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Bioremediation kinetics in diesel oil polluted soil, aimed to geophysical monitoring

[Carla Maria Raffa, Andrea Vergnano, Fulvia Chiampo, Alberto Godio, Francesca Bosco, Barbara Ruffino]

***Abstract*—In this work the kinetics of aerobic bioremediation of diesel oil polluted soil was evaluated comparing microcosms at different values of water content (u%) and carbon to nitrogen ratio (C/N). The percentage of degraded diesel oil is influenced by these two parameters due to their relevance for microbial metabolism. In addition, water content influences substrate dispersion and the contact between microorganisms and pollutant. The experimental runs allowed to model the process kinetics by the first and the second order model. In general, the best removal efficiency is achieved with C/N = 120 and u% = 8%, with the half-life time in the order of 70 days. On this base, a geophysical model was tested to predict the dielectrical permittivity of a sandy soil partially saturated with water, gas and diesel oil. The result of the modelling activity can be useful to the experimental design for monitoring the diesel oil degradation at laboratory scale.**

***Keywords*— biodegradation, diesel oil, kinetics, microcosms, soil, electrical permittivity, geophysical parameters.**

I. Introduction

Bioremediation process is strongly influenced by the parameters required for the optimal microbial metabolism. Among them, water content (u%) and carbon to nitrogen ration (C/N) have high relevance. Therefore, to get good process performance, these parameters must have proper values and to this purpose their monitoring is essential.

In this frame, knowledge of the optimized values can be of help to maximize the process kinetics. At the same time, process monitoring must be adequate to the measurement kind and range.

Thinking to the field scale, water content is rather easy to monitor by geophysical measurements, for example by electrical conductivity and dielectrical permittivity.

This study shows the experimental findings achieved in 6 microcosms having different C/N ratio and water content, where diesel oil aerobic degradation occurred.

The pollution removal efficiency was useful to define the optimal parameters and to model the process kinetics.

Based on these results, a geophysical model was applied to the microcosm showing the best results to check the sensitivity of the model itself, in view of in-field experimental runs monitored by geophysical methods.

Carla Maria Raffa, Andrea Vergnano, Fulvia Chiampo, Alberto Godio, Francesca Bosco, Barbara Ruffino

Politecnico di Torino
Italy
Corresponding author: F. Chiampo (*fulvia.chiampo@polito.it*)

II. Experimental

A. *Soil*

The soil used in this study came from 3 m under the surface and sieved to obtain a particle size distribution between 0.15 and 2 mm, according to ASTM C method 136.

The physical and chemical properties were estimated in previous studies [1].

The soil was contaminated with commercial diesel oil and stimulated with Mineral Salt Medium suitable for Bacteria (MSMB). This medium was found to be optimal for biostimulation, as described in a previous paper [1].

B. *Soil microcosms*

Microcosms were set up to evaluate biodegradation in different physical and chemistry conditions. The parameters that were changed are carbon to nitrogen ratio (C/N) and water content (u% by weight) in soil. In each sample the concentration of diesel oil was 70 $g \cdot kg^{-1}$ of soil.

The microcosms were prepared in sealed glass jars (0.2 l) with 200 g of soil (layer height = 3 cm) and different quantities of MSMB, depending on C/N ratio and water content. The C/N ratios were 120 and 180, water contents were 8%, 12% and 15%, with a total number of 6 microcosms.

Each microcosm had two replicas.

Microcosm aeration was carried out by mixing the content every 3-4 days.

C. *Analysis*

The residual diesel oil concentration was measured at t = 0, 35, 71, 112, 131,138 days in sample extracts achieved from each microcosm. The extraction was done with the EPA method 3546. The diesel oil concentration was determined by gas-chromatographic analysis of the extract, according to the EPA method 8015.

Each analysis was done in triplicate.

D. *Kinetic modeling*

The amount of diesel oil at different time was used to study the kinetic of soil bioremediation.

The reaction rate, R, follows the law:

$$R = dC_t/dt = - k \cdot C_t^{n} \qquad (1)$$

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where C_t is the residual diesel oil concentration at time t, k is the reaction rate constant and n is the reaction order.

The diesel oil biodegradation process can be described with first order model (n = 1) or second order one (n = 2). According to previous studies [2, 3], these models fit well the experimental data.

If n = 1, the equation (1) becomes:

$$R = -k \cdot C_t \tag{2}$$

and the residual diesel oil concentration can be express as:

$$C_t = C_0 \cdot \exp(-kt) \tag{3}$$

where C_0 is the initial diesel concentration at t = 0.

To evaluate when the diesel oil concentration is halved ($C_t = C_0/2$), the half-life time $t_{1/2}$ can be calculated. Considering the equation (3), it is possible to define this parameter as:

$$t_{1/2} = (\ln 2)/k = 0.693/k. \tag{4}$$

In the first order reaction rate model, $t_{1/2}$ does not depend on the initial oil concentration.

With the second order model (n = 2), the equation (1) becomes:

$$R = -k \cdot C_t^2 \tag{5}$$

and the residual oil concentration is:

$$1/C_t = 1/C_0 + k \cdot t \tag{6}$$

with the half-life time equal to:

$$t_{1/2} = 1/(k \cdot C_0). \tag{7}$$

In this case, $t_{1/2}$ depends on the initial diesel oil concentration.

Fitting of the experimental data can give the most suitable order for the process kinetics.

E. *Geophysical issues*

One of the most sensitive physical parameters to the fluid content of the soil is the dielectric permittivity; it is a basic electromagnetic property, controlling the radio-wave propagation into the soil.

Several models were proposed to predict the dielectric permittivity of soils composed by sandy grains and partially saturated with gas (air), water and hydrocarbons. One of the most popular ones is the Complex Refractive Index Model (CRIM) [4]. It predicts the bulk dielectric permittivity by accounting for the contribution of each fraction. The general formulation of the CRIM model is given by the following formula:

$$\epsilon^{\alpha}_{bulk} = (1-\phi)\,\epsilon^{\alpha}_{grain} + (\phi S_w)\,\epsilon^{\alpha}_{water} + (\phi\, S_o)\,\epsilon^{\alpha}_{oil} + \phi\,(1 - So - S_w)\,\epsilon^{\alpha}_{water} \tag{8}$$

where ϕ is the soil porosity, and S_w and S_o are the water and oil saturation, respectively, while ε defines the dielectric permittivity of the different materials.

The typical range of the α-exponent is 0.25–0.6.

III. Results and discussion

A. *Removal of diesel oil*

The gas-chromatographic analysis measured the residual diesel oil concentration at t = 0, 35, 71, 112, 131, 138 days in each microcosm. The experimental results allowed the calculation of pollutant removal. The results are shown in Figs. 1 and 2.

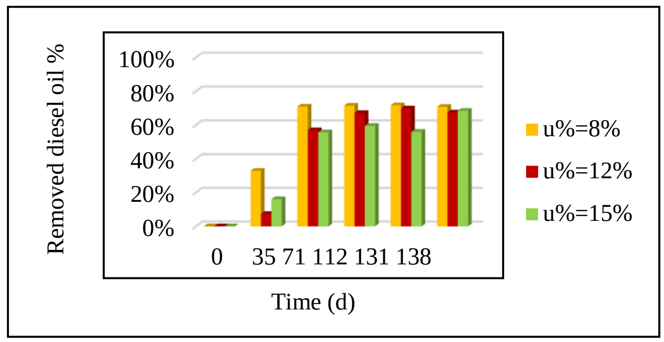

Figure 1. Percentage of diesel oil removed by the microcosm with C/N = 120

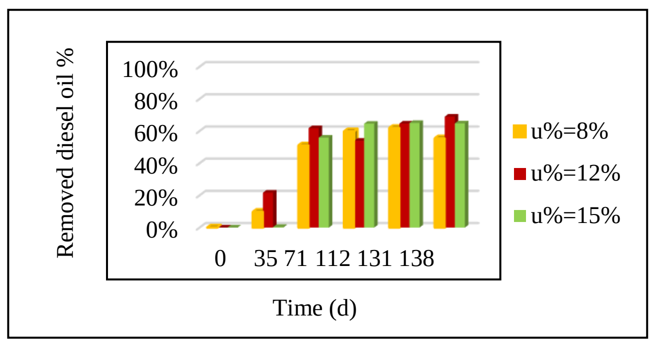

Figure 2. Percentage of diesel oil removed by the microcosm with C/N = 180

The amount of degradation is strongly influenced by water content and the C/N ratio, and in the first 35 days the microcosms show more evident differences. In particular, the microcosm with C/N = 120 and u% = 8% b.w. gives better efficiency than the other microcosms, with removal equal to 70% since the 70th day. After this time, the microcosm does not show removal improvement.

The experimental results show that as a whole the process is efficient and permits the diesel oil reduction of 70% for microcosms with C/N = 120 and of 65% for microcosms with C/N = 180 after 131 days.

The effect of water content is evident in the first days, whereas in the last run period the percentage of removed diesel oil is similar in all microcosms with the same C/N ratio.

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B. *Kinetic modelling*

The data of residual diesel oil concentration were used to model the process kinetics.

Figs. 3 and 4 show the data fitting with first order model, while in Figs. 5 and 6 the data are fitted with the second order model.

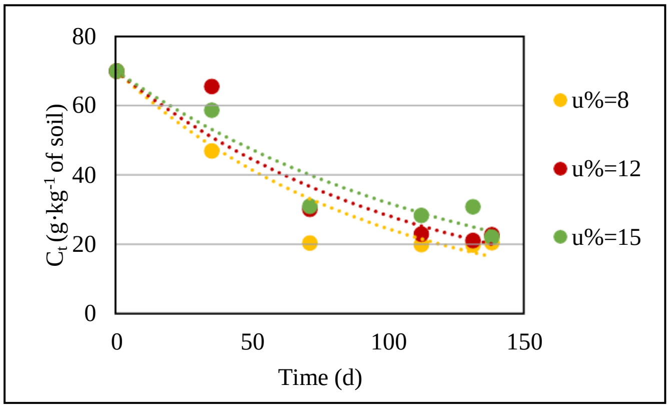


Figure 3. First order rate model for microcosms with C/N= 120

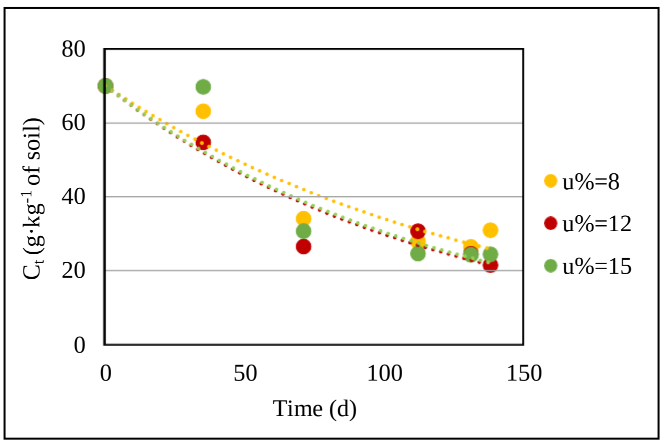
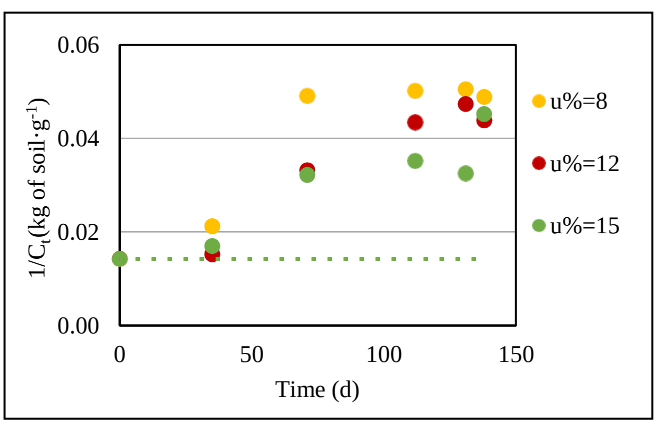


Figure 4. First order reaction rate model for microcosms with C/N=180

Considering the equations (3) ÷ (7), it is possible to calculate the reaction rate constant and the half-life time for all the tested microcosms.



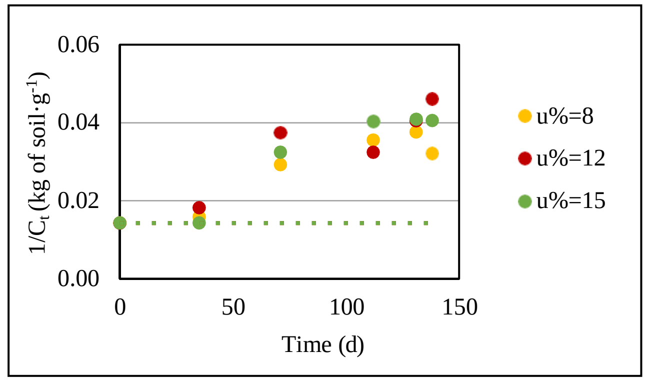


Figure 5. Second order reaction rate model for microcosms with C/N=120

Figure 6. Second order reaction rate model for microcosms with C/N=180

For microcosms with C/N = 120, the reaction rate constants of the first order model are in the range 0.0113-0.008 d^{-1}, respectively for water content 8%, 12% and 15%. Their calculated half-life time is equal to 61, 77 and 87, respectively, in according to percentage of removed diesel oil.

Table 1 shows the reaction rate constant for the studied microcosms.

In the same way, for microcosms with C/N = 180 the reaction rate constants are in the range 0.0072-0.0085 d^{-1}, and half-life times are 96, 82, 84 days, respectively for water content 8%, 12% and 15%.

TABLE I. REACTION RATE CONSTANT, K, FOR THE TESTED MICROCOSMS

C/N	*u% (b.w.)*	*First order model k (d^{-1})*	*R^2*	*Second order model k (kg of soil·g^{-1}·d^{-1})*	*R^2*
120	8	0.0113	0.800	0.0003	0.814
	12	0.0090	0.914	0.0002	0.928
	15	0.0080	0.878	0.0002	0.850
180	8	0.0072	0.878	0.0002	0.874
	12	0.0085	0.862	0.0002	0.854
	15	0.0083	0.881	0.0002	0.907

The half-life time is reported in Table 2 for each microcosm.

TABLE II. HALF-LIFE TIME , $T_{1/2}$, IN THE TESTED MICROCOSMS

C/N	*U% b.w.*	*First order model $t_{1/2}$ (days)*	*Second order model $t_{1/2}$ (days)*
120	8	61	48
	12	77	71
	15	87	71
180	8	96	71
	12	82	71
	15	84	71

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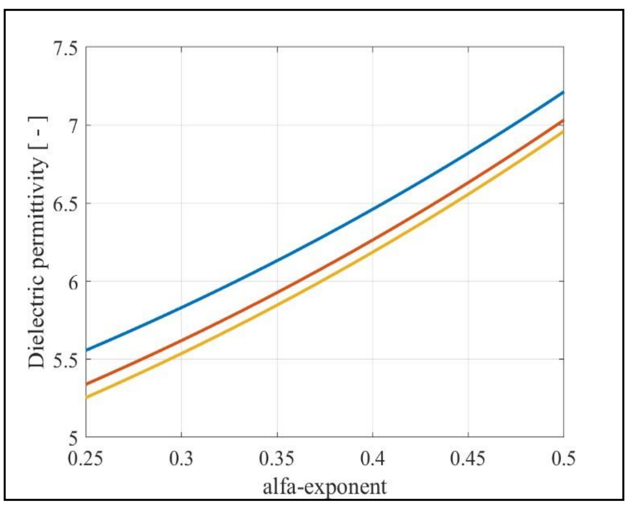
Comparing the half-life times, it is possible to affirm that in general the microcosms with C/N = 180 have longer times than microcosms with C/N = 120.

Like the first order model, the second order one describes rather well the experimental data, as demonstrated by R^2 values, that are not much different in the two studied cases.

C. *Geophysical issues*

We computed the theoretical value of the dielectric permittivity by adopting the equation (8). The following values of the physical properties of the materials were assumed: average porosity = 0.4; soil density = 2700 $kg \cdot m^{-3}$; diesel oil density = 800 $kg \cdot m^{-3}$; water content: 0.13 $m^3\ m^{-3}$; initial diesel oil concentration = 70 $g \cdot kg^{-1}$ of soil, equivalent to diesel oil volume of 0.14 $m^3 \cdot m^{-3}$ of the total volume (the mixture oil–water–soil–air); relative electrical permittivity of water = 78.

The response of the model of the dielectric permittivity is computed for different values of diesel oil within the pore volume: 0.14 m^3 which corresponds to a concentration of 70 $g \cdot kg^{-1}$ of soil at the beginning of the experiment, 0.07 $m^3 \cdot m^{-3}$ and 0.042 $m^3 \cdot m^{-3}$ which is the corresponding volume of diesel oil at the end the experiment, when about 70 % of the diesel oil was degraded. The plot of Fig. 7 shows the computed response of the permittivity versus the values of the exponent (α) of the equation (8). The computed response shows that the degradation of the diesel oil slightly affects the geophysical response. A degradation of about 70% of diesel oil only provides for a decrease of the theoretical response of the



dielectric permittivity of about 10-15%.

Figure 7. Theoretical response of the dielectric permittivity versus the values of α-exponent of equation (8): the blue curve refers to a volume of diesel oil of 0.14 $m^3 \cdot m^{-3}$, the red curve is the trend for a volume of diesel oil equal to 0.07 $m^3 \cdot m^{-3}$, the orange one is the result for a diesel oil volume of 0.042 $m^3 \cdot m^{-3}$.

IV. Conclusions

This study allowed to evaluate the aerobic biodegradation in microcosms with different carbon to nitrogen ratio and water content.

The results show that in the microcosms with C/N = 120 the diesel oil removal is always higher than in the ones with C/N = 180. Moreover, the water content influences the biodegradation process in the first period, but at the end of the experimental runs the percentage of removed diesel oil is similar in the tests with identical C/N ratio.

As far the kinetic modelling concerns, both the adopted orders of reaction fit well the data, even if the process complexity is not adequately considered, especially for the co-metabolites generation. Finally, the theoretical computation of the expected geophysical response pointed out that the dielectric permittivity of the sandy soil with a certain degree of water content is only slightly affected by the degradation process.

Acknowledgment

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