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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 populations[4] and plant growth.[5] Methylene blue (MB) is a dye cationic azo molecule with the molecular formula of $C_{16}H_{18}N_3SCI$, which high resistance to environmental degradation in

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soil due to the presence of benzene rings in its structure. Unlike inorganic pollutants (e.g., heavy metals) and some organic pollutants that have permissible levels in soil quality standards, the permissible level of soil contaminated with synthetic dyes have not been recorded in soil quality standards. Nevertheless, the toxicity and environmental hazards of organic dyes are significantly higher compared to organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls.[2] Therefore, determination of the permissible levels and refining of these pollutants (especially in calcareous soils of Iran) is of paramount importance.

Several methods are used for the removal of dye contaminants from aquatic environments; however, data is scarce regarding their refining in soil environments due to the heterogeneous structure of soil.[6, 7] Among the common methods for the removal of dyes from aqueous solutions, degradation and adsorption are considered to be most appropriate for dye removal,[2] the application of which in the soils contaminated with these contaminants has rarely been investigated.

In the photocatalytic degradation processes of organic contaminants, contaminants are completely degraded and converted into CO_2 and H_2O in the presence of semiconductor catalysts (e.g., T), especially under UV radiation.[8] T nanoparticles are strong photocatalysts that could effectively remove numerous Environmental organic contaminants and convert them into environmentally friendly products.[8] On the other hand, pollutants are not degraded in the adsorption process and are adsorbed by various adsorption mechanisms (e.g., adsorption, precipitation, coprecipitation, and formation of surface complexes).[9] Various adsorbents are used in this process, and agricultural wastes have been considered as cost-efficient and environmentally friendly adsorbents in this regard. Biochars produced from agricultural waste and acts as a proper adsorbent for cationic and anionic dyes owing to its unique

properties, such as high specific surface area and specific functional groups.[10] The functional groups at the B surface (e.g., carboxyl, hydroxyl, and phenolic) effectively bind to soil pollutants, and these properties of biochar indicate its potential as an effective sorbent to be used for organic and inorganic contaminants in soil and water.[10]

To date, no studies have been focused on the use of photocatalytic materials in the soil heterogeneous environment for the removal of organic contaminants, as well as the effects of B on the behavior of MB dye in the soil environment. The present study aimed to evaluate the effects of T nanoparticles and B on the degradation/adsorption of MB dye in two soils with various textures as affected by different light radiation (UV and VS).

Materials and methods

In this study, two soil samples were collected from different areas in Kerman, Iran. After filtration through a two-millimeter sieve, the physical and chemical properties of the samples were determined using conventional methods.[11] The soils samples had sandy loam (SL) and loam (L) textures. The other properties of the studied soils are presented in Table 1.

Table 1. Selected chemical and physical properties of studied soils

Properties	Sandy loam soil	Loam soil
Clay (%)	5	11.6
Sand (%)	71	48.4
Silt (%)	24	40
Organic matter (%)	0.69	0.98
Calcium carbonate equivalent (%)	8.32	17.3
Electrical conductivity (dS/m)	2.39	7.84
pH	7.5	6.8
Cation exchange capacity (cmol(+)/kg)	8.93	14.8

In order to investigate the effects of T (Platonic Nanotech, 99% Anatase, 30-50 nm), B (produced from sheep manure at the temperature of 500 °C for 4 h in anaerobic

conditions), and the combination of these materials on the degradation/adsorption of MB in the soils, the soil samples were initially contaminated with the MB source at the concentrations of 100, 200, and 300 mg/kg and incubated for one week in field capacity (FC; moisture maintained at 20%V for SL and 32% V for L) in the dark. Following that, the T nanoparticles at 1 and 3%, B at 1 and 3%, and their combination with equal weight percentages (T0.5 + B0.5

and T1.5 + B1.5%) were separately added to the contaminated soil samples. Subsequently, the samples were individually exposed to UV and VS radiation in closed boxes containing UV LEDs (365 nm) and VS (555 nm) 3W individually, and 20 light in 0.3 m^2 were assigned individually to each irradiation 8 h per day for 60 days. The boxes were placed in a room at the constant temperature of 25±3 °C. Fig. 1 shows the schematic of the experimental setup.
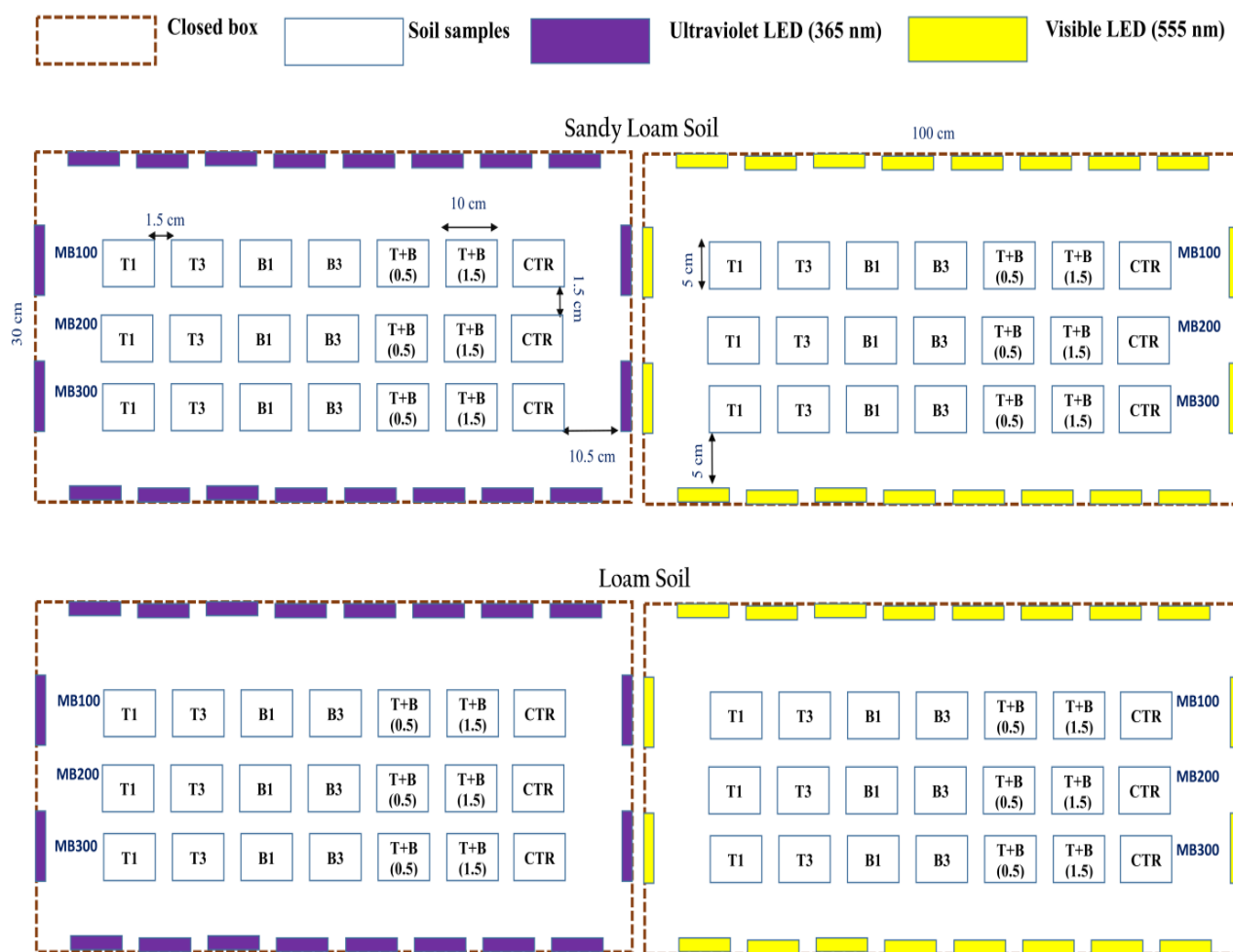

Fig. 1. Schematic of experimental setup (each soil sample in three replicates)

During 60 days of incubation, the samples were stored in FC moisture conditions and stirred once daily. After this period, the samples were extracted using distilled water (soil-to-water ratio: 1:2). Afterwards, the samples were shaken for 2 h at 190 rpm and centrifuged immediately at 2,500 rpm. The supernatants were filtered

through the Whatman 42 filter paper, and the MB concentration was determined using the spectrophotometric method (Cary 50 UV-VIS spectrophotometer) at the maximum MB wavelength (644 nm). Finally, MB was calculated based on the MB standard curve.

Data analysis was performed in the SAS software using the analysis of variance, mean

comparison, and Tukey's test (alpha 0.05), and graphs were also drown using the Excel software version 2016.

Results and discussion

The results of the analysis of variance (ANOVA) indicated that various levels of MB contamination, amendments, radiation sources, and their interactions had significant effects on the extracted MB in the SL and L soils, with the exception of the interactive effects of the amendments and irradiation, at 0.01 significance level of Tukey's test (Table 2). Fig. 2 depicts the effects of various concentrations of MB on the extracted MB from the SL and L soils.

Table 2. Analysis of variance of extracted methylene blue in sandy loam and loam soils affected by Cd levels and chelating agents

Source of variation	DF†	Mean squares	
		Sandy loam	Loam
MB levels	2	85134.3**	65911.8**
Amendments	6	5914.2**	2324.2**
Radiation sources	1	920.1**	232.6**
MB levels × Amendments	12	10658.8**	7427.4**
MB levels × Radiation sources	2	34246.8**	26424.9**
Amendments × Radiation sources	6	2831.5ns	1096.77ns
MB levels × Amendments × Radiation sources	12	5235.2**	3636.6**
Error	84	70.73	28.86

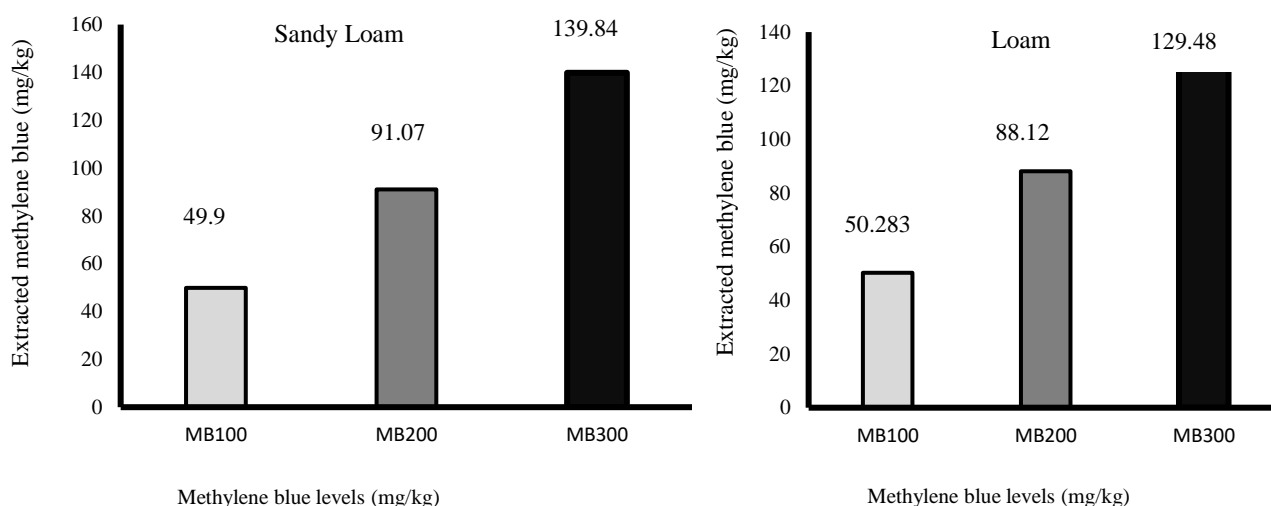†Degrees of freedom; *, **Significant at 5% and 1%, respectively; ns: Non-significant

Fig. 2. Effects of various MB concentrations on extracted MB from SL and L soils (each column with average of 42 samples; different letters indicate significant differences in the mean of different treatments; P<0.05)

The extracted MB from both soils significantly increased at higher MB concentrations, which was predictable. Another important finding in this regard was the difference between the soil samples in terms of the extracted MB, which was approximately equal at low MB concentration (100 mg/kg), while at the high concentrations of MB (200 and 300 mg/kg), the extracted MB level from the SL soil was higher compared to the L soil. This difference could be attributed to the lower clay content in the SL soil samples compared to the L soil samples. Due to the higher specific surface area and higher cation exchange capacity of clay and silt than the sand particles, these particles were able to retain greater amounts of MB, thereby preventing MB desorption.[12] As results, the initial level of MB (100 mg/kg) led to the extraction of 50% of MB

from the soils, and increasing the applied MB to 200 and 300 mg/kg led to the MB extraction of approximately 45 and 43% of each the initial MB concentrations, respectively, which indicated the increased degradation or adsorption process, resulting in the increased MB concentration in the soil samples. This increment could be attributed to degradation or adsorption, as well as the increased availability of MB for T or B as the added MB to the soil was greatly adsorbed on the soil particle surfaces at low concentrations (physical adsorption on the negative surfaces of the soil particles), and B and T could not affect these samples properly. At the time of extraction, MB was attached to the soil particles (weak binding) and extracted more rapidly, showing higher levels of MB. Furthermore, the investigation of the effects of the studied amendments on the extracted MB from the SL and L soils (Fig. 3) demonstrated that in both soils, the highest level of the extracted MB was obtained in the control samples (no amendments).
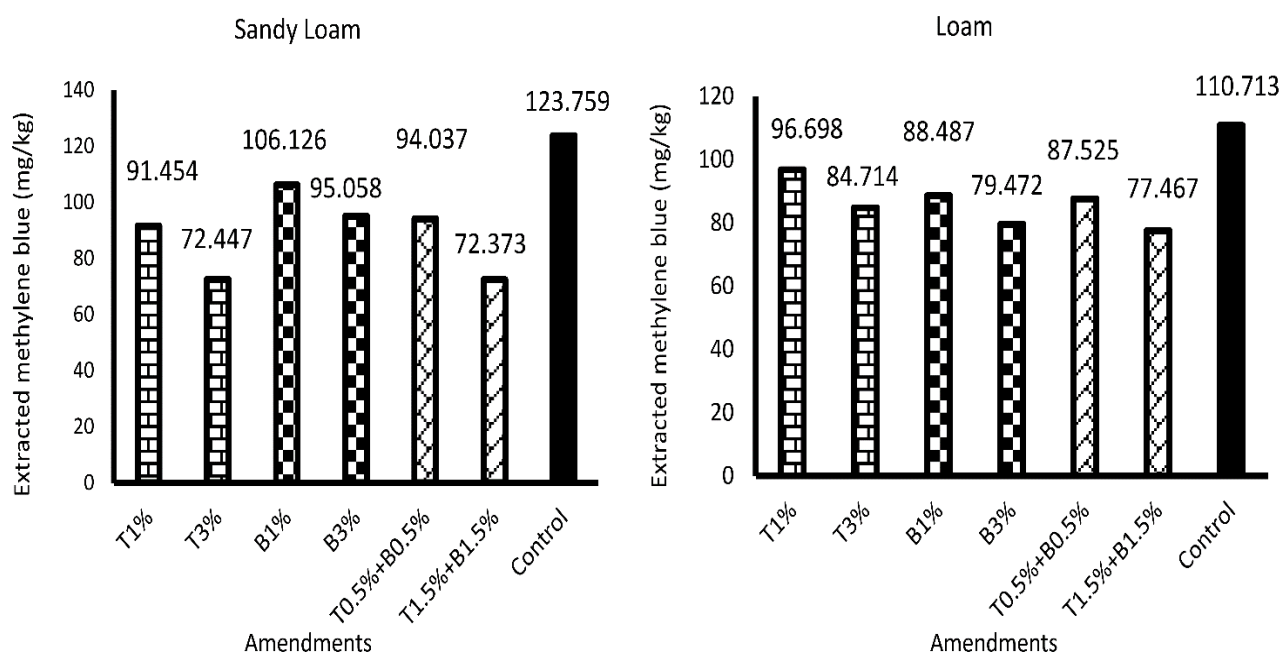

Fig. 3. Effects of various levels of T and B on extracted MB from SL and L soils (each column: mean of 18 samples; different letters indicate significant differences in means of different treatments; P<0.05)

According to the findings of the current research, the extracted MB in the control treatment of SL soil was 1.2 times higher than the L soil, indicating the lower surface adsorption of MB in the SL soil. On the other hand, the highest reduction of the extracted MB in both soil samples was obtained in treatment of T1.5% + B1.5%. In the SL soil samples, the application of T1%, T3%, B1%, and B3% was observed to reduce the extracted MB by 26, 41, 14.2, and 23.2%, respectively compared to the control treatment. In addition, the application of T0.5% + B0.5% and T1.5% + B1.5% was observed to decrease the extracted MB by 24 and 41.5%, respectively compared to the control treatment in the SL soil. The application of T1%, T3%, B1%, B3%, T0.5% + B0.5%, and T1.5% + B1.5% decreased the extracted MB by 12.6, 23.4, 20, 28.2, 20.9, and 30%, respectively compared to the control samples in the L soil. In the photocatalytic degradation of organic contaminants such as MB, the light energy (hv: UV or sunlight) in the form of a photon with a specific wavelength (>387.5 nm) excites the electrons (e^-) on the surface of T, moving the electron from the valence bands to the conduction bands, thereby resulting in the electron-hole ($e^- + h^+$) pair generation (Eq.

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1).[13]

$$Catalyst + hv \rightarrow e^- + h^+ \qquad (1)$$
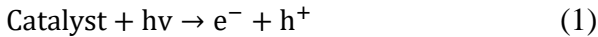
The generated electron-hole pair produces superoxide ($O_2^{-°}$) and hydroxyl free radicals ($OH^°$) through the reduction of oxygen molecules and water oxidation, respectively. During the following reactions, the superoxide radicals were neutralized by the proton, producing unstable hydrogen peroxide (Eqs. 2-4).

$$O_2^{-°} + H^+ \rightarrow HO_2^° \qquad (2)$$
$$2HO_2^° \rightarrow H_2O_2 + O_2 \qquad (3)$$
$$H_2O_2 + e^- \rightarrow OH^° + OH^- \qquad (4)$$
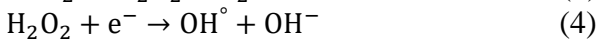
Finally, the produced hydroxyl free radicals reacted with MB as a dye, leading to its degradation[14] (Eq. 5).

$$OH^° + Dye = Oxidized\ dye \qquad (5)$$
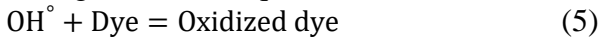
Due to the observed degradation mechanism of T, the reduction of MB in the soil was predictable although as expected of the strong photocatalyst, the reduction trend was gradual. In this regard, the low efficiency of T could be attributed to the high thickness of soil layers, lower photon absorption to the photocatalyst surface (decreased hydroxyl radicals), and inappropriate intensity of the applied photon to the system.

In a research in this regard, Daneshvar *et al.* reported that the zero point of charge of T was 6.8, and at higher pH than this value, the surface charge of T was negative due to the absorbed hydroxyl.[15] Therefore, it was concluded that increased pH in the environment caused the negative charge on the T surfaces to increase, and the conditions of the formation of hydroxyl radicals improved, increasing degradation. Based on the pH values for the SL (7.5) and L soils (6.8), it was expected that higher levels of MB degraded in the SL soil due to the increased production of destructive hydroxyls. However, the heterogeneous soil conditions led to the failure of this assumption. Moreover, the application of B reduced the extractable MB in both the SL and L soils through adsorption and distribution mechanisms.

According to the findings of Chen and Yuan, the adsorption of organic contaminants in the prepared B at low temperatures occurred through the adsorption mechanism on the non-carbonated biochar fraction, while in the prepared B at high temperatures, the main mechanism was adsorption on the carbonized sections.[16] Electrostatic adsorption and desorption between organic contaminants and B was reported to be another possible mechanism in the mentioned study.[17]

The biochar surface often has a negative charge, which could adsorb cationic organic contaminants through electrostatic adsorption. This electrostatic adsorption has been reported by Xu *et al.*[18] With regard to the MB adsorption on B in aquatic solutions, Yao *et al.* have stated that as biochar increases in soil, the ion exchange capacity of the soil increases as well, which in turn affects the adsorption of cationic contaminants.[19] Fig. 4 shows the effects of UV and VS radiation sources on the level of extracted MB from the SL and L soils. Accordingly, a significant difference was observed between the UV and VS radiation sources on the MB content of both soils, so that the extraction rate of MB in the samples with VS radiation was higher compared to the UV samples, indicating the more significant effects of the UV source compared to the VS samples on MB degradation. The changes in the extracted MB in the L soil compared to the SL soil indicated that the L soil was less affected by UV radiation (Fig. 4). Since the T energy band gap was 3.2 eV, it could only adsorb the wavelength of 370-370 nanometers, as well as small amounts of visible energy.[20] According to the results of the present study, due to the specific energy band gap of T, it had significantly lower efficiency in the presence of VS light. Numerous studies have reported the effectiveness of UV radiation compared to VS light in the improvement of the photocatalytic activity of T.[21, 22]
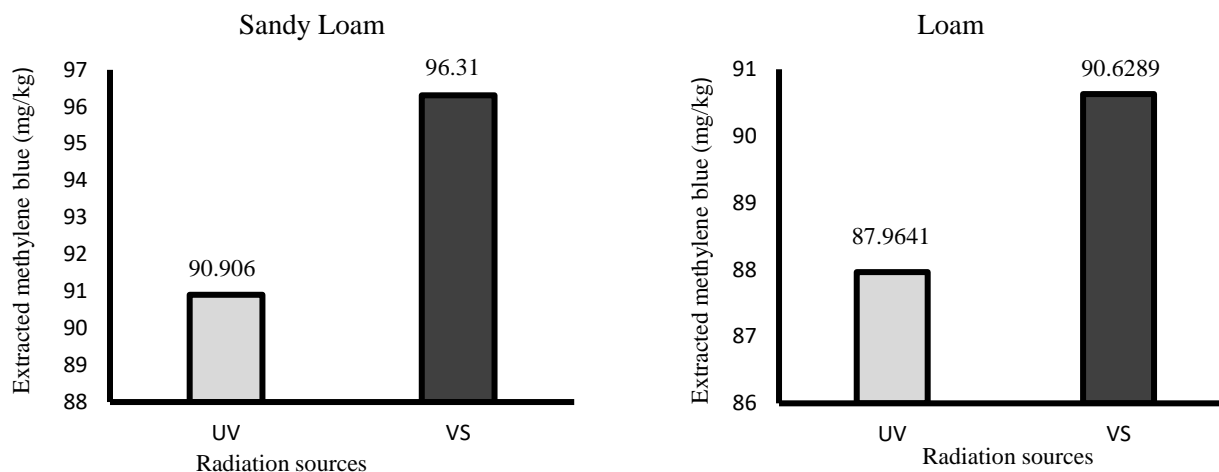
Sandy Loam

Loam

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, TiO_2[rutile and anatase], and ferric oxide) could be excited by UV irritation, 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.
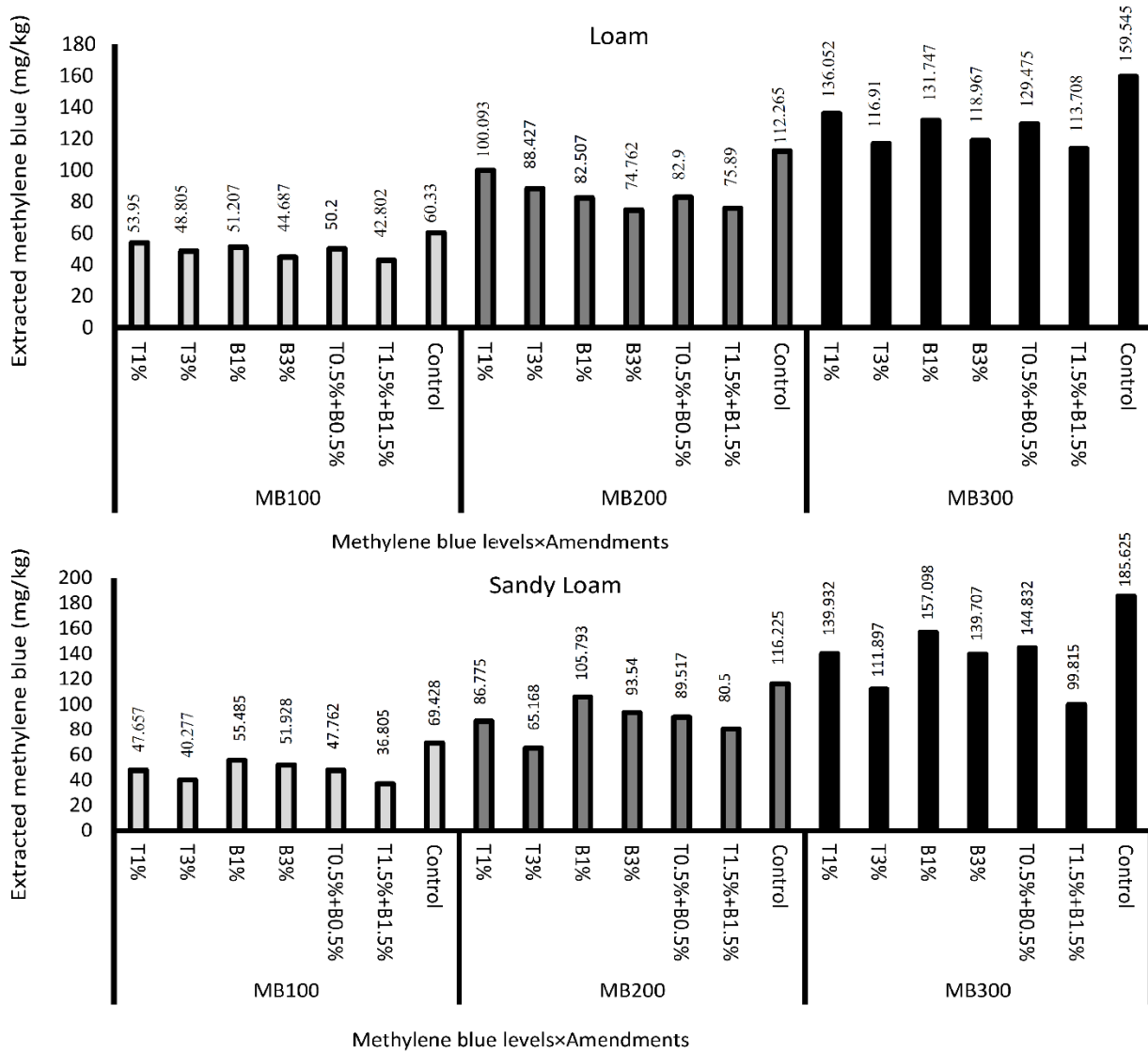
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Fig. 5. Effect of MB contamination levels and amendment treatments on extracted MB from SL and L soils (each column with mean of six samples; different letters indicate significant differences in means of different treatments; $P < 0.05$)
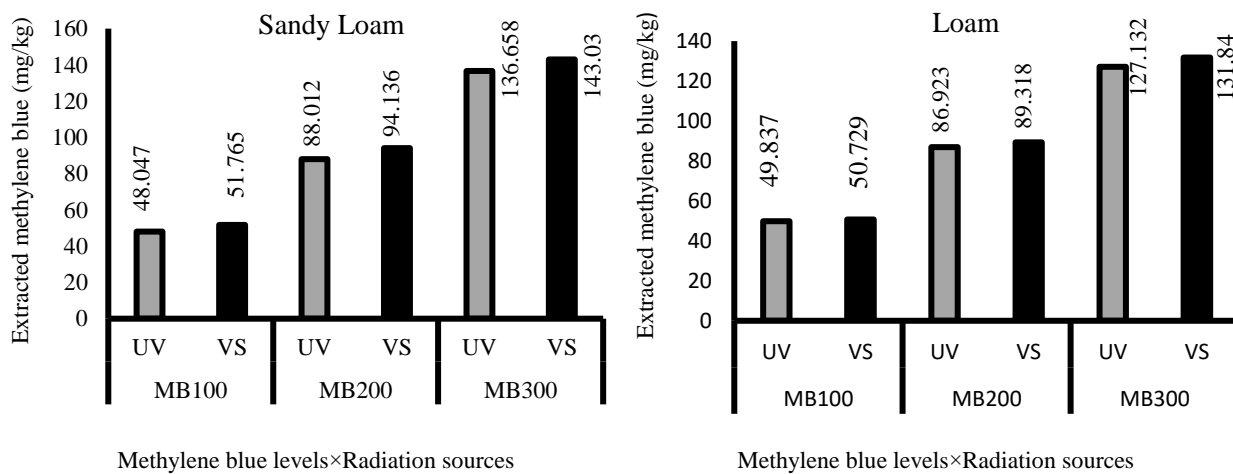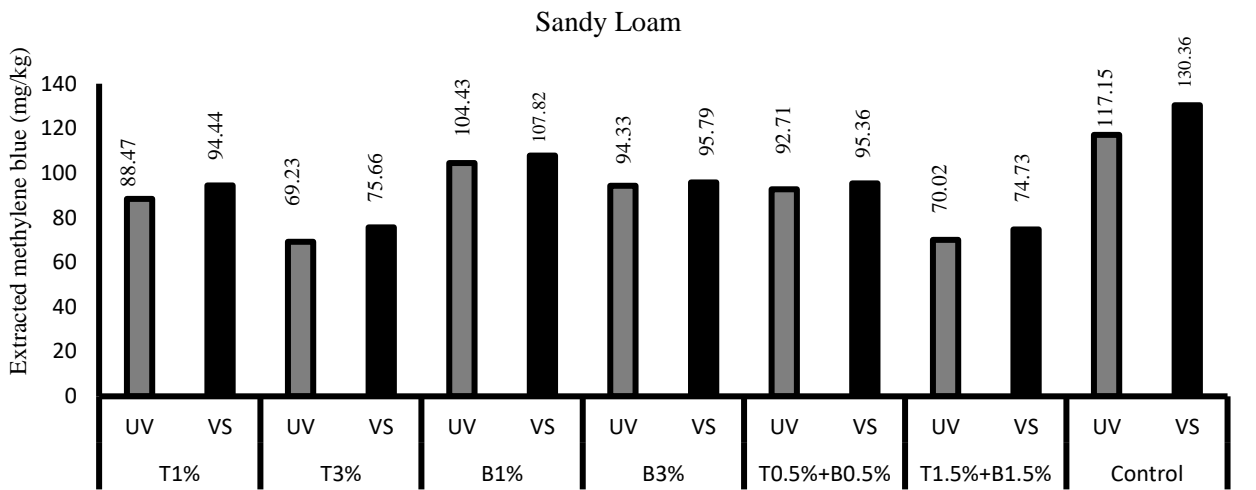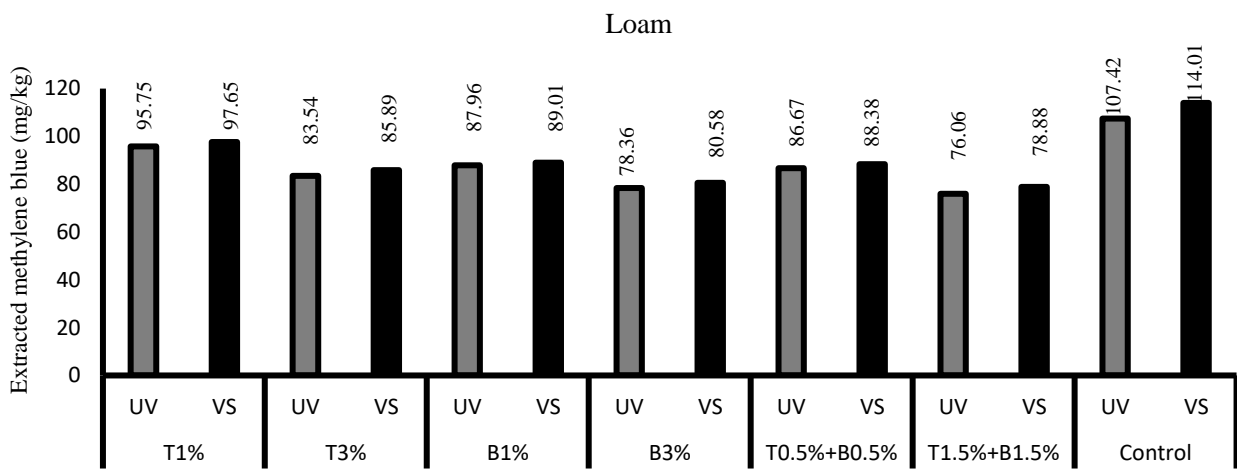

Fig. 6. Effect of MB contamination levels and radiation sources on extracted MB from SL and L soils (each column with mean of 21 samples; different letters indicate significant differences in means of different treatments; $P < 0.05$)

Sandy Loam

Amendments×Radiation sources

Loam

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)
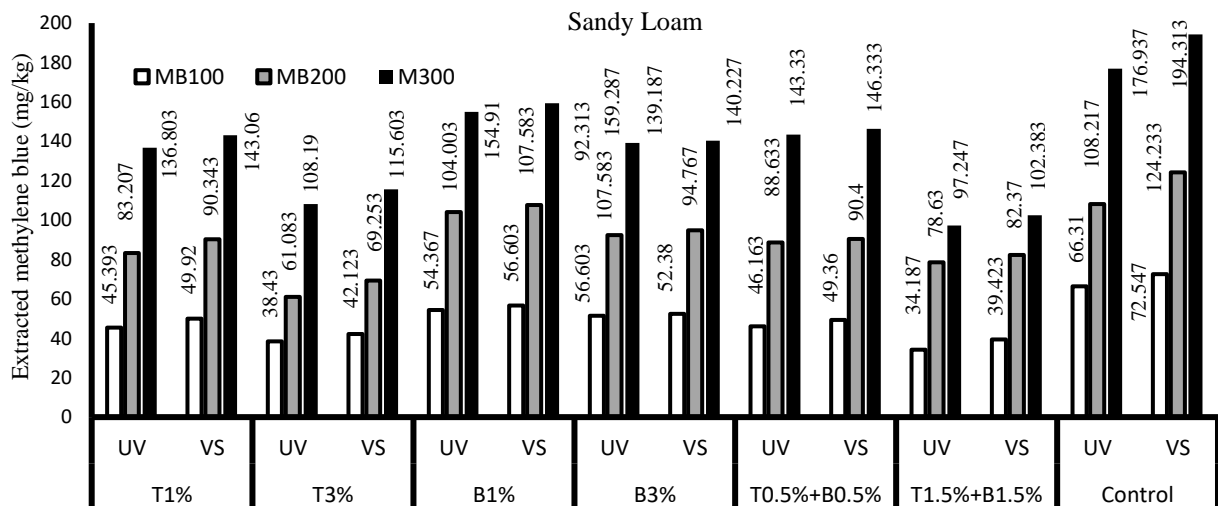
Sandy Loam

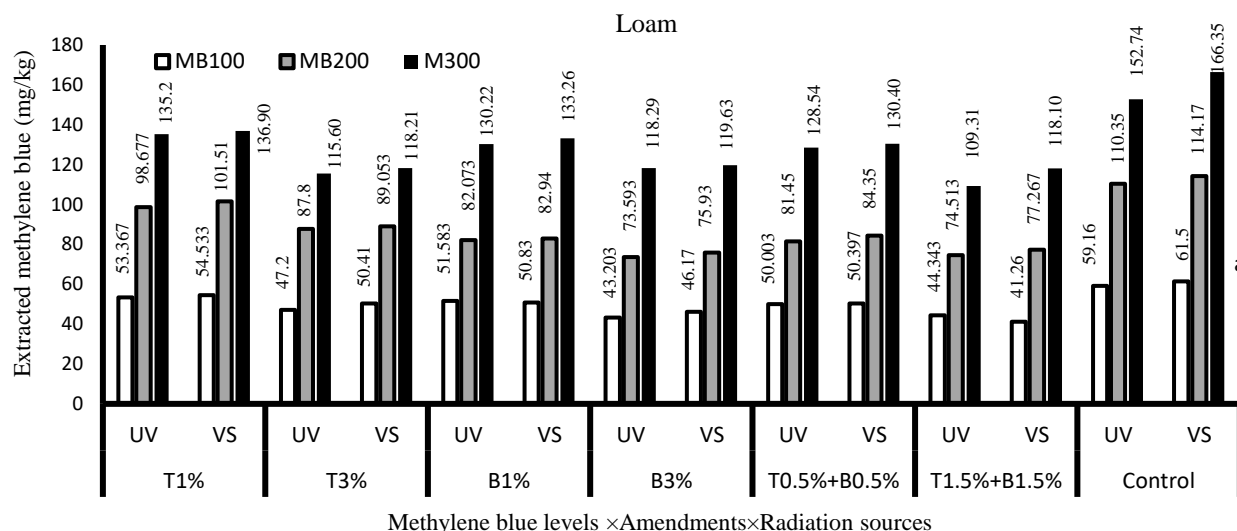Methylene blue levels ×Amendments×Radiation sources

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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) <

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 enviroment.[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, H_2O_2, 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.

Acknowledgments

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 Biotecnol 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. Jayanthy V, Geetha R, Rajendran R, Prabhavathi P, Sundaram SK, Kumar SD, *et*

al. Phytoremediation of dye contaminated soil by Leucaenaleucocephala (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 Cu_2O-CuO/TiO_2 anatase powders. J Environ Chem Eng 2016; 4(2): 2138-46.

14. Zhang F, Zhao J, Shen T, Hidaka H, Pelizzetti E, Serpone N. TiO_2-assisted photodegradation of dye pollutants II. Adsorption and degradation kinetics of eosin in TiO_2 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 TiO_2 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 TiO_2 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 TiO_2/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 TiO_2 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 TiO_2 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.