

Effects of titanium dioxide nanoparticles and sheep manure biochar on the behavior of methylene blue organic contaminant in sandy loam and loam soils

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ABSTRACT

The present study aimed to evaluate the effects of titanium dioxide nanoparticles (T: 1 and 3%), sheep manure biochar (B: 1 and 3%), and their combination (T0.5% + B0.5% and T1.5% + B1.5%) on the degradation/sorption of methylene blue (MB: 100, 200, and 300 mg/kg soil) in sandy loam (SL) and loam (L) soils with variable light radiation (ultraviolet_(UV) and visible_(VS)). According to the results, the application of T (especially with UV radiation exposure), B, and their combination significantly reduced the MB concentration in the soils compared to the control treatment (without T and B). In addition, the combined application of T and B (T1.5% + B1.5%) was significantly more efficient than the other treatments in the reduction of the MB extraction in the studied soils. However, B and T application decreased the soil MB concentration, but due to the competition between the ions in the soils and MB for adsorption on the B and T surfaces, insufficient water in the soils to form appropriate amounts of degradable hydroxyl radicals, low absorption of UV radiation by T (due to the high thickness of the soil layer), and consumption of large amounts of T for soil organic matter degradation, the efficacy of these amendments decreased. Moreover, lack of using specialized biochar for this cationic contaminant (modification of the B functional groups) diminished the efficiency of this adsorbent in the soil, which requires further investigations.

Keywords: Titanium dioxide nanoparticles, Biochar, Methylene blue, Soil, Ultraviolet

Introduction

In recent decades, the release of various contaminants (e.g., dye contaminants) into the environment has increased dramatically due to the remarkable growth of industrial activities.¹ Dye contaminants are water-soluble, synthetic, aromatic, organic pigments with potential application in various industries. Wastewater containing dyes could pollute surface and subsurface water and soil.²

According to a study by Zhou,² the levels of azo dyes in the surface soil in the proximity of dyeing and printing industries were 12-456 mg/kg on average, and these dyes could stabilize within the soil colloids after a few weeks, being retained in soil for a long time. As dyes mainly have complex, aromatic structures and are manmade, they are often highly stable, and their removal from environmental sources is difficult.³

Azo dyes are a large group of synthetic dyes with one or more -N=N- bonds, which adversely affect soil microbial populations⁴ and plant growth.⁵ Methylene blue (MB) is a dye cationic azo molecule with the molecular formula of $C_{16}H_{18}N_3SCl$, which has high resistance to environmental degradation in

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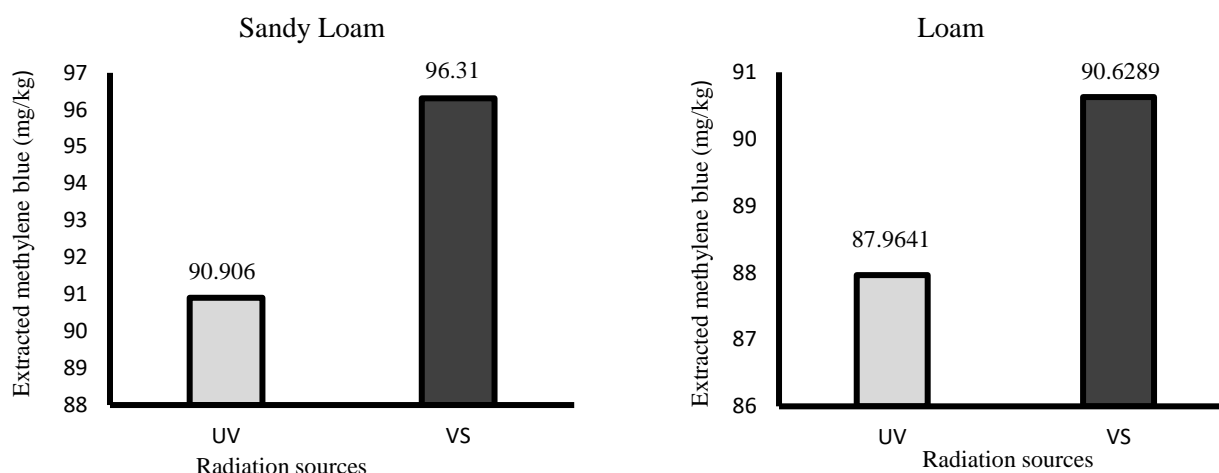


Fig. 4. Effects of radiation sources on amount of extracted MB from SL and L soils (each column with mean of 63 samples; different letters indicate significant differences in means of different treatments; $P < 0.05$)

Fig. 5 shows the interactive effects of the MB levels and amendment treatments on the extracted MB from the SL and L soils. As can be seen, at all the levels of the applied MB in both the studied soils, the soils without amendments (control) had the highest level of extracted MB compared to the other treatments. At the MB concentrations of 100 and 300 mg/kg, T1.5% + B1.5% treatment had the most significant effect on the reduction of the extracted MB from the SL and L soil, while 200 mg/kg of MB led to the most significant decrease in the SL soil and L soil at T3% and B3%, respectively. The interactive effects of various MB pollution levels and radiation sources on the level of the extracted MB from the SL and L soil (Fig. 6) indicated that at all the applied MB levels, there was no statistically significant difference between the two irradiations (same contamination level) despite the lower extractable MB in the UV samples compared to the VS samples in both soils. Furthermore, the findings of the current research demonstrated that the extraction of MB was higher in the SL soil compared to the L soil, which was observed at all the MB concentrations and irradiation sources.

Fig. 7 shows the interactive effects between the amendments and radiation sources on the extracted MB from the SL and L soil. As is shown, various levels of different amendments with the irradiation sources were

not statistically significant. Contrary to the prediction regarding the B treatments, the amount of the extracted MB with UV irradiation showed lower levels of extracted MB compared to the VS irradiation, which was unexpected. In the previous studies in this regard, the effect of UV irradiation on the decomposition of organic compounds (even soil organic matters) has been confirmed,²³ while the involved mechanism has not been elucidated. However, it is assumed that the presence of various photocatalytic compounds in soil (e.g., zinc oxide, TiO₂[rutile and anatase], and ferric oxide) could be excited by UV irradiation, degrading more MB compared to VS irradiation. According to our findings regarding the interactive effects of various levels of MB pollution, different amendments, and radiation sources on the amount of the extracted MB from the SL and L soil (Fig. 8), there was a significant difference in all the soils treated with the control treatment at every level of contamination, so that the highest extracted MB was observed in the control soil. In addition, the lowest extracted MB in MB100 and MB300 in the SL soil was observed in the treatment with T1.5% + B1.5% (UV irradiation) and treatment T1.5% + B1.5% (VS irradiation) in the L soil. On the other hand, the highest extracted MB at both levels of MB (100 and 300 mg/kg) was observed in the control treatment with VS irradiation.

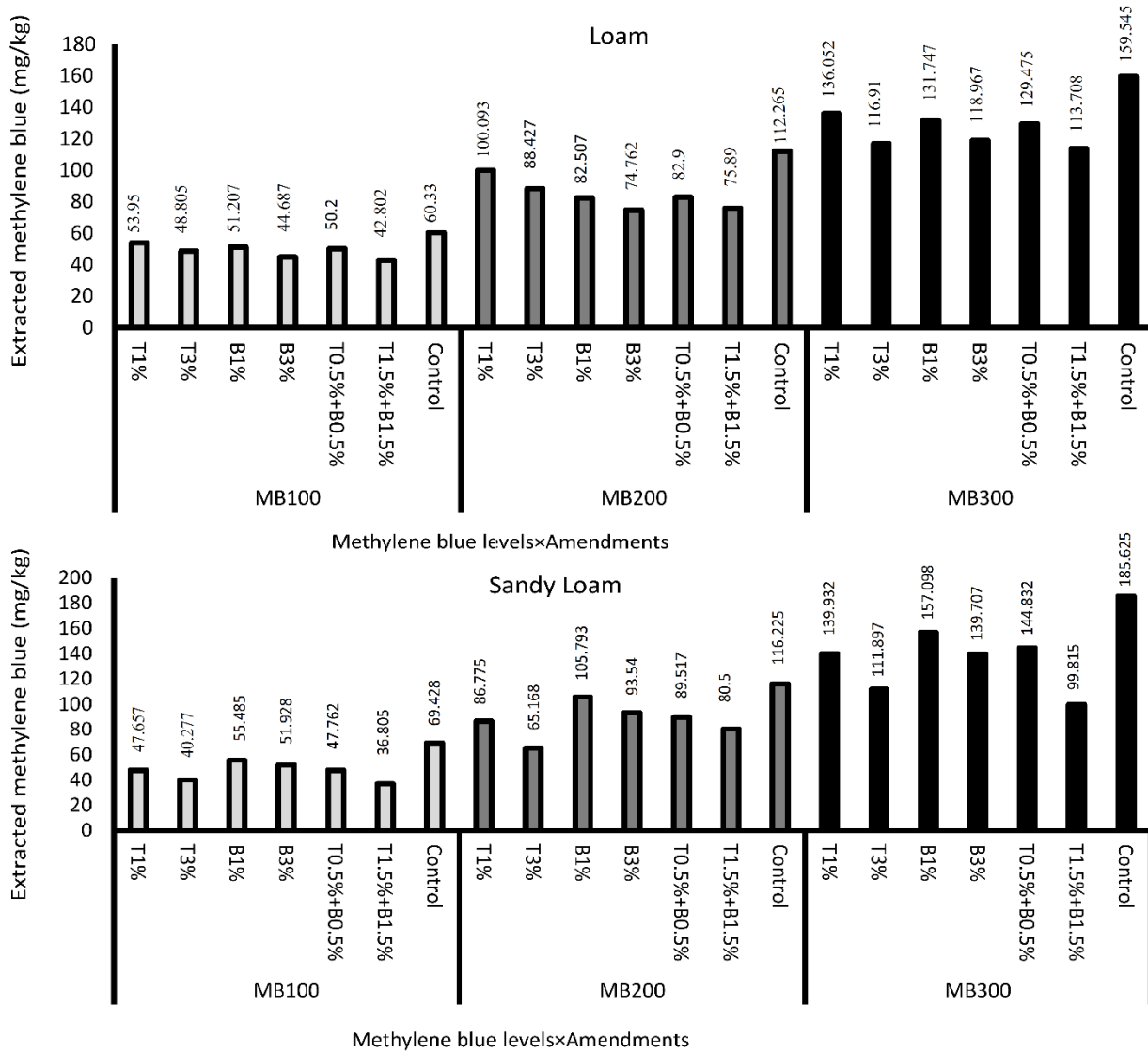


Fig. 5. Effect of MB contamination levels and amendment treatments on extracted MB from SL and L soils (each column with mean of six samples; different letters indicate significant differences in means of different treatments; $P < 0.05$)

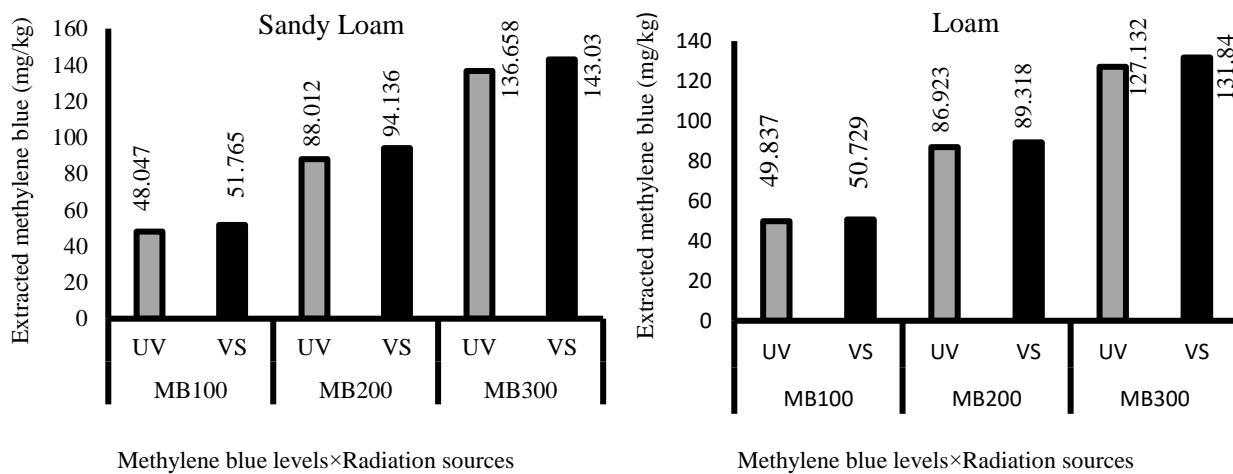
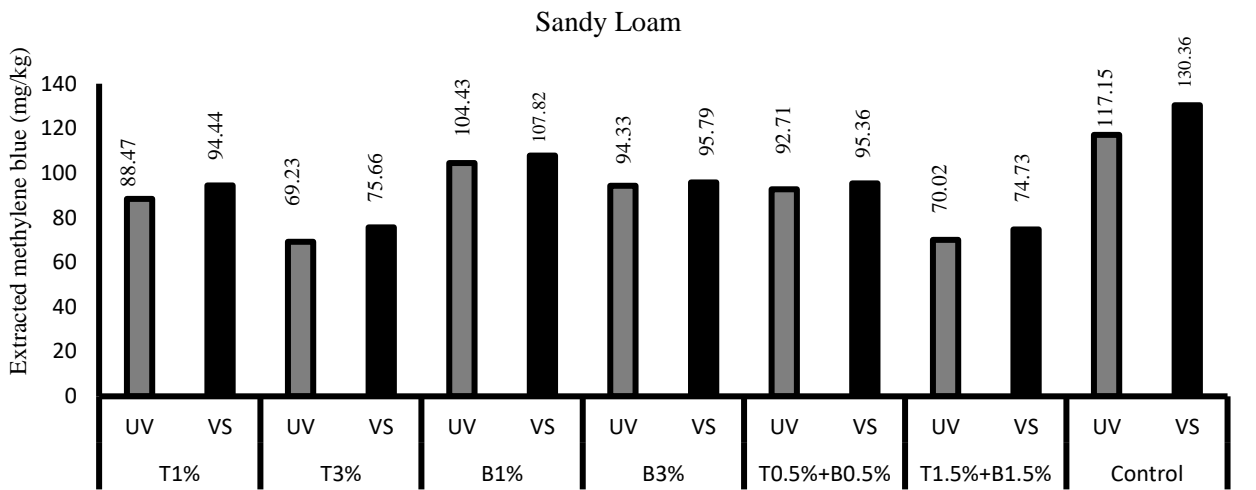
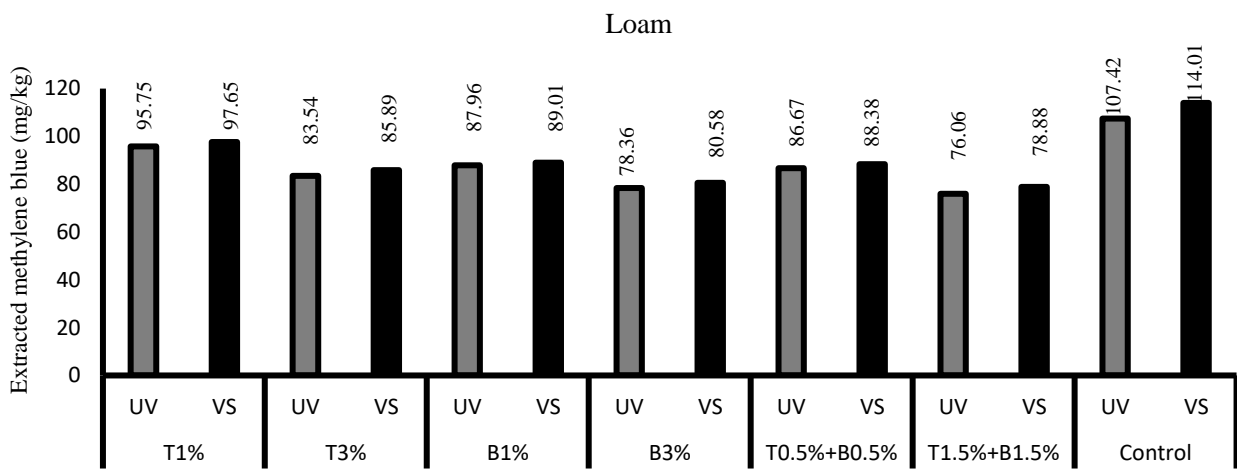


Fig. 6. Effect of MB contamination levels and radiation sources on extracted MB from SL and L soils (each column with mean of 21 samples; different letters indicate significant differences in means of different treatments; $P < 0.05$)

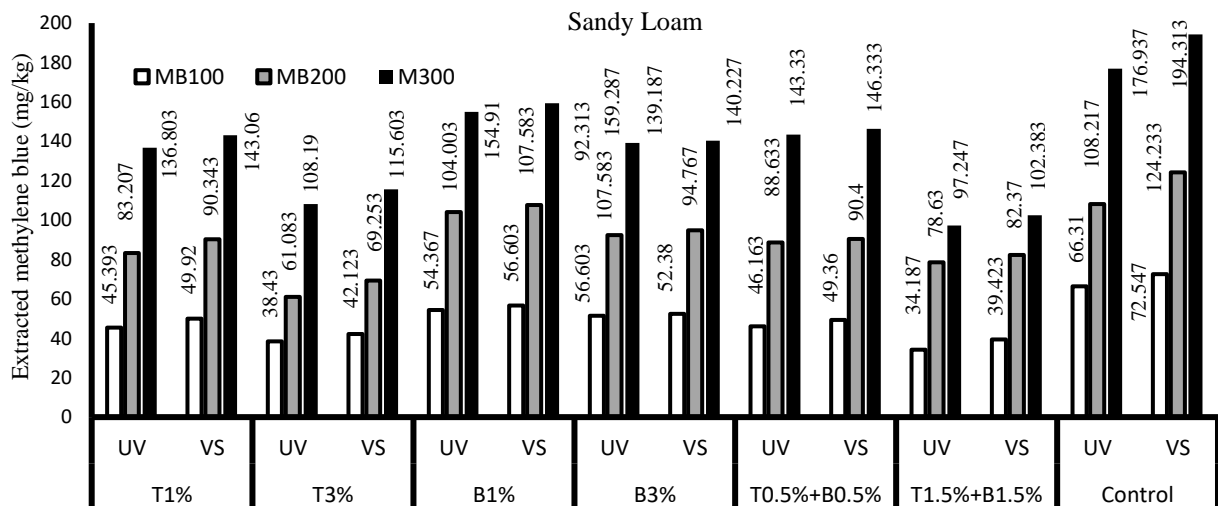


Amendments×Radiation sources



Amendments×Radiation sources

Fig. 7. Effects of amendment treatments and radiation sources on extracted MB from SL and L soils (each column with mean of nine samples; different letters indicate significant differences in means of different treatments; $P < 0.05$)



Methylene blue levels ×Amendments×Radiation sources

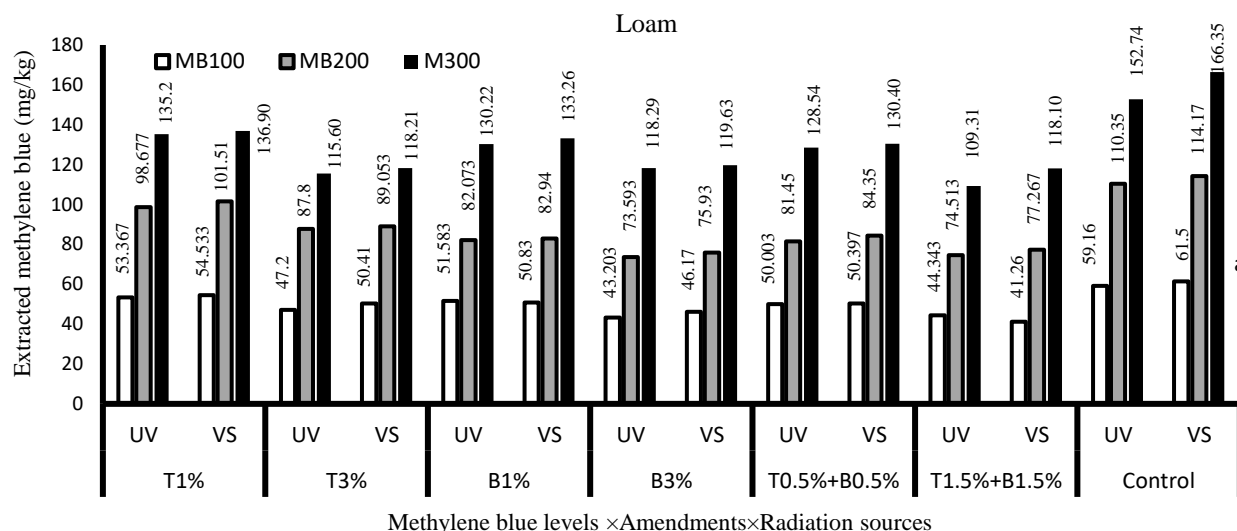


Fig. 8. Effects of MB contamination levels, amendment treatments, and radiation sources on extracted MB from SL and L soils (each column with mean of three samples; different letters indicate significant differences in means of different treatments; $P < 0.05$)

In the MB200 treatment of the SL soil, the lowest and highest extracted MB was observed in the T3% treatment with UV irradiation and control samples with the VS irradiation, respectively. Unexpectedly, the L soil had the lowest amount of the extracted MB, which was observed in the B3% treatment with UV irradiation. In addition, the highest amount of the extracted MB in this soil was observed in the control samples with VS irradiation. In general, the reduction of the extracted MB at various concentrations of MB in the SL and L soil was as follows:

SL soil with MB100 contamination:

- $T1.5\%+B1.5\%(UV) < T3\%(UV) < T1.5\%+B1.5\%(VS) < T3\%(VS) < T1\%(UV) < T0.5\%+B0.5\%(UV) < T0.5\%+B0.5\%(VS) < T1\%(VS) < B3\%(UV) < B3\%(VS) < B1\%(UV) < B1\%(VS) < Control(UV) < Control(VS)$.

L soil with MB100 contamination:

- $T1.5\%+B1.5\%(VS) < B3\%(UV) < T1.5\%+B1.5\%(UV) < B3\%(VS) < T3\%(UV) < T0.5\%+B0.5\%(UV) < T0.5\%+B0.5\%(VS) < T3\%(VS) < B1\%(VS) < B1\%(UV) < T1\%(UV) < T1\%(VS) < Control(UV) < Control(VS)$.

SL soil with MB200 contamination:

- $T3\%(UV) < T3\%(VS) < T1.5\%+B1.5\%(UV) < T1.5\%+B1.5\%(VS) < T1\%(UV) < T1\%(VS) < Control(UV) < Control(VS)$.

$T0.5\%+B0.5\%(UV) < T1\%(VS) < T0.5\%+B0.5\%(VS) < B3\%(UV) < B3\%(VS) < B1\%(UV) < B1\%(VS) < Control(UV) < Control(VS)$.

L soil with MB200 contamination:

- $B3\%(UV) < T1.5\%+B1.5\%(UV) < B3\%(VS) < T1.5\%+B1.5\%(VS) < T0.5\%+B0.5\%(UV) < B1\%(UV) < B1\%(VS) < T0.5\%+B0.5\%(VS) < T3\%(UV) < T3\%(VS) < T1\%(UV) < T1\%(VS) < Control(UV) < Control(VS)$.

SL soil with MB300 contamination:

- $T1.5\%+B1.5\%(UV) < T1.5\%+B1.5\%(VS) < T3\%(UV) < T3\%(VS) < T1\%(UV) < B3\%(UV) < B3\%(VS) < T1\%(VS) < T0.5\%+B0.5\%(UV) < T0.5\%+B0.5\%(VS) < B1\%(UV) < B1\%(VS) < Control(UV) < Control(VS)$.

L soil with MB300 contamination:

- $T1.5\%+B1.5\%(UV) < T3\%(UV) < T1.5\%+B1.5\%(VS) < T3\%(VS) < B3\%(UV) < B3\%(VS) < T0.5\%+B0.5\%(UV) < B1\%(UV) < T0.5\%+B0.5\%(VS) < B1\%(VS) < T1\%(UV) < T1\%(VS) < Control(UV) < Control(VS)$.

In a similar study regarding the effects of T nanoparticles on a type of PAH (phenanthrene) in the soil contaminated with this pollutant, the optimum removal condition

for the degradation of phenanthrene (85%) was observed at 2% (w/w) of T in the presence of water (100%; water saturated soil), which indicated the significant effect of water on the photocatalytic process in the soil environment.²⁴ In another research assessing the destructive effects of T on phenanthrene degradation in soil, Gu *et al.* claimed that T had high efficiency in the degradation of the pollutant, which in turn increased the radiation intensity, H₂O₂, humic acid, and efficiency of phenanthrene degradation.²⁵ Furthermore, Shi *et al.* reported that the application of B (rice straw) in phenanthrene-contaminated soil decreased the phenanthrene uptake by the maize seedlings.²⁶

In another research, Beesley *et al.* applied B in the contaminated soil by PAH, demonstrating that B could decrease the PAH by 50% in the soil pore water concentration.²⁷ Based on the aforementioned studies, use of T and B has been successful in the reducing the availability of organic pollutants (non-dyes) in soil. However, the present study did not provide satisfactory results that may be indicative of the stable molecular structure of the dye (MB) compared to other organic pollutants in soil.

Conclusion

According to the results, the application of T nanoparticles with UV irradiation could reduce the extracted MB in the studied soil samples compared to the control samples. However, these findings were not satisfactory, and further investigations are required regarding the changes in the type of the T nanoparticles using particle doping for better particle separation to enhance the effects of light, changed soil conditions to saturate the soil and increase the production of hydroxyl free radicals to degrade MB, and developing a thin layer of soil to enhance the effectiveness of light in the T nanoparticles in order to improve MB degradation by T nanoparticles. Although the B application alone could reduce the extracted MB in the soils compared to the control samples, the obtained results indicated that the adsorbent was not

efficient, and further assessment is required regarding the changes in the biochar type (engineered B) in order to enhance MB degradation B. Moreover, use of various B in aquatic environments has yielded favorable outcomes, while the complex nature of the soil environment compared to aqueous solutions renders the use of B in the soil environment inefficient, urging additional research.

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References

1. Padhi BS. Pollution due to synthetic dyes toxicity and carcinogenicity studies and remediation. *Int J Environ Sci* 2012; 3(3): 940-55.
2. Zhou Q. Chemical pollution and transport of organic dyes in water–soil–crop systems of the Chinese Coast. *Bull Environ Contam Toxicol* 2001; 66(6): 784-93.
3. Robinson T, McMullan G, Marchant R, Nigam P. Remediation of dyes in textile effluent: A critical review on current treatment technologies with a proposed alternative. *Bioresour Technol* 2001; 77(3): 247-55.
4. Imran M, Crowley DE, Khalid A, Hussain S, Mumtaz MW, Arshad M. Microbial biotechnology for decolorization of textile wastewaters. *Rev Environ Sci Biotechnol* 2015; 14(1): 73-92.
5. Rehman K, Shahzad T, Sahar A, Hussain S, Mahmood F, Siddique MH, *et al.* Effect of Reactive Black 5 azo dye on soil processes related to C and N cycling. *Peer J* 2018; 6: e4802.
6. Pazos M, Cameselle C, Sanromán MA. Remediation of dye-polluted kaolinite by combination of electrokinetic remediation and electrochemical treatment. *Environ Eng Sci* 2008; 25(3): 419-28.
7. Jayanthi V, Geetha R, Rajendran R, Prabhavathi P, Sundaram SK, Kumar SD, *et*

- al.* Phytoremediation of dye contaminated soil by *Leucaena leucocephala* (subabul) seed and growth assessment of *Vignaradiata* in the remediated soil. *Saudi J Biol Sci* 2014; 21(4): 324-33.
8. Mc Cullagh C, Skillen N, Adams M, Robertson PK. Photocatalytic reactors for environmental remediation: A review. *J Chem Technol Biotechnol* 2011; 86(8): 1002-17.
 9. Yagub MT, Sen TK, Afroze S, Ang HM. Dye and its removal from aqueous solution by adsorption: A review. *Adv Colloid Interface Sci* 2014; 209: 172-84.
 10. Liu Y, Zhao X, Li J, Ma D, Han R. Characterization of bio-char from pyrolysis of wheat straw and its evaluation on methylene blue adsorption. *Desalin Water Treat* 2012; 46(1-3): 115-23.
 11. Sparks D L. *Methods of Soil Analysis: Part 3, Chemical methods*. Madison, WI: Soil Science Society of America. 1996.
 12. Shaheen I, Ahmad KS, Jaffri SB, Zahra T, Azhar S. Evaluating the adsorption and desorption behavior of triasulfuron as a function of soil physico-chemical characteristics. *Soil Environ* 2016; 35(1): 99-105.
 13. Ajmal A, Majeed I, Malik RN, Iqbal M, Nadeem MA, Hussain I, *et al.* Photocatalytic degradation of textile dyes on Cu₂O-CuO/TiO₂ anatase powders. *J Environ Chem Eng* 2016; 4(2): 2138-46.
 14. Zhang F, Zhao J, Shen T, Hidaka H, Pelizzetti E, Serpone N. TiO₂-assisted photodegradation of dye pollutants II. Adsorption and degradation kinetics of eosin in TiO₂ dispersions under visible light irradiation. *Appl Catal, B* 1998; 15(1-2): 147-56.
 15. Daneshvar N, Salari D, Niaei A, Rasoulifard MH, Khataee AR. Immobilization of TiO₂ nanopowder on glass beads for the photocatalytic decolorization of an azo dye CI Direct Red 23. *J Environ Sci Health, Part A* 2005; 40(8): 1605-17.
 16. Chen B, Yuan M. Enhanced sorption of polycyclic aromatic hydrocarbons by soil amended with biochar. *J Soil Sediment* 2011; 11: 62-71.
 17. Deng Y, Zhang T, Wang Q. Biochar adsorption treatment for typical pollutants removal in livestock wastewater: A review. *Engineering applications of biochar*. 2017; <http://dx.doi.org/10.5772/intechopen.68253>
 18. Xu RK, Xiao SC, Yuan JH, Zhao AZ. Adsorption of methyl violet from aqueous solutions by the biochars derived from crop residues. *Bioresour Technol* 2011; 102(22): 10293-8.
 19. Yao Y, Gao B, Zhang M, Inyang M, Zimmerman AR. Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil. *Chemosphere* 2012; 89(11): 1467-71.
 20. Mesgari Z, Gharagozlou M, Khosravi A, Gharanjig K. Spectrophotometric studies of visible light induced photocatalytic degradation of methyl orange using phthalocyanine-modified Fe-doped TiO₂ nanocrystals. *Spectrochim Acta A* 2012; 92: 148-53.
 21. Ehrampoosh M, Moussavi GH, Ghaneian M, Rahimi S, Ahmadian M. Removal of methylene blue dye from textile simulated sample using tubular reactor and TiO₂/UV-C photocatalytic process. *J Environ Health Sci Eng* 2011; 8(1): 34-40.
 22. Tayade RJ, Natarajan TS, Bajaj HC. Photocatalytic degradation of methylene blue dye using ultraviolet light emitting diodes. *Ind Eng Chem Res* 2009; 48(23): 10262-7.
 23. Munter R. Advanced oxidation processes—current status and prospects. *Proc Estonian Acad Sci Chem* 2001; 50(2): 59-80.
 24. Asadi M, Shayegan J, Alaie E. Photocatalytic degradation of PAHs contaminated soil in south pars economic and energy zone with TiO₂ nanocatalyst. *Iran J Chem Eng* 2007; 4(1): 14-20.
 25. Gu J, Dong D, Kong L, Zheng Y, Li X. Photocatalytic degradation of phenanthrene on soil surfaces in the presence of nanometer anatase TiO₂ under UV-light. *J Environ Sci* 2012; 24(12): 2122-6.
 26. Shi M, Hu LC, Huang ZQ, Dai JY. The influence of bio-char inputting on the adsorption of phenanthrene by soils and by maize seedlings. *J Agro Environ Sci* 2011; 30: 912-6.
 27. Beesley L, Moreno-Jiménez E, Gomez-Eyles JL. Effects of biochar and greenwaste compost amendments on mobility, bio-availability and toxicity of inorganic and organic contaminants in a multi-element polluted soil. *Environ Pollut* 2010; 158(6): 2282-7.