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# Phytoremediation modeling in soil contaminated by oil-hydrocarbon under salinity stress by eucalyptus (A comparative study)

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ABSTRACT

This study is designed to compares the efficiency of three models about behavior of plants under crude oil pollution and stress salinity. To model phytoremediation of a soil contaminated with oil hydrocarbons under salinity stress the models of Maas-Hoffman, Van Genuchten and Hoffman, Dirksen were used. The first factor was crude oil at 5 levels (control, 1, 2, 3, 4% W/W), and the second factor salinity at 5 levels (control, 4, 5.5, 7, and 9 dS/m). To understand about the efficiency of Eucalyptus to decrease the content of hydrocarbons, oil hydrocarbon concentration was compared before and after planting. The results showed that crude oil and salinity affected fresh and dry weights of the root and the shoot, root volume, stem diameter, number of leaves, leaf area, and stem height ($p < 0.05$). All of the models used in this study could determine the behavior of plants against these stresses ($R^2 > 0.98$). Additionally, the potential of eucalyptus seedlings to reduce the concentrations of total petroleum hydrocarbons (TPH) was studied by measuring TPH concentration in the soil before and after planting. Generally it can be resulted that the model of Dirksen had the highest accuracy with the highest $R^2$ (99%) and lowest RMSE (from 0.0001 to 0.0002) and SSE (from 0.005 to 0.0007). As a prudent suggestion for practical application, the Dirksen model can be used with more confident compared to two other models just after its local calibration.

## 1. Introduction

Soil pollution with crude oil and its derivatives has been considered to be the most dangerous environmental pollution, which is inevitable in oil producing countries. Crude oil exploration has resulted in economic development especially in developing countries, but environment of these countries has also destroyed by undesirable effects of oil industry, for example the water resources in the Niger Delta are no longer suitable for human consumption, but oil exploration in Nigeria cannot be stopped because approximately 90% of Nigeria's foreign exchange earnings is due to crude oil exploration industry (Okotie et al., 2018). Beside of harmful effects of oil industry on our environment, there are a lot of reports of multiple studies from Middle East (Binns et al., 2014) to Mexico Gulf (Gay et al., 2010) that show the negative effects on human health such as psychological problems, respiratory tract irritation, and disturbance of blood profile by exposure to crude oil spills (Ramirez et al., 2017). Since the majority of the world's oil reserve is in salty and very salty areas, many oil-contaminated sites are facing salinity as well. Salinity is one of the most important environmental factors that reduces the growth, development, and production of plants around the world (Sevengor et al., 2011). Today, due to the high use of petroleum compounds around the world, pollutions with these compounds are widespread globally (Chris, 2006). Petroleum compositions can be affected by various factors and transfer by air, water and organisms all around the polluted location (Doran and Zeiss, 2000). Based on a study by the European Environmental Agency (EEA) at least 34% of contaminated locations in Europe were polluted by mineral oil (EEA, 2011).

'Hydrocarbons' are one of the most important groups of organic pollutants. They are often entered into the environment through the oil and gas industries. These compounds have undesirable effects on agricultural products, surface water, ground water, and soil quality, and they consequently enter the food chain from the contaminated air, polluted soil, and water, thereby threatening human health. Therefore, the waste from the oil industries must be refined before it is disposed in the environment (Wang et al., 2007).

There are various methods for the removal of crude oil and other pollutants from the soil. Generally, these methods are divided into three categories, including physical (such as extraction of polluting fumes from the soil), chemical (such as soil washing), and biological (such as phytoremediation). Physical and chemical methods usually have many complications due to their administration costs and the harmful

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changes that they do to the physical and chemical properties of the soil. Phytoremediation is the use of green plants to refine contaminated sites, a method compatible with environment, and also an interesting way for the elimination of contaminants. This method is less costly and is also simpler compared to other refining methods. In this method, organic pollutants are refined by different processes such as plant stabilization, plant extraction, plant evaporation, rhizosphere decomposition, rhizosphere purification, plant decomposition, and hydraulic control (Joner et al., 2002). Plants that have high absorption potency and high biomass can be appropriate for phytoremediation. Fast-growing tree species are suitable for this purpose considering such properties as high biomass potential, extensive root system, and high transpiration, which successfully affect the phytoremediation process (Minhas et al., 2007). Phytoremediation has been used for treating contaminants including heavy metals (Gong et al., 2018; Anning and Akoto, 2018; Chandra et al., 2018; Cristaldi et al., 2017) and crude oil (Asemoloye et al. 2017; Liao et al., 2016; Tao et al., 2009; Zhang et al., 2010; Peng et al., 2009; Lin et al., 2007), also multiple research results have published about application of phytoremediation for remediation of saline soils (Romeh, 2017; Nouri et al., 2017; Jesus et al., 2015; Al-Nasir, 2009; Kushiev et al., 2006) but there are a few researches which have compared simultaneous effects of salinity and crude oil on effectiveness of phytoremediation (Cai et al., 2016).

A model is a small component reconstructed from a great object or phenomenon and is the same as the actual object or phenomenon in terms of its operation. Thus, under a situation that it is difficult, costly and time-consuming to access all the details of the affairs and phenomena, the model plays an important role, granting us the ability to analyze and predicts the results (Razzaghi, 2002).

The main purpose of the modeling in phytoremediation is to see to what extent a plant can remediate a particular pollutant such as oil, heavy metals, salinity, drought and *etc*. Pollutant absorption and accumulation models have a major role in our understanding of the refining processes and help us better manage contaminated areas.

Davari and Homaee (2015) have developed an analytical deterministic model for simultaneous phytoremediation of Ni and Cd. The results indicated that elevated Ni and Cd concentrations in soil inhibited growth of both ornamental kale (*Brassica oleracea*) and land cress (*Barbarea verna*) plants. The newly proposed model, which assumes that metal uptake rate inversely depends on total soil metal ion concentration, reasonably well predicted the cleanup time of Ni, Cd, and Ni in the presence of Cd. The model also predicts that phytoremediation process takes much longer time when soil is contaminated with multi-metal ions.

Considering the necessity of the investigation of the role of plants in the removal of pollutions, this research was aimed at modeling the green refining of a hydrocarbon oil contaminated saline soil by Eucalyptus plants and a presentation of comparative analysis between three models (Mass-Hoffman, Van Genuchten – Hoffman and Dirksen models). This type of models are the basic models which related to reducing transpiration simulation, their efficiency has demonstrated about modeling of plants behavior under saline stress but no research has been done about crude oil pollution.

## 2. Materials and methods

A non-contaminated clay loam soil was selected, and then, the contaminations (1, 2, 3, and 4% w/w) (Moubasher et al., 2015) were created through spraying and appropriate amount of hydrocarbon oils on each pot as evenly as possible. Next, for the equilibration, the polluted pots were incubated at 30–35 °C for 3 months. During the incubation, the pots were irrigated weekly with distilled water and the salts were allowed to go deep in the pot by irrigation and then be re-transferred to the soil surface by evaporation (Kornfeild and Susskind, 1977). The salinity was applied by adding sodium chloride (NaCl) and calcium chloride ($CaCl_2$) salts at 1:1 ratio reported by Hosseini et al. (2009) that the presence of calcium chloride along with sodium chloride reduced the harmful effects of sodium, lowered its absorption and increased the Ca/Na ratio (Hosseini et al., 2009). Salinity levels were: 4, 4.5, 5, 7 and 9 dS/m. Because a more accurate prediction based on models, at least 5 stress levels is needed to model the absorption and stress evaluation process. Therefore the models will require these five levels of salt stress and crude oil pollution for more accurate prediction. Accordingly, five levels of salinity and crude oil are considered. In current study we used a nonlinear least square regression for curve fitting. Mathematically the number of measurement points for curve fitting must be at least two points greater than the number of fitting parameters. In this study we used some models in which the largest number of fitting parameters in the model was 3; thus we can fit this equation on our measurement data (numbers of stress point indicates the number of measurement data). In curve fitting the variation in treatments is more important than the number of measurement points. In this study the number of stress levels was 5 but we have low and high level of oil concentration. 75 one-year old *Eucalyptus camaldulensis* seedlings with a height of 23 cm, a stem diameter of 1.75 cm, and ~25 leaves were obtained from the Isa Parre terrarium, Dezful, Khuzestan, Iran (32°22′N 48°24′E). For any level of treatment including salinity and crude oil three repetitions was considered. After the administration of the incubation period, the pots were transferred to the greenhouse for the Department of Soil Science, University of Tehran. The light, moisture, and temperature (25–35 °C) were controlled to be optimized based on ecological requirements of eucalyptus. A eucalyptus seedling was planted in each 5 kg pot. The pots were irrigated at 70% field capacity, and a 12-h brightness was applied. During the planting period, the pots were irrigated with distilled water. In addition, in order to minimize evaporation from soil surface, the surface of soil in all pots were covered with perlite so that almost guaranties all of the water consumed by plant transpiration. Before irrigation, all pots were weighed to find the amount of water used by plants. To minimize the effect of evaporation, a number of pots without a plant were also included. The basis of the models used in this study is based on transpiration. Considering the soil analysis results, the plant's nutrient requirements was addressed by fertilization, the plants were harvested 150 days after planting. A gas chromatography (GC) instrument which equipped with the FID[1] detector was used to measure the concentration of THP, the concentration of oil hydrocarbons was determined based on standard method of United States Environmental Protection Agency (EPA: UNEP/IOC/IAEA). For modeling of the phytoremediation of the hydrocarbon-contaminated saline soil by eucalyptus, the models of Maas and Hoffman (1977), Van Genuchten and Hoffman (1984) and Dirksen et al., (1993) were used. For this purpose, optimal values of the parameters and constants of the models were reported from the software Solver Excel 2013 by using the data obtained from experimental studies. Then, the relative transpiration rate was calculated by these models and compared with the total amount of water given to the seedlings during the cultivation period, and evaporation effects were subtracted from it and considered as true transpiration.

Water absorption by plants can be expressed quantitatively using the general equation of flow:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial Z}\left[K(h)\frac{\partial h}{\partial Z} + K(h)\right] + S \tag{1}$$

Where θ is volumetric moisture content of soil ($L^3\,L^{-3}$), t time (T), z direction of flow (L), K non-saturated hydraulic conductivity coefficient ($L\,T^{-1}$), h water pressure in soil (L), and S the sink/source term, which indicates the amount of water absorbed by the plants in terms of the soil volume and time unit ($L^3\,L^{-3}\,T^{-1}$). In these models, the amount of water absorbed by the plant is assumed to be equal to the actual transpiration from the area limited to root growth. Hence, in the

[1] Flame Ionization Detection