Phenol Transport and Biodegradation Model in an Unsaturated Porous Media from Wastewater Discharge

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***Abstract:** To minimize groundwater pollution and suggest appropriate remedial actions, sound numerical models must be developed to predict the fate, transport and biodegradation of pollutants in partially treated or untreated industrial wastewater. Phenol is an aromatic organic compound produced on a large scale and is also released as major organic pollutant from several industrial wastewater (pharmaceutical, petroleum, coal refineries etc.,). Biodegradation of phenol in soil is generally rapid especially in presence of nutrients and acclimated microbes which are discharged along with the partially treated wastewater. A numerical model has been developed to predict the fate of phenol from industrial wastewater discharged on to a porous unsaturated soil media. The transport processes of advection, dispersion, and biodegradation process using Haldane growth and inhibition have been incorporated in the numerical model. The results suggest that acclimated microbes in the wastewater has a potential to degrade phenol up to 1500 mg/L at a bacterial concentration of 0.1 mg/L and soil depth of 50 cm. The results also show that phenols desorb at a depth of 100cm from 12th day and are simultaneously acted upon by the increased microbial concentration. In essence, high microbial concentration significantly decreases the phenol movement in the unsaturated zone, particularly at a larger depth and at higher time levels which eventually affects the groundwater quality.*

***Keywords:** Phenol, Transport model, Biodegradation model, Wastewater discharge, Haldane Kinetics.*

I. INTRODUCTION

Continuous or intermittent release of partially treated or untreated wastewater from several industries could lead to accumulation of several organic and toxic compounds in soils, which eventually will leach through soil to accumulate in groundwater. Presence of significant concentrations of phenol in groundwater mainly near or at hazardous waste sites have been reported (ATSDR, 2008). United States Environmental Protection Agency (USEPA) has enlisted phenols and their derivatives as priority pollutants and therefore the treatment and safe disposal of these pollutants are of primary concern due to their toxic and long term effects on humans and animals (Meena et al., 2015). Partially treated or untreated phenolic wastewater when discharged into soil or subsoil surface culminates in accumulation of these compounds which may affect the groundwater quality. Due to volatility few of the phenolic compounds are also released into the atmosphere through industrial and vehicular activities and eventually reach water bodies. Phenolic compounds have been proven to cause various diseases and inebrieties in both animals and humans either through skin absorption or intake from contaminated groundwater (Meena et al., 2015). In spite of several advanced phenol removal techniques (such as membrane-based separation method, electro-Fenton method, biodegradation, photo catalysis and so on), industrial wastewater treatment in many developing countries does not follow regulatory standards and wastewater are discharged untreated or in many cases partially treated (Kahru et al, 2002). Water resources can be restored by careful application of domestic or industrial wastewater for irrigation; this prevents contamination of surface water sources and mitigates water scarcity. In the past two decades, wastewater has been applied for irrigation of several crops and has become a common practice in several developing countries, adversely the applied wastewater if consists of toxic compounds could affect the groundwater quality and cause several food and water borne diseases, especially if the wastewater is not treated to standards, it contains, organic pollutants, inorganic chemicals and acclimated microbes from the secondary treatment units (Haruvy, 2006). Comparatively, modeling studies which includes the biodegradation process of phenolic pollutants along with its transport in an unsaturated porous media are few, here an attempt is made to develop a numerical model based on Haldane's inhibition kinetics and Richard's transport equation to predict the fate and transport of phenol when discharged on a soil media from a partially treated industrial wastewater discharge.

II. MODEL DESCRIPTION

In this study, a one-dimensional model is proposed which incorporates for the following phenomena: water flow, phenol and cresol transport along with the biodegradation.

A. Water flow modeling

Richard's equation is commonly used for one-dimensional downward movement of water in the unsaturated zone of soil with water uptake by plant roots (Antonopoulos, 2006):

$$C(h)\frac{\partial h}{\partial t} = \frac{\partial}{\partial z}K\left(\frac{\partial h}{\partial z}\right) - \frac{\partial K}{\partial z} + S_w \quad (1)$$

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Where: $C(h) = \frac{\partial\theta}{\partial h}$ is specific moisture capacity (1/L); h is the pressure head (L); K is the hydraulic conductivity of unsaturated soil (L/T); S_w is the water abstraction by plant ($L^3 L^{-3}T^{-1}$); t is the time (T); z is the downward depth (L).

In the present study, the hydraulic conductivity and the hydraulic soil functions of water retention are used as follows:

$$S_e = \frac{\theta_w - \theta_r}{\theta_s - \theta_r} \quad (2)$$

$$\theta_w = \theta_r + \frac{\theta_s - \theta_r}{(1+|\alpha h|^{\beta})^{\eta}} \quad (3)$$

$$K(h) = K_s S_e^{1/2}\left[1 - \left(1 - S_e^{1/\eta}\right)^{\eta}\right]^2 \quad (4)$$

where: θ_w is the water content (L^3/L^3); θ_s is the saturated water content; θ_r is the residual water content; K_s is the saturated hydraulic conductivity(L/T); S_e is the effective saturation; α, β and η are fitting parameters.

B. Phenol transport and biodegradation

The one-dimensional transport of phenol in under saturated soil conditions are described by the equation 5:

$$R\frac{\partial\theta C}{\partial t} = \frac{\partial}{\partial z}\left(\theta D\frac{\partial C}{\partial z}\right) - \frac{\partial qC}{\partial z} - \Phi_1 \quad (5)$$

where C is the concentration of phenol/cresol; $D=D_0*\tau+q*\lambda_L$, D_0 is the molecular diffusion coefficient; q is the Darcy velocity; λ_L is the longitudinal dispersivity; τ is the tortuasity; ρ is the bulk density; D is the dispersion coefficient; Φ_1 is the biodegradation rate of phenol/cresol per unit soil volume; R is the retardation factor for phenol/cresol based on the linear partitioning coefficient ($R = 1 + \frac{\rho_b K_d}{\theta_w}$); ρ_b is the bulk density of soil; K_d is the linear partitioning coefficient.

The biodegradation term Φ_1 describe the kinetic behavior of phenol/cresol which is described by Haldane model shown in equations 6 and 7.

$$\Phi_1 = \frac{dC}{dt} = \frac{M}{Y_T}\frac{\mu_{max}C}{K_c + C + \frac{C^2}{K_i}} \quad (6)$$

$$\frac{dM}{dt} = M\frac{\mu_{max}C}{K_c + C + \frac{C^2}{K_i}} \quad (7)$$

where M is the bacterial concentration, μ_{max} is the maximum specific growth rate, Y_T is the yield coefficient, K_c is the half saturation constant, K_i is the inhibition constant.

The water flow equation (1) and phenol transport equations (5) and (6) pertains the following initial and boundary conditions:

$$h\ (z,\ t = 0) = h_i,\ C\ (z,\ t = 0) = C_i \quad (8)$$

$$h\ (z = 0,\ t) = h_1 \text{ and } h\ (z = L,\ t) = h_2 \quad (9)$$

$$C\ (z = 0,\ t) = C_1 \text{ and } \partial C/\partial z\ (z = L,\ t) = 0 \quad (10)$$

where h_1 and C_1 are the surface boundary condition of the pressure head and phenol/cresol concentrations, respectively, h_i and C_i are the initial distribution of the pressure head and phenol/cresol concentrations, respectively. h_2 is the pressure head at the bottom of the domain, L is the total depth of unsaturated zone.

III. NUMERICAL SOLUTION

The partial differential equations (1), (5), (6) and (7) pertaining water movement and contaminant migration model, with their initial and boundary conditions Eqs. (8) – (10), are solved by the finite difference scheme. The prevalent technique to solve Eq. (1) has been the implicit finite difference scheme with explicit linearization of K(h) and C(h) (van Dam and Feddes, 2000). The phenol/cresol model represented by Eqs. (5) - (7) are solved by fully implicit finite difference method. Thomas algorithm is employed to resolve the subsequent tri-diagonal system of linear algebraic equations. The pressure head values in the unsaturated soil profile are obtained by unsaturated flow model. The acquired values of pressure head $h(z,t)$ are used to find $q(z,t)$, $\theta(z,t)$, and $D(z,t)$ which available in the transport equation of phenol. Later, the phenol migration model is solved for assumed initial and boundary condition. The base values of the parameters used in the study for transport process is given in Table.1 while the biodegradation kinetics for phenol metabolism for a mixed microbial consortia is given in Table 2 (Sharma et al., 2012).

IV. RESULTS AND DISCUSSION

Phenol transport and biodegradation in under saturated porous media has been predicted successfully by the developed numerical model. The numerical result of present water flow model in vadoze zone is endorsed with the existing reported analytical/numerical results. From Fig. 1, it is observed that the current model outcomes are in good agreement match with the available results (Mitchell and Mayer, 1998). The effect of microbial concentration on phenol removal is revealed in Fig. 2.

It is noted that with 0.1 mg/L of initial microbial concentration, phenol is completed removed at a soil depth of 40 cm from initial phenol concentration of 1500 mg/L. However, with 0.001mg/L of initial microbial concentration, complete removal is observed at 160 cm of soil depth. The phenol biodegradation kinetics for the acclimated culture here has relatively better growth rate and half saturation constant as is was already acclimated with phenolic compounds.

Table 1. Base values of parameters used in this study

Parameter	Symbol	Value	Reference
Depth of unsaturated zone	--	500 cm	Assumed
Simulation time	--	5 hours	Assumed
Van Genuchten parameter	α	0.0335 (cm^{-1})	Mitchell & Mayer (1998)

Van Genuchten parameter	β	2.0	Mitchell & Mayer (1998)
Van Genuchten parameter	η	0.5	Mitchell & Mayer (1998)
Saturated water content	θ_s	0.381 (cm^3/cm^3)	Mitchell & Mayer (1998)
Residual water content	θ_r	0.102 (cm^3/cm^3)	Mitchell & Mayer (1998)
Saturated hydraulic conductivity	K_s	0.00922 cm/s	Mitchell & Mayer (1998)
Soil bulk density	ρ_b	1.56×10^6 mg/l	Lee et al., (2006)
Molecular diffusion coefficient	D_0	0.12 cm^2/h	Kaluarachchi & Parker (1988)
Tortuasity	τ	1	Assumed
Longitudinal dispersivity	λ_L	0.5 cm	Lee et al., (2006)
Distribution coefficient	k_d	3×10^{-8} to 8×10^{-8} l/mg	Viotti et al., (2005)

Table 2: Bio-kinetic constants for Haldane model (Sharma et al., 2012)

Parameter	Symbol	Phenol
Maximum growth rate (1/h)	μ_{max}	0.13
Half saturation constant (mg/L)	K_c	29.1
Yield coefficient (mg/mg)	Y_T	0.31
Inhibition concentration (mg/L)	K_i	432.2

As the microbial concentration increases so does the biodegradation of phenol, this effect could be observed as both the 0.01 and 0.001 mg/L of initial microbial concentration reaches undetectable levels of phenol at the depth of 160 cm. Fig 3 shows the vertical transport of phenol at different time interval along with the adsorption and biodegradation process. The results show that the concentration becomes undetectable at the depth of 100 cm and 180 cm after 5th and 10th day respectively. On the other hand, the concentration become nearly zero at the depth of approximately 80 cm and again increase to 350 mg/l at the depth of nearly 140 cm and reaches zero at the depth of 200 cm at 12th day. This initial decrease is due to the high consumption of phenol by the bacteria in the shallow depths and the same has been shown in Fig 4. However, the increase in concentration observed between the depths of 80 cm to 200 cm is due to the advection and dispersion phenomena. Hence, it can be concluded that the physical processes such as advection and dispersion may be predominant in the initial time and later the biodegradation become more predominate. Similarly, the 13th day concentration profile is also follows the previous day trend with more reduction. This is due to the further concentration increase in bacteria in the shallow depths (Fig 4). The adsorption and desorption potential of phenol is reflected in Fig. 3.

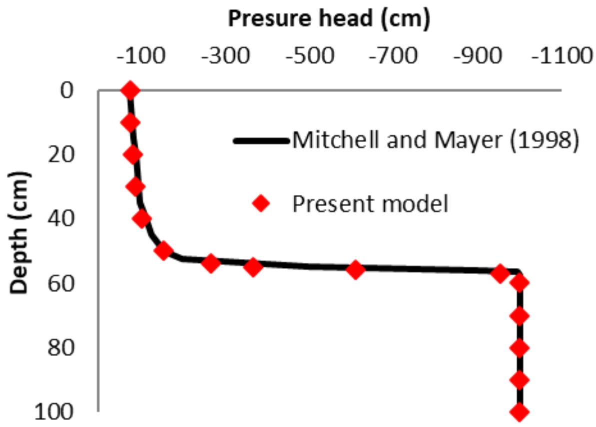

Fig 1: Validation of the present model for flow in unsaturated soil after 1 day

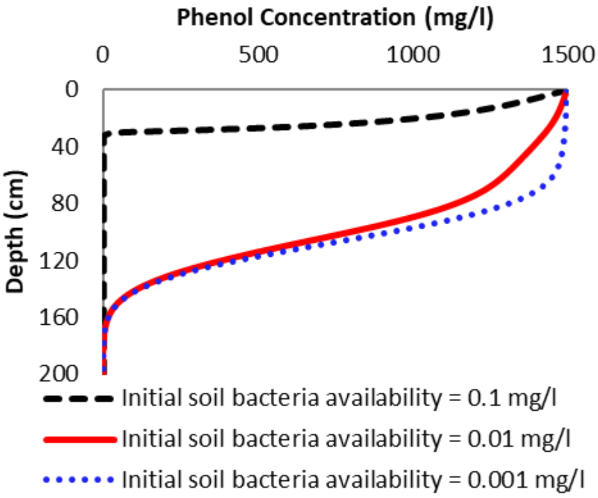

Fig.2: Concentration profile for phenol in the presence during the variation in initial soil bacteria concentration (refer to Tables 1 and 2 for other data)

Up to 10th day, phenol is completely utilized by the microbes and no adsorption of the pollutants to soil media is observed. At a depth of 200 cm and 10 days of phenol wastewater discharge (1500 mg/L), biodegradation is the primary process for phenol removal. However, after 12 d of phenol application to the soil, much of the phenol adsorbs to the soil media along noticeable biodegradation removal. However, at the depth of 100 cm, phenol is dispersed from the soil surface and is available for bacterial degradation, which quickly occurs and A similar pattern could be observed on 13th day where there is desorption of phenol molecules and gradual biodegradation, till reaches a depth of 200 cm. With continuous phenol discharge at initial concentration of 1500 mg/L, both adsorption and biodegradation process significantly remove phenol in the soil media. A considerable increase in microbial concentration could be seen at 10, 12 and 13 days upto 800 mg/L from initial microbial concentration of 0.01 mg/L (Fig. 4). Since the microbes have already been acclimated to phenolic compounds, the mixed consortia dominated by *Pseudomonas* and *Bacillus sp*, could easily metabolize phenol as primary carbon source and therefore increased biomass concentration.

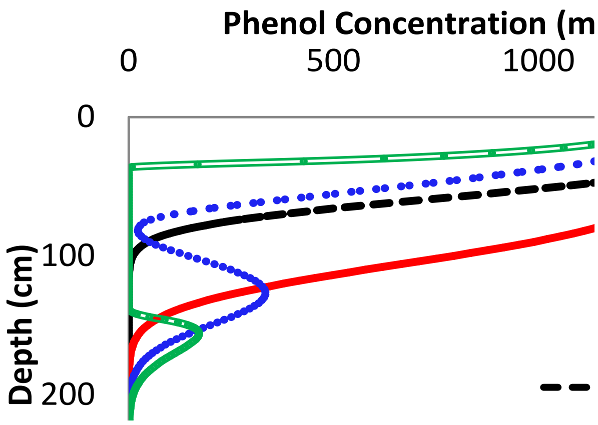

Fig.3: Concentration profile for phenol at different time with the initial soil bacterial concentration of 0.01 mg/l (refer to Tables 1 and 2 for other data)

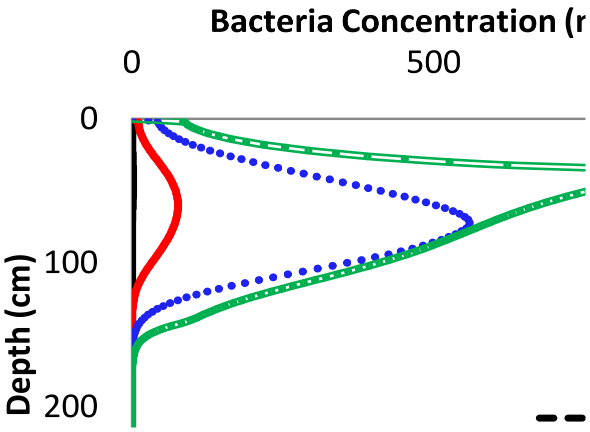

Fig.4: Concentration profile for bacteria at different time with the initial soil bacterial concentration of 0.01 mg/l (refer to Tables 1 and 2 for other data)

VI. CONCLUSION

In this study, a numerical model is developed which describes the transport, adsorption and transformation of phenol in presence of acclimated biomass using Haldane inhibition model. With continuous phenol discharge (initial concentration 1500 mg/L) from partially treated wastewater containing acclimated microbes (0.1 mg/L initial biomass concentration), it could be seen that with phenols are undetected at a depth of 40cm. Also, advection and dispersion of phenol on soil media was noticed with very heavy phenol discharge by 12 and 13th day of application. However, due to increased biomass, the desorbed phenol could be utilized by the microbes by the depth of 200 cm.

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