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MATHEMATICAL MODEL AND PARAMETER ANALYSIS OF PHENOL DEGRADATION IN BIOFILTER

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Abstract: A mathematical model consisting of mass balance equation and accounting for reaction, mass transfer is presented to describe steady state phenol degradation along the length of a packed bed reactor. For solving the model developed along with boundry conditions software BIOPHEN in the language ForTran 77 was developed and subsequently solved using Backward Implicit Scheme. The reactor is packed with a mixture of compost, perlite, sawdust and an activated sludge from paddy soil is taken for modelling purpose. Sensitivity analysis was carried altogether out of seven parameters namely specific surface area ,rate constant, biofilm thickness, porosity, effective diffusivity, gas flow rate and initial concentration.
Key Words: Biofilter, mathematical modelling, Simulation.

1. INTRODUCTION

Phenol (C_6H_6O) is a white, crystalline solid at room temperature. Phenol is classified by OSHA as a "hazardous chemical." It is corrosive and combustible. Phenol produces dense smoke when burned. Vapors are heavier than air and may accumulate in low-lying areas. Phenol is present naturally in the environment and is also manufactured. Phenol is present in plant and animal organic wastes as a result of decomposition. Phenol is an important industrial chemical and enters the environment in air emissions and wastewater connected with its use as a chemical intermediate, disinfectant and antiseptic.

Skin contact with phenol or swallowing products containing phenol may lead to increased exposure. This type of exposure is expected to occur infrequently and generally occurs over a short time period. At the workplace, exposure to phenol can occur from breathing contaminated air. However, skin contact with phenol during its manufacture and use is considered the major route of exposure in the workplace. (J.Michalowicz.et.al.2007)

Biofiltration is a new and effective technology .instead of transferring contaminant from one medium to another, or using large amount of energy to destroy or remove pollutants, utilizes the efficiency of microorganism to degrade the pollutant. (S.Zarook,1997)

To predict the concentration degradation of pollutant gas in biofilter, a model is required which can widely be used for regulatory and planning purposes. Furthermore the monitoring of odorous and toxic gas is costly, time consuming and risky for health. Reliable model is needed to safeguard the public interest by contributing towards the monitoring & clean up of odour & toxic gases in biofilter. The factor like porosity, moisture content, sp.surface area,effective diffusivity of gas in biofilm & decay constant affecting the degradation of polluted gas in biofilter . The model can therefore also be used as a design tool and also to predict the effect of varying operating conditions.

This study involves the development of a new technology that has the potential to help improve the air quality of the environment. Biofiltration has the potential to treat phenol and other hydrocarbon causing compounds in a cost effective, reliable, utilizing natural and waste material that are available on site. This work is relevant not only from an academic perspective but also from an industrial standpoint because it will advance engineering design and operation principles, which is key for commercial applications.

2. MATHEMATICAL MODEL

The degradation of phenol in the biofiltration is described through a simple model based on mass balance equations The biofilter is modeled as a packed bed bio reactor of packing material which supports the growth of micro-organisms as biofilms. When air flows in the bed, oxygen and phenol are continuously transferred from the gas phase to the biofilm, where they diffuse and are consumed by aerobic microbial activity.

A general transient biofiltration model should incorporate dispersion, diffusion, reaction and adsorption phenomena. At steady-state conditions, the adsorption process is in equilibrium and thus, it does not come into play. However, under transient conditions, adsorption process needs to be explicitly accounted for in the model development. Fig 1 illustrates a diagram of a single particle in the biofilter, covered with a uniform layer of biofilm in which the simultaneous degradation of phenol take place.

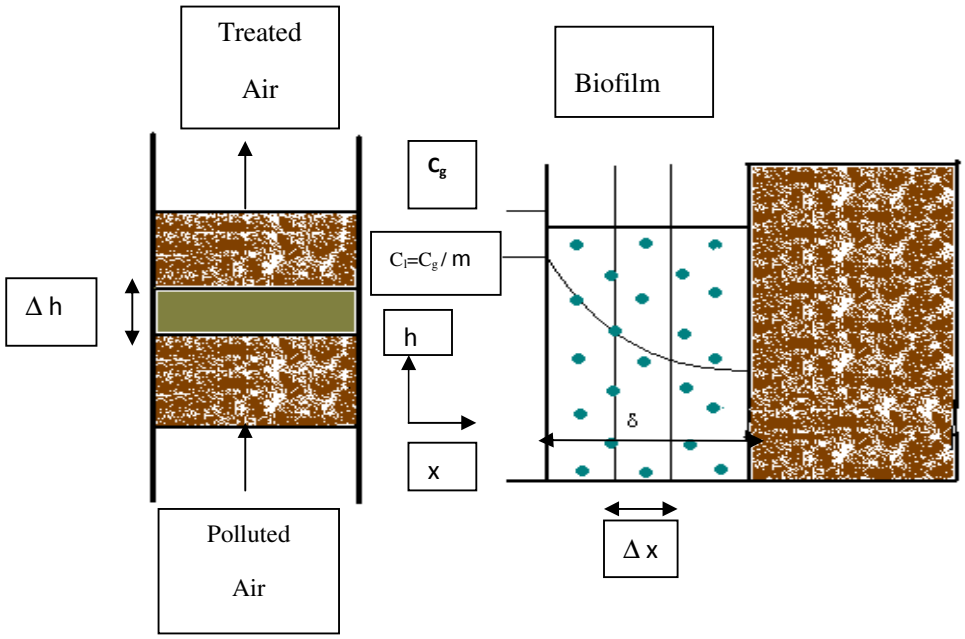


Fig-1 Schematic Representation of the Model; h is the distance of the biofilter, x is the distance into the biofilm , δ is the biofilm thickness.

The theoretical model describing the elimination of phenol in the biofilter bed is based on the following assumptions.

(1) The biofilter is a porous and homogeneous body and biofilter assumed to behave as a bioreactor.

(2) The biofilm is formed on the exterior surface of the particles. Biomass does not grow in the pores of the particles, and thus no reaction occurs in the pores. Sizes of these pores are too small for microbial growth (Deshusses et al., 1995a).

(3) The biofilm is not necessarily formed uniformly around particles.

(4) Adsorption of the pollutant on the solid particles occurs only through the direct bare solid/air interface.

(5) Oxygen is not adsorbed on the solid particles since concentration gradient of oxygen between the gas phase and the solid is almost negligible.

(6) The thickness of the biofilm is small relative to the main curvature of the solid particles, and thus planar geometry can be used.

(7) The extent of the biofilm patch is much larger than its depth. Hence, the phenol and oxygen transported into the biofilm through the side surfaces of the biofilm patch can be neglected, and diffusion and reaction in the biofilm can be considered in a single direction only.

(8) The phenol and oxygen at the biofilm and air interface are always in equilibrium as dictated by Henry's law.

(9) The phenol and/or oxygen are depleted in a fraction of the actual biofilm. This fraction is called the effective biolayer or active biofilm thickness (Zarook et al., 1993).

(10) Diffusivities of the phenol is equal to the diffusivities of the same compounds in water, corrected by a factor depending on the biofilm density. (Fan et *al* . 1990).

(11) The biofilm density, defined as the amount of dry biomass per unit volume of biofilm, is constant.

(12) There is no accumulation of biomass in the filter bed and thus, the specific biofilm surface area is constant.

(13) The biodegradation rate depends on the concentration of the biofilm and oxygen.

(14) Direction of flow of phenol in vertical upward.

(15) Reaction in the bed is first order irreversible type.

(16) No axial dispersion

These assumptions result in the following set of equations.

A mass balance of C_6H_6O in the bulk gas phase

$$\varepsilon\frac{\partial C_{C_6H_6O}}{\partial t}+Vg\frac{\partial C_{C_6H_6O}}{\partial h}=A_S D_e\left(\frac{\partial C_l}{\partial x}\right)_{x=0} \tag{1}$$

A mass balance of C_6H_6O in the biofilm

$$\frac{\partial C_l}{\partial t}=D_e\left(\frac{\partial^2 C_l}{\partial x^2}\right)-(-r_{C_6H_6O}) \tag{2}$$

Microkinetics

Micro kinetics is characterized by first order rate of reaction. Thus the reaction rate for C_6H_6O is given by

$$(-r_{C_6H_6O})=k_1 C_l \tag{3}$$

Where, $(-r_{C_6H_6O})$ is degradation rate of C_6H_6O, gm m^{-3} h^{-1}

k is rate constant , h^{-1},C_l is concentration in the biofilm (g/m^3), equation (2) becomes

$$\frac{\partial C_l}{\partial t} = D_e\left(\frac{\partial^2 C_l}{\partial x^2}\right) - k_1 C_l \tag{4}$$

Assuming dynamic equilibrium between the gas phase and the surface of the biofilm, a pseudo-steady state assumption is made for the biofilm and accumulation term is set to 0. in Equation (4)

$$D_e\left(\frac{\partial^2 C_l}{\partial x^2}\right) - k_1 C_l \tag{5}$$

Boundry conditions

For t > 0 , x = 0 , $C_l = \frac{C_{C_6H_6O}}{H_c}$

B.C. 2

At t > 0 , x = δ , $\frac{dC_l}{dx} = 0$

Where H_c is Henry's constant

Solution can be obtained as equation (5)

$$\left(\frac{\partial C_l}{\partial x}\right)_{x=0} = -m\frac{C_{C_6H_6O}}{H_c}\tanh(m\delta) \tag{6}$$

Where $m = \sqrt{\frac{k_1}{D_e}}$

Put equation (6) in equation (1) ,the final equation is

$$\varepsilon\frac{\partial C_{C_6H_6O}}{\partial t} + Vg\frac{\partial C_{C_6H_6O}}{\partial h} = -\varphi \bullet C_{C_6H_6O} \tag{7}$$

Where, $\varphi = \frac{A_S D_e m}{H_c}\tanh(m\delta)$

Initial and Boundary Conditions

IC

At t = 0 , h= 0 , $C_{C_6H_6O} = C_0$

For t = 0 , 0 < h ≤ H , $C_{C_6H_6O} = 0$ (8)

BC

At $t > 0$, $h = H$, $\frac{\partial C_{C_6H_6O}}{\partial h} = 0$

3. DESCRETIZATION

For the Descretization the differential terms are first descretized using Taylor series expansion .The descretized terms are

$$\frac{\partial C_{C_6H_6O}}{\partial x} = \frac{C_{i+1,j} - C_{i-1,j}}{2h} \tag{9}$$

$$\frac{\partial C_{C_6H_6O}}{\partial t} = \frac{C_{i,j} - C_{i,j-1}}{k} \tag{10}$$

Putting (9),&(10)in the model equation (7) & we get ,

$$\varepsilon \frac{C_{i+1,j} - C_{i-1,j}}{2h} + Vg \frac{C_{i,j} - C_{i,j-1}}{k} = -\varphi \bullet C_{i,j} \tag{11}$$

Where h and k are the step sizes in height and time of biofilter Final Descretized Descretized equation is given below.

$$C_{i+1,j}\left[\frac{Vg}{2h}\right] + C_{i,j}\left[\frac{\varepsilon}{k} + \varphi\right] + C_{i-1,j}\left[-\frac{V_g}{2h}\right] + C_{i,j-1}\left[-\frac{\varepsilon}{k}\right] = 0 \tag{12}$$

Concentration at the bottom i.e. i=1,j=1 at initial time t=0 is known .It is desired that the concentration of C_6H_6O inside the biofilter is to be calculated. Therefore the concentration of C_6H_6O inside the biofilter is calculated by transforming equation (12) at grid points where concentration is unknown .The intial and boundry conditions are also incorporated where it is required

$$C_{i+1,j}\left[\frac{Vg}{2h}\right] + C_{i,j}\left[\frac{\varepsilon}{k} + \varphi\right] = C_{i-1,j}\left[\frac{V_g}{2h}\right] + C_{i,j-1}\left[\frac{\varepsilon}{k}\right] \tag{13}$$

$C_{i-1,j}$ and $C_{i,j-1}$ are known concentration therefore they are brought to right hand side (RHS) .For i =1 and i = 2, M-1 equation (13) holds good.

For i=2 and i=M,equation (13) along with the boundry condition i.e.model equation is used. The proposed model equation (12) is nonlinear partial differential equation. Finite

difference Backward Implicit scheme. Fig (2) is used for computing the concentration at various heights with variation of time.

For j=2 and i=2

$$C_{3,2}\left[\frac{Vg}{2h}\right]+C_{2,2}\left[\frac{\varepsilon}{k}+\varphi\right]=C_{1,2}\left[\frac{V_g}{2h}\right]+C_{2,1}\left[\frac{\varepsilon}{k}\right]$$

Or

$$C_{2,2}\left[\frac{\varepsilon}{k}+\varphi\right]+C_{3,2}\left[\frac{Vg}{2h}\right]=C_{1,2}\left[\frac{V_g}{2h}\right]+C_{2,1}\left[\frac{\varepsilon}{k}\right]$$

For i=3 and j=2

$$C_{2,2}\left[-\frac{Vg}{2h}\right]+C_{3,2}\left[\frac{\varepsilon}{k}+\varphi\right]+C_{4,2}\left[\frac{V_g}{2h}\right]=C_{3,1}\left[\frac{\varepsilon}{k}\right]$$

For i=4 and j=2

$$C_{3,2}\left[-\frac{Vg}{2h}\right]+C_{4,2}\left[\frac{\varepsilon}{k}+\varphi\right]+C_{5,2}\left[\frac{V_g}{2h}\right]=C_{4,1}\left[\frac{\varepsilon}{k}\right]$$

Similarly, For i = m-1 and j = 2

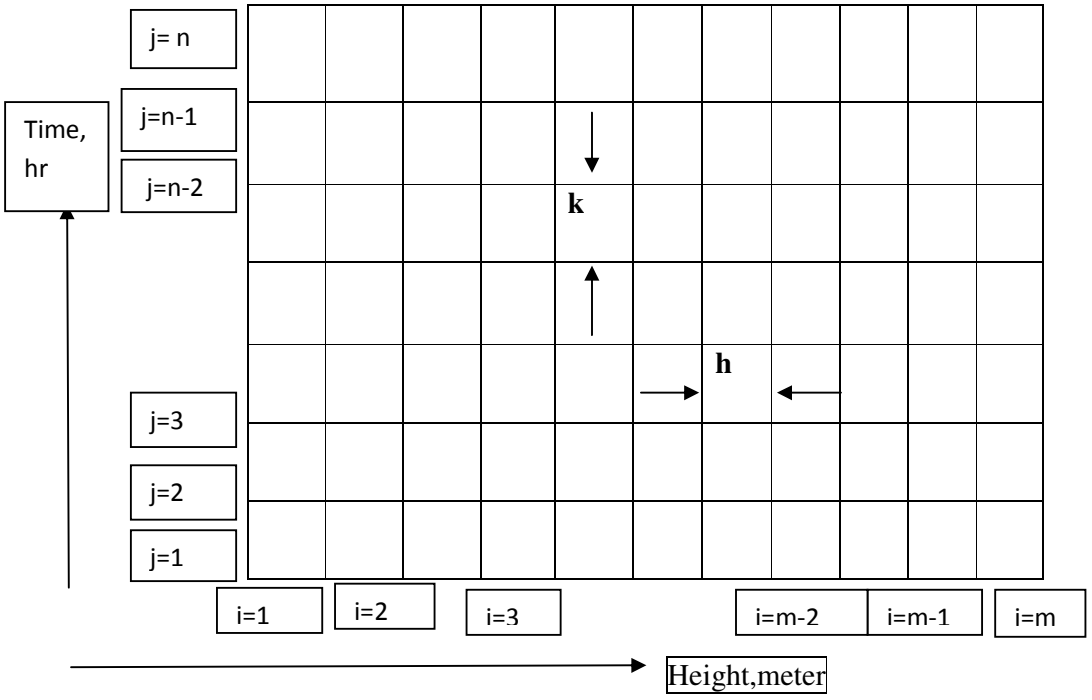


Fig 2 : Grid for the flow of phenol into Bio reactor bed

$$C_{m-2,2}\left[-\frac{Vg}{2h}\right]+C_{m-1,2}\left[\frac{\varepsilon}{k}+\varphi\right]+C_{m,2}\left[\frac{V_g}{2h}\right]=C_{m-1,1}\left[\frac{\varepsilon}{k}\right]$$

For i=M and j=2 (from boundry condition)

$$C_{m+1,2}-C_{m-1,2}=0 \tag{14}$$

The model equation along with the boundry conditions, results in a tridiagonal banded matrix i=1 (bottom of biofilter),i=2 to m-1 and i=m (top of biofilter).

$$\begin{bmatrix}
\frac{\varepsilon}{k}+\varphi & \frac{V_g}{2h} & 0 & 0 & 0 & 0 & - & - & 0 & 0 \\
\frac{Vg}{2h} & \frac{\varepsilon}{k}+\varphi & \frac{V_g}{2h} & 0 & 0 & - & - & - & - & 0 \\
0 & \frac{Vg}{2h} & \frac{\varepsilon}{k}+\varphi & \frac{V_g}{2h} & 0 & - & - & - & - & 0 \\
0 & 0 & \frac{Vg}{2h} & \frac{\varepsilon}{k}+\varphi & \frac{V_g}{2h} & 0 & - & - & - & 0 \\
- & - & - & - & - & - & - & - & - & - \\
- & - & - & - & - & - & - & - & - & - \\
- & - & - & - & - & - & - & - & - & - \\
- & - & - & - & - & - & - & - & - & - \\
0 & - & - & 0 & 0 & \frac{Vg}{2h} & \frac{\varepsilon}{k}+\varphi & \frac{V_g}{2h} & 0 & 0 \\
0 & 0 & - & - & 0 & 0 & \frac{Vg}{2h} & \frac{\varepsilon}{k}+\varphi & \frac{V_g}{2h} & 0 \\
0 & 0 & 0 & - & - & 0 & 0 & \frac{Vg}{2h} & \frac{\varepsilon}{k}+\varphi & \frac{V_g}{2h} \\
0 & 0 & 0 & 0 & - & - & - & 0 & -1 & 1
\end{bmatrix}
\times
\begin{bmatrix}
C_{2,2} \\ C_{3,2} \\ C_{4,2} \\ C_{5,2} \\ - \\ - \\ - \\ - \\ C_{m-3,2} \\ C_{m-2,2} \\ C_{m-1,2} \\ C_{m,2}
\end{bmatrix}
=
\begin{bmatrix}
C_{1,2}\left[\frac{V_g}{2h}\right]+C_{2,1}\left[\frac{\varepsilon}{k}\right] \\
C_{3,1}\left[\frac{\varepsilon}{k}\right] \\
C_{4,1}\left[\frac{\varepsilon}{k}\right] \\
C_{5,1}\left[\frac{\varepsilon}{k}\right] \\
- \\ - \\ - \\ - \\
C_{m-3,1}\left[\frac{\varepsilon}{k}\right] \\
C_{m-2,1}\left[\frac{\varepsilon}{k}\right] \\
C_{m-1,1}\left[\frac{\varepsilon}{k}\right] \\
C_{m,1}
\end{bmatrix}$$

The above tridiagonal matrix is utilized for computation of the unknown concentration from i=2 to i=m at the unknown level i=2 from the known concentration at level i=1.Once the concentration at i=2 is computed,it is possible to compute the concentration at i=3 and the process could be continued iteratively further,depending upon the condition of the problem,and in this case till the time when no further change in concentration is observed (say j = n).

The above representation result in a tridiagonal matrix of the solution,and in order to conserve the storage space in the computer, the m×m matrix is converted to m×3 matrix.The above equation in matrix form is

$$A \times C = P \tag{15}$$

C is the solution vector at i=2 to m, denoting the change in concentration at a particular i , when the values at i=1 are known at prior point. The model equation along with the boundry conditions reduces in a set of algebraic equations and form tridiagonal matrix. The tridiagonal matrix was solved using a computer code developed in FORTRAN 77 language.

The simulation is based on the model parameters listed in Table 1

Variables	**Parameters**	**Units**	**Value**
$\mathbf{A_S}$	Specific surface area	$m^2\ m^{-3}$	413
He	Henry's Constant	-	0.42
$\mathbf{D_e}$	Effective Diffusivity	$m^2\ h^{-1}$	15.48×10^{-5}
$\mathbf{k_1}$	First order Rate Constant	h^{-1}	0.35
ε	Porosity	-	0.50
H	Height of Biofilter	m	0.4
δ	Biofilm Thickness	m	0.0003
Δ**h**	Differential length along the column	m	0.04
Δ**t**	Differential time element	h	15

4. RESULT AND DISCUSSION

The results obtained are presented here in the form of graph and analysed objectively.

4.1. Simulated result for higher efficiency

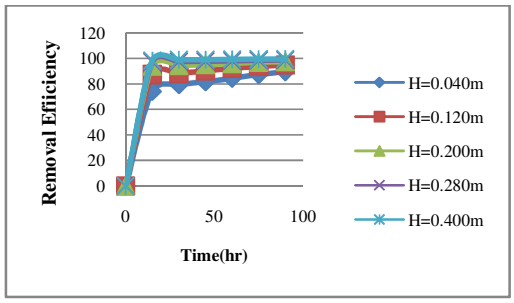


Fig.3:Removal efficiency Vs Time at various Heights

Fig 3 shows the effect of the biofilter bed height increase in height on the efficiency. The removal efficiency is increase with increase in the bed height. Since the capacity is increasing therefore removal efficiency is also increasing.

4.2 Experimental validation of the model

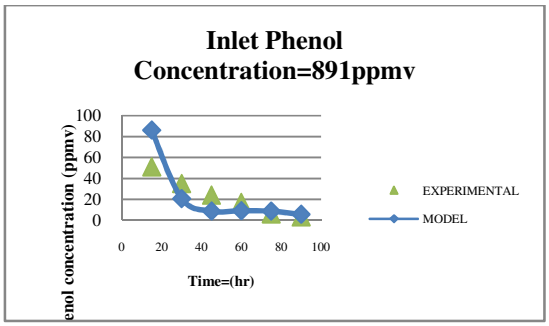


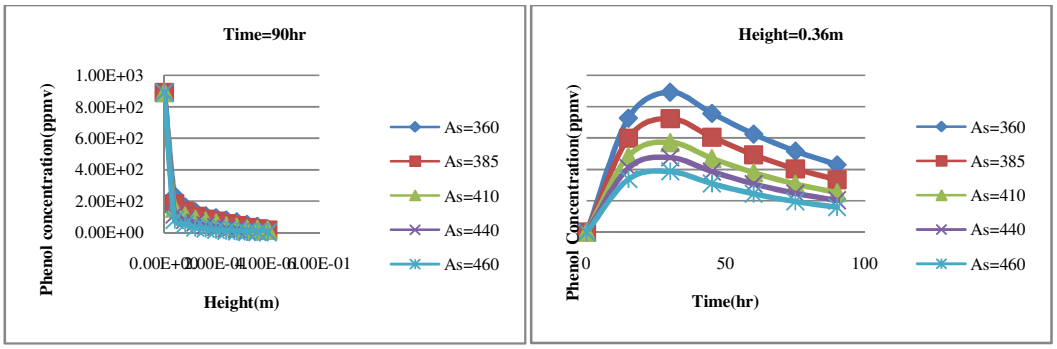
Fig 4 Comparison of Phenol concentration vs time between model and experimental results

fig 4 the result obtained from the model are validated with the experimental data presented by (Kenneth F. Reardon .et.al.2000).The experimental results for the outlet phenol concentration are compared with simulated results. It is observed that the model results follow the same trend as that of experimental results. Further it could be observed that the two results are close to each other.

4.3. Effect of Specific Surface Area of Biofilter Media (A_s) on Phenol Concentration in Biofilter

Increasing Height

Fig 5 and fig 6 shows the effect of specific surface area of biofilter media on phenol concentration in the biofilter with respect to time an height. The effect of the specific surface area on the exit gas concentration, the outlet phenol concentration is found to be decreasing with the increase in specific surface area.From this ,it is evident that with higher specific surface area the removal is increased.This is intuitively expected because for a given biofilm thickness increased surface area increases the reaction volume and area of mass transfer .

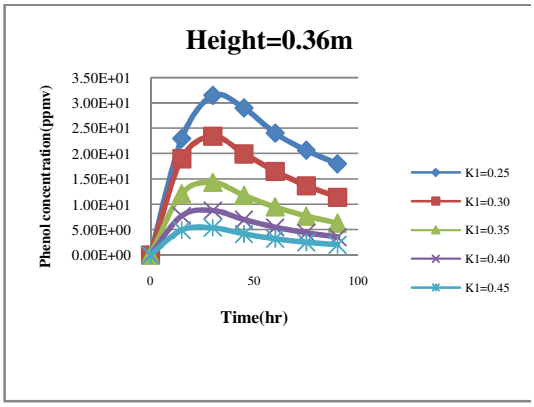


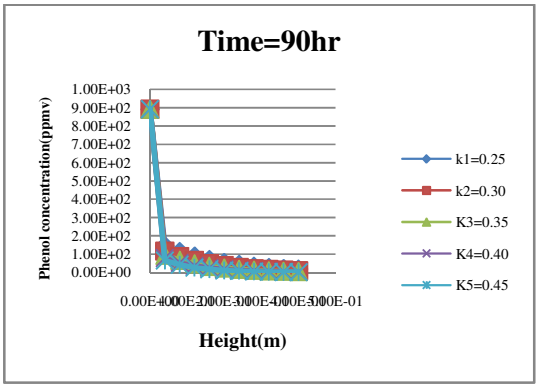
C_0=891ppmv,D_e=15.48×$10^{-5}$$m^2$/h,δ=0.0003m,$k_1$=0.35$h^{-1}$,Q=0.0125$m^3$/h,ε=0.50

Fig.5 and 6: Phenol concentration Vs Time & height at Various As (Specific surface Area)

4.4 Effect of Rate Constant (k_1) on Phenol Concentration in Biofilter

Fig 7 and 8 shows the effect of rate constant on phenol concentration in the biofilter with respect to time and height .The phenol concentration is found to decrease with increase in rate constant. This is due to the fact that with the increase in rate constant more and more phenol concentration is consumed in the reactions, which occurs in the biofilter. This shows that with the increase of rate constant the phenol concentration in the biofilter decreases.



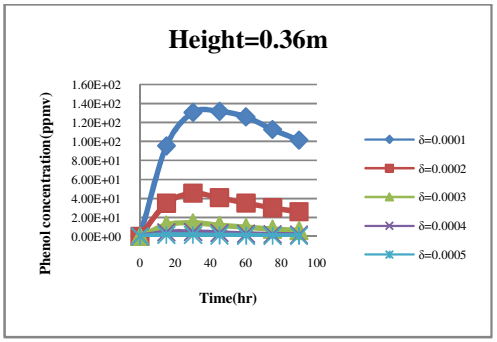


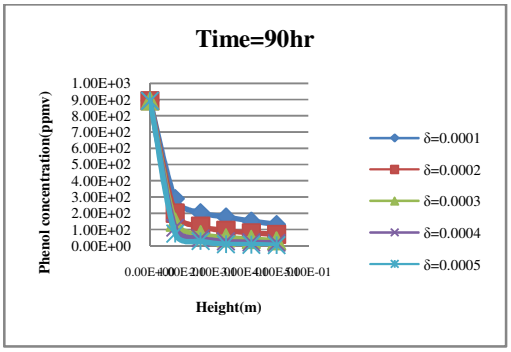
C_0=891ppmv,A_S=413m^2/m^3,D_e=15.48×$10^{-5}$$m^2$/h,δ=0.0003m ,Q=0.0125$m^3$/h,ε=0.50

Fig.7 and fig8: Phenol concentration Vs Height and time at Various k_1 (Rate Constant)

4.5 Effect of Biofilm Thickness (δ) on Phenol concentration in Biofilter

Fig 9 and 10 shows the effect of biofilm thickness on phenol concentration in the biofilter with respect to time. The phenol concentration is found to decrease with the increase in the thickness of biofilm. This is due to the fact that with the increase in biofilm thickness more and more phenol concentration is consumed as a result of reactions, resulting in the decrease of the outlet phenol concentration from the biofilter .





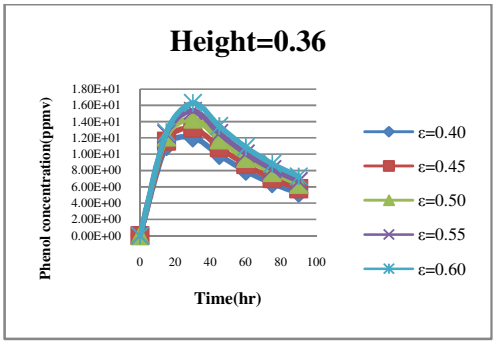
C_0=891ppmv,A_S=413m^2/m^3, D_e=15.48×$10^{-5}$$m^2$/h, k_1=0.35h^{-1}, Q=0.0125m^3/h,ε=0.50

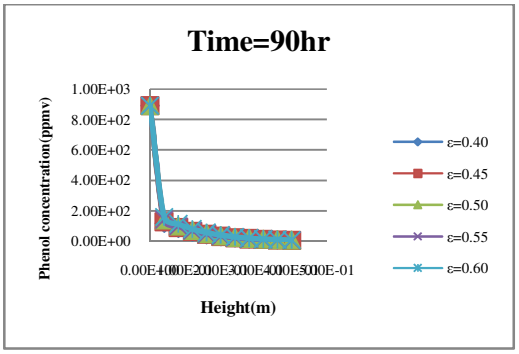
Fig.9and fig 10: Phenol concentration Vs Height at Various δ(Biofilm Thickness)

4.6 Effect of Porosity of the biofilter media (ε) on Phenol Concentration in Biofilter

Fig 11 and fig 12, shows the effect of porosity of the biofilter media on phenol concentration in the biofilter with respect to time and height.The phenol concentration

is found to be increasing with the increase in porosity .This is due to fact that with the increase in porosity ,the biofilter media available for the degradation decreases, hence there is an increase in the phenol concentration .



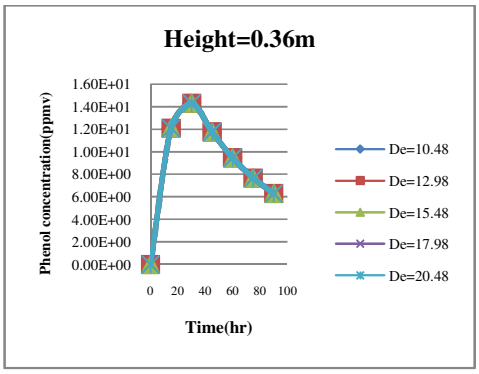


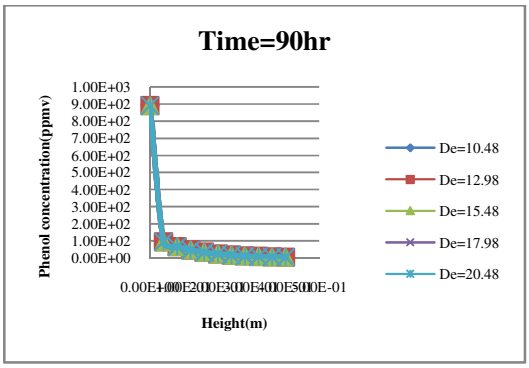
C_0=891ppmv,A_S=413m^2/m^3, k_1=0.35h^{-1}, D_e=15.48×$10^{-5}$$m^2$/h ,δ=0.0003m ,Q=0.0125$m^3$/h

Fig.11 and 12: Phenol concentration Vs Height at Various ε(Porosity)

4.7 Effect of Effective Diffusivity (D_e) on Phenol Concentration in Biofilter

Fig 13 and 14 show the effect of effective diffusivity on phenol concentration in the biofilter with respect to time and height. There is not much of effect of diffusivity on the outlet concentration of phenol. This is due to the biofilter operation is convection dominated.



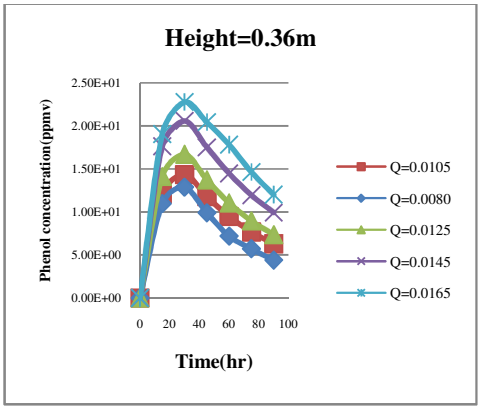


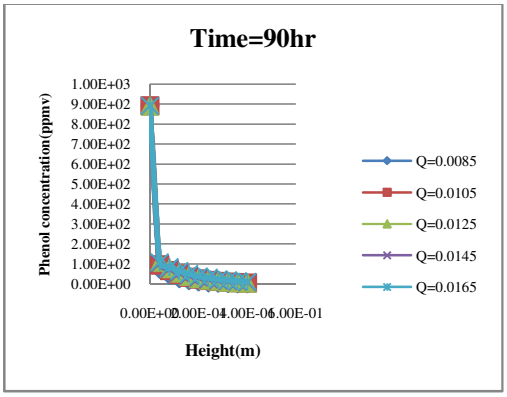
C_0=891ppmv,A_S=413m^2/m^3, k_1=0.35h^{-1},δ=0.0003m ,Q=0.0125m^3/h,ε=0.50

Fig.13 and 14: Phenol concentration Vs Height at Various D_e(Effective Diffusivity)

4.8 Effect of Air Flow Rate (Q) on Phenol Concentration in Biofilter

Fig 15 and 16, shows the effect of air flow rate of the bulk gas phase on phenol concentration in the biofilter with respect to time and height. The outlet phenol concentration is found to be increases with the increase in air flow rate in the bulk gas phase. The outlet phenol concentration increases due to the reason that, as the flow rate increases more and more phenol is pumped in the biofilter as a result of which the driving force is increased and retention time of phenol in biofilter decreased, resulting in low degradation.



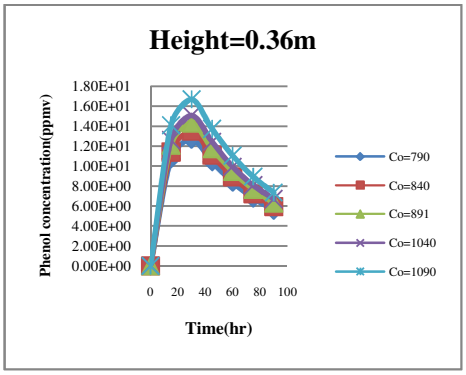


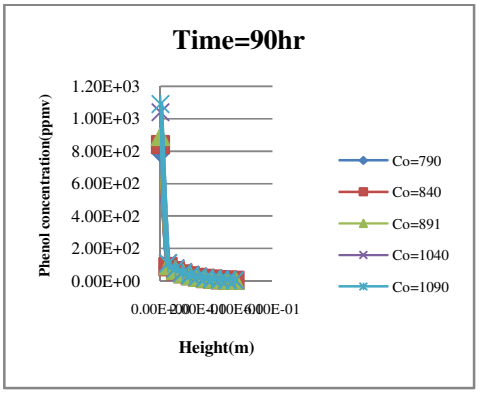
C_0=891ppmv,A_S=413m^2/m^3, D_e=15.48×$10^{-5}$$m^2$/h, k_1=0.35h^{-1},δ=0.0003m ,ε=0.50

Fig.15 and16 : Phenol concentration Vs Height at Various Q(Air Flow Rate)

4.9 Effect of Initial Concentration (C_0) on Phenol Concentration in Biofilter

Fig 17 and 18 show the effect of initial concentration on phenol concentration in the biofilter with respect to time and height. The phenol concentration is found to be increasing with the increase initial concentration. This is due to fact that as bed height increases as a result of which capacity of biofilter increases resulting in the decreased outlet phenol concentration.





A_S=413m^2/m^3, k_1=0.35h^{-1}, D_e=15.48×$10^{-5}$$m^2$/h, δ=0.0003m ,Q=0.0125$m^3$/h,ε=0.50

Fig.17 and 18: Phenol concentration Vs Height at Various C_0(Inlet Concentration)

5. CONCLUSIONS

The conclusions drawn from the modeling and simulation studies are shows that the outlet phenol concentration is found to decrease with increases the value of parameters specific surface area, biofilm thickness and rate constant .However phenol concentrations increase in the parameters porosity air flow rate and initial phenol concentration. It is also found that outlet phenol concentrations do not change with change in effective diffusivity parameter. It is observed that results are good agreement with experimental results. Simulated maximum phenol removal efficiency is observed to be 99.9%.

NOMENCLATURE

Symbol	Quantity	Units
A	Area of cross section of biofilter column	m^2
A_S	Specific surface area	m^2m^{-3}
$C_{C_6H_6O}$	C_6H_6O gas phase concentration	gm m^{-3}
C_1	Concentration of C_6H_6O in Biofilm	gm m^{-3}
C_g	Pollutant gas phase concentration	gm m^{-3}
C_{in}	Contaminant concentration in the influent	ppmv
C_{out}	Contaminant concentration in the effluent	ppmv
D_e	Effective diffusion coefficient	m hr^{-1}

dp	Particle diameter	m
H_e	Henry's constant	-
Δh	Height increment of the control volume	m
i	Increment for the height	m
j	Increment for the time	hr
h	Step size in height	m
k	Step size in time	hr
k_1	Rate constant	hr^{-1}
Q	Air Flow rate	$m^3 hr^{-1}$
RE	Removal Efficiency	-
$(-r_{C_6H_6O})$	$C_6 H_6O$ Degradation rate	$gm\ m^{-3}\ hr^{-1}$
V_g	Superficial air velocity of the bulk gas phase	$m\ hr^{-1}$
V	Volume of the filter material	m^3
ΔV	Incremental control volume	m^3
X_i	Mass fraction biofilter material	-
Δx	Thickness of the control volume of biofilm	m
Greek Constant		
ε	Porosity of the biofilter packing material	-
δ	Biofilm thickness	m
τ	Empty Bed Residence Time	

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