars, data of adsorption isotherms was fitted through two models applied (Liang *et al.* 2022).

Freundlich:

$$q_e = KfCen \quad (5)$$

Langmuir;

$$q_e = q_{max}KLCe / 1 + KLCe \quad (6)$$

2.4.5. Desorption study and reusability of biochar

The modified and unmodified biochar was regenerated via extraction with 25mL of Milli-Q water. After being washed and dried in an oven, the materials performed three adsorption-desorption cycles, separately. This was followed through continuously for 24h at room temperature. The desorption efficiency of modified and unmodified biochar was calculated using equation (7):

$$\%\,desorption, doxycycline = C_{des} / C_{ads} \times 100 \quad (7)$$

Where, C_{des} and C_{ads} are desorbed volume (mg/L) of doxycycline in the solution and adsorbed volume of doxycycline through biochar, respectively.

Table 1. Elemental composition (%), and surface area of unmodified and modified biochar

Sample	C	H	O	N	S	O/C	N/C	H/C	(O+N)/C	Ash %	SSA (m^2 g^{-1})
Unmodified Biochar	32.16	0.64	11.61	1.04	0.11	0.19	0.04	0.01	0.24	61.34	13.64
Modified Biochar	34.15	0.66	6.32	1.45	0.14	0.33	0.03	0.02	0.22	53.29	129.41

Table 2. Kinetic adsorption parameters of doxycycline onto unmodified and modified biochar

Sample	Pseudo-1st-order			Pseudo-2nd-order		
	qe (mg g^{-1})	K_1 (h^{-1})	R^2	qe (mg g^{-1})	K_2 (h^{-1})	R^2
Unmodified BC	131.4	0.04	0.804	143.1	0.0003	0.902
Modified BC	154.8	0.08	0.842	174.4	0.0006	0.913

3. Results and discussion

3.1. Biochars characterization

Table 1 exhibits the ash content, elemental compositions, aromatic ratio, surface area, and pore volume of modified and unmodified biochar. The surface area significantly increased after modification (129.41 m^2 g^{-1}) .It was much higher than unmodified biochar (13.64 m^2 g^{-1}). Pyrophosphoric acid treatment could increase the biochar's surface area (Liang *et al.* 2022; Zou *et al.* 2024). Pyrophosphoric acid treatment generally increased the content of S, N and C but decreased O content as compared to pristine biochar. The H content showed no obvious alteration between before and after modification. Moreover, the ash content reduced after modification from 61.34 to 53.29%. Pyrophosphoric acid modification could partially eliminate ash of pristine biochar (Liu *et al.* 2012; Zhang *et al.* 2024). A substantially negative association was observed between ash and C contents in this work. Additionally, it was observed that the aromatic ratios O/C, H/C, (O + N)/C of modified biochar were reduced compared to pristine biochar. This decrease showed the biochar treated by pyrophosphoric acid turned into material with a less hydrophilic-nature with weak polar groups (Liu *et al.* 2012; Ma *et al.* 2014; Li and Lei 2024).

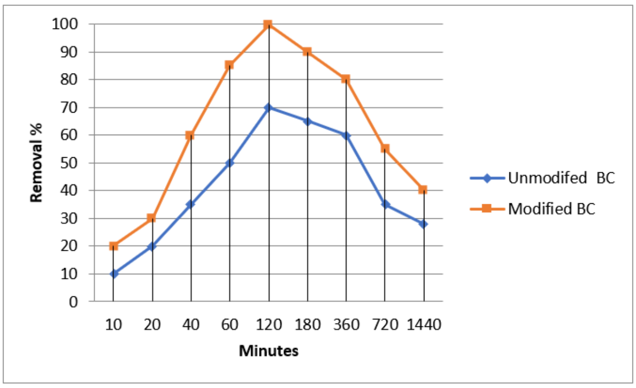


Figure 1. Sorption kinetics of doxycycline on modified and unmodified biochar

3.2. Reaction Time and Kinetic Modelling

Figure 1 and **Table 2** represent the doxycycline removal percentage and sorption capacity by modified and unmodified biochar at different times. After 120 minutes, there was an ambiguous difference between 180 and 1440 minutes, thus, 120 minutes was deemed to be a maximum equilibrium time for doxycycline sorbed onto modified and unmodified biochar. Besides, it was observed that the sorption efficiency of treated-biochar was higher than unmodified biochar. In this study, pseudo-1st-order and pseudo-2nd-order models were applied to arrange the sorption data for understanding possible mechanism related with the doxycycline sorption on modified and unmodified biochar. R^2 values of the pseudo-second-order model (0.902-0.913) were greater than those of the pseudo-first-order model (0.804–0.842) (**Table 2**), comparable the most of antibiotics adsorption findings (Murtaza *et al.* 2021; Peiris *et al.* 2017; Setiawatie *et al.* 2018). Furthermore, values of q_e were closer to theoretical q_e values considered through the pseudo-second-order model; additionally proposing that kinetics doxycycline's sorption onto modified and unmodified biochar could be preferably reported by the pseudo-2nd-order model. The pseudo-2nd-order model exhibits chemisorption mechanism occurred between doxycycline and modified biochar including valency forces through electrons exchange between biochar and doxycycline (Wang *et al.* 2018; Wang *et al.* 2024). On the contrary, the q_e values of pyrophosphoric acid-treated biochar were greater than for unmodified-biochar. For instance, theoretical q_e of doxycycline on modified biochar was 174.4mgg^{-1}, significantly greater than the pristine biochar. It is evident that pore volume and SA of modified biochar significantly enhanced after pyrophosphoric acid modification (**Table 1**), signifying pore-filling and surface adsorption might explicate the greater qe of modified biochar than un-modified biochar (**Figure 1** and **Table 2**). Moreover, pyrophosphoric acid treatment could enhance functional groups number amount of adsorbent (Liu *et al.* 2012; Wang *et al.* 2017; Xia *et al.* 2025)., thus, chemical interactions between functional groups of modified biochar and doxycycline molecules might also partly lead to greater qe values of modified biochar compared to pristine biochar (Wang *et al.* 2017). Therefore, possible cause for greater qe values of modified biochar than pristine biochar might be explicated via the increased interactions between modified biochar and doxycycline owing to the improved number of functional groups, i.e. –OH and –COOH (Liu *et al.* 2012).

3.3. Influence of Initial doxycycline -Concentration and Isothermic sorption

Since the pyrophosphoric acid-modified biochar exhibited greater sorption capacity compared to unmodified biochar (**Table 2**). Sorption data of doxycycline onto modified and unmodified biochar are represented in **Figure 2**. The sorption data exhibited significantly greater sorption capacity compared to unmodified biochar. The data of doxycycline sorbed to modified and unmodified biochar fitted thru Freundlich and Langmuir models (**Table 3**). Both the Freundlich and Langmuir models presented isothermic sorption well because R^2 value of Langmuir (0.961–0.983) was same as R^2 of Freundlich model (0.982–0.989). Conforming to, q_{max} fitted via Langmuir model, the q_{max} of doxycycline via modified biochar (153.9mgg^{-1}) was significantly higher than untreated biochar (87.6mgg^{-1}). According to Freundlich, Kf of modified biochar (89.5mg^{-1}-nLn g^{-1}) were also higher compared to untreated biochar (63.2 mg^{-1}-n Ln g^{-1}). These findings suggested that modified biochar had hefty sorption capability and greater sorption ability as compared to untreated biochar, which might be mainly explicated by the higher O/C ratio and surface area of pyrophosphoric acid-modified biochar than pristine biochar. In this work, Langmuir and Freundlich both models could fit for adsorption data of doxycycline on modified and unmodified biochar well, signifying the doxycycline adsorption on biochar might be influenced via several processes. (Ma *et al.* 2014) Summarized primary sorption process of antibiotic on adsorbent surface, such as EDA interaction, surface complexation, cation exchange, electrostatic interaction, and Hydrogen bonding. Pyrophosphoric acid-treatment removed the cations, for example, Ca^{2+}, Na^{+} and Mg^{2+}, signifying the surface complexation and cation exchange should not be primary mechanisms for doxycycline adsorption on modified and unmodified biochars (Wang *et al.* 2017). Simultaneously, **Table 2** and **Figure 1** exhibited that doxycycline was sorbed mainly via chemisorption mechanism including EDA-interaction and H bonding. In comparison, O/C contents of modified biochar with unmodified biochar (**Table 1**), greater O/C ratio of modified biochar proposed that modified biochar might have additional oxygen-enrich functional groups which could aid as hydrogen-bond acceptors and therefore doxycycline adsorption on modified biochar was greater raw adsorbent (Wu *et al.* 2017). Contrastingly, physical adsorption might also partly bestow to greater adsorption ability of modified biochar due to SA of modified biochar was greater than pristine adsorbent (**Table 1**), though chemical adsorption was most influenced in this work. Nonetheless, it is difficult to value the support of π-π EDA-interaction, H-bonding and physical adsorption for doxycycline sorption on modified and unmodified biochars (Liu *et al.* 2012).

Table 3. Isothermic adsorption parameters of doxycycline onto unmodified and modified biochar

Sample	Langmuir			Freundlich		
	qmax (mg g^{-1})	K_L(L mg^{-1})	R^2	Kf (mg^{-1-n} g^{-1})	n	R^2
Unmodified BC	87.6	0.12	0.961	63.2	0.11	0.982
Modified BC	153.9	0.26	0.983	89.5	0.14	0.989

Table 4. Sorption isotherm parameters of doxycycline onto unmodified and modified biochar at different initial pH of solution.

Sample	Langmuir			Freundlich		
	qmax (mg g^{-1})	K_L(L mg^{-1})	R^2	Kf (mg^{-1-n} g^{-1})	n	R^2
			Initial pH=5			
Unmodified BC	119.2	0.22	0.929	65.2	0.1	0.949
Modified BC	139.8	0.57	0.941	79.1	0.1	0.973
			Initial pH=7			
Unmodified BC	166.8	0.21	0.901	68.6	0.2	0.964
Modified BC	258.7	0.07	0.984	50.4	0.3	0.996
			Initial pH=9			
Unmodified BC	358.8	0.03	0.967	32.4	0.4	0.982
Modified BC	562.1	0.02	0.993	26.4	0.5	0.998

3.4. Effect of pH

Effect of different pH values on adsorption of doxycycline on pyrophosphoric acid treated biochar was examined because doxycycline form and adsorption mechanism of doxycycline on biochar was significantly affected via pH. **Figure 3** displays the impact of pH in sorption of doxycycline on modified and unmodified biochar at 25 °C. Increasement in adsorption capacity with increased pH was noticed on modified and unmodified biochar, and highest adsorption of doxycycline onto modified and unmodified biochar was observed at 9 pH. The adsorption data of doxycycline on modified and unmodified biochar under several pH solutions were arranged by Freundlich and Langmuir models (**Table 4**). The R^2 values showed the Freundlich and Langmuir could fit the adsorption data well, particularly Freundlich model. Generally, Kf of doxycycline adsorption on biochars reduced but n enhanced with enhancing pH. Besides, the initial pH enhancing from 5-9, the fitted Kf of unmodified biochar reduced from 65.2 to 32.4 mg^{-1}-n Ln g^{-1} and modified biochar decreased from 79.1 to 26.4 mg^{-1}-n Ln g^{-1}. As well as, q_{max} of doxycycline on modified biochar enhanced from 139.8 mg g^{-1} to 562.1 mgg^{-1} with pH elevating from 5-9 which was much higher than unmodified biochar (119.2 to 358.8 mgg^{-1}). These findings evidently proposed that adsorption ability of doxycycline on modified biochar was improved thru raised pH 5 to 9. In general, the doxycycline properties and biochar were changed through solution pH, and subsequently inducing sorption volume of doxycycline on the biochar. pH_{PZC} of biochar and pKa of doxycycline was suggested as key reason for alterations of adsorption capability of doxycycline onto biochar under various pH values (Yan *et al.* 2018; Xia *et al.* 2025; Wen *et al.* 2025; Wen *et al.* 2024). Moreover, biochar surface charge was positive, when solution pH was lower compared to their pHPZC and vice versa. At lower pH, doxycycline was cationic and the biochar surface is generally positive, thus, the π-π electron (electron-donor- acceptor) interactions were weak. As well as pH elevating, doxycycline turned zwitterionic and electron-donor-acceptor interactions between biochar and doxycycline was strengthened. Therefore, increased adsorption of doxycycline was noticed. In brief, changed charges of biochar and doxycycline should reasonably elucidate the variations of adsorption volume of doxycycline on modified and unmodified biochar under different pH values. Thus, the increased sorption of doxycycline on modified biochar at increased pH could be mainly enlightened by the strengthened electrostatic attraction between negative charges of doxycycline and positive surface charges of biochar.

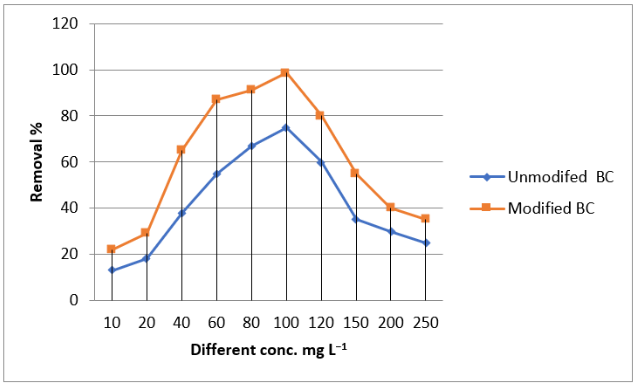


Figure 2. Sorption isotherms of doxycycline on modified and unmodified biochar

3.5. Desorption analysis

After successful doxycycline adsorption, the modified and unmodified biochars were exposed to regeneration experiments in order to measure the stability and reusability of biochar. The experiments conducted based on three adsorption desorption cycles to scrutinize repetitive use of biochar under the optimum condition. Findings exhibited that sorption capabilities of modified biochar somewhat decreased after three adsorption-desorption cycles (**Figure 4**). Very low desorption amount was noticed with Milli-Q water for modified biochar (12.36-1.25 %) (**Figure 4**). Results proposed that pyrophosphoric acid-modified biochar was efficiently recycled and can be used in repeated doxycycline sorption batches at least three times with minimum loss in their sorption volumes, using Milli-Q water as ideal desorption material (Yang *et al.* 2021; Wang *et al.* 2024; Tong *et al.* 2024; Lei and Xu 2024; Jin *et al.* 2024).

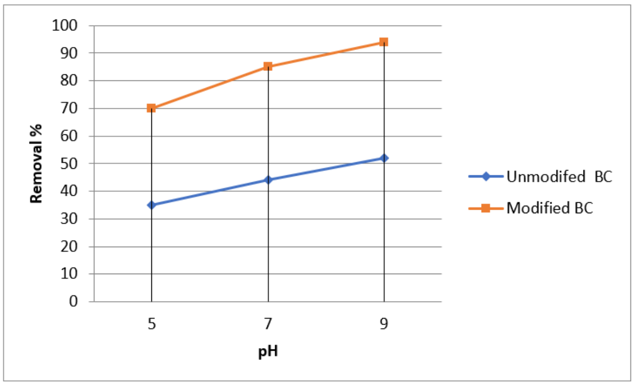


Figure 3. Effect of various pH solutions on doxycycline removal

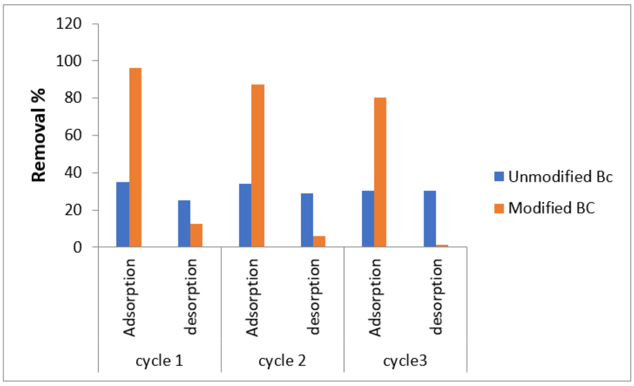


Figure 4. Adsorption-desorption of modified and unmodified biochar

4. Conclusions

Pyrophosphoric acid-modification improved the doxycycline sorption on modified biochar, (about 30% enhancement). The doxycycline sorption on pyrophosphoric acid-modified sesame adsorbent was greatly enhanced along with increasing pH from 5 to 9. The π-π EDA interactions and H-bonding might be the primary adsorption mechanism for doxycycline adsorption onto treated and un-treated biochar. With respect to the pristine adsorbent, modified biochar revealed higher sorption capacities and volumes of doxycycline and might be a virtuous adsorption agent for doxycycline elimination from the water, though the doxycycline adsorption on unmodified biochar was low compared to modified biochar. The findings of the current study demonstrated that sorption was spontaneous and multi-layered as evidenced by Langmuir and Freundlich models, and endothermic as elimination efficacy can be enhanced by raising the temperature.

Acknowledgments

The authors extend their appreciation to the Researchers supporting project number (RSP2025R247) King Saud University, Riyadh, Saudi Arabia.

References

An, X., Wang, Y., Yu, C. and Hu, X. (2024). Biochar-bacteria coupling system enhanced the bioremediation of phenol wastewater-based on life cycle assessment and environmental safety analysis. *Journal of Hazardous Materials*, **480**, 136414. doi: https://doi.org/10.1016/j.jhazmat.2024.136414

Chen, S., Yang, Z., Sun, W., Tian, K., Sun, P and Wu, J. (2024). TMV-CP based rational design and discovery of α-Amide phosphate derivatives as anti plant viral agents. *Bioorganic Chemistry*, **147**, 107415. doi: https://doi.org/10.1016/j.bioorg.2024.107415

Jin, X. and Lei, X. (2024). The Impact of China's New Environmental Law on the Financial Performance of Heavy Polluting Enterprises. *Polish Journal of Environmental Studies*, **33**(4).

Jin, X., Huang, S. and Lei, X. (2024). Research on the impact mechanism of green innovation in marine science and technology enabling dual economic circulations. *Sustainability*, **16**(19), 8421.

Lei, X. and Xu, X. (2024). Storm clouds over innovation: Typhoon shocks and corporate R&D activities. *Economics Letters*, **244**, 112014.

Li, H. and Lei, X. (2024). "The Impact of Climate Change on the Development of Circular Economy in China: A Perspective on Green Total Factor Productivity", *Global NEST Journal*, **26**(4).

Liang H., Meng Y., Ishii K. (2022). The effect of agricultural greenhouse gas emissions reduction policies: evidence from the middle and lower basin of Yangtze River, China. *Discover Sustainability*, **3**(1), 43.

Liang H., Zhu C., Ji S., Kannan P., Chen F. (2022). Magnetic Fe2O3/biochar composite prepared in a molten salt medium for antibiotic removal in water. *Biochar*, **4**(1), 3.

Liu P., Liu W. J., Jiang H., Chen J. J., Li W. W., Yu H. Q. (2012). Modification of bio-char derived from fast pyrolysis of biomass and its application in removal of tetracycline from aqueous solution. *Bioresource Technology*, **121**, 235–240.

Lu, Y., Wang, H., Lu, Y., Ren, Z., Gao, N., Wang, J and Jin, R. (2025). In-situ synthesis of lanthanum-coated sludge biochar for advanced phosphorus adsorption. *Journal of Environmental Management*, **373**, 123607. doi: https://doi.org/10.1016/j.jenvman.2024.123607

Ma Y., Liu W. J., Zhang N., Li Y. S., Jiang H., Sheng G. P. (2014). Polyethylenimine modified biochar adsorbent for hexavalent chromium removal from the aqueous solution. Bioresource Technology, **169**, 403–408.

Murtaza G., Ditta A., Ahmed Z., Usman M., Faheem M., Tariq A. (2021). Co-biosorption potential of Acacia nilotica bark in removing Ni and amino azo benzene from contaminated wastewater. *Desalination and Water Treatment*, **233**, 261–271.

Ouwen, L., Jiajun, L. and Xue, L. (2024). "Evolutionary game analysis of enterprises' green production behavior in the context of China's economic green transformation", *Global NEST Journal*, **26**(3). Available at: https://doi.org/10.30955/gnj.005781.

Peiris C., Gunatilake S. R., Mlsna T. E., Mohan D., Vithanage M. (2017). Biochar based removal of antibiotic sulfonamides and tetracyclines in aquatic environments: a critical review. Bioresource Technology, **246**, 150–159.

Peng, C., Xu, W., Wang, X., Meng, F., Zhao, Y., Wang, Q and Peng, L. (2025). Alginate oligosaccharides trigger multiple defence responses in tobacco and induce resistance to Phytophthora infestans. *Frontiers in Plant Science*, **16**, 1506873. doi: 10.3389/fpls.2025.1506873 .

Setiawatie E. M., Lestari V. P., Astuti S. D. (2018). Comparison of anti-bacterial efficacy of photodynamic therapy and doxycycline on aggregatibacter actinomycetemcomitans. *African Journal of Infectious Diseases*, **12**, 95–103.

Sun, L., Jiang, Z., Yuan, B., Zhi, S., Zhang, Y., Li, J and Wu, A. (2021). Ultralight and superhydrophobic perfluorooctyltrimethoxysilane modified biomass carbonaceous aerogel for oil-spill remediation. *Chemical Engineering Research and Design*, **174**, 71–78. doi: https://doi.org/10.1016/j.cherd.2021.08.002

Tong, L. *et al.* (2024). "Study on the Impact of China's Digital Economy on Agricultural Carbon Emissions", *Global NEST Journal*, **26**(6). Available at: https://doi.org/10.30955/gnj.06183.

Wang H., Fang C., Wang Q., Chu Y., Song Y., Chen Y., Xue X. (2018). Sorption of tetracycline on biochar derived from rice straw and swine manure. *RSC Advances*, **8**(29), 16260–16268.

Wang S., Zhao M., Zhao Y., Wang N., Bai J., Feng K., Wang J. (2017). Pyrogenic temperature affects the particle size of biochar-supported nanoscaled zero valent iron (nZVI) and its silver removal capacity. *Chemical Speciation & Bioavailability*, **29**(1), 179–185.

Wang, C., Liu, H. and Ma, S. (2024). "Analysis of the effect of digital financial inclusion on agricultural carbon emissions in China", *Global NEST Journal*, **26**(8). Available at: https://doi.org/10.30955/gnj.06313.

Wang, Z., Wang, F. and Ma, S. (2024). Research on the Coupled and Coordinated Relationship Between Ecological Environment and Economic Development in China and its Evolution in Time and Space. *Polish Journal of Environmental Studies*.

Wang, Z., Wu, Q. and Ma, S. (2024). "Research on Carbon Emission Peaks in Large Energy Production Region in China —Based on the Open STIRPAT Model", *Global NEST Journal*, 26(5).

Wen, L., Ma, S., Wang, C., Dong, B., Liu, H. (2024). A Study of Green Strategy Choice and Behavioral Evolution of Consumers and Producers under the Double Subsidy Policy. *Polish Journal of Environmental Studies*. https://doi.org/10.15244/pjoes/188455

Wen, L., Ma, S., Zhao, G., Liu, H. (2025). The Impact of Environmental Regulation on the Regional Cross-Border E-Commerce Green Innovation: Based on System GMM and Threshold Effects Modeling. *Polish Journal of Environmental Studies*, **34**(2), 1347–1362. https://doi.org/10.15244/pjoes/187118

Wu W., Li J., Lan T., Müller K., Niazi N. K., Chen X., Wang H. (2017). Unraveling sorption of lead in aqueous solutions by chemically modified biochar derived from coconut fiber: a microscopic and spectroscopic investigation. *Science of the Total Environment*, **576**, 766–774.

Xia, W., Ruan, Z., Ma, S., Zhao, J. and Yan, J. (2025). Can the digital economy enhance carbon emission efficiency? Evidence from 269 cities in China. *International Review of Economics & Finance*, **97**, 103815.

Yan Q., Li X., Ma B., Zou Y., Wang Y., Liao X., Wu Y. (2018). Different concentrations of doxycycline in swine manure affect the microbiome and degradation of doxycycline residue in soil. *Frontiers in Microbiology*, **9**, 3129.

Yang C. X., Zhu Q., Dong W. P., Fan Y. Q., Wang W. L. (2021). Preparation and characterization of phosphoric acid-modified biochar nanomaterials with highly efficient adsorption and photodegradation ability. *Langmuir*, **37**(30), 9253–9263.

Yang, X., Xia, X., Zhang, Z., Nong, B., Zeng, Y., Wu, Y and Li, D. (2019). Identification of anthocyanin biosynthesis genes in rice pericarp using PCAMP. *Plant Biotechnology Journal*, **17**(9), 1700–1702. doi: https://doi.org/10.1111/pbi.13133

Yu, K., Chai, B., Zhuo, T., Tang, Q., Gao, X., Wang, J and Chen, B. (2023). Hydrostatic pressure drives microbe-mediated biodegradation of microplastics in surface sediments of deep reservoirs: Novel find-ings from hydrostatic pressure simulation experiments. *Water Research*, **242**, 120185. doi: https://doi.org/10.1016/j.watres.2023.120185 .

Zhang, D., Wang, Y., Gu, Q., Liu, L., Wang, Z., Zhang, J and Zhang, Y. (2025). Cotton RLP6 Interacts With NDR1/HIN6 to Enhance Verticillium Wilt Resistance via Altering ROS and SA. *Molecular Plant Pathology*, **26**(1), e70052. doi: https://doi.org/10.1111/mpp.70052

Zhang, K., Li, Y., Ma, S., Fu, C. (2024). Research on the Impact of Green Technology Innovation in the Manufacturing Industry on the High-Quality Development of the Manufacturing Industry Under “Dual Circulation”. *Polish Journal of Environmental Studies*. https://doi.org/10.15244/pjoes/189480

Zhuo, T., He, L., Chai, B., Zhou, S., Wan, Q., Lei, X and Chen, B. (2023). Micro-pressure promotes en-dogenous phosphorus release in a deep reservoir by favouring microbial phosphate mineralisation and solubilisation coupled with sulphate reduction. *Water Research*, **245**, 120647. doi: https://doi.org/10.1016/j.watres.2023.120647 .

Zou, F. *et al.* (2024). “Do Technological Innovation and Environmental Regulation Reduce Carbon Dioxide Emissions? Evidence from China”, *Global NEST Journal*, **26**(7).