EXPERIMENTAL INVESTIGATION OF A TRICKLE BED BIOREACTOR: HYDRODYNAMICS TO BIODEGRADATION

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EXPERIMENTAL INVESTIGATION OF A TRICKLE BED BIOREACTOR: HYDRODYNAMICS TO BIODEGRADATION

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Supervisors' Certificate

This is to certify that the work presented in the dissertation entitled "*Experimental Investigation of a Trickle Bed Bioreactor: Hydrodynamics to Biodegradation"* submitted by "*Karri Sesha Surya Vara Prasad Reddy"*, Roll Number 214CH1110, is a record of original research carried out by him under our supervision and guidance in partial fulfillment of the requirements of the degree of *Master of Technology* in *Chemical Engineering*. Neither this dissertation nor any part of it has been submitted earlier for any degree or diploma to any institute or university in India or abroad.

Prof. Hara Mohan Jena

Dedicated to my parents

Mr. SIVA REDDY

&

Mrs. SUBHASINI DEVI

Declaration of Originality

I, *Karri Sesha Surya Vara Prasad Reddy*, Roll Number 214CH1110 hereby declare that this dissertation entitled *Experimental Investigation of a Trickle Bed Bioreactor: Hydrodynamics to Biodegradation* presents my original work carried out as a postgraduate student of NIT Rourkela and, to the best of my knowledge, contains no material previously published or written by another person, nor any material presented by me for the award of any degree of NIT Rourkela or any other institution. Any contribution made to this research by others, with whom I have worked at NIT Rourkela or elsewhere, is explicitly acknowledged in the dissertation. Works of other authors cited in this dissertation have been duly acknowledged under the sections "Reference" or "Bibliography". I have also submitted my original research records to the scrutiny committee for evaluation of my dissertation.

I am fully aware that in case of any non-compliance detected in future, the Senate of NIT Rourkela may withdraw the degree awarded to me on the basis of the present dissertation.

May 26, 2016

NIT Rourkela *Karri Sesha Surya Vara Prasad Reddy*

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Abstract

Experimental investigations have been carried out to study the performance of trickle bed bioreactor in degrading, the most common pollutant; phenol in synthetic water. The effect of key parameters that play predominate role such as hydrodynamic, mass transfer and microbial degradation were characterized under different conditions such as at various superficial liquid velocity, superficial gas velocity and phenol concentrations. The experiments were conducted in a laboratory scale trickle bed bioreactor with cylindrical plexiglas column of height 1.28 m and internal diameter of 0.091 m. Air, Phenol solutions and water and glass beads are used as gas, liquid and solid phases.

In hydrodynamic studies, the effect of superficial liquid and gas velocities and concentration of phenol solutions on pressure drop and dynamic liquid saturation were studied. It was observed that both pressure drop and dynamic liquid saturation increases with superficial liquid velocity. With increasing superficial gas velocity pressure drop increases but dynamic liquid saturation decreases. In mass transfer studies, the effect of superficial liquid and gas velocities were studied. The results shows that both solid-liquid, gas-liquid mass transfer coefficients increase with increase in superficial liquid and gas velocities.

Microbial degradation study on phenol was investigated by using a microbe, *Pseudomonas putida* in trickle bed bio reactor. The effect of initial phenol concentration (100 to 1500 ppm) and liquid flow rate (2-4 LPM) were studied. The analysis shows that the microbe, *Pseudomonas putida* is capable of degrading 1000 ppm phenol solution within 54 hours completely. The impact on rate of biodegradation was successfully determined between external mass transfer and biochemical reaction by correlating Colburn factor (J_D) and Reynolds number (N_{Re}) as $J_D = K * N_{Re}^{-(1-n)}$, in which n and K values for present investigation are 0.97, 5.7 respectively.

Keywords: *Hydrodynamics, Mass transfer, Foaming effect, Microbial degradation, Pseudomonas putida*

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Nomenclature

a_t	Total external surface area of particles per unit volume of empty tube, cm^2/cm^3
a_s	Wetted active area of bed per unit bed volume, 1/m
A_m	Surface area per unit weight of immobilized bead, cm^2/g
$(C_{L,O2})_e$	Concentration of dissolved oxygen in water at exit, $kmol/m^3$
$(C_{L,O2})_e'$	Concentration of dissolved oxygen in water at exit of empty bed, $kmol/m^3$
$\left(C_{L,O2}\right)_f$	Concentration of dissolved oxygen in water in feed, $kmol/m^3$
$\left(C_{L,O2}\right)_f'$	Concentration of dissolved oxygen in water in feed of empty bed, $kmol/m^3$
c_s	Solubility of benzoic acid, g/l
c_f	Solubility of benzoic acid in feed stream, g/l
c_e	Solubility of benzoic acid in exit stream, g/l
D, D_f	Diffusivity of solution, cm^2/s
G	Mass flux of phenol solution, g/cm^2h
h	Height of reactor bed
J_D	Colburn factor, dimensionless
k	Intrinsic first-order degradation rate constant L/cm^2 h
k_m	Mass transfer coefficient, L/cm^2 h
k_p	Observed first-order biodegradation rate constant, L/g h
$K_{ls}a$	Volumetric solid-liquid mass transfer coefficient, 1/s
$K_{gl}a$	Volumetric gas–liquid mass transfer coefficient,1/s
N_{Re}	Reynolds number, dimensionless
Q	Volumetric flow rate, L/h
r	Phenol removal rate
W	Dry weight of biomass
U_l	Superficial liquid velocity, m/s
U_g	Superficial gas velocity, m/s
ε	Void fraction or porosity
ρ	Feed density, g/cm^3
ρ	Bead density, g/cm^3
μ	Feed viscosity, g/cm s
σ	Surface tension, N/m

Chapter 1

Introduction and Literature Review

1.1. Overview

With rapid urbanization and industrialization, pollution due to man-made has become a major problem (Ghisalba, 1983). In a survey on quality of potable water, out of 122 countries India ranks 120, which tells us about the water problem persisting in our country (Kasturi mandal, 2008). It is estimated that by 2020, India may become a water-stressed nation. To major extent, the industrial activities were polluting the surface and ground water. Phenol is one of the toxic organic pollutants in industrial effluent and it is toxic even at lower concentrations. Phenol and its derivatives can be generated as wastes from coking operations, petrochemicals, pharmaceuticals, crude oil refineries, phenolic resins production, pulp and paper manufacturing. Due to these adverse health effects of phenolics as per Indian Standards, the permissible limit for phenol for the discharge into inland surface water is 1.0 ppm and in public sewer and marine disposal 5 ppm. The World Health Organization (WHO) has given maximum permissible limit of 0.1 ppm for phenols (Kumaran and Paruchuri, 1997). Table 1.1 presents phenol concentrations from various industrial effluents.

Table 1.1 Concentrations of phenol from various industries (Busca et al., 2008)

Category	**Phenol discharge (mg/l)**
Coal industry	9 – 6800
Gas production	4000
Coking operations	28 – 3900
Pulp and paper	0.1 - 1600
Petrochemicals	2.8 – 1220
Pharmaceuticals	1000

In view of phenols toxicity, it is extremely necessary to treat effluent before discharging into water bodies. The choice of method depends on the amount of phenol discharged, cost.

Table 1.2 Methods of treating phenolic compounds

Treatment method	Advantages	Disadvantages
Adsorption	Low cost, higher percentage of phenol removal	Produces a large amount of solid waste
Chemical oxidation	Less space, Fast reduction in contaminant concentrations	Higher cost, formation of harmful byproducts
Ion exchange	Long life of resins, cheap maintenance	Higher cost of the resins and Selectivity of resins in removing contaminants.
Chemical precipitation /coagulation	Less space, ease of process control	Higher maintenance cost, large sludge production

Hence, development of new technology is required which enhances the phenol biodegradation without any drawbacks. Biological treatment can be employed with mixed or pure microbial cultures, which is considered as an efficient process for the treatment of industrial effluents containing phenol because it doesn't produces any toxic products and it is cost effective than other physico-chemical methods (Kumaran and Paruchuri, 1997).

1.2. Trickle bed reactor

Solid–liquid-gas or solid-liquid reactors find importance in chemical processes because of wider applications in petroleum industries such as hydrocracking, hydrodenitrogenation, hydrodesulfurization, petro chemical industries as hydrogenation, oxidation and chemical industries. Among various reactors, trickle bed reactors are one of the commonly employed reactors. Trickle bed reactor plays an important role in effluent treatment plants and biochemical industries (immobilized enzymes or cells). Trickle beds are operated either co-current or counter current manner. Most of the reactors are co-current down-flow because it gives a better mechanical stability, relatively lesser pressure drops, no flooding condition, where higher throughputs of liquid may processes (Saroha and Khera, 2006). In down-flow reactors, liquid and gas flows downwards in cocurrent manner, where the flows of liquid on the solids like rivulets or films or droplets. Trickle bed

bioreactors are successfully used in the treatment of wastewater as it provides higher specific surface area for the growth of biomass and better retention for slow growing microorganisms (Soccol et al., 2003). To design and operation of a successful trickle bed bioreactor it is an important phenomenon to understand its hydrodynamics, mass transfer and degradation performance.

1.2.1. Trickle bed reactor applications

Trickle bed reactors are used in petroleum (hydrocracking, hydrodenitrogenation, hydrodesulfurization etc.) chemical industries, petro chemical industries (oxidation, hydrogenation). In recent years, trickle bed reactor plays a major role in biochemical industries (immobilized enzymes or cells) and effluent treatment plants. In wastewater treatment, trickle beds remove organics from wastewater by the action of microbes. Mixed microbial growth is attached to solids; stones etc in which effluent stream is allow trickling in presence of air.

1.2.2. Advantages

There are several advantages of TBRs listed below (Gianetto and Specchia, 1992)

- Higher conversion can be observed due to plug flow behavior.
- Simple construction due absence of moving parts.
- Larger reactor size.
- Lower investment and operating costs.
- Pressure drop across the bed is less which reduces operating costs.
- Different flow regimes can be observed and depending on demands it has more flexibility.
- Operating can be done at high temperature, pressure.
- Less catalyst loss which is necessary when costly catalysts are used.

There are some drawbacks in trickle bed reactors like flow mal distribution, formation of hot spot. Hot spot formation is due to reaction occurring in unwetted regions without any liquid phase. These hot spots cause the catalyst particles to sinter; damage the reactor casing and lead to reactor run away (Boelhouwer, 2001).

1.3. Effluent Treatment in Bioreactors

Effluent treatment needs larger place while employing lagoons or activated sludge process. In this treatment, time of retention may depend on number of days (Sokol, 2003). For 10-550 mg/lit of effluents with concentration of phenol can be treated in the reactors such as lagoons, activated sludge, oxidation ponds, etc. The problems in using reactors in which free cells for degradation includes sludge removal and cell concentration maintenance.

Over the mentioned conventional bioreactors, continuous bioreactors are having many advantages such as operation of reactor at constant flowrate, higher growth rate microbial cultures, higher gas-liquid mass transfer rate etc. Most commonly used bioreactors in effluent treatment are Continuous stirrer tank bioreactors (CSTBR), Airlift bioreactors (ABR), Slurry bioreactors, Rotating discs biological reactors (RDBR), Hollow fiber membrane bioreactor (HFMBR), Moving bed bioreactor, Membrane bioreactor, Fluidized bed bioreactors (FBBR) and Trickle bed bioreactors (TBBR).

TBBR is suitable one because of its simple design and lower operating costs. TBBR provides higher specific surface area for the growth of biomass. Trickle bed bioreactor permits control over the microbe's growth with optimum living conditions. It gives better retention for slow growing microorganisms.

1.3.1. Trickle bed bioreactor for effluent treatment

In recent years, TBBR plays a major role in effluent treatment plants. Microbial cultures are attached to solids, stones or supports (such as rock, slag, ceramic, plastic, etc). As effluent trickles down the bed of solids, the microbes which form as a bio-film have an ability to degrade the toxic contaminants present in wastewater effluents. For maintaining higher activity of microbes, these supports are necessary (Tziotzios et al., 2005). Table 1.3 shows the comparison of trickle bed bioreactor with other bioreactors in effluent treatment. Table 1.4 gives the comparison of various reactor performances.

Table 1.3 Comparison of TBBR with other bioreactors in effluent treatment applications (Tziotzios et al., 2005, Jena et al., 2005, Alemzadeh et al., 2002)

Parameter	**RDBR**	**HFMBR**	**FBBR**	**TBBR**
Specific surface area per bioreactor volume (m^2/m^3)	40-50	8-10	800-1200	1000-1100
Biomass concentration (kg/m^3)	Upto 6	Upto 22	30-40	25-75

Table 1.4 Comparison of various reactors performance (Holladay et al., 1978, Prieto et al., 2002)

	CSTBR	**FBBR**	**TBBR**
Phenol degradation rate	2.67 gm/l.d	11.2 gm/l.d	18.0 gm/l.d
Effluent phenol concentration	0.25-1.00 mg/l	0.01-0.5 mg/lit	0.5–1.0 mg/lit

Due to higher biomass concentration (75 kg/m^3), TBBR has capability to achieve treatment in lesser time. In terms of degradation, TBBR has highest phenol degradation rates (18 gm/l.d). Clogging is one of the practical problems while trickle-bed bioreactor operation. This is due to excess biomass formation. Excess formation of biomass causes obstruction of bed which leads to pressure drop increase (Weber et al., 1996). For prevention of this problem, it is necessary to adopt an active thin biofilm. This clogging problem can be eliminated by two approaches. Excessive biomass accumulation can be prevented by limiting the nutrients (may be in the form of MSM) available for growth the biomass formation. Another approach to prevent clogging is the use of NaOH wash for removal of biomass (Weber et al., 1996).

1.4. Hydrodynamic parameters

1.4.1. Flow regime

Trickle bed reactors can be operated in various flow regimes, which depend on gas and liquid velocities, fluid properties, design parameters. Usually two broad regimes are classified as low interaction and high interaction regimes (Al-Dahhan and Dudukovic, 1994). At moderate gas and low liquid velocities, trickle flow regime exists. In this regime, flow of liquid can be film or rivulet flow as in figure 1.1(a). Heat and mass transfer rates are lesser in trickle flow regime. Due to lower heat and mass transfer, many industrial reactors operate in this regime for achieving the specific goals. At relatively

high gas and liquid velocities, pulse flow regime exists (figure 1.1b). In Pulse flow regime, particle wetting occurs. This regime is advantageous in terms of higher heat and mass transfer rates, wetting, effective utilization of catalyst bed. At high gas and low liquid velocities, spray flow regime (figure 1.1c) exists. The flow will be in droplets, when semi-continuous nature was lost by liquid. The boundary of the spray flow and trickle flow regimes is very difficult for identification. At low gas and high liquid velocities, liquid becomes continuous by occupying entire void spaces. Gas flows as bubbles in a dispersed phase, bubbling flow occurs (figure 1.1d). Pressure drop across the bed becomes higher. Advantages of bubbling flow regime are complete wetting and higher rates of heat and mass transfer.

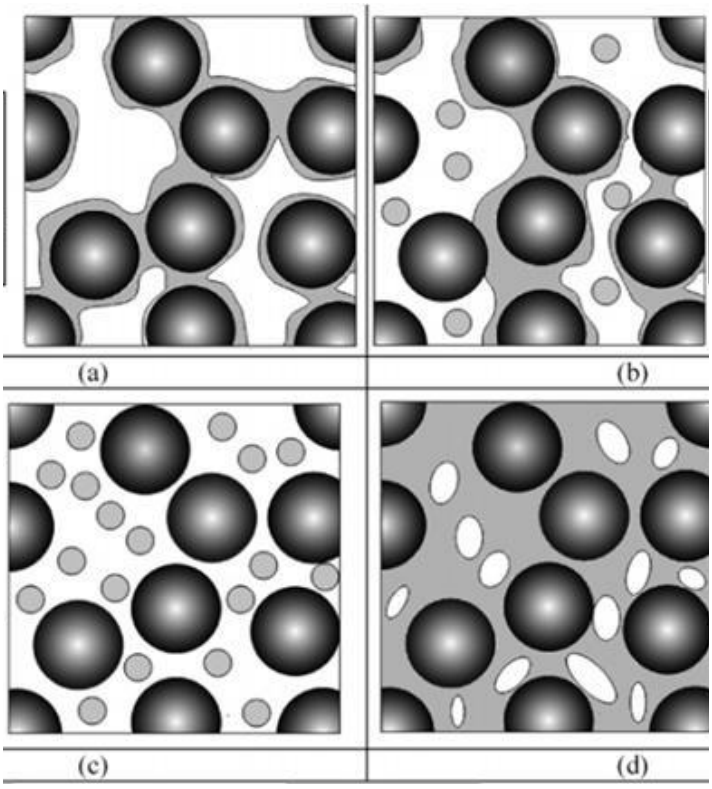


Figure 1.1 Flow regimes in trickle bed reactor (Prashant et al., 2005)

1.4.2. Pressure drop and Liquid holdup

Pressure drop and liquid holdup are the two basic hydrodynamic characteristics which are inter-linked with selectivity, power consumption, conversion that takes place in trickle bed reactors. So, it is worthwhile to investigate the hydrodynamics of trickle bed reactor.

Industrial trickle bed reactors are usually operated in pulse flow regime or in the trickle flow regime to achieve the high throughput (Gupta and Bansal, 2010).

1.4.2.1. Pressure drop

Two-phase pressure drop is an important parameter which associates with operating costs of trickle bed reactors as they affects the energy requirements (Bansal et al., 2008). Pressure drop depends on various operating variables like diameter of column, particle shape and size, gas-liquid velocities and fluid properties like density, viscosity and surface tension (Charpentier and Favier, 1975).

1.4.2.2. Liquid holdup

Liquid holdup is the ratio of the amount of liquid to the reactor volume. Holdup can be broadly classified into external and internal liquid holdups. Internal liquid accounts for the liquid volume that held due to the capillary forces in catalysts pores. External liquid holdup accounts for the outside liquid occupied by the void spaces of the bed. External holdup may broadly classify as dynamic and static liquid holdup. The dynamic liquid holdup is the fraction of the bed volume occupied by the liquid phase and it is measured as the ratio of amount of the liquid flowing out when inlets and outlets are closed to the volume of reactor (Al-Dahhan and Highfill, 1999). Liquid hold-up has ability to control and enable more wetting which tends to the prevention of the hot spot formation in exothermic reactions (Sodhi and Bansal, 2011).

1.4.2.3. Measuring techniques for Liquid Hold-up

Different techniques used to determine liquid holdup is classified as integral, semi-integral and local measurements techniques.

a) Integral Measurement techniques

There are mainly five methods, which provide information about bed volume.

- **Draining technique**

  In draining technique, liquid hold-up can be determined closing outlet and inlet values simultaneously and then liquid is drained. Static and dynamic holdups can be determined by using draining technique (Larkins et al., 1961).

- **Weighing technique**

  In weighing technique, liquid hold-up can be determined by weighing when liquid is flowing out of the reactor. To measure total hold-up, the weight of dry bed must be subtracting from measured reactor weight. To measure dynamic holdup, the weight of drained bed must be subtracting from measured reactor weight (Holub, 1990).

- **Tracer technique**

  Liquid hold-up can be determined by the residence time distribution of liquid. Total hold-up is mean of RTD of liquid (Mills and Dudukovic, 1981).

- **Closed Loop technique**

  Liquid hold-up can be obtained by circulation of liquid through the solids in a closed loop. Difference of volume of the liquid out and loop volume gives total holdup (Charpentier et al., 1968)

b) Semi-Integral techniques

These techniques give info about a section of the bed. By applying in different positions, more information can be obtained like absorbance technique

c) Local Measurements techniques

This method uses a sensor which is inserted at certain position. These can be based on conduction, optical signal, absorbance of radiation, electrical, etc. (Blok and Drinkenburg, 1982).

1.4.2.4. Previous studies on Hydrodynamic Studies

Specchia and Baldi, 1977 considered various types of packing to correlate hold-up and pressure drop in packed beds. They developed correlations by considering both low and high interaction regime. Correlations were formulated for both foaming and non-foaming systems.

Wammes et al., 1991 found that hold-up increases with liquid flow rate while decreases with gas flow rate, densities of gas. They also found that pressure drop increases with liquid and gas flow rates. When they compared results of nitrogen to helium, hydrodynamic state are same when densities of gas are equal.

Larachi et al., 1991 studied the pressure drop dependency on liquid and gas mass flow rates. They concluded that pressure drop increases with both mass flow rates, similar results were obtained when changing the value of the total pressure also showed that pressure drop is lesser for non-foaming liquids than foaming liquid and reported that with increase in particle size, pressure drop decreases.

Sodhi et al., 2011 investigated the variation of gas, liquid velocities and surface tension on the pressure drop in a down flow trickle bed reactor. They used Sodium Lauryl Sulphate which produces a moderate to extensive foam formation ability. This foaming nature depends on the concentration used and other parameters.

Sodhi et al., 2011 investigated on dependency of gas and liquid flow rates dynamic liquid saturation. They concluded that in the low interaction regime, dynamic liquid saturation increases with increase in liquid flow rate and then decreases sharply with a change in regime transition from lower interaction to high interaction regime. They also concluded that, this phenomenon observed in non-foaming air-water system was opposite.

Table 1.5 gives brief summary on hydrodynamic literature studies. Various researchers have published their hydrodynamic data obtained using the techniques discussed. Table 1.6 gives available correlations for pressure drop in trickle bed reactors. Table 1.7 gives available correlations for liquid holdup.

Table 1.5 Summary on Hydrodynamics previous studies

Author	**Type of system used**	**Parameters studied**
Turpin and Huntington, 1967	Air/water/tabular alumina/drainage technique	Pressure drop, liquid saturation
Sato et al., 1973	Air/water/glass spheres/electric conductivity probe, pressure transducer	Pressure Loss, Liquid holdup
Midoux et al., 1976	Air, N_2, CO_2, He/Water, cyclohexane, kerosene, gasoline, petroleum ether/ spherical and cylindrical Al_2O_3/ weighing method	Flow Patterns, Pressure loss, liquid holdup
Specchia and Baldi., 1977	Air/Water, Glycerol aqueous solution, Water with	Pressure drop and holdup

	surfactant/Glass spheres and Glass cylinders	
Ellman et al., 1990	Air/Water/Spherical and cylindrical Glass, ceramics, porous alumina particles/tracer technique	Liquid Hold-Up
Benkrid et al., 1997	Air/kerosene, cyclohexane/glass spheres /drainage technique	Pressure drop, liquid saturation
Saroha et al., 2006	air/water/glass beads/tracer technique	liquid holdup, pressure drop, Axial dispersion
Bansal et al., 2009	air/water, SLS, glycerol, CMC, PEO/glass beads, solid cylinders, raschig rings/draining method	liquid saturation

Table 1.6 Correlations for pressure drop in trickle bed reactors

Author	**Correlation proposed**	**Flow Regime**
Turpin and Hunington, 1967	$\ln f_{\lg} = 7.96 - 1.34\ln Z + 0.0021(\ln Z)^2 + 0.0078(\ln Z)^3,$ $f_{\lg} = \frac{\delta_{\lg} d_{pe}}{2u_g^2 \rho_g}; d_{pe} = \frac{2}{3} d_p \frac{\varepsilon_B}{1-\varepsilon_B}; 0.2 < Z = \frac{\mathrm{Re}_g^{1.167}}{\mathrm{Re}_l^{0.767}} < 500$	All
Sato et al., 1973	$\log(\frac{\delta_{\lg}}{\delta_l + \delta_g}) = \frac{0.70}{(\log \chi / 1.2)^2 + 1}, \quad 0.1 < \chi < 20$	All
Midoux et al., 1976	$(\frac{\delta_{\lg}}{\delta_l})^{0.5} = 1 + \frac{1}{\chi'} + \frac{1.14}{\chi^{0.54}}, 0.1 < \chi < 80$	All
Specchia and Baldi, 1977	$\ln f_{\lg} = 7.82 - 1.30\frac{Z}{\psi^{1.1}} - 0.0573[\ln(\frac{Z}{\psi^{1.1}})]^2$	High interaction regime
Clements and Schmidt, 1980	$\frac{\delta_{gl}}{\delta_g} = 1507\mu_1 d_p (\frac{\varepsilon_B}{1-\varepsilon_B})(\frac{\mathrm{Re}_g We_g}{\mathrm{Re}_l})^{-1/3},$ $We_g = u_g^2 \rho_g d_p / \sigma_1$	Trickle and pulsing
Sai and Varma, 1987	$F=1320(\frac{\mathrm{Re}_g}{\mathrm{Re}_l})^{1.0}(\frac{\sigma_w}{\sigma_l})^{0.05}(\frac{\mu_w}{\mu_l})^{1.4}(\frac{\rho_l}{\rho_w})^{1.3}$ $F=1950(\frac{\mathrm{Re}_g}{\mathrm{Re}_l})^{0.7}(\frac{\sigma_w}{\sigma_l})^{0.05}(\frac{\mu_w}{\mu_l})^{1.1}(\frac{\rho_l}{\rho_w})^{1.3}$	Gas continuous Pulse flow (foaming and non-foaming)

Ellman et al., 1990	$f = A(X_g\xi_1)^j + B(X_g\xi_1)^k; \xi_1 = \frac{\mathrm{Re}_1^{0.24} We_1^{0.2}}{(1+3.17\,\mathrm{Re}_1^{1.65} We_1^{1.2})^{0.1}}$ $f = C(X_g\xi_2)^j + D(X_g\xi_2)^k; \xi_2 = \frac{\mathrm{Re}_1^2}{(0.001+\mathrm{Re}_1^{1.5}}$; $A = 6.96; B = 53.27; C = 200; D = 85;$ $j = -2; k = -1.5; m = 1.2; n = -0.5$	High interaction Low interaction
Bansal et al., 2008	$f_{LGL,T} = 102\frac{We_G^{0.6} S_1^{3.443} S_2^{1.065}}{\mathrm{Re}_{L,M}^{1.4}}(\frac{\sigma_L}{\sigma_M})^{-\frac{4}{3}}(\frac{\mu_L}{\mu_W})^{-1.15}$ $f_{LGL,T} = 2*102\frac{We_G^{0.6} S_1^{3.443} S_2^{1.065}}{\mathrm{Re}_{L,M}^{1.4}}(\frac{\sigma_L}{\sigma_M})^{-\frac{4}{3}}(\frac{\mu_L}{\mu_W})^{-1.15}$ $S_1 = \frac{a_s d_p}{\varepsilon}, S_2 = (l/d_{ps})^{\frac{1}{\phi_s}}$	Low interaction High interaction

Table 1.7 Correlations for liquid holdup in trickle bed reactors

Author	Correlation proposed	Flow Regime
Turpin and Hunington, 1967	$\varepsilon_d = \{0.132(\frac{L}{G})^{0.24} - 0.017\}\varepsilon_B$	High Interaction
Sato et al., 1973	$\varepsilon_1 = 0.185 A_v^{1/3} \chi^{0.22} \varepsilon_B; \chi = (\delta_l/\delta_g)^{0.5};$	Low interaction
Midoux et al., 1976	$\varepsilon_1 = \varepsilon_B \frac{0.66\chi^{0.81}}{1+0.66\chi^{0.81}}$	Low interaction
Specchia and Baldi, 1977	$\varepsilon_d = A\varepsilon_B(Z/\psi^{1.1})^{-a}(ad_p/\varepsilon_B)^{0.65}$ $Z = \mathrm{Re}_g^{1.164}/\mathrm{Re}_l^{0.767}; \psi = \frac{\sigma_w}{\sigma_l}[\frac{\mu_l}{\mu_w}(\frac{\rho_w}{\rho_l})^2]^{\frac{1}{3}}$	High interaction for foaming A=0.0616, a=0.172; non foaming A=0.125, a=0.312
Sai and Varma, 1987	$\beta_d = 0.245*a_s^{1/3}(\frac{\mathrm{Re}_l}{\mathrm{Re}_g})^{1/3}(\frac{\sigma_w}{\sigma_l})^{0.8}(\frac{\mu_l}{\mu_w})^{0.5}(\frac{\rho_l}{\rho_w})^{0.2}$ $\beta_d = 0.065*a_s^{1/3}L^{1/3}(\frac{\sigma_w}{\sigma_l})^{0.8}(\frac{\mu_l}{\mu_w})^{0.15}(\frac{\rho_l}{\rho_w})^{0.2}$	Pulse and trickle Foaming pulse flow
Ellman et al., 1990	$\log\beta_1 = -RX_g^m \mathrm{Re}_1^n We_1^p(\frac{A_v d_k}{1-\varepsilon_B})^q;$ $R = 0.42; m = 0.24; n = 0.14; p = 0; q = -0.14$	Low interaction

1.5. Mass transfer studies

Interactions between liquid, solid and gas phase are important to study the performance and efficiency of a bioreactor. These interactions may be solid-liquid, gas-liquid or gas-solid. More interactions and transfer of phase materials between solid, liquid and gas phases increase the efficiency of bioreactor. So it is worthwhile to investigate mass transfer interactions between different phases.

1.5.1. Solid-Liquid Mass Transfer

Various researches have been carried out experiments to evaluate the solid-liquid mass transfer effects. Majority of literature emphasis on the dissolution and electrochemical methods. Other techniques like absorption and chemical reaction also investigated by some of the researchers. A brief notes about measuring techniques were presented.

1.5.1.1. Different techniques for measuring solid-liquid mass transfer coefficients

a) Electrochemical method

This technique used to determine the mass transfer coefficient instantaneously at any position within the bed. Liquid and gas are pumped to the reactor in cocurrent manner. A cathode is placed within the bed in axial position, with the same geometry and size as inert packing. An anode is placed at the reactor outlet. The liquid phase contains a solvent, an electrolyte. By electrons transfer, current is generated in the electrochemical cell (Hanratty and Campbell, 1983).

b) Dissolution technique

This method is used at to determine the overall solid-liquid mass transfer coefficient in a trickle bed reactor. There are two methods for making of active particles i.e coating or casting particles. This prevents larger changes in properties of bed. Some of the solid materials used by researchers are benzoic acid, a mixture of benzoic acid and a Rhodamine B, naphthalene and β-napthal (Al-Dahhan et al., 1997). Investigators used either a longer beds or short beds with a section of particles. By this, saturation of the effluent can be avoided.

Different techniques have been developed to determine the amount of solid material in the outlet samples. Researchers have been employed some of the techniques like UV spectrometer, fluorometer, titration with *NaOH* etc. By the assumption of plug flow, Goto et al., 1975 suggested a relation to determine volumetric solid-liquid mass transfer coefficient given in equation 1

$$k_{ls}a = \frac{U_l}{z_B}\ln\left(\frac{c_s - c_f}{c_s - c_e}\right) \qquad (1.1)$$

c) Chemical reaction

Liquid and gas flows down into solid catalyst. At higher temperatures, products are formed from reactants. By determining product concentration, mass transfer coefficient can be evaluated (Satterfield et al., 1969). Hydrogenation, hydration etc are some of the examples.

d) Absorption

Liquid and gas flows down in a cocurrent manner in which carbon as solid phase. Benzaldehyde is added to liquid phase. Absorption can be determined by benzaldehyde concentration in outlet stream

1.5.1.2. Previous studies on solid-liquid mass transfer

Various studies come into existence to investigate the effects of the mass transfer in a trickle bed. Many researchers suggested correlations to evaluate solid-liquid mass transfer coefficients by considering different systems. The table below shows some of the previous studies on solid-liquid mass transfer. Techniques used and operating regimes (flooded, trickle, transition, pulse, dispersed bubble flow) are indicated in Table 1.8.

Jolls & Hanratty, 1969 investigated mass transfer studies by using electrochemical technique. A test sphere, located at the top, and a section of nickel-coated pipe which was located outside the column acts as the cathode and anode respectively. The electrolyte used was $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$. For complete wetting of the electrode, this electrolyte was injected from the bottom of the column. They concluded that the effect of reynolds number was slightly larger power than 0.5, on the mass transfer

coefficient of inert spheres.

Sylvester & Pitayagulsarn, 1975 used dissolution technique to investigate mass transfer studies. Water and Air were considered as liquid and gas phase respectively which were pumped to the top of the column in co-current manner. The dissolution technique by coating of benzoic acid on cast spheres was employed by Sylvester & Pitayagulsarn, 1975. Effluent samples were collected and analysed by titrating against *NaOH* (0.01N) solution in which phenolphthalein was added as an indicator.

Hirose et al., 1976 used two different systems to investigate mass transfer. In system A, coating of particles with benzoic acid was employed in dissolution technique. In system B, a redox reaction which occurs in sulphuric acid electrolyte, between metallic copper and dichromate ions was employed. To avoid channeling in system A, it's not employed at lower rates because of lesser wettability nature of benzoic acid. In system B, as handling of corrosive materials was difficult, it's not used at high liquid flow rates. They concluded that both systems A and B yield mass transfer coefficients which were similar when operated in transition regime.

Satterfield et al., 1978 investigated mass transfer effects by using dissolution technique. In this method, benzoic acid solids of cylindrical shape were used as solid phase. They operated in wide range of flow regimes from trickle flow to pulsing flow regime. They concluded that trickle flow regime and pulse flow regime was characterized by incomplete wetting and complete wetted conditions respectively. Some of the correlations given by Satterfield et al., were given in table 1.9.

Chou et al., 1979 investigated mass transfer studies by electrochemical method. Nickel cathode, electrolytic solution of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ and alumina spheres were employed. They concluded that, in the trickle regime, a large scatter of data was observed at different positions in bed of alumina spheres, however they observed time averaged data was independent of the position of electrode in the pulse flow regime. They suggested a correlation for only in pulse flow regime but not in trickle flow regime because of the large scatter in trickle flow data.

Reuther et al., 1980 investigated mass transfer studies in a packed bed reactor. They employed dissolution by coating with benzoic acid and rhodamine B. In this study, packed bed was divided as two inert sections and an active section in central portion of the packed bed. The packing material used was berl saddles. The effluent concentrations were analysed by fluorometer.

Lakota & Levec, 1990 evaluated mass transfer coefficients by using dissolution technique. The packing material in this study was made by a mixture of naphthalene, stearate and talc. Water and Air were considered as liquid and gas phase respectively which are passed through the bed of cylinders co- current manner. Firstly, gas flow rate kept constant and the flow rate of liquid increased from lower interaction and higher interaction regimes. A correlation was given by Lakota & Levec, 1990 which pertains entire range of flow regimes.

Various researchers have published their mass transfer data obtained using the techniques discussed. It should be noted that most of the literature was found to be dependence of sherwood number on liquid reynolds number. Table 1.9 gives available correlations for the evaluation of solid-liquid mass transfer coefficients.

Table 1.8 Summary on solid-liquid mass transfer studies

Author	Technique used	Operating regime
Al-Dahhan et al. (2000)	Dissolution of naphthalene	none specified
Bartelmus (1989)	Electrochemical	flooded, trickle & pulse
Chou et al. (1979)	Electrochemical	trickle & pulse
Goto et al. (1975)	Dissolution of naphthalene	trickle
Hirose et al. (1976)	Dissolution of benzoic acid	dispersed bubble & pulse
Jolls & Hanratty (1969)	Electrochemical	trickle & pulse
Lakota & Levec (1990)	Dissolution of naphthalene	trickle & pulse

Latifi et al. (1988)	Electrochemical	flooded & trickle
Lemay et al. (1975)	Dissolution of benzoic acid	pulse
Rao & Drinkenburg (1985)	Electrochemical	trickle & pulse
Reuther et al. (1980)	Dissolution of benzoic acid	gas continuous, transition, pulse and dispersed bubble
Satterfield et al. (1978)	Dissolution of benzoic acid	trickle & pulse
Specchia et al. (1978)	Dissolution of benzoic acid	flooded & trickle
Sylvester & Pitayagilsarn (1975)	Dissolution of benzoic acid	gas continuous, transition, pulse
Tan & Smith (1980)	Dissolution of benzaldehyde	trickle
Trivizidakis & Karabelas (2006)	Electrochemical technique	flooded, trickle & pulse

Table 1.9 Correlations for the prediction of solid-liquid mass transfer coefficients

Author	**Correlation proposed**	**Flow regime**
Jolls and Hanratty, 1969	$ShSc^{-1/3} = A\mathrm{Re}^{n}$ $\mathrm{Re} < 35, A = 1.64; n = 0.6$ $35 < \mathrm{Re} < 140, A = 1.44; n = 0.58$ $140 <, A = 1.59; n = 0.56$ $\mathrm{Re} > 1120, A = 6.4; n = 0.5$	trickle & pulse
Sylvester and Pitayagulsarn, 1975	$k_{ls} = 1.634 * 10^{-4}[L^{-0.78}(1-\frac{\varepsilon^{y}}{1+\varepsilon^{y}})]G^{0.38}$ $y = 4L/6350$	Gas continuous, transition, pulse
Hirose et al., 1976	$\phi Sh = 1.56\,\mathrm{Re}_{l}^{1/2}\,Sc^{1/3}$	Pulse flow
Satterfield et al., 1978	$\phi Sh = 0.815\,\mathrm{Re}_{l}^{0.822}\,Sc^{1/3}$ $\phi Sh = 0.334K_{o}^{0.202}Sc^{1/3}$	different

Specchia et al., 1978	$Sh' = (2.14\,\mathrm{Re}_l^{0.5} + 0.99)Sc^{1/3}$ $Sh' = (10.8(1-\varepsilon)\,\mathrm{Re}_l^{0.5})Sc^{1/3}$	Trickle
Reuther et al., 1980	$Sh = \frac{0.0819\,\mathrm{Re}_l^{0.77}\,Sc^{1/3}}{\varepsilon}$ $\phi Sh = \frac{0.00437\,\mathrm{Re}_l^{1.517}\,Sc^{1/3}}{\varepsilon}$ $\phi Sh = \frac{0.68\,\mathrm{Re}_l^{0.416}\,Sc^{1/3}}{\varepsilon}$	Gas continuous, transition, pulse and dispersed bubble flow
Chou et al., 1979	$\phi Sh = \frac{0.72\,\mathrm{Re}_l^{0.54}\,\mathrm{Re}_g^{0.16}\,Sc^{1/3}}{\varepsilon}$	Gas continuous
Rao and Drinkenburg, 1985	$\phi Sh = 0.24\,\mathrm{Re}_l^{0.75}\,Sc^{1/3}$ $\phi Sh = \frac{0.77\,\mathrm{Re}_l^{0.45}\,\mathrm{Re}_g^{0.223}\,Sc^{1/3}}{\varepsilon}$ $\phi Sh = 0.71K_o^{0.21}Sc^{1/3}$	Trickle Pulse flow
Latif et al., 1988	$j_D = 0.667\,\mathrm{Re}_l^{-0.34}$	flooded & trickle
Lakota and Leves, 1990	$Sh = 0.487\,\mathrm{Re}_l^{0.495}\,Sc^{1/3}$	trickle & pulse
Trivizidakis and Karabelas, 2006	$Sh = 0.35\,\mathrm{Re}_l^{0.6}\,Sc^{1/3}$	Trickle flow
Bartelmus et al., 1989	$Sh/Sc^{1/3} = (1.19 + 0.0072\,\mathrm{Re}_G^{*})^{1.1}(\mathrm{Re}_L^{*})^{0.494}Ga^{-0.22}$ $Sh/Sc^{1/3} = 2.269(\mathrm{Re}_L^{*})^{0.494}(\mathrm{Re}_G^{*})^{0.178}Ga^{-0.276}$	Trickle Pulsing
Tan and Smith., 1982	$Sh/Sc^{1/3} = 4.25\,\mathrm{Re}_L^{0.48}$	trickle
Lemay et al., 1975	$k_{ls}Sc^{2/3} = 0.2(E_L''\mu_L/\rho_L)^{1/4}$	all
Goto and Smith., 1975	$k_{ls}\,a/D = \alpha_s(G_L/\mu)^{n_s}(\mu/\rho D)^{1/3}$	all

1.5.2. Gas-Liquid Mass Transfer

Gas-liquid mass transfer is one of the most important steps in determining the absorption rate. This is because in any absorption process, the gas must be dissolved in the liquid (Charpentier, 1976). According to the two-film concept, the overall gas-liquid mass transfer coefficient may be expressed, in terms of the liquid side and the gas side mass transfer coefficients (Herskowitz & Smith, 1983):

$$\frac{1}{K_L a} = \frac{1}{H * k_g a} + \frac{1}{k_L a} \qquad (1.2)$$

In the case of a highly insoluble gas can be assumed that vapor-liquid equilibrium is established between the gas and the gas-liquid interface, that means there is no significant mass transfer resistance in the gas phase (Satterfield, 1975). This can be observed from the above equation. For a slightly soluble gas, like hydrogen or oxygen, the value of the Henry's constant is larger than unity. This results in the term, ($H*k_g a$) which is greater than $k_L a$ over a range of liquid and gas velocities. Thus, $K_L a$ can be approximated as $k_L a$ (Herskowitz & Smith, 1983)

However, if the gas is soluble in the liquid, carbon dioxide in water as an example, it can be assumed that there is negligible mass transfer resistance in the liquid film then the experimental study is concerned only on the evaluation of mass transfer in the gas film. (Iliuta, Iliuta & Thyrion, 1997)

1.5.2.1. Methods for finding Gas-Liquid Mass Transfer Coefficient

For finding the gas-liquid mass transfer coefficient, mainly different techniques were discussed in literature;

- Absorption
- Desorption

Absorption or desorption techniques are by far the most frequently used. In these methods, either oxygen may be transferred from air to water (absorption) or water to nitrogen (desorption). The driving force for desorption into nitrogen is easier to measure accurately due to its driving concentration difference $C_A \rightarrow 0$. The driving concentration difference for the absorption from air, on the other hand, is $C_A^* \rightarrow C_A$, and is more difficult

to measure accurately (Lara-Marquez *et al*, 1994a).

The equation prescribed for finding volumetric mass transfer coefficient is based on correlation proposed by Goto and Smith (1975).

For absorption technique,

$$k_{gl}a = \frac{U_l}{z_B} \ln[\frac{C^*_{L,O2} - \left(C_{L,O2}\right)'_e}{C^*_{L,O2} - (C_{L,O2})_e}] \quad (1.3)$$

For desorption technique,

$$k_{gl}a = \frac{U_l}{z_B} \ln[\frac{\left(C_{L,O2}\right)'_e * (C_{L,O2})_f}{(C_{L,O2})_e * \left(C_{L,O2}\right)'_f}] \quad (1.4)$$

1.5.2.2. Previous studies on gas-liquid mass transfer

Mass transfer has adverse effect on the performance of trickle bed reactor. This means, for scale-up or reactor design the estimation of the mass transfer parameter is necessary (Al-Dahhan *et al*, 1997).

Reiss 1967 determined the gas-liquid mass transfer by desorption method. In this method, air and water as gas and liquid phases respectively flows in cocurrently downwards. Three columns of different diameters of were used (3, 4, and 16 in). The packing material was raschig rings. They developed a correlation by considering dissipation energy.

Sato et al., 1972 evaluated mass transfer coefficients within bed of 65.8-mm diameter, which was packed of glass beads to a height of 25 cm. the process of desorption was used to evaluate gas-liquid mass transfer by using nitrogen and water as gas and liquid phases respectively**.** They obtained data in pulsing flow and dispersed bubble flow regimes. They concluded that increase in gas flowrate increases the mass transfer coefficient value ten times the values at low gas flowrates, increased with increasing liquid flowrate. They also concluded that an increase in packing size decreases the mass transfer coefficients at the constant gas and liquid flowrates.

Gianetto et al., 1973 determined mass transfer coefficient by employing desorption technique. In this method, air and 2 N sodium hydroxide solution were used. The column has inner diameter of 8 cm and the solids used were glass berl saddles, spheres, glass and ceramic rings. The flow of gas was cocurrent downwards to the liquid phase. They

concluded that the height of bed has effect on mass transfer coefficient. They compared results with Reiss 1967 studies, which showed that values by Gianetto et al., 1973 were lesser than Reiss 1967 studies.

Ufford and Perona, 1973 evaluated mass transfer coefficient by absorption rate of carbondioxide into water. The flow of gas was cocurrent downwards to the liquid phase. The experiments were investigated in a packed column. They used packing material like raschig rings, berl saddles of different diameters. The reported that mass transfer is independent on gas rate rather than liquid rate.

Shende and Sharma, 1974 determined mass transfer coefficients by employing gas absorption technique. Different packings like ceramic, metal and plastic were employed. They obtained data in both cocurrent and counter-current operations.

Sylvester and Pitayaguisarn, 1975 measured gas-liquid transfer coefficients, in a downflow column which was packed with cylindrical pellets by using absorption method in which tap water and carbondioxide were considered. The experimentation covers a range of flow regimes.

Goto and Smith, 1975 employed absorption technique by using oxygen and water as gas and liquid phases respectively. Nitrogen and water were used as gas and liquid phases respectively in desorption technique. Mass transfer rates were measured in a tube, packed with glass beads and granular CuO.ZnO catalyst particles. They concluded that mass transfer coefficients were increased with liquid rate but unaffected by gas flow rate.

Table 1.10 Summary on Gas-Liquid mass transfer studies

Reference	**Packing used**	**Gas and liquid phases used**		
		Solute	**Gas**	**Liquid**
Reiss, 1967	Rasching rings and Saddles	Ammonia and oxygen	Air	Water
Gianetto et al., 1970	Spheres, Rasching rings and Saddles	Carbondioxide, Ammonia and oxygen	Air	Sodium hydroxide and sodium sulphate
Ufford and Perona, 1973	Rasching rings and Saddles	Carbondioxide	Air	Water

Sato et al., 1974	Spheres	Oxygen	Nitrogen	Water
Goto and Smith, 1975	Spheres and pellets	Oxygen	Nitrogen and oxygen	Water
Sylvester and Pitayaguisarn, 1975	Cylindrical pellets	Carbondioxide	Carbondioxide	Water
Lemay et al., 1975	Spheres	Oxygen	Air	Water
Shende and Sharma 1974	Spheres and Raschig rings	Oxygen	Air, Nitrogen	Sodium hydroxide

Various researchers have published their mass transfer data obtained using the techniques discussed. It should be noted that most of the researchers found that the volumetric mass transfer coefficient has dependence on the liquid Reynolds number, liquid velocity etc. Table 1.11 gives available correlations for the prediction of gas-liquid mass transfer coefficients.

Table 1.11 Correlations for prediction of gas-liquid mass transfer coefficients

Author	Correlation proposed	Flow regime
Sylvester and Pitayaguisarn, 1975	$k_{gl}a = 1.295 * 10^{-6} * L^{1.2} * G^{0.3}$	gas continuous, transition, and pulsing flow regimes
Reiss (1967)	$k_L a = 0.12 * E_L^{0.5}; E_L = [\frac{\Delta P}{\Delta L}]_{LG} * V_L$	Trickle flow
Turek and Lange, 1981	$k_L a = 16.8 * D * Ga_L^{-0.22} * \mathrm{Re}_L^{0.25} * Sc_L^{0.5}$	Trickle and pulse flow
Fukushima and Kusaka (1977)	$k_L a = 2.8 * \frac{D[1 - H_t / \varepsilon_B]}{d_h^2} * \mathrm{Re}_L^{0.73} * \mathrm{Re}_G^{0.2} * Sc_L^{0.5} (\frac{d_p}{D_C})^{0.2}$	All regimes
Goto and Smith, 1975	$\frac{k_L a}{D} = \alpha_L (\frac{G_L}{\mu})^{n_L} (\frac{\mu}{\rho D})^{0.5}$, where α_L, n_L are parameters	Not specified
Gianetto et al. (1973)	$\frac{k_L \varepsilon}{v_L} = 0.0305\{[(-\frac{\Delta P}{\Delta z}) \frac{g_c \varepsilon}{a_v \rho_L v_L^2}]^{0.068} - 1\}$	Not specified

1.6. Microbial phenol degradation studies

1.6.1. Phenol and its uses

Among the major toxic compounds, phenol and its substituent phenolic compounds contribute an adverse effect to the environment. These phenolic compounds often found in the wastewaters discharged from the industries such as paper and pulp, textiles, gas and coke, fertilizers, pesticides, steel and oil refineries etc. During the last two decades, phenolic compounds have become the one of the major research areas to preserve our environment. Due to severe impact of phenolics, US Environmental Protection Agency (EPA, 1979) had classified them as high toxic contaminants. The physical and chemical properties of phenol have been enlisted in table 1.12.

Table 1.12 Physical and chemical properties of phenol

Formula	C_6H_5OH
Molecular weight (g/mol)	94.14
Melting point (ºC)	43
Flash point	87 ºC
Water solubility(g/L at 25 ºC)	87
Boiling point (ºC)	181.8

Phenol is used in the preparation of slimicides, disinfectants, mouthwashes etc (ATSDR, 2008). Phenol is also used in the preparation of creams, shaving soaps because of its germicidal properties, in veterinary medicine as an antiseptic. Industrially phenol is used for the preparation of bakelite. Phenol is used in the production of drugs (Busca et al., 2008).

1.6.1.1. Toxic nature of phenol

Phenol is one of the major pollutants which are included in EPA (1979. Phenol is toxic to microbial cells, which was evaluated by Kahru et al., 2002. Exposure to phenol by orally causes disorders in nervous system, liver, cardiac depression and reduced blood pressure (Khare, 2011). Myocardial depression, eye irritation, skin rashes are causes reported by Tziotzios et al., 2005. World Health Organization set a maximum permissible limit as 0.1 ppm for phenolics reported by Kumaran and Paruchuri, 1996**.**

1.6.1.2. Research carried on phenol degradation in trickle bed reactor

Sa and Boaventura, 2001 isolated pure microbe of *Pseudomonas putida* which as inoculum for reactor start-up. After operating for 65 days, the phenol removal efficiency was recorded as 43%. If we consider phenol in the feed stream i.e 90 mg/l, the overall removal efficiency increases to 90%. They concluded that rate of phenol degradation is about 0.25 g/l which is greater than in stirred tank bioreactor. The degradation rate reported by Prieto et al., 2002 is higher than the values reported by Mordocco et al., 1999 and Pai et al., 1995. In latter cases, immobilization of *Rhodococcus erythropolis* cells was done in calcium alginate beads. This lowers the degradation rates. They concluded that this is due to the unstability of a gel support. Sgountzos et al., 2006 isolated the pure culture of *Pseudomonas fluorescens* from creosote contaminated site of tar factory at Ringe, Denmark. The experimentation is carried for 80 days. For first 15 days, phenol removal is about 45 -50%. After 50 days, phenol removal was about 55-57%. For entire 80 days, 98% of phenol degradation was achieved. They reported that degradation rate of phenol is higher in batch experiments than packed reactors. Chirwa and Smit, 2010 isolated *Pseudomonas Putida* as a phenol degrading species. They concluded that the bioreactor is capable of degrading 86% of phenol within 50 hours after the shock loading treatment. They reported that the bioreactor is capable of degrading 86% of phenol within 50 hours after the shock loading treatment. This may be due to the effect of the performance of the microbes by pre-exposure to the waste stream.

Table 1.13 Various phenol removal efficiencies in TBR listed by various researchers

Microorganism used	Packing medium	Phenol degradation	Reference
Pseudomonas putida	Poraver	Removal efficiency was 43%. If phenol in feed is 90 mg/l, the efficiency increases to 90%.	Sa et al., (2001)
Rhodococcus erythropolis	Biolite	Influent concentration-400 mg/l, rate of phenol degradation is 7.2 gm phenol/l per day.	Prieto et al., (2002)
Pseudomonas testosterone	Celite R-635	Phenol is fed at 20 mg/l it took 10 h for complete degradation.	Kim et al., (2002)

Alcaligenes, Acinetobacter	Gravel	It requires 5.5 hours for degradation when feed concentration is 1885 mg/l.	Tziotzios et al., (2005)
Phanerochaete chrysosporiumm, Trametes versicolor	Pinewood chips, foam glass beads	In R-1, phenol removal is 51.8% whereas it is 81% in R- 2.	Ehlers and Rose (2005)
Pseudomonas fluorescens	silicate sand	For entire 80 days, 98% of phenol degradation was achieved.	Sgountzos et al., (2006)
Isolated from Municipal treatment plant	liapor clay beads	Phenol removal rate is 2.3 g/l at initial phenol concentration of 4.9 g/l	Bajaj et al., (2008)
Isolated from Municipal treatment plant	liapor clay beads	Maximum phenol removal rate is 37.47 mmol/l. 94% degradation was achieved.	Bajaj et al., (2009)
Pseudomonas Putida	coarse stones	Phenol degradation is 86% within 50 hours.	Chirwa and Smit (2010)

Kim et al., 2002 conducted phenol degradation in conical flasks and a packed reactor. *Pseudomonas testosterone* was used to degrade phenol. Phenol was fed at a rate of 20 mg/l, degradation complete in 10 hours. Complete degradation in continuous stirred tank reactor was achieved within 16 h. They concluded that the rate of degradation is highest in PBR than CSTR. They also concluded that packed bed reactor was not suitable for aerobic microbes. Tziotzios et al., 2005 isolated a mixed bacterial culture of *Alcaligenes* and *Acinetobacter* from olive mill waste waters which contains significant amounts of phenolics. They compared the results of both batch reactor and pilot plant packed bed reactor for phenol degradation. They concluded that phenol removal was higher in packed bed reactor than batch reactor. They reported that 300 hours was requires to degrade 1850 mg/l of phenol in batch reactor where it requires less than 5.5 hours in packed bed reactor when phenol feed concentration is 1885 mg/l.

Ehlers and Rose 2005 isolated mycelial suspensions of *Phanerochaete chrysosporiumm, Trametes versicolor* and *Lentinula edodes* as inoculum for reactor. They fabricated two different reactors with packings pinewood chips and foam glass beads. In Reactor-1, they didn't added glucose. In Reactor -2 they added glucose in reduced amount because of absence of carbon content. They reported that phenol removal efficiency in Reactor -1 was recorded as 51.8% whereas it was recorded as 81% in Reactor- 2. This may be due to

the presence of available glucose in Reactor-2. Bajaj et al., (2008, 2009) designed an aerobic and anaerobic reactors for the biodegradation of high phenol in synthetic water. The biomass collected from a sludge plant. They evaluated performance of reactor on degradation basis. They reported that, under aerobic conditions, the phenol removal rate is 2.3 g/l at initial phenol concentration of 4.9 g/l whereas under anaerobic conditions, the maximum phenol removal observed to be 39.47mmol/l.

1.6.2. Effect of external mass transfer with biodegradation

1.6.2.1. Biodegradation

Mass balance for phenol in the trickle bed bioreactor at steady state, considering spherical immobilized beads, no axial dispersion and plug flow, can be established as (Chen and Lin, 2007)

$$(\frac{hQ}{W})\frac{dC}{dz} = -r \qquad (1.5)$$

Assuming first-order biodegradation (valid assumption at low phenol concentrations by Dursun and Tepe, 2005), the relation between the observed biodegradation rate constant k_p (L/g h) and phenol concentration C (mg/L) in TBR can be expressed as

$$r = k_p C \qquad (1.6)$$

Substituting equations (1.5), (1.6)

$$(\frac{hQ}{W})\frac{dC}{dz} = -k_p C \qquad (1.7)$$

Integrating Eq. (1.7) with boundary condition of $C = C_0$ at $z = 0$ and $C = C$ at $z = h$, Eq. (1.8) is obtained. Different values for k_p can be calculated by using Eq. (1.8).

$$\ln(\frac{C_o}{C}) = \frac{W}{Q}k_p \qquad (1.8)$$

1.6.2.2. External film diffusion and mass transfer

As the liquid passes over the immobilized beads in a PBR, regions develop near the periphery of the beads where the velocity of the fluid is less (Nath and Chand, 1966). of Fluid stagnant film exists in such regions near the surface of the beads. Now, the substrate (such as phenol in the present study) needs to be transported through this fluid film by

molecular diffusion (Nath and Chand, 1966). The rate of film diffusion is proportional to the driving force and area for mass transfer.

Hence, the following equation can be developed for the mass transfer:

$$r_m = k_m A_m (C - C_S) \tag{1.9}$$

Am can be calculated experimentally by

$$A_m = \frac{6}{\rho_p d_p} = \frac{6}{2.5 * 4} = 6\,\text{cm}^2/\text{gm} \tag{1.10}$$

1.6.2.3. Biodegradation and mass transfer (Banerjee and Ghosal, 2016)

The biodegradation rate of phenol on immobilized beads can be expressed as

$$r = kA_m C_S \tag{1.11}$$

Now, the rate of phenol removal and the rate of mass transfer will be same at steady state. Equating (1.9) and (1.11), C_s can be calculated as:

$$C_S = \frac{k_m C}{k + k_m} \tag{1.12}$$

From (1.6), (1.11) and (1.12), the observed biodegradation rate (k_p) can be expressed as:

$$k_p = \frac{kA_m k_m}{k + k_m} \tag{1.13}$$

Or

$$\frac{1}{k_p} = \frac{1}{A_m k_m} + \frac{1}{kA_m} \tag{1.14}$$

Eq. (1.14) shows the effect of biodegradation and mass transfer rates on the rate of phenol biodegradation.

1.6.2.4. Model development (Banerjee and Ghosal, 2016)

Usually, Colburn factor is used for correlation with mass transfer coefficient which is dimensionless group, defined as

$$J_D = \frac{k_m \rho}{G} \left(\frac{\mu}{\rho D_f}\right)^{2/3} = K N_{\text{Re}}^{-(1-n)} \tag{1.15}$$

Where J_D can be defined in relation with reynolds number (N_{Re}). D_f, r and m represents diffusivity, density and viscosity of feed fluid, respectively. The superficial mass velocity, G (g/cm^2 h) can be calculated as:

$$G = \frac{Q\rho}{1000 * A} \tag{1.16}$$

Various correlations of mass transfer have been reported in literature indicating the dependence of both of these values on bacterial strain as well as the configuration and operational parameters (Tepe, A.Y. Dursun, 2008). Reported values of n ranges from 0.1 to 1.0 (Nath and Chand, 1966).

From Eq. (1.15), the mass transfer coefficient can be expressed as:

$$k_m = NG^n$$

where,

$$N = \frac{K}{\rho}\left(\frac{\mu}{\rho D_f}\right)^{-2/3}\left(\frac{d_p}{\mu}\right)^{-(1-n)} \tag{1.17}$$

Substituting Eq. (1.17) in Eq. (1.14), the following equation can be developed:

$$\frac{1}{k_p} = \left(\frac{1}{NA_m}\right)\left(\frac{1}{G^n}\right) + \frac{1}{kA_m} \tag{1.18}$$

Eq. (1.18) implies that the plot of $1/k_p$ vs. $1/G^n$, based on the experimentally measured values, will yield a straight line having slope $1/NA_m$ and intercept $1/kA_m$. Thus, by assuming different values of K and n, various Am values can be calculated. Now, comparing these calculated values of Am with the experimentally obtained Am value, most suitable n and K values can be predicted to propose the best external mass transfer correlation for our present study of phenol biodegradation by immobilized cells. Table 1.14 shows different mass transfer correlations reported in literature.

Table 1.14 Different Mass transfer correlations reported in literature (Banerjee and Ghoshal, 2016)

Author	**Mass transfer correlation**	**Value of K**
Tepe and Dursun	$j_D = 1.34N_{Re}^{-0.35}$	1.34
Rovito and Kittrell	$j_D = 1.625N_{Re}^{-0.507}$	1.625
Wilson and Geankoplis	$j_D\varepsilon = 1.09N_{Re}^{-0.67}$	$1.09/\varepsilon = 3.47$

Nath and Chand	$j_D = 5.7 N_{Re}^{-0.59}$	5.7
Dizge and Tansel	$j_D = 5.7 N_{Re}^{-0.18}$	5.7

1.7. Objectives of the work

The main objectives of the present investigation are;

- Characterization of trickle bed bioreactor for hydrodynamics, mass transfer and biodegradation performance.
- To evaluate the effect of superficial gas and liquid velocities and surface tension on two phase bed pressure drop and dynamic liquid saturation.
- To evaluate the effect of flow velocities of the gas and liquid phases on solid-liquid mass transfer and gas-liquid mass transfer.
- To investigate the effect of initial concentration of phenol and liquid flowrate on biodegradation of phenol.
- To evaluate the combined effect of external mass transfer and biodegradation reaction on the observed biodegradation of phenol by a correlation between the Colburn factor (J_D) and Reynolds number (N_{Re}).

1.8. Layout of the thesis

This thesis consists of mainly of four chapters; Introduction and Literature review, Experimental Methodology, Results and discussion, Conclusions.

***Chapter 1*:** Deals with the introduction, literature review and objectives of present work.

***Chapter2*:** Deals with different methodologies of experimental work and techniques used for the characterization of trickle bed bioreactor.

***Chapter 3*:** Discuss about results obtained from hydrodynamic, mass transfer studies and microbial phenol degradation studies.

Chapter 4: Deals with conclusion of present work and future scope based on outcomes of present work.

Chapter 2

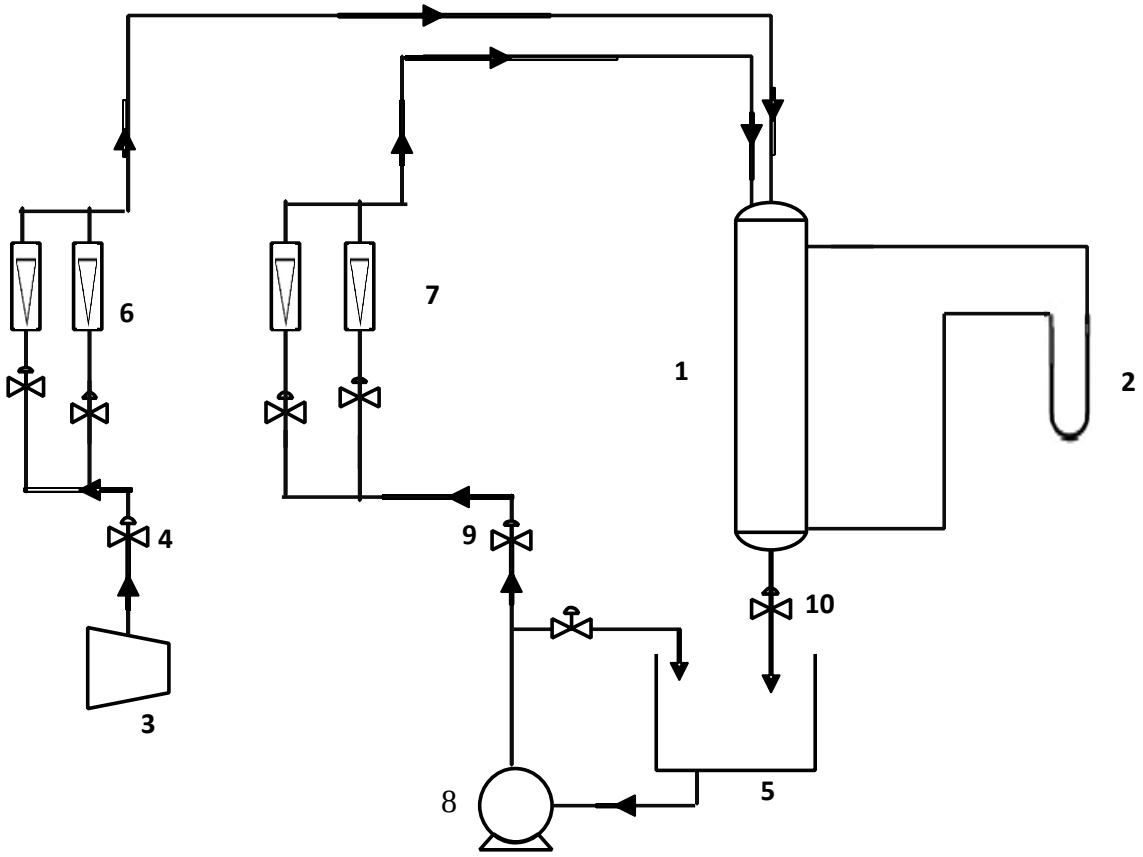
Experimental Methodology

2.1. Introduction

This chapter describes the detailed experimental setup and techniques used for hydrodynamic, solid-liquid and gas-liquid mass transfer and microbial degradation experiments. This chapter also gives the information about materials used for the characterization of effluents of solid-liquid, gas-liquid mass transfer and biodegradation experiments. Figure 2.1 shows the schematic representation of the experimental setup used in this study. Figure 2.3 gives the photographic representation of the experimental setup.

2.2. Experimental setup

Trickle bed mainly consists of three sections; the test section, the gas-liquid distributor section and the gas-liquid disengagement section. Test section is a cylindrical Plexiglas column of 0.091 m internal diameter and 1.28 m height. The gas-liquid distributor is located at the top of the test section which sends uniformly distributed liquid and gas mixture to the test section interfaced with a perforated plate (figure 2.2) consisting of 127 holes of 3 mm size. The gas–liquid disengagement section at the bottom of the column is a conical section of 0.31m height, assembled to the test section. The packing material in the column is supported on a stainless steel mesh. Firstly gas was pumped into the column at a desired flow rate using air rotameters and then the liquid was pumped using water rotameters at a desired flow rate. Four calibrated rotameters with different ranges each for water as well as for air were used for the accurate record of the flow rates. Table 2.1 gives the characteristics of experimental set-up and packing material.



1- Plexiglas column, 2- U tube manometer, 3-Air compressor 4- Air control valve, 5- Liquid storage tank, 6- Air Rotameter, 7- Liquid rotameter, 8- Pump, 9- Liquid control valve, 10- Liquid outlet valve

Figure 2.1 Schematic representation of the experimental setup

Figure 2.2 Photographic representation of distributor plate

Table 2.1 Characteristics of experimental set up and packing material

Test section (Cylindrical Plexiglas column)	
Column diameter	0.091 m
Column height	1.28 m
Gas-liquid distributor section (fructo-conical)	
Height, m	0.31 m
Diameter of the ends, m	0.1 m
Gas-liquid disengagement section (fructo-conical)	
Height, m	0.31 m
Diameter of the ends, m	0.1 m
Liquid reservoir	
Capacity, lit.	50 lit
Bed characteristics	
Packing material	Glass beads
Diameter of particle	0.004 m
Density of particle	2500 kg/m^3
Porosity	0.319

2.3. Techniques for Measuring Properties of Fluids

2.3.1. Liquid Density

The densities of water and aqueous solutions of SLS has been measured using standard 10 ml specific gravity bottle. The recommended standard procedure was followed.

2.3.2. Viscosity of Liquids

Viscosity of the liquids used in the experiment has been determined by using standard Ostwald (U-tube) viscometer. The standard procedure for determination of viscosity as recommended for Ostwald viscometer has been followed.

2.3.3. Surface Tension

Surface tension is the contractive quality of the surface of a liquid that allows it to resist external force. Tensiometer is an instrument used to measure the surface tension (γ) of liquids.

Figure 2.3 Photographic representation of the experimental setup

Table 2.2 Properties of Liquids and gases

Fluid phase	**Density, (kg/m^3)**	**Viscosity, (kg/m.s)**	**Surface tension, (N/m)×10^{-3}**
Air	1.166	1.794x10^{-5}	-
Water	995.7	0.000798	72.3
100 ppm phenol solution	993.5	0.000799	71.48
200 ppm phenol solution	993.86	0.000805	71.126
400 ppm phenol solution	994.0	0.000812	70.954
500 ppm phenol solution	994.45	0.000813	70.743
600 ppm phenol solution	994.7	0.000815	70.587
800 ppm phenol solution	995.2	0.000826	70.586
1000 ppm phenol solution	995.77	0.000837	70.131
1250 ppm phenol solution	996.82	0.000857	69.663
1500 ppm phenol solution	998.07	0.000876	68.130

2.1. Operating Conditions and Procedures

The experiments were performed in trickle and pulse flow regime for a range of superficial liquid and gas velocities. The range of operating conditions in the present work was given in Table 2.3.

2.1.1. Hydrodynamic studies

For the measurement of pressure drop across the bed, the pressure ports have been provided and fitted to the manometers filled with mercury as manometric fluid. Adjust the initial level of manometer to zero level. Firstly air was pumped to the column at a desired flow rate using air rotameters and then the liquid was pumped at a desired flow rate using water rotameters. Due to the flow of liquid and gas through trickle bed, some fluctuations can be seen in manometer level. After five minutes, make sure that the steady state was reached. Note the readings of manometer. This procedure was repeated for different values of liquid and gas flowrates.

The dynamic liquid saturation was determined by drainage method. In drainage system, the inlet and outlet valves of the system were closed simultaneously. The liquid in the column was collected for 30 minutes. Note the volume of liquid collected. This procedure was repeated for different values of liquid and gas velocities. The ratio of volume of liquid collected to the reactor volume gives dynamic liquid holdup. Dynamic liquid saturation is the ratio of dynamic liquid holdup to porosity of bed.

Table 2.3 Range of operating conditions in the present work

A. Hydrodynamics studies	
System	Air/Water, Phenol solution/Glass Beads
Superficial liquid velocity, m/s	0.0026- 0.0231 m/s
Superficial gas velocity, m/s	0.026-0.128 m/s
B. Solid-Liquid mass transfer studies	
System	Air/Water/Glass beads coated with benzoic acid
Superficial liquid velocity, m/s	0.0026-0.013 m/s
Superficial gas velocity, m/s	0.026-0.205 m/s
C. Gas-Liquid mass transfer studies	
System	Air, Nitrogen/ Water/Glass beads
Superficial liquid velocity, m/s	0.0026-0.0179 m/s
Superficial gas velocity, m/s	0.026-0.128 m/s
D. Microbial degradation studies	
System	Air/ Phenol solution/Glass beads
Liquid flow rate, LPM	2-4 LPM
Gas flow rate, LPM	3 LPM

2.1.2. Solid-liquid mass transfer studies

For solid-liquid mass transfer studies, dissolution technique was used. In this technique, glass beads were coated with molten benzoic acid when it is heated to its melting point. The column was divided into three sections for employing dissolution method. The first section was 50cm section at the bottom of the column packed with 4 mm glass spheres. The second section was 32cm section filled with active particles, 4 mm glass spheres coated with benzoic acid. The column was then filled, up to 128 cm, with glass beads. After loaded of column the distributor cap was placed on the top and the column was closed. Air and water were pumped and fed to the top of the column at a desired flow rates by using air rotameters and water rotameters respectively. The liquid samples were collected and analysed by titrating against sodium hydroxide solution.

2.1.3. Gas-liquid mass transfer studies

For gas-liquid mass transfer studies, both absorption and desorption techniques were used. In absorption method, air and water were used as gas and liquid phase respectively. When both water and air were introduced into column, the oxygen from air transfers to water, so that there is an increase in concentration of dissolved oxygen in effluent stream. In desorption method, nitrogen and water were used as gas phase and liquid phases respectively. In this process, as nitrogen having zero dissolved oxygen concentration, there is a transfer of oxygen from water to nitrogen so that there is a decrease in concentration of dissolved oxygen in water. Gas and liquid phases were pumped and fed to the top of the column at a desired flow rates by using gas rotameters and liquid rotameters respectively. The liquid samples were collected and analysed by using D.O meter.

2.1.4. Microbial degradation of phenol

2.1.4.1. Selection of microorganisms

Microorganism *Pseudomonas putida* was used for degradation of phenol in trickle bed bioreactor. Microorganism was taken from one of the research scholars of chemical engineering department, NIT Rourkela.

2.1.4.2. Chemicals and Reagents

All the chemicals & reagents were of analytical grade. All the chemicals were procured from Merck, Fischer and HIMEDIA.

2.1.4.3. Preparation of phenol Stock Solution

The phenol stock solution was prepared by adding 10g of phenol to double distilled autoclaved water and the final volume should be 1000ml. The final concentration of the stock solution was 10000 PPM (10000 mg/L) and the stock solution was diluted to the required concentration for its use in the experiments.

2.1.4.4. Inoculum production medium and Reaction medium

The MSM composition used in the study is as per Mordocco et al (1999). Phenol was used as a sole carbon source and phenol solution was added to MSM at a concentration of 100 PPM. The media was sterilized by autoclaving and the phenol was used after sterilization.

2.1.4.5. Experimental Procedure

Inoculum production medium was sterilized in an autoclave and incubated for 24 hours at 30^{o}C. The incubated medium was added to the bed from the top of the column. The reaction medium was prepared as given per above composition for 20 liters of water. The amount of phenol added to reaction medium, such that the final concentration must be 1000 ppm. Samples were collected for every 3 hours and analysed for final concentrations of phenol.

Table 2.4 Composition of inoculum production medium and reaction medium

Component	Inoculum Production Medium (mg/lit)	Reaction Medium (mg/lit)
K_2HPO_4	750	95
NaCl	60	60
KH_2PO_4	840	105.5
$FeCl_3$	60	60
$(NH_4)_2SO_4$	488	488
$CaCl_2$	60	60
$MgSO_4$	60	60

2.2. Analytical Methods

2.2.1. Benzoic acid concentration estimation

Sodium hydroxide of 0.01N was prepared in a round bottomed flask of 500 ml. The liquid samples were collected and titrated against 0.01 N sodium hydroxide solution to determine benzoic acid concentration in effluent samples. The phenolphthalein was used as indicator.

2.2.2. Dissolved oxygen estimation

Dissolved oxygen content can be estimated by two ways; by using winkle's method or by dipping a dissolved oxygen sensor directly. In this work, Inlet and outlet concentrations of oxygen in water were measured by D.O sensor (HACH LDO HQ10).

2.2.3. Phenol concentration estimation

Direct photometric method (APHA, 1998) was used for estimation of phenol effluent samples. Firstly, the samples were centrifuged at 8000 rpm for 10 minutes. The

supernatant was used for determination of phenol concentration. In this method, Phenolic compounds in supernatant reacts with 4-aminoantipyrine at a pH 7.9 ± 0.1 in the presence of potassium ferricyanide to give reddish-brown antipyrene dye with maximum absorbance at 500 nm. Determination of phenol concentration was done by using UV/Visible spectrophotometer. Procedure for estimation and calibration graph of phenol are given in *Appendix-A.*

Chapter 3

Results and Discussion

3.1. Hydrodynamic Studies

3.1.1. Pressure drop

Figures 3.1, 3.2, show the variation of bed pressure drop with liquid velocity for non-foaming (water) and foaming systems (phenol solution) respectively. At constant gas velocity, for both the systems, the pressure drop increases with liquid velocity. At lower velocities of gas and liquid, bed pressure drop increases slightly but beyond a particular liquid velocity, there is a significant increase in pressure drop which may be because of the transition from trickle flow to pulse flow regime as reported by Bansal et al. 2005. As seen from figure 3.2, for 500ppm phenol solution, the pressure drop is higher than air-water system because of the foaming effect of phenol solution which induces more bed pressure drop according to Sodhi et al. 2011.

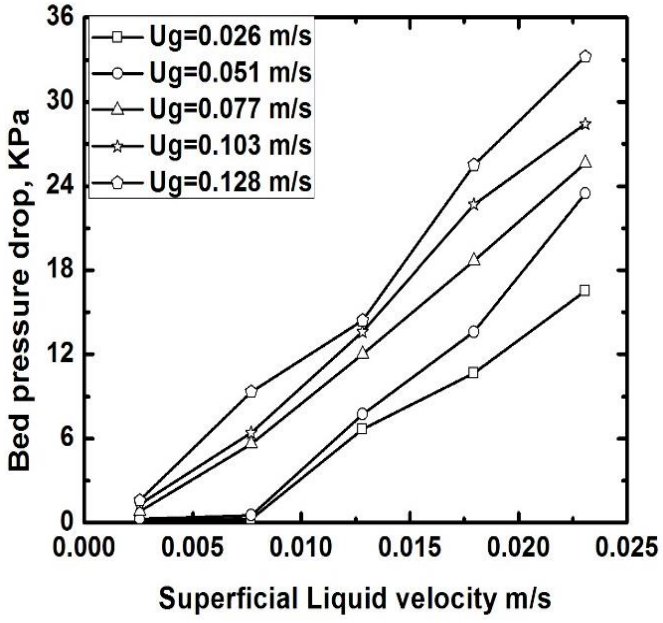


Figure 3.1 Variation of pressure drop with liquid velocity (water as the liquid)

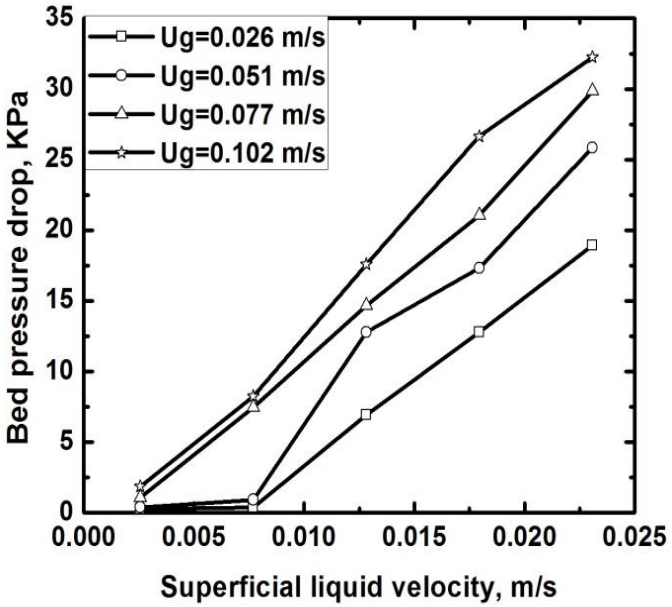


Figure 3.2 Variation of pressure drop with liquid velocity (phenol solution as the liquid)

Figures 3.3, 3.4 show the variation of pressure drop with gas velocity for non-foaming and foaming systems respectively. At constant liquid velocities, for both foaming and non-foaming system, pressure drop increases with gas velocity. At lower gas velocities, pressure drop increases slightly with gas velocity. But at higher liquid and gas velocities, pressure drop increase significantly in both systems.

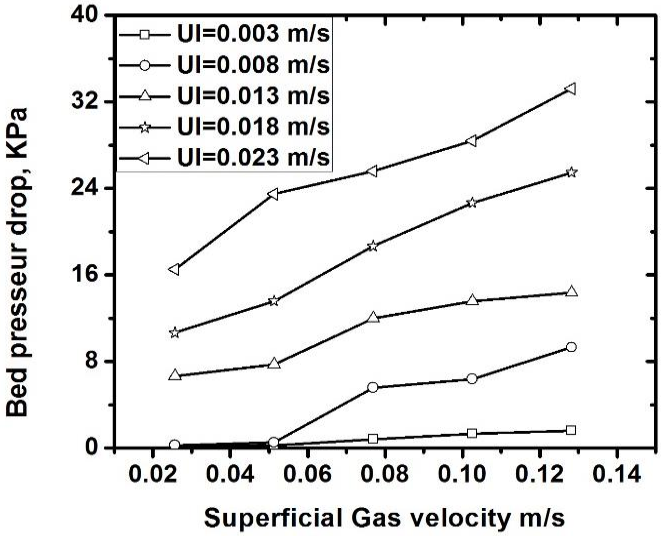


Figure 3.3 Variation of pressure drop with gas velocity (water as the liquid)

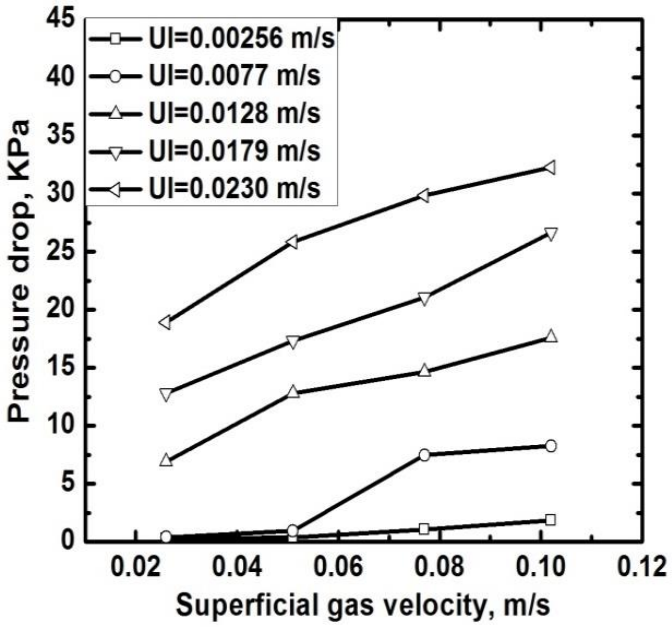


Figure 3.4 Variation of pressure drop with gas velocity (phenol solution as the liquid)

Surface tension of water is more than that of phenol solution. As lower surface tension leads to higher pressure drop because of foaming (Bansal et al, 2008), thus the variation on bed pressure drop by surface tension property is also studied. Figure 3.5 shows the variation of surface tension on pressure drop. By increasing phenol concentration or decreasing surface tension, an increase in bed pressure drop is observed.

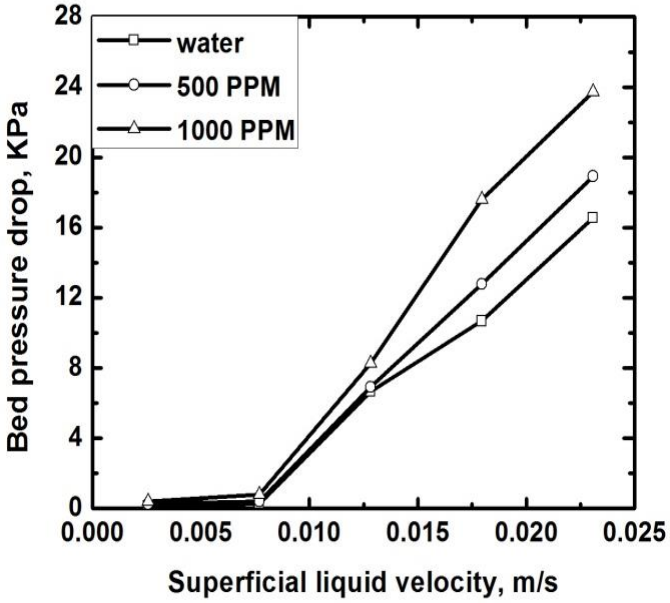


Figure 3.5 Effect of surface tension on bed pressure drop at superficial gas velocity of 0.026 m/s

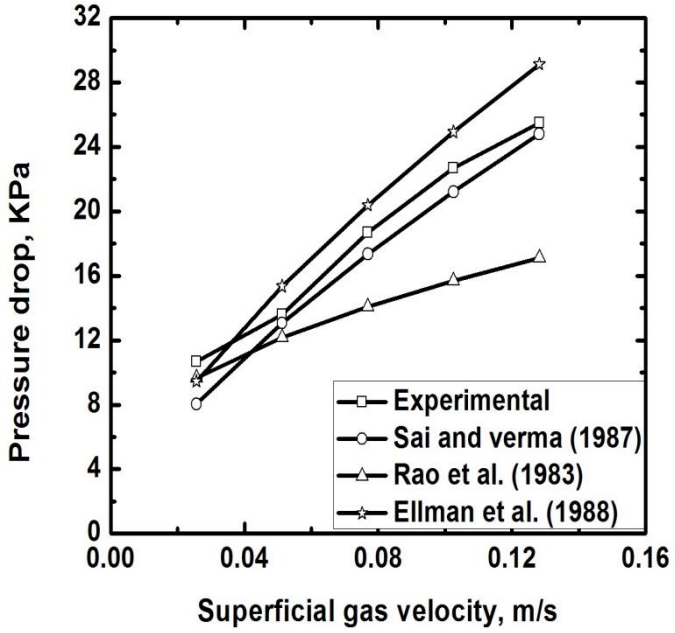


Figure 3.6 Comparison of pressure drop results with previous studies

Figure 3.6 shows a comparison of pressure drop results obtained in the present investigation with those of previous studies. The experimental results are almost closer to the results of Ellman et al., 1988 and Sai and Varma, 1987. The Present experimental results are almost between the ones of Ellman et al., 1988 and Sai and Varma, 1987. Rao et al., 1983 has conducted experiments in packed beds for both foaming and non-foaming systems. At lower gas velocities the experimental results are close to the results of Rao et al., 1983, but at higher gas velocities, the experimental results are almost 1.5 times greater.

3.1.2. Dynamic liquid saturation

The variation in dynamic liquid saturation with superficial liquid velocity for air- water and air-50ppm phenol solution systems are shown in figure 3.7, 3.8. It is observed that for both systems, increase in liquid velocity increases the dynamic liquid saturation. This may be due to the inventory and the space occupied by the gas at lower liquid velocities, is occupied by the liquid at higher liquid velocities.

Figures 3.9, 3.10 show the variation of liquid saturation with superficial gas velocity on for air- water and air-500 ppm phenol solution systems. It is observed that by increasing gas velocity, there is decrease in dynamic liquid saturation. Normally, void spaces are shared by both gas and liquid phases. In figure 3.10, for air-500 ppm phenol solution,

dynamic liquid saturation decreases significantly with gas velocity. This may be due to foam formation in higher interaction regimes, which decreases dynamic liquid saturation. For all the cases the liquid saturation is found to be less in case of air-phenol solution than for the air-water system.

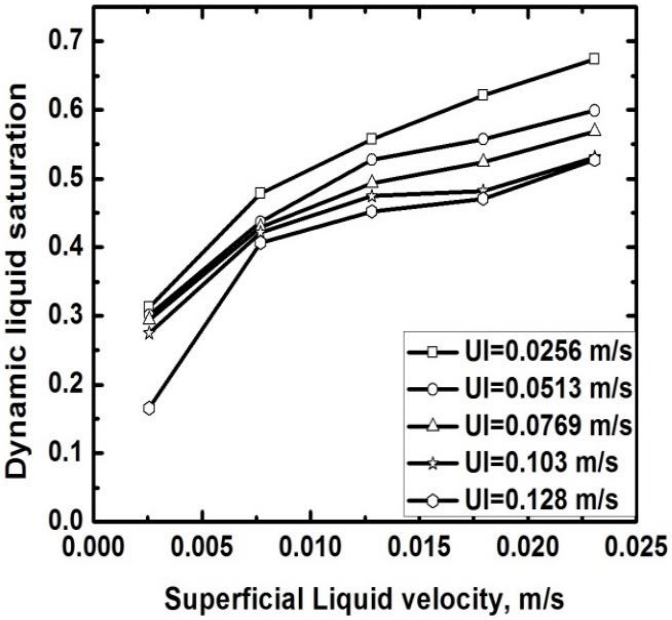


Figure 3.7 Variation of dynamic liquid saturation with liquid velocity (water as liquid)

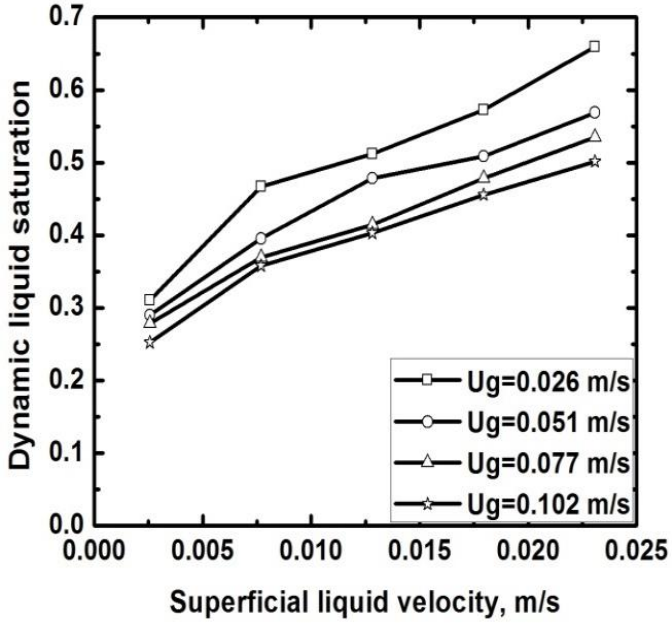


Figure 3.8 Variation of dynamic liquid saturation with liquid velocity (phenol solution as liquid)

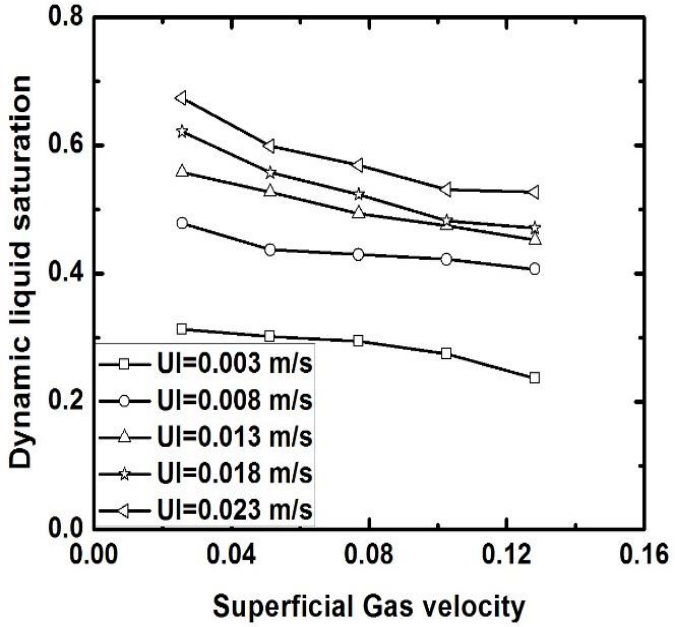


Figure 3.9 Variation of dynamic liquid saturation with gas velocity (water as liquid)

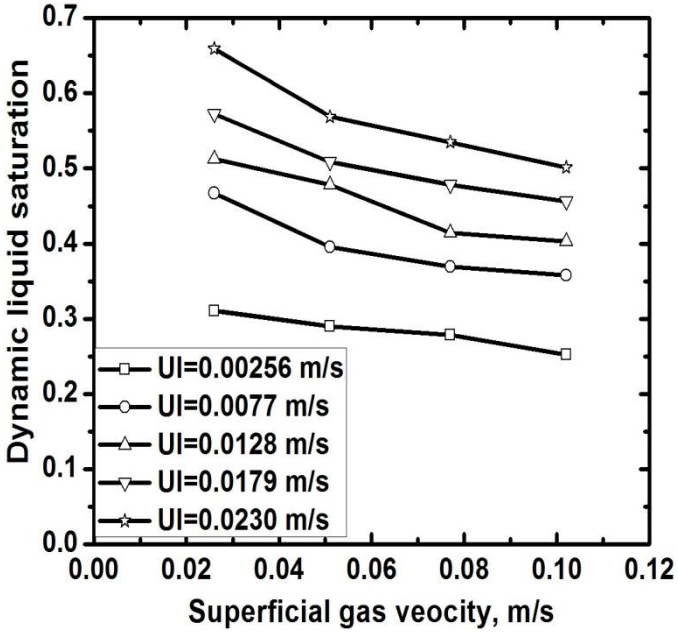


Figure 3.10 Variation of dynamic liquid saturation with gas velocity (phenol solution as liquid)

Figure 3.11 shows the effect of surface tension on liquid saturation at gas velocity of 0.077 m/s with varying liquid velocity. Lower value of liquid saturation results for higher concentrations of phenol. The phenol solutions (lower surface tension than water) produce

excess foam in higher interaction regimes, which results in decrease in dynamic liquid saturation values. Due to the foaming effect it is observed that higher concentration of phenol in aqueous solution yields lower values of dynamic liquid saturation. Similar results are also obtained by Sodhi and Bansal, 2011.

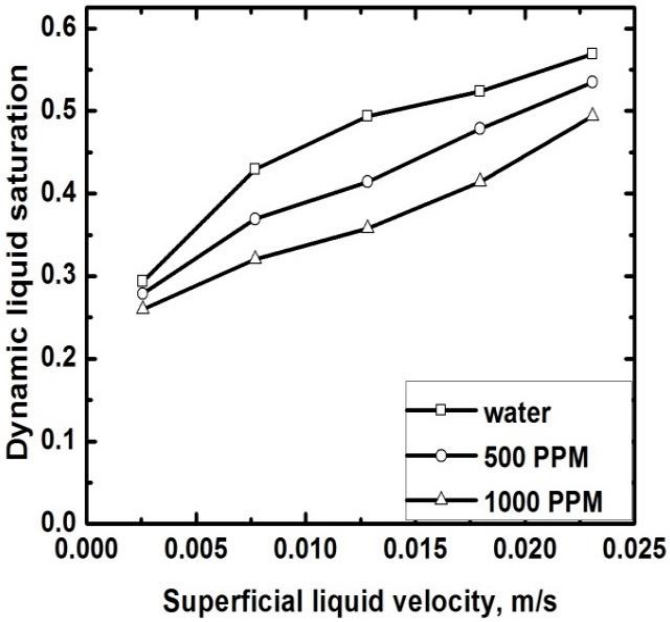


Figure 3.11 Effect of surface tension on dynamic liquid saturation at superficial gas velocity of 0.077 m/s

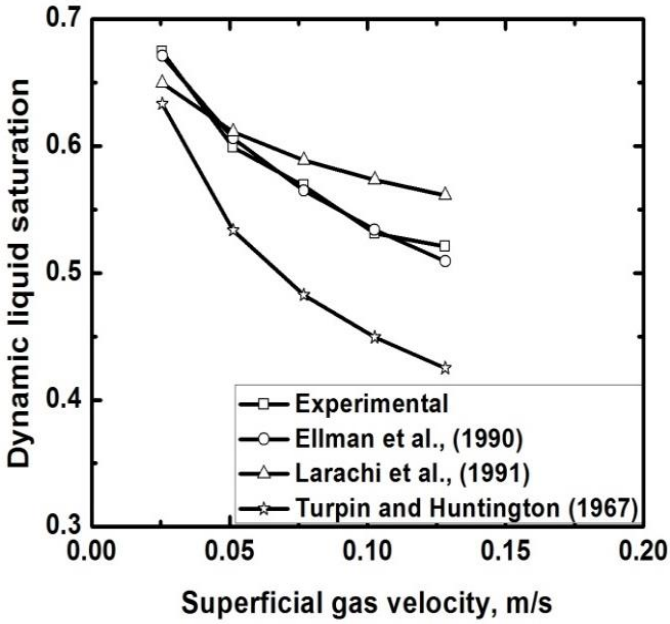


Figure 3.12 Comparison of liquid saturation results with previous studies

Figure 3.12 shows the comparison of results obtained in the present investigation and with those of previous studies. The experimental results are almost same to the ones obtained by Ellman et al., 1900 The agreement with the results of Lararchi et al., 1991 is close at lower gas velocities, but as the gas velocity increases the present results underestimates the ones of Lararchi et al., 1991. This may be because of experiments by Lararchi et al., 1991 is using different liquid phases such as ethanol, ethylene glycol solutions which are foaming liquids and the gas phase used was nitrogen gas which is almost similar to water in properties. Turpin and Huntington, 1967 experiments were mainly based on viscosity property, which is non effective for foaming liquids. The present experimental results are different and nearly 1.2 times greater than values reported by Turpin and Huntington 1976.

3.2. Mass Transfer Studies

3.2.1. Volumetric solid-liquid mass transfer coefficients

Figure 3.13 shows the variation of solid-liquid mass transfer coefficients with superficial liquid velocity. Mass transfer coefficient increases linearly with liquid velocities.

Figure 3.14 shows the variation of solid-liquid mass transfer coefficients with gas velocities. At lower gas velocities, mass transfer coefficients are little influenced by gas velocities due to low interactions as the flow regime may be trickles one. But at higher gas velocities, mass transfer rate increases may be due to the change in flow regime from trickle flow to pulse flow. Increase in mass transfer rates may be due to increased effective interfacial area in pulse flow regime than in trickle flow regime (Hirose et al., 1976).

Figure 3.15 shows the comparison of experimental results obtained in the present investigation and with those of previous studies. It is evident that the studies of electro-chemical technique by Rao and Drinkenburg, 1985 and Latifi et al., 1988 results in higher mass transfer coefficients than present work. The higher values of mass transfer rates than Lakota and Levec, 1980 is because of higher solubility of benzoic acid than naphthalene.

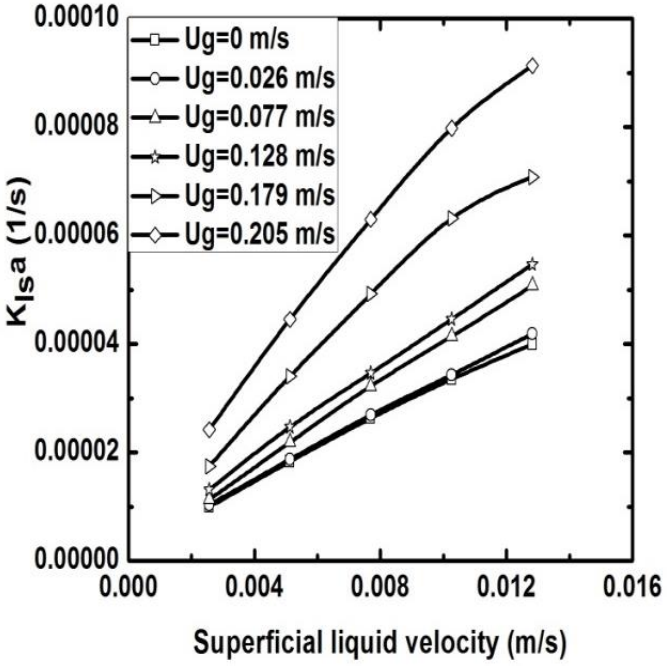


Figure 3.13 Variation of solid-liquid mass transfer coefficients with liquid velocity

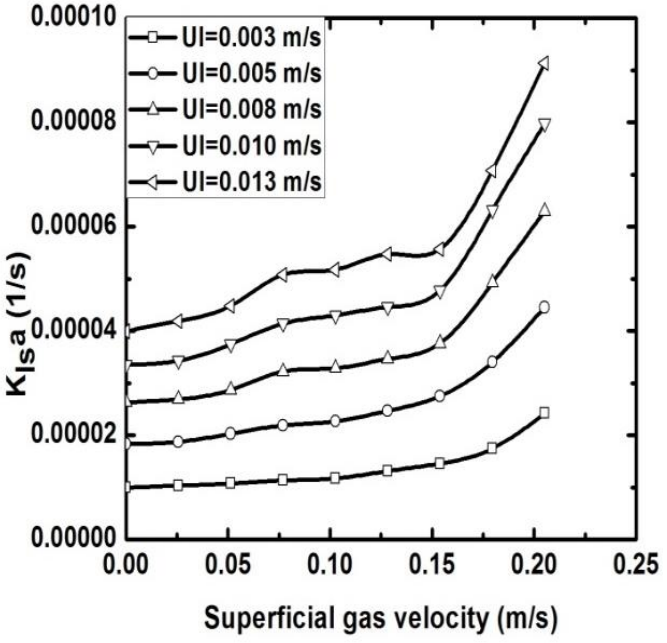


Figure 3.14 Variation of solid-liquid mass transfer coefficients with gas velocitity

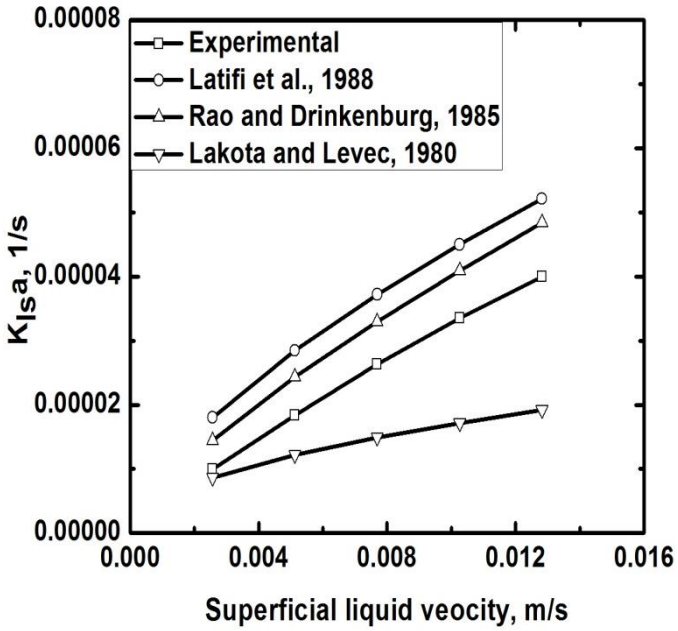


Figure 3.15 Comparison of experimental results with previous studies at gas velocity 0.179 m/s

3.2.1. Volumetric gas-liquid mass transfer coefficients

Both absorption and desorption methods as discussed in chapter-2 were used to determine the gas-liquid mass transfer coefficient. The results of both the methods follow the similar trend but in desorption method the coefficients obtained is little higher as shown in figure 3.16. Thus the results of the desorption method which is considered to be better because of higher driving force concentration differences (Lara-Marquez et al, 1994).

Figure 3.17 shows the variation of volumetric gas-liquid mass transfer with superficial liquid velocity. At lower liquid velocities, mass transfer coefficients increase with liquid velocity. The effect is little more pronounced at higher velocities, may be due to the transition from trickle flow regime to pulse flow regime (Hirose et al., 1974).

Figure 3.18 shows the variation of volumetric mass transfer coefficients with superficial gas velocities. At lower gas velocities, it can be observed that mass transfer coefficients are almost constant and independent of gas velocities. This may be due to poor distribution of liquid (Hirose et al., 1974). But at higher flow rates, an little increase in mass transfer coefficients is observed may be due to the transition from trickle flow to pulse flow regime.

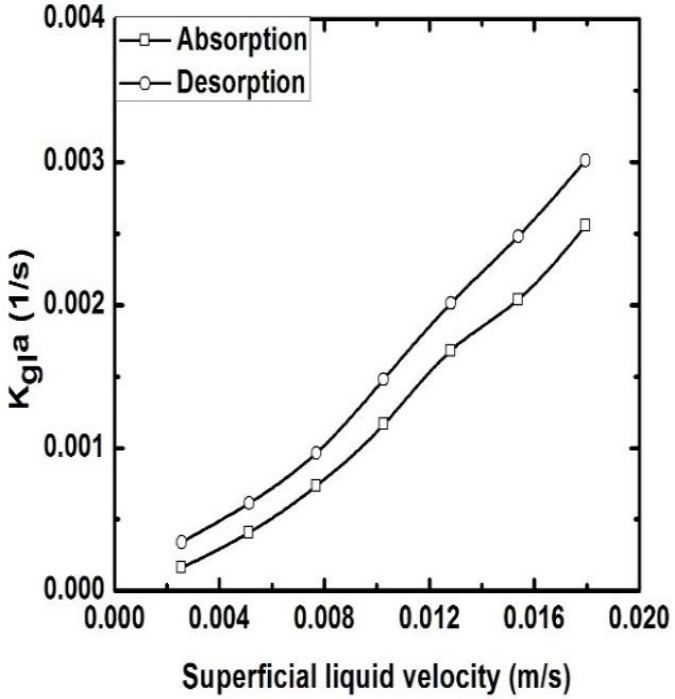


Figure 3.16 Comparison of mass transfer coefficients in absorption and desorption

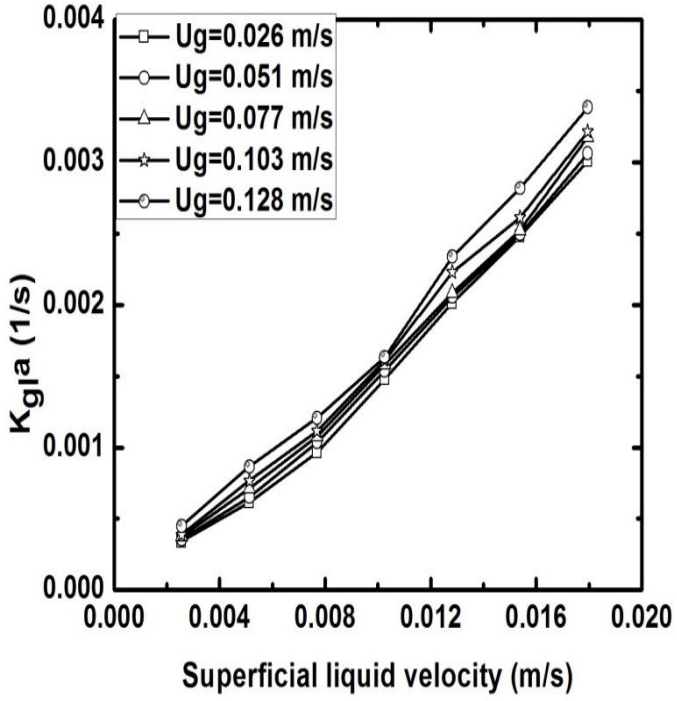


Figure 3.17 Variation of gas-liquid mass transfer coefficients with liquid velocities

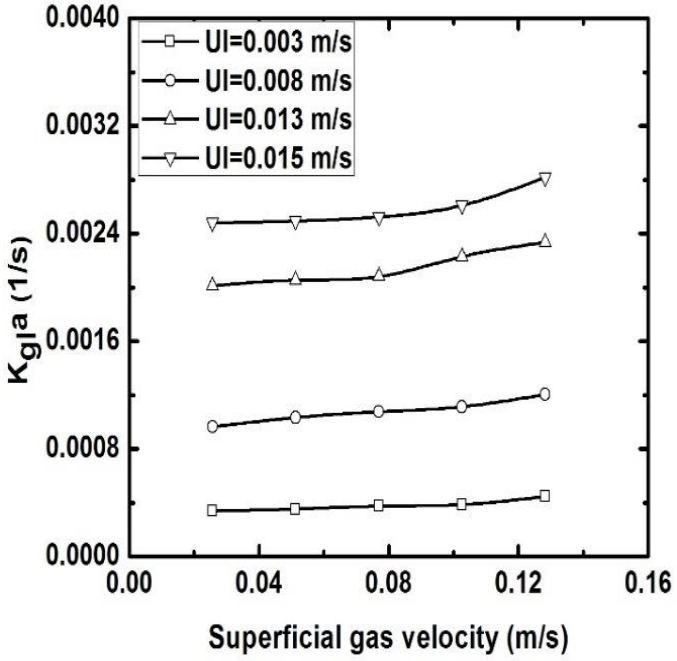


Figure 3.18 Variation of gas-liquid mass transfer coefficients with gas velocities

3.3. Microbial degradation of phenol

Phenol biodegradation studies by *Pseudomonas putida* on glass beads in the trickle bed leads to the following results. Figure 3.19 shows the FESEM image of immobilized *Pseudomonas putida* on glass beads.

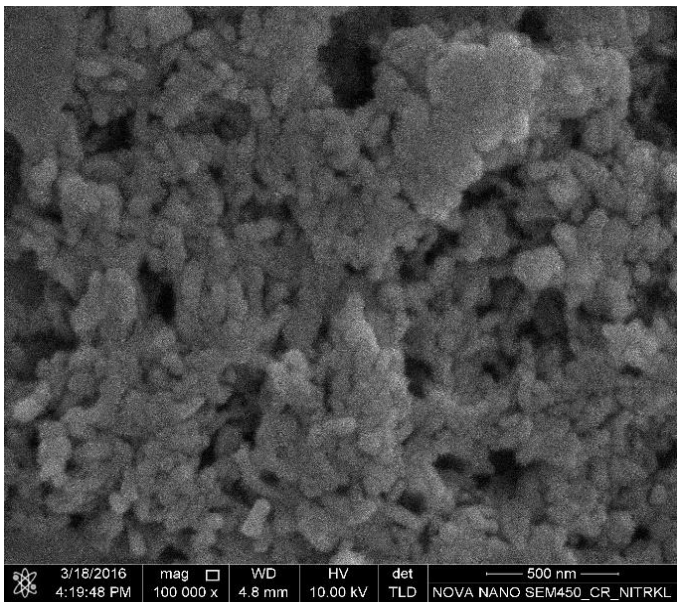


Figure 3.19 FESEM image of immobilized Pseudomonas putida on glass bead

Phenol degradation behavior was studied between 100-1500 ppm of initial phenol concentrations in the semi-batch mode. The liquid phase flow rate was constant at 3 lpm. Figure 3.20 shows the effect on phenol degradation in percentage at different initial concentrations from 100 to 1000 ppm.

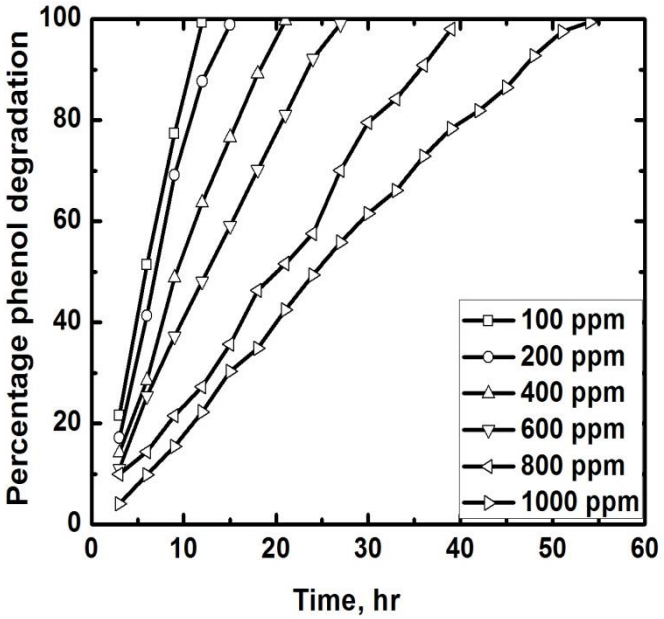


Figure 3.20 Effect of initial concentration on percentage phenol biodegradation

Figure 3.21 also show the effect initial concentration of phenol on degradation from 1000 to 1500 ppm. It shows that the phenol is completely degraded by *Pseudomonas putida* upto an initial concentration of 1000 ppm. Percentage degradation was only 81%, 43% for 1250 ppm and 1500 ppm phenol solutions respectively. That means the phenol biodegradation reduces at higher concentrations like 1250, 1500 ppm. The inability of *Pseudomonas putida* to degrade phenol completely may be due to substrate (phenol) inhibition and the toxicity of phenol at higher concentrations as reported by Luo et al., 2009.

The variation of flow rate on degradation rate was investigated by operating the trickle bed at different flow rates ranging from 2-4 lpm with initial concentration of 200 ppm. From figure 3.22, low rates of biodegradation were observed at low flow rates this may be due to the higher mass transfer resistance at the liquid film layer around bead which might be reduced by increasing the flow rate (Tepe and Dursun, 2008).

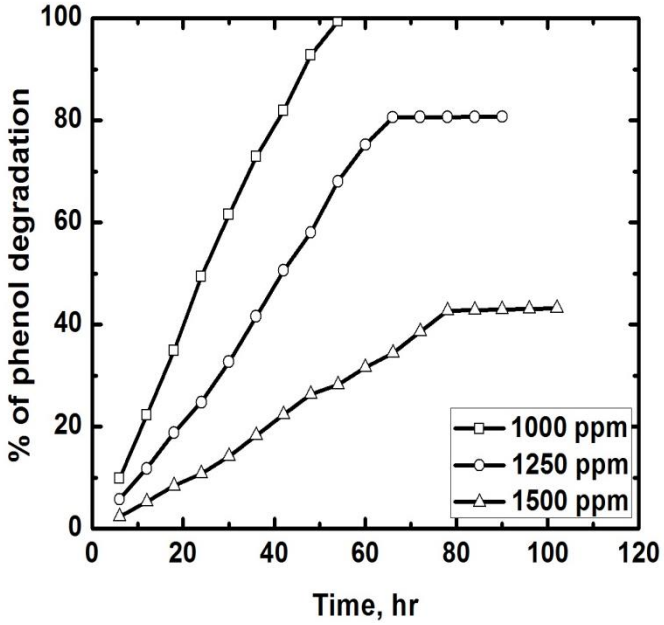


Figure 3.21 Effect on percentage phenol degradation at higher concentrations of phenol

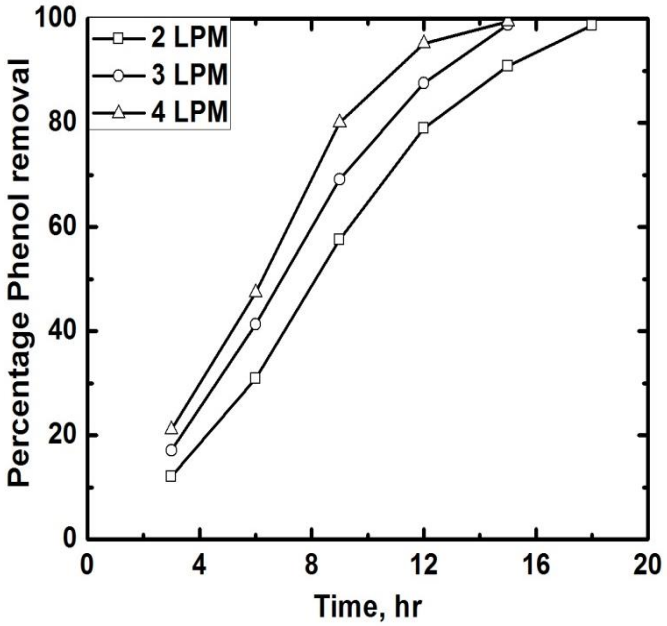


Figure 3.22 Effect of liquid flow rates on percentage phenol degradation

A correlation is developed from the experimental data which shows the effect of external mass transfer and biochemical reaction on the phenol biodegradation. Impact of the external mass transfer on the biodegradation (at initial phenol concentration of 200 mg/L) is analyzed by calculating Reynolds numbers (N_{Re}) and mass fluxes (G) for different experimental flow rates.

According to equations 1.17 and 1.18 mentioned in chapter 1,

$$N = \frac{K}{\rho}\left(\frac{\mu}{\rho D_f}\right)^{-2/3}\left(\frac{d_p}{\mu}\right)^{-(1-n)} \quad (1.17)$$

$$\frac{1}{k_p} = \left(\frac{1}{NA_m}\right)\left(\frac{1}{G^n}\right) + \frac{1}{kA_m} \quad (1.18)$$

The graph between $1/k_p$ vs $1/G^n$ gives slope as $1/NA_m$ and intercept as $1/kA_m$. The tabular values of slope and intercept details are given in Appendix-B. Values of N are calculated by using equation 1.17. Then A_m and k are determined from slope and intercept by equation 1.18. Among several calculated values, the A_m obtained for K = 5.7 and n = 0.97 is closest to the experimental A_m value of 6 cm^2/g as determined by Equation 1.10. All the calculated values of A_m were given in Appendix-B.

Based on present study, the developed mass transfer correlation is,

$$j_D = 5.7 N_{Re}^{-0.003}$$

Chapter 4

Conclusion

The characterization of trickle bed bioreactor was successfully carried out in the present investigation from hydrodynamics to biodegradation. The variation of key parameter which plays an important role in the performance of trickle bed bioreactor was successfully studied.

Pressure drop increases with both gas and liquid velocities. The foaming nature of phenol solution induces more pressure drop in high interaction regions when compared with air-water system. Higher pressure drop was observed in 1000ppm phenol solution as 37.58 KPa whereas its value for water is only 28.42 KPa at U_g= 0.103 m/s and U_l= 0.023m/s. Dynamic liquid saturation increases with liquid velocity, but decreases with increase gas velocity. Lowest value of dynamic liquid saturation was recorded as 0.237 for 1000ppm solution, whereas 0.275 for water at U_g= 0.103 m/s and U_l= 0.0026 m/s. This may be due to void space occupied by excess foam formed in higher interaction regime.

In mass transfer studies, both solid-liquid, gas-liquid mass transfer coefficients is found to increase with superficial liquid and gas velocities. This may be due to higher interaction between the phases and higher effective interfacial area in pulse flow regime than in trickle flow regime.

Microbial degradation of phenol was successfully examined by using *Pseudomonas putida.* It completely degraded phenol solutions up to 1000 ppm within 54 hours respectively. But it was unable to degrade higher concentrations of phenol completely, for initial concentrations of 1250 ppm and 1500 ppm the degradation is only 81%, 43% respectively because of substrate inhibition. Higher liquid flow rate results in enhanced biodegradation rate in the experimental domain may be due to decrease in mass transfer resistance at the liquid film layer around bead. A correlation which gives the effect of the external mass transfer and biodegradation reaction on biodegradation rate is developed.

4.1. Future Scope

- Using different packings and column diameters to determine the on hydrodynamics, mass transfer and biodegradation studies for the characterization of more improved trickle bed bioreactor.
- Other parameters like wetting efficiency, axial dispersion must be investigated.
- Isolation of a microbe is necessary, which is efficient to degrade higher phenol concentrations
- The present work is totally an experimental based. It is necessary to simulate the behavior of the system by using advanced analysis tool such as computational fluid dynamics (CFD) to simulate the behavior of the system.

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Appendix-A

Calibration Curve for standard phenol concentrations

Different solutions of phenol (2-20 mg/l) were used for the preparation of curve. R^2 was found to be equal to 0.992 (Fig.1)

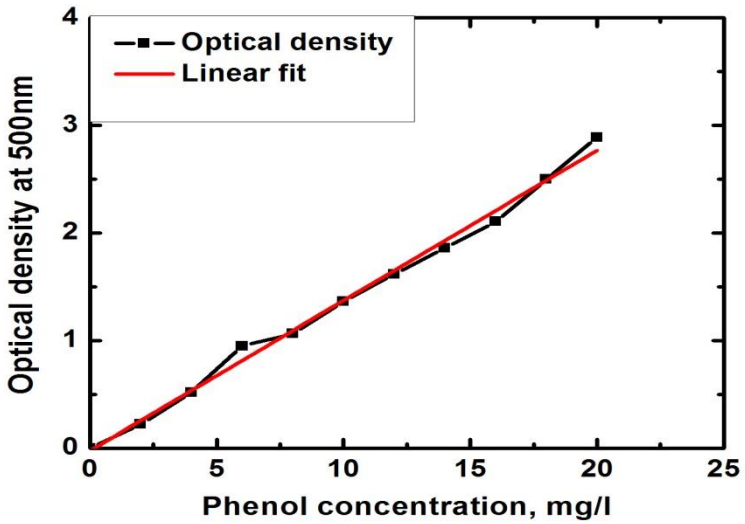

Figure 1 Calibration Curve for standard phenol concentrations

Phenol estimation

Reagents required

Ammonium hydroxide **(0.5N):** 35 ml concentrated ammonia solution was mixed with 1 liter of water.

Phosphate buffer solution: 104.5 g K_2HPO_4 and 72.3 g KH_2PO_4 was dissolved in water and diluted to 1 l. The pH has been adjusted to 6.8.

4-Aminoantipyrine solution: 2.0 g 4-aminoantipyrine mixed with 100 ml of water.

Potassium ferricyanide solution: 8.0 g $K_3Fe(CN)_6$ was mixed with 100 ml of water. Solution was stored in a brown glass bottle.

Procedure:

- For 100 ml sample taken, 2.5 ml NH_4OH solution was mixed.
- With the help of buffer, pH was adjusted to 7.9 ± 0.1.
- 4-aminoantipyrine solution of 1 ml, was mixed.
- $K_3Fe(CN)_6$ solution of 1 ml was mixed.
- Absorbance was taken against 500 nm in UV/Vis spectrophotometer, after 15 min.

Appendix-B

Table 1 Calculated value of $1/k_p$ and $1/G^n$ for different n

					$1/G^n$				
$1/K_p$	n=0.1	0.2	0.4	0.5	0.6	0.7	0.8	0.9	1
0.08984	0.941106	0.88568	0.78443	0.738231	0.694754	0.653837	0.61533	0.57909	0.544985
0.043632	0.903711	0.816693	0.666987	0.602763	0.544724	0.492272	0.444872	0.402035	0.363324
0.023881	0.878083	0.771029	0.594486	0.522008	0.458367	0.402484	0.353414	0.310327	0.272493

Table 2 Slope and intercept values of equation 18 for different values of n

	n=0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
Slope	0.9295	1.6946	2.318	2.8196	3.2165	3.5239	3.7548	3.9207	4.0315	4.095
intercept	0.8589	0.7356	0.628	0.5341	0.4523	0.3811	0.3193	0.2656	0.219	0.178

Table 3 Calculated values of A_m for different values of K, n

For K=1.34

n	Am	k
0.1	3359.884	0.002976
0.2	1247.039	0.004009
0.3	616.8896	0.005403
0.4	343.1682	0.007285
0.5	203.5563	0.009825
0.6	125.724	0.013257
0.7	79.84146	0.017893
0.8	51.73986	0.024159
0.9	34.04833	0.032633
1	22.67816	0.044095

For K=1.625

n	Am	k
0.1	2770.612	0.00042
0.2	1028.328	0.001322
0.3	508.6967	0.00313
0.4	282.9817	0.006616
0.5	167.8556	0.013172
0.6	103.6739	0.02531
0.7	65.83849	0.047569
0.8	42.66548	0.088246
0.9	28.07677	0.162633
1	18.70076	0.29907

For K=5.7

n	Am	k
0.1	789.8676	0.001474
0.2	293.1636	0.004637
0.3	145.0232	0.01098
0.4	80.67462	0.023208
0.5	47.85358	0.046202
0.6	29.55616	0.08878
0.7	18.76975	0.166856
0.8	12.16341	0.30954
0.9	8.004343	0.570467
1	5.331358	1.049046

n	Am	k
0.95	6.523823	0.773382
0.96	6.264382	0.822001
0.97	6.01601	0.873939
0.98	5.777921	0.928501
0.99	5.549943	0.987299
1	5.331358	1.049046