Evaluation of Kinetic and Equilibrium studies for Phytoremediation of Methylene Blue Dye (Triarylmethane) and Congo Red (Diazo) using *Trachyspermum Ammi* L.

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Research Article

Keywords: Methylene Blue Dye, Congo Red dye, Phytoremediation, Kinetics, Adsorption

Posted Date: August 19th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-746247/v1>

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Title: Evaluation of Kinetic and Equilibrium studies for Phytoremediation of Methylene blue dye (triarylmethane) and Congo red (Diazo) using *Trachyspermum ammi* L.

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Abstract

Phytoremediation developed as a green-clean, solar-driven and innovative technique for the eradication of contaminants from the environment from last two decades. In the present research work, phytoremediation potential of an ornamental plant *Trachyspermum ammi* L. (*T. ammi*) was examined for the removal of a triarylmethane-Methylene blue (MB) and di-azo-Congo red (CR) dye. The various parameters such as initial dye concentration, contact time, and pH were focused to explore the dye removal capability of *T. ammi*. The increase in initial dye concentration affects the decolorization potential of the *T. ammi*. The decolorization potential of *T. ammi* found to be reduced with enhancing the initial dye concentration of both the dyes. The plant achieved condition of equilibrium after the 40 h of contact time with both MB and CR dye. The favorable pH for *T. ammi* for the MB dye was observed as 5 while for CR dye was 6. The kinetics of phytoremediation reaction with both MB and CR dyes were studied with help of pseudo-first order, pseudo-second order, and Elovich models and the results were well appropriated to pseudo-first order with the correlation value $R_2 \geq 0.95$ for MB and $R_2 \geq 0.97$ for CR. The Langmuir and Freundlich isotherms studies of phytoremediation reaction found in favor of Freundlich equilibrium isotherm with correlation $R_2 \geq 0.99$ for both MB and CR dyes. The mechanism of *T. ammi* for removal of dyes was supported with the help of analytical techniques such as Fourier Transform-Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM).

Key words: Methylene Blue Dye; Congo Red dye; Phytoremediation; Kinetics; Adsorption

Introduction

Synthetic dyes used in textile industry are mostly allergic, carcinogenic, and mutagenic in nature. Furthermore, if these dyes are discharged in wastewater as such in the water bodies, it resulted into a deadly threat to aquatic life such as fishes, microbes, and other creatures of water bodies (Konicki et al. 2013; Aljeboree et al. 2014). The dye contaminated water is also unsuitable for human consumption. Subsequently, their complete expulsion from textile wastewater is a matter of great concern for research community. Various physio-chemical techniques such as adsorption, photo catalysis, advanced oxidation, precipitation, coagulation, solvent extraction, membrane removal etc. were proposed in the literature to remove dyes from textile wastewater (Ahmad et al. 2015; Ali et al. 2018; Kang et al. 2019). But, these types of techniques have less productivity, costly and produce intermediate contaminants. Because to these issues, there are lot of significant methods to develop eco-friendly, cost effective and resourceful method for treatment of textile dyes wastewater (Ullah et al. 2020). Some researchers also proposed the use of enzymes and microbes such as bacteria and fungi as an eco-friendly approach but in actual practice, microbial administration appears to be quite difficult (Khandare and Govindwar 2015; Sarkar et al. 2017; Arfin et al. 2019). In last two decades, another clean-green innovative plant-based technique known as phytoremediation comes into view as an eco-friendly and cost-effective method for the removal of the contaminants from wastewater in contrast with physio-chemical and biological methods (enzymatic, microbial) etc (Kabra et al. 2013, Khandare and Govindwar 2015). Phytoremediation technology is the best suitable, accepted as natural and sustainable development strategies to change over contaminated areas into the fruitful one with use of different varieties of plants. In literature, aquatic plant species such as *Azolla pinnata* (Al-Baldawi et al. 2018), *Chara vulgaris* (Mahajan et al. 2019; Mahajan and Kaushal 2020), *Lemna minor* (Imron et al. 2019), *Eichhornia crassipes* (Tan et al. 2016; Sharma et al. 2021), *Pistia stratiotes* (Mahajan and Kaushal 2019; Ekanayake et al. 2021), *Salvinia molesta* (Kaushal and Mahajan, 2015; Al-Baldawi et al. 2020), *Typha angustifolia* (Chandanshive et al. 2017) are more focussed for the phytoremediation of dye wastewater due to their easy administration in aqueous form. Many terrestrial plants also proved their potential for dye removal due to the effective enzymatic system in their roots. As illustration, the ornamental flowering plant *Blumea malcolmii* was reported to degrade the Direct Red 5B with involvement of number of enzymes present in its roots (Kagalkar et al. 2009). *Aster amellus*, *Portulaca grandiflora*, *Glandularia pulchella*, *Petunia grandiflora* and *Nopalea cochenillifera* were some other terrestrial garden ornamental plant species reported for the degradation of Remazol Red, Navy Blue HE2R, Green HE4B, Brilliant Blue Green and Red HE7B respectively (Kabra et al. 2011; Khandare et al. 2011a, b; Kabra et al. 2011; Adhi et al. 2012). Recently, some other commonly grown ornamental plants such as *Asparagus officinalis*, *Alcea rosea*, and *Bacopa monnieri* plant species reported for remediation of hazardous azo dyes (Watharkar et al. 2018, Mahmoudabadi et al. 2019, Shanmugam et al. 2020). In the present study, *Trachyspermum ammi* ornamental plant species of Apiaceae family explored for the removal of dyes. Previously, *T. ammi* was reported for the removal of heavy metals from the soil (Javed et al. 2020). Revathi et al. 2018 utilised the biomass of leaves of *T. ammi* as an adsorbent for removal of Grey BL dye from aqueous solution. As per our knowledge, no work is reported in literature for removal of dyes from aqueous solution by *T. ammi* plant in the living state. Hence, the present study was planned to examine the phytoremediation ability of *T. ammi* plant for removal of two structurally different dyes, a diazo dye Congo Red (CR) and a triaryl methane dye Methylene Blue (MB) in aqueous form. To optimise the phytoremediation process, the effect of contact time, initial dye concentration and pH were studied. The mechanism of dye removal by plant in living conditions was analysed

through study of kinetic and equilibrium isotherms. FTIR and SEM studies were also performed to support the dye removal mechanism of *T. ammi* plant.

Material and methods

Synthetic dye Solution

The two structurally different dyes, a triarylmethane dye, Methylene Blue (MB) and a diazo dye Congo Red (CR) were used in present research work (Fig. 1). The solid form of MB and CR dyes used in experimental work was in a high analytical grade and acquired from Merck Limited, Mumbai. The MB and CR dyes are soluble in double distilled water, so the stock solutions of both dyes were prepared in water. The various initial dye concentrations were prepared by diluting the stock solution to required extents.

Plant collection and cultivation

T. ammi plants (Fig. 2) of same size and growth were collected from the botanical garden of the Guru Nanak Dev University, Amritsar, Punjab (India). Initially, plants were gently washed under the tap water thoroughly to remove soil for 10-15 minutes and after that kept in distilled water for 24 h so that plants become free from any soil particles. Before experimentation, plants were grown in half-strength Hoagland nutrient solution for one week so that plants can adjust themselves as medium changes from soil to water (Leggett and Frere 1971). The growth of plants has been observed after one week. It has been observed that plants grow faster in aqueous medium with extensive growth of roots. Thereafter, plants were transferred into dye solution (100 mL) in the beakers with support system for phytoremediation experiment.

Phytoremediation experiments

The phytoremediation experiments were performed with different concentrations of dyes (10, 20, 30, 40 and 50 mg L⁻¹) of MB and CR dyes by using *T. ammi*. The progress of the phytoremediation experiment was analysed by measuring absorbance of dye solution with the help of Shimadzu-2550 UV-visible double beam spectrophotometer. The samples of dye solution up to 2 mL were taken every 8 h up to 40 h for measuring absorbance and then decolorization percentage was calculated as given below (Kabra et al. 2011):

$$\text{Decolorization (\%)} = \frac{\text{Initial absorbance} - \text{Final absorbance}}{\text{Initial absorbance}} \times 100 \quad (1)$$

The quantity of dye removed by the *T. ammi* at any time is 'q_t' (mg g⁻¹) and 'q_e' (mg g⁻¹) at equilibrium determined from equations 2 and 3 respectively (Mahajan and Kaushal 2020):

$$q_t = \frac{(C_0 - C_t)}{w} \times v \quad (2)$$

$$q_e = \frac{(C_0 - C_e)}{w} \times v \quad (3)$$

'C₀' is the initial dye concentration, 'C_t' is the dye concentration any time 't' and 'C_e' is the equilibrium dye concentration in mg L⁻¹, 'v' is the volume of the solution in mL and 'w' is the weight of the plant in g. The fresh weight of the plant is taken after drying several times in folds of filter paper.

Kinetics and Equilibrium studies

The kinetics of *T. ammi* for the removal of the MB and CR dyes was interpreted by using the pseudo-first order, pseudo-second order and Elovich models as demonstrated by equations 4, 5 and 6 respectively (Ahmed et al. 2014):

$$\log (q_e - q_t) = \log q_e - K_1 t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

$$q_t = \frac{1}{\beta} \ln (\alpha \beta) + \frac{1}{\beta} \ln t \quad (6)$$

where 'K₁' and 'K₂' are the rate constants for pseudo-first order and pseudo-second order, respectively. In eq. 6 'α' determine the chemisorption, and 'β' find out that how much adsorption takes place at adsorbent surface.

The application and importance of suitability of the kinetic models to experiment data are predicted with the regression value (R²) and standard deviation of normalized value (Δ q_t%). The normalized standard deviation value is computed with following equation (Mahajan and Kaushal 2020):

$$\Delta q_t \% = 100 \sqrt{\frac{\sum \left| \frac{q_t(\text{exp}) - q_t(\text{theor})}{q_t(\text{exp})} \right|^2}{n-1}} \quad (7)$$

where q_t (exp) and q_t (theory) are the practical and theoretical values of the amount of dye remediated from aqueous solution where "n" corresponds to the numeral count of experiment. The rationality of kinetics models is based upon the value of Δq_t %. The lower is its value for the kinetic model, higher is the acceptability of the data for that model.

The equilibrium studies of phytoremediation reactions were determined with the help of Langmuir and Freundlich models represented by equations (8) and (9) respectively (Wang et al. 2018).

$$\frac{C_e}{q_e} = \frac{1}{b Q_0} + \frac{1}{Q_0} C_e \quad (8)$$

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (9)$$

The Langmuir adsorption constants 'b' and 'Q₀' were related to the high ability of adsorption of the dye at equilibrium and rate of adsorption correspondingly. The value 'n' finds the spontaneity in behaviour of dye molecules toward phytoremediation process in case of Freundlich adsorption isotherm, and 'K_f' is the adsorption capacity for the plant. The valuable Langmuir isotherm parameter 'R_L' is suggested for equilibrium parameter and determined by following equation (Mahajan and Kaushal 2020):

$$R_L = \frac{1}{b + C_0} \quad (10)$$

When there is irreversible process, the R_L value corresponds to the zero, and it is for favourable conditions. The value becomes more than one for the unfavourable process (Kaur et al. 2015).

Characterization techniques

The root surface of *T. ammi* plant was evaluated by FTIR and SEM techniques. The FTIR of dried sample of *T. ammi* was examined before and after phytoremediation of both MB and CR dyes. The infrared spectra were taken with Agilent (CARRY-630) spectrophotometer with range of 400– 4000 cm⁻¹. The surface analysis of the *T. ammi* was examined with the help of scanning electron microscope (JEOL-JSM-6100 Ltd, Japan). *T. ammi* particles were placed on stubs and coated with gold foil by the gold- coating machine- JEOL-JSM-6100 Ltd, Japan....

Result and discussion

T. ammi has shown the efficient removal of the MB and CR dyes up to 40 h and found to active after eliminating the maximum percentage of the dyes. The equilibrium stage of experiment was achieved after 40 h and both MB and CR dyes solution decolorised up to maximum extent. The different parameters, kinetics, and absorption mechanism of *T. ammi* have been detailed on the obtained results.

Surface Characterisation of *T. ammi* roots

To characterize the functional group present on *T. ammi* roots, its FTIR spectra was taken before and after phytoremediation of both MB and CR dyes. The FTIR spectra *T. ammi* roots before and after dye adsorption was shown in Fig. 3 and comparative interpretation of results of FTIR spectra was presented in Table 1.

The FTIR spectra depicts the presence of functional groups such as phenolic and carboxyl group which is indicated in roots of *T. ammi* and these results agree with the previous spectra reported for *T. ammi* plant extract (Qamar et al. 2020). Mathew et al. 2008 also confirmed the presence of Thymol (2-isopropyl-5-methyl phenol) as main active constituent of *T. ammi* plant extract. It has been inferred in Fig. 3 that most of the FTIR peaks changes its position after the adsorption of dye due to interaction among functional group of dye and root. For instance, the FTIR spectrum for *T. ammi* exhibits a strong broad band at 3431 cm^{-1} assigned to the O-H stretching vibration of phenolic group which on adsorption of MB and CR dye changes its position at 3364.4 & 3371.4 cm^{-1} respectively and gets more broader due to extensive intermolecular H-bonding (Mahajan and Kaushal 2019). Similarly, peaks appear due to carbonyl group stretching 1248.7 & 1036.2 cm^{-1} shifts their position and it has also been observed that the intensities of these peaks changed from strong to medium or weak. These results strongly recommended that functional group interaction plays an important role in adsorption of dyes from their solution by *T. ammi* plant roots. The feeble peaks appear at 1584 , 1509 & 1451 cm^{-1} (after MB adsorption) and 1653 , 1507 & 1458 cm^{-1} (after adsorption of CR dye) confirmed the adsorption of dye molecules.

Scanning electronic micrograph (SEM) analysis have been also done to confirm the surface absorption of dye by roots of *T. ammi* during phytoremediation process. As SEM is one of the best technologies for the surface characterization of adsorbent, so surface analysis of *T. ammi* roots confirmed the absorption of dye by roots through phytoremediation process (Aljeboree et al. 2017). SEM of *T. ammi* roots is recorded for both before and after the phytoremediation experiment with MB and CR and results are presented in form SEM micrographs (Fig. 4). Fig. 4a, indicates the smooth surface having prominent pores in the fresh roots of *T. ammi* before phytoremediation process while Fig. 4 b and c the dye loaded surface of *T. ammi* roots. It has been clearly depicted from Fig. 4 b and c shows that surface of *T. ammi* roots is covered with MB and CR dyes, respectively. The SEM images of *T. ammi* roots show prominent colored marks which could be assumed as indication of adsorption of dyes by *T. ammi* roots acts as the adsorbent for removal of dyes from its solution during phytoremediation process (Qamar et al. 2020).

Kinetic and equilibrium studies

The kinetic studies of phytoremediation for different dyes in aqueous phase in living forms were suggested by classical kinetic models and limiting methods to understand the mechanism of transfer of mass during

phytoadsorption (Mosoarca et al. 2018; Saber et al. 2018; Mahajan and Kaushal 2019, 2020; Kaushal and Mahajan 2021). Therefore, the phytoremediation kinetics study of MB and CR dyes with the help of *T. ammi* was studied with pseudo-first order, pseudo-second order, and Elovich models. The kinetic graphs of various models at different concentrations of MB and CR dyes are shown in Fig. 5-7. The constants of kinetics and other used parameters determined from kinetic plots for MB and CR dye are presented in Table 2 and 3 respectively. Fig 5a-b depicts the pseudo-first order straight-line graph with negative value of slope when $\log (q_e - q_t)$ against time (t) had plotted at various concentrations for *T. ammi*. Figure 6a- b depicted a linearized plot with the positive slope when t/q_t plotted versus “t” for pseudo-second order kinetic model and k_2 and $q_{e (theor)}$ values are predicted with the help of intercept and slope respectively for different concentration for both the dyes. The Elovich constants α and β has been determined by the slope and intercept, of the plot between q_t vs $\ln t$ depicted in Fig. 7a- b. From Table 2 and 3, it has been clearly depicted that R_1^2 values lies either above 0.90 or near to it for most of concentrations of both the dyes in case of pseudo-first order only in comparison to pseudo-second order and Elovich model. Moreover, $q_{e (theor)}$ values for *T. ammi* are found to be more consistent to $q_{e (exp)}$ for pseudo-first order in case of both of dyes MB and CR while for pseudo-second order and Elovich model $q_{e (theor)}$ values are far away from $q_{e (exp)}$. Also, the values of Δq_{t1} (%) in comparison to Δq_{t2} (%) and Δq_{t3} (%) are lower which indicate toward the acceptability of the data for pseudo-first order for both the dyes. Hence, the value of experimental data of the phytoremediation of MB and CR dyes by *T. ammi* showed better compliance with pseudo-first order. It has been also observed that when there is increase in the initial dye concentration then the rate constant (k_1 and k_2) value decrease gradually for MB and CR dye removal by *T. ammi* (Table 2 and 3). There is probability of competition in co dye molecules to acquire available adsorbent sites on surface of plant. Hence, there is decrease in electrostatic interaction on increasing the initial dye concentration and the reduction in the dye interaction towards the plant surface. Therefore, chemisorption mechanism may restrict by the rate of the adsorption of MB and CR dyes by *T. ammi* (Sánchez-Galván et al. 2008). In Table 2, the value of constant β has been decreased by the enhancement in the dye concentration which shows that the site of adsorption for MB and CR dye was low in value in the *T. ammi* surface and therefore, MB and CR uptake dyes by plant surface might occur through functional group interaction (Kaushal and Mahajan 2021). Additionally, the constant value α_{EI} decreased by the increase in initial dye concentration, which indicated that more than one mechanism which drives the phytoremediation process.

The equilibrium studies on phytoremediation were also work out by using the Langmuir and Freundlich adsorption isotherm. The monolayer adsorption is depicted by Langmuir isotherm with specific and uniform adsorption sites on the surface while Freundlich model is affected by the heterogeneous nature of surface sites (Hameed et al. 2007). The evaluation of regression coefficient (R^2) and other various constant values had been predicted by linear regression plot are presented in **Table 4**. The value of R^2 Langmuir adsorption isotherm was found to be 0.987 and 0.983 for MB and CR and the equilibrium constant R_L value has been found to be decreases with increase in concentration. R_L value was determined to be 0.0197, and for CR the value for R_L is 0.0198 at 50 mg L⁻¹ MB dye concentration, indicated that MB and CR dye adsorption by *T. ammi* is highly favorable in high concentration due to bonding between functional groups present on *T. ammi* root cells and dye molecules (Mi-Hwa et al. 2010). The little bit better fitting of Freundlich model ($R^2 = 0.999$) during the adsorption for CR dye than for MB ($R^2 = 0.990$) on *T. ammi* which suggested the heterogenous nature of *T. ammi* surface (**Table 4**). As the value $1/n$ of Freundlich isotherm obtained to be lower than 1, hence it has been predicting the surface with

heterogeneity (Hameed et al. 2007). If the value of n is equal to unity, if the value of n below to unity the process is chemical and if the value of n comes more than unity then process is physical and favorable. The $1/n$ value for of MB adsorption on the surface of *T. ammi* has been obtained to be 0.1784, which determine the valuable adsorption of MB dye on the *T. ammi* surface (Fytianos et al. 2000) and for the CR dye value of $1/n$ was obtained as 0.3175 which is supportive adsorption at surface of *T. ammi*.

Impact of contact time, initial dye concentration, pH parameters on the adsorption capacity of phytoremediation of *T. ammi*

For examine the effect of time on increasing dye concentration on decolourisation percentage of *T. ammi* plants were dipped in 250 mL beaker containing 100 mL of MB and CR dye solutions containing 10, 20, 30, 40 and 50 mg L⁻¹. The amount of dye removed by the plant was determined up to 40 h because maximum adsorption takes place up to 40 h and further no more adsorption observed. The rate of adsorption and decolourisation becomes high with increase in the time. The plot of amount of MB and CR dye adsorbed by plant as a function time is shown in Fig. 8 a and b respectively. Initially the rate of adsorption may be high due to proximity of the uncovered surface area of the adsorbents, however, it has been observed that the phytoremediation capacity of *T. ammi* to decolorise MB and CR dyes solution decreases with further increase in concentration. This is because of high concentration pores of adsorbent become blocked due to blockage of high concentration of adsorbate particles and rate of adsorption becomes decreases. These types of results were reported in research study of *Glandularia pulchella* for remediation of Green HE4B (sulphonated azo dye). The reduction in decolorization capacity might be toxic on plant system due to the influence of enhancing concentration which hinders the metabolism of plant, and thus, reduces the metabolic activity of the plant system (Kabra et al. 2011). The fast adsorption at initial phase of experiment is caused by the high amount of dye particles in the solution and large number of unoccupied sites available on plant which behaves as driving force for remediation process, while on last phase the driving force reduces. The decrease in the driving force could be due to saturation of the active sites available on adsorbent surface as a plant root surface.

Fig 9 (a) reveal the decolorization percentage of MB dye versus time. Maximum MB decolorization was observed in 10 mg L⁻¹ after that, it reduces in 20, 30, 40 and 50 mg L⁻¹. Fig 9 (b) predicts the decolorization of CR with time. After 24h the concentration 10 mg L⁻¹ and 20 mg L⁻¹ follow same pattern of decolorization. Afterwards the percentage decolorization of 10 mg L⁻¹ becomes high than 20, 30, 40 and 50 mg L⁻¹. Similar work was reported for removal of MB dye by using *L. minor* plant (Muhammad et al. 2019) and *Chara vulgaris* for the decolorization of the CR dye (Mahajan and Kaushal 2020).

The pH values of dyes solution have great effect on phytoremediation process for removing the dyes in their aqueous phase. In the current study, pH effect on MB and CR dyes remediation by *T. ammi* was projected by performing experiment from in the pH range 3 to 10 along with 20 mg L⁻¹ MB and CR dyes solutions. It was examined that both at high and low pH, decolorization ability of plant get effected. The maximum decolorization 95.7% is obtained at pH 8 in case of MB dye by using *T. ammi* while with CR dye, maximum decolorization 97.3% was observed at value of pH 5 (Fig. 10). The pH of dye solution might be having large impact on the functional groups of dyes and the plant surface. The pH value above 8, there was a sharp reduction in the decolorization of MB and decrease in decolorization was observed at above pH 5 in CR. Earlier also the similar

effect of pH was documented in studies to remediate the acidic dyes in their aqueous state (Khataee et al. 2012). Therefore, the optimum value of pH for removal of MB and CR by *T. ammi* is at pH value 8 and 5 respectively.

Mechanism of Phytoremediation of dyes by *T. ammi*

Based on these result and discussions, a hypothetical mechanism is also proposed for phytoremediation of dyes by *T. ammi* plant (Fig. 11). The roots of *T. ammi* plant plays an important role in removal of dyes from solution. The phytoabsorption of MB and CR dye by plant root has been confirmed through SEM studies of roots of *T. ammi* (Fig. 4). It has been clearly inferred the presence of phenolic and carboxyl functional groups in roots of *T. ammi* from FTIR results. Kinetic and equilibrium studies also indicate the the adsorption of dye occur on surface through chemical interaction of functional groups. Hence, it can be assumed that dye molecules get adsorbed through intermolecular H-bonding, electrostatic and aromatic $\pi - \pi$ interactions between functional group present on surface of roots of *T. ammi* and dye molecules as shown in Fig. 11. (Kaushal and Mahajan 2021). Once the dye gets phytoadsorbed on surface of roots then get assimilated inside the plant root cell where it gets detoxified by the internal mechanism of plant cell (Kabra et al. 2013). As the growth of *T. ammi* plant was not restricted and even rejuvenate after absorption of dye which implies that *T. ammi* plant has potential of remediate structurally different types of dyes. However, the future studies are required to explore mechanism for detoxification of dyes inside root cells.

Cost effectiveness of the MB and CR removal through Phytoremediation

Phytoremediation is the cost-effective solar driven technology in contrast with any-other physical, chemical, and biological processes (Khandare and Govindwar 2015). This technique provides the neutral and resourceful application to the removal of harmful pollutants out of the surrounding environment (Dietz and Schnoor 2008). Some of the physical and chemical processes which are reported for the removal of MB and CR dyes, need large amount of money for their operations. The oxidation method using the various catalysts proved to be a fast and effective method for removal of MB and CR dyes, but it involves high energy and large amount of chemical for its processing and that is the major limitation of the process (Tavares et al. 2012). The description of the results in current research work, proved the capacity of *T. ammi* to degrade the dyes MB and CR in natural forms without any additional chemicals. Therefore, the textile industrial area could implement the cost-effective and eco-friendly technology of phytoremediation by using ornamental plant for the treatment of the dye loaded wastewater rather than the using costly techniques for removal of the harmful dyes from the wastewater.

Conclusion

Phytoremediation studies were performed with *T. ammi* to remediate MB and CR dyes from the synthetic wastewater. The results of this research work indicated the capacity of *T. ammi* to treat the dyes wastewater for the water remediation methods. The various effect such as the influence of initial dye concentration, time and pH on the phytoremediation mechanism were observed. The decolorization potential of *T. ammi* toward MB and CR dye was decreased on increase in the initial dye concentration of these dye (10 to 50 mg L⁻¹) while adsorption capacity found to be increased. The maximum decolorization MB and CR dye solution was found 99 and 85% respectively. The pH of dye solution also found to influences the phytoremediation process as 97% decolorization

of 20 mg L⁻¹ CR dye observed at pH 5 while 95% decolorization at pH 8 for MB. The maximum decolorization capacity by *T. ammi* explored its utilization for removal of the contaminants from the wastewater, especially dyes and can be grown in the dye contaminated area. The adsorption isotherms of Langmuir and Freundlich models investigate the adsorption pattern of MB and CR dyes on the *T. ammi* surface and Freundlich model found to be a little bit better fit for adsorption of both dyes MB ($R^2 \geq 0.990$) and CR ($R^2 \geq 0.990$) dye molecules on *T. ammi* root surface. The kinetic studies results supported the pseudo-first order kinetic model with the maximum correlation value $R^2 \geq 0.95$ and 0.97 for MB and CR respectively for phytoremediation by *T. ammi*. FTIR and SEM studies confirmed that dye molecules get phytoadsorbed by plant roots through the functional group interaction. After phytoadsorption, dye get finally assimilated inside the root cells where it gets detoxified. Future research work will plan to explore detoxification mechanism inside the plant cells. Hence, the observed outcomes suggested that the *T. ammi* is an efficient ornamental plant for phytoremediation of noxious dyes from the environment and can be utilized as an effective phytoremediator which provide sustainable solution for wastewater treatment in present scenario of environmental safety crisis.

Declarations

Competing interests: The authors declare that there is no competing interests.

Ethics approval and consent to participate: “Not applicable”, as research does not report on or involve the use of any animal or human data or tissue.

Consent for publication: Not Applicable.

Funding: No

Authors' contributions

Navjeet Kaur: Conducted the experimental studies and drafted the manuscript; Jyotsna Kaushal: Conceptualization, expert view, data interpretation and overall Supervision; Pooja Mahajan: Data interpretation. All authors read and approved the final manuscript.

Acknowledgements

The authors express their gratitude to the Chitkara University, Rajpura for providing required lab facilities to complete this research work.

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478 Table1. Comparative analysis of FTIR peaks of *T. ammi* roots before and after adsorption of Methylene Blue and
 479 Congo Red dye

S. No.	Peak position (cm ⁻¹) in FTIR spectra of <i>T. ammi</i> roots			Functional group assigned	Intensity
	Before dye adsorption	After MB adsorption	After CR adsorption		
1	3431.0	3466.4	3371.4	O-H (hydroxyl group stretch)	Strong, broad
2	2926.0-2851.4	2926.0-2855.1	2920.4-2851.4	-CH ₂ - (methylene group stretching)	Medium
3	2374.3	----	2316.5	O=C=O (carboxyl group stretch)	Medium
4	1699.0	----	-----	-C=O (Non-conjugated stretch)	Strong
5	----	----	1653.1	N-H bending (amide interaction)	Medium, broad
6	---	1584.1	-----	-C=O (Conjugated stretch)	Medium
7	---	1509.6	1507.7	C-C stretching (aromatic group)	Weak
8	1490.9	----	-----	C=C stretching (aromatic)	Medium
9		1451.8	1418.3	C-O stretching	Weak
10	1343.7	1323.2	1321.3	O-H bending (phenol)	Medium, Weak, weak
11	1248.7	1233.7	1261.7	C-O (carbonyl)	Medium, Medium, Weak
12	1183.4	1187.2	1156.5	C-O stretch (alcohol)	Weak
13	1036.2	1058.6	1034.3	C-N stretching	Weak, medium, medium
14	950.5	----		=C-H (alkene)	Medium

Table 2. Kinetic model constant values for phytoremediation of Methylene Blue dye by *T. ammi*.

Kinetic Model	Kinetic Parameters	Initial dye concentration mg L ⁻¹				
		10	20	30	40	50
Pseudo-First Order	q _{e (exp)} (mg g ⁻¹)	0.049	0.085	0.105	0.124	0.135
	K ₁	0.030	0.022	0.026	0.017	0.022
	q _{e (theor)} (mg g ⁻¹)	0.056	0.091	0.116	0.125	0.140
	R ₁ ²	0.887	0.943	0.904	0.951	0.881
	Δq _{t1} (%)	0.432	0.241	0.168	0.143	0.112
Pseudo-Second Order	q _{e2 (theor)} (mg g ⁻¹)	0.086	0.179	0.202	0.232	0.244
	K ₂	11.5	5.57	4.93	4.33	4.08
	R ₂ ²	0.844	0.780	0.847	0.915	0.933
	Δq _{t2} (%)	2.85	2.14	1.85	0.94	0.87
Elovinch Equation	q _{e3 (theor)} (mg g ⁻¹)	0.729	1.313	1.613	2.654	1.952
	α	0.005	0.008	0.011	0.014	0.014
	β	53.1	29.41	23.98	14.47	19.84
	R ₃ ²	0.912	0.909	0.929	0.637	0.854
	Δq _{t3} (%)	16.55	16.02	14.43	14.21	14.14

Table 3. Kinetic model constant values for phytoremediation of Congo Red (CR) dye by *T. ammi*

Kinetic Model	Kinetic Parameters	Initial dye concentration mg L ⁻¹				
		10	20	30	40	50
Pseudo First Order	q _{e (exp)} (mg g ⁻¹)	0.0473	0.084	0.1105	0.1315	0.1512
	K ₁	0.028	0.015	0.018	0.043	0.020
	q _{e (theor)} (mg g ⁻¹)	0.0516	0.0709	0.0958	0.1244	0.1349
	R ₁ ²	0.9718	0.909	0.9509	0.9676	0.9785
	Δq _{t1} (%)	0.445	0.267	0.156	0.142	0.125
Pseudo Second Order	q _{e2 (theor)} (mg g ⁻¹)	0.0533	0.1074	0.1444	0.1677	0.2015
	K ₂	13.73	9.30	6.90	5.96	4.96
	R ₂ ²	0.684	0.790	0.873	0.929	0.931
	Δq _{t2} (%)	2.74	2.12	1.94	0.97	0.79
Elovinch Equation	q _{e3 (theor)} (mg g ⁻¹)	0.5874	0.9037	1.2351	1.4383	1.8139
	α	0.00702	0.01338	0.01824	0.0248	0.02484
	β	65.78	43.66	31.94	27.54	22.42
	R ₃ ²	0.747	0.745	0.839	0.896	0.914
	Δq _{t3} (%)	16.25	16.14	14.41	14.13	14.02

Table 4. Langmuir and Freundlich constants for Phytoremediation of Methylene Blue (MB) and Congo Red (CR)

Equilibrium Model	Constants	MB	CR
Langmuir Isotherm	Q_0 (mg g ⁻¹)	0.138	0.162
	b (mg g ⁻¹)	0.700	0.388
	R^2	0.987	0.983
Freundlich isotherm	1/n	0.1784	0.3175
	K_F	0.0745	0.0576
	R^2	0.990	0.999

List of Figures:

Fig. 1 Chemical Structure of (a) Congo red (CR) (b) Methylene blue (MB)

Fig. 2 Image and Classification of *Trachyspermum ammi*

Fig 3. IR spectra of *T. ammi* roots before and after MB dye adsorption

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572 Fig. 4 SEM of *T. ammi* roots (a) Before phytoremediation (b) After phytoremediation of MB (c) After
573 phytoremediation of CR dye

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578 Fig. 5 Pseudo first order kinetic model for (a) Methylene blue (b) Congo red dye
579 phytoremediation by *T. ammi*

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Fig. 6 Pseudo second order kinetic model for (a) Methylene blue (b) Congo red dye
phytoremediation by *T. ammi*

Fig. 7 Elovinch equation kinetic model for (a) Methylene blue (b) Congo red dye
phytoremediation by *T. ammi*

Fig. 8. Adsorption capacity of *T. ammi* (a) Methylene blue (b) Congo red dye as a function of time

Fig. 9 Decolorization variation of (a) Methylene blue and (b) Congo Red dye by *T. ammi* with time

Fig. 10 Effect of pH on decolorization pattern of *T. ammi* for MB and CR

Fig. 11 Proposed Mechanism for Phytoadsorption of Methylene Blue (MB) and Congo Red (CR) dye by *T. ammi* roots