# Removal of Phenolic Compounds From Industrial Waste Water by SemifluidizedBed Bio-Reactor

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*The harmful effects due to the presence of phenolic compounds in industrial waste waters have been highlighted. Primary sources alon with the concentration level in indus trial effluents are presented. Degradation technique for the above mentioned compounds by conventional methods has been described. The drawbacks of the traditional technique have been mentioned. Use of semifluidized bed reactor with immobilized cells for the above treatment has been emphasized. Salient design feautres for such a reactor have been outlined.*

## 1.0 Introduction

Presence of phenolic compounds even at low concentration in the industrial waste water adversely affects aquatic as well as human life directly or indirectly when disposed off to public sewage, river or surface water. Sometimes these form complex compounds with metal ions, discharged from other industries, which are more carcinogenic in nature than the phenolic compounds. The toxicity imparted by phenolic compounds is responsible for health hazards and dangerous to aquatic life. Different conventional processes generally being used to remove phenolare: solvent extraction, incineration, chemical oxidation, free-cultured biological degradation, adsorpation and membrane separation. However, depending upon the quality and quantity of waste water, the treatment methods are to be chosen. At lower concentration of phenol, all the above mentioned techniques will not be suitable to treat the waste water; in addition these become uneconomical for its industrial scale-up operation. Application of semi-fluidized bed immobilized bioreactor is a novel technique in the treatment of waste water containing phenolic compounds. A detailed study with various types of immobilized culture bio-reactor and their applicability under varied conditions of waste water have been highlighted in this article.

## 2.0 Sources Of Phenols And Phenolic Compounds

The primary sources of phenolic compounds present in industrial effluents are: petroleum refineries, plastic manufacturing plants, pharmaceutical industries, coal carbonization and tar distillation units, wood chacoal pro-

duction units, coke ovens, phenol-formaldehyde plants, bisphenol - A and other synthetic resin manufacturing units. Table-1 presents some of the industrial waste water comparatively rich with phenol along with their phenol concentration.

**Table 1.**
**Concentration of phenolic compounds in industrial waste water.**

| Sl. No. | Source of waste water | Phenol Concentration mg/lit. |
|---|---|---|
| 1. | Coal Carbonisation process | |
| | (i) Low temperature | 1000-8000 |
| | (ii) High temperature | 800-1000 |
| 2. | Metallurgical coke manufacturing process | |
| | (i) Spent liquor after phenol recovery | 900-1000 |
| | (ii) Coke oven effluent | 35-250 |
| 3. | Oil Refineries | 1500-2000 |
| 4. | Phenol formaldehyde resin manufacturing plants. | 800-2000 |

**3.0 Immobilized specific culture for phenol degradation**

**3.1 Immobilization**

Immobilization is considered as a physical confinement or localization of micro-organisme that permits the economical resue of the micro-organisms.

**3.2 Methods of preparation of immobilization culture**

There are four techniques which are used commonly. These are:

(i) Absorpation
(ii) Gel Entrapping
(iii) Encapsulation
(iv) Metal Binding

**3.3 Selection of specific culture**

A pseudbmonas sp. which was islocated from phenol containing soil was immobilized in alginate and Poly Acryl Amide (PAA) and cultivated in a fermenter batch wise. This immobilized cells can degrade phenol even at an initial concentration of 2000mg/lit. On the other hand, free-cultured cells can not grow at all at this high concentration or even at a substantially lower concentration. The carriers act as a protective cover against phenol and in this contest PAA is more effective than alginate.

**3.4 Entrapped immobilization cells for degradation of phenol**:

Different entrapping carriers can be used, including calcium alginate.PAA, K-carrangeenan and Cellulose acetate. Among these calcium alginate and K-carrangeenan gel can be prepared easily, as dissolution rate of these two gels are more. It is difficult to

produce poly acrylamide gel which is too weak for aeration. The mechanical resistance of alginate and K-carrangeenan is reported to be too weak. They become fragile and higher amounts of free cells will be detected at the end of semi-fluidized bed operation. According to Yang. et. al. cellulose triacetate might restrict the diffusion of large molecules. So a new carrier has been developed to combine the advantages of cellulose triacetate and the lower diffusion limitation of calcium alginate.

## 4.0 Tretment of phenolic waste water

### 4.1 Conventional methods of treatment

The conventional treatment methods adopted for removal of phenol depend upon the maintenance of the toxic limit of phenol Concen tration and adequate acclamatization of the bio-mass. The trick ling filter and the activated sludge process are generally in use for the treatment of phenolic waste water. In activated sludge process the requirment of air for aeration increase with phenol concentration. The phenol loading removal is effective only upto a certain level. The discharged effluent standard being 0.1 mg/lit, the conventional methods are not efficient to bring down the phenol concentration to such a low level in the treated effluent. Generally to reduce the concentrartion of phenol to such low level immobilization cultured semi-fluidized bed bio-reactors are effective.

## 5.0 Novel technique : Semi fluidized bed bio-reactor

A semifluidized bio-ractor is a new and novel technique of contacting immobilized culture in solid support (preferably polymer) with industrial wastewater (fluid). In this type of bioreactor, simultaneous formation of packed bed and fluidized bed is achieved by the prevention of free expansion of a fluidized bed with the introduction of an adjustable top screen, which allow the fluid to pass trough. The bottom portion of the bed will be in fluidized condition while the top portion of the bed will be a packed bed. As a result, this method will overcome the disadvantages of fiudized bed namely, back mixing, attrition and corrosion of solids. Semifluidized bed will also overcome certain drawbacks that of the packed bed, such as segregation, non uniformity in temperature and channeling. A semifluidized bed immobilized bioreactor like fluidized bed, rotating disk, basket type batch reactor, which are as under,

(i) The bed particles in both fluidized and semifluidized bed bio-reactor are coated with viable microbes. The loss of these bed particles through elutriation in the fluidized bed bioreactor can drastically reduce the concentration of culture in the reactor and thus, impair the effectiveness of the system. Elutriation of fluidizing particles could result from an instability of the fluidized bed, the reduction in the specific gravity of the fluidizing practicle and the occurance of the slugging.

(ii) Instability of fluidized bed due to fluctuation in flow rate of waste water would result both in a channeling effect, where waste water flows through the bed without being treated and in substantial loss of microbe

coated particles through wash out.

(iii) Excess bacterial growth formed on fluidizing particles in the fluidized bed bio-reactor causes agglomeration. Gases inherent to biological degradation of waste water are trapped in these aggregates. As a result, the specific gravity of aggregate is greatly reduced, and leads to elutriation of these valuable immobilized cultured particles.

(iv) A large amount of the gas must be pumped through the fluidized bed bioreactor, if direct injection of air or oxygen into the bioreactor is employed to supply the essential oxygen for the bacterial digestion of waste water.

(v) To reduce and compensate for particle elutriation, mechanical devices, a solid retention tank and solid re-entry line are needed in the fluidized bed bioreactor to remove excess bacterial growth, to capture the washed out praticles and to return them to bed, respectively. These of course, lead to higher costs and additional inconvenience., In a semifluidized bed bioreactor, bacteria-coated bed particles are retained in the bioreactor, regardless of their specific gravity or operating conditions, by the top fixed bed and the restrining plate. Thus, the need for additional devices is eliminated. To prevent slugging of the semifluidized bed bioreactor by bacterial growth, the top restraining plate can be elevated to fluidize the entire bed, there by utilizing the shear force of the fluid on the particles to remove excess cells. Injection of gases or liquids into the bed may also accomplish the task.

(vi) Mass transfer rates attainable in a semifluidized bed are always higher than those attainable in other bioreactors. Operation of bioreactors, which results in high transfer of oxygen to bacteria, leads to lower operation cost through efficient use of oxygen. The improved mass transfer characteristics of a semifluidized bed, as compared to a fluidized bed, are attained at the cost of a higher pressure drop.

(vii) In a semifluidized bed bioreactor, main treatment of waste water is performed in the fluidized portion of the reactor where intensive mixing occur. The effluent from the fluidized portion, which is lean in contaminants, is treated in the packed bed portion where mixing is not intensive. This arrangement gives the most efficient waste removal in a given volume. In the semifluidized bed bioreactor, the packed bed portion complements the fluidized bed portion by acting as a polishing section. The final effluent from the semifluidized bed biorector should have a much lower level of contaminants compared to a fluidized bed bioreactor.

(viii) The structure of a semifluidized bed bioreactor is such that the system can have a self-regulatory effect. The amount of bed particles in the fluidized and packed portions of the bed is directly related to effluent flowrate. If the waste water flowrate is fluctuated upward, additional particles will be shifted to the packed portion of the bioreactor. This shift will have two major effects: one is the formation of a large polishing section, which compensates for the increased load to the bioreactor, the other is that the increased pressur drop will cause the flowrate to de-

crease, thereby returning the bed to a normal operating mode. This self-regulating feature or fluidic effect reduces the need for human supervision.

### 5.1 Proposed pilot Plant For Degradation of Phenolic Waste Water

In proposed pilot plant for the treatment of phenolic waste water, it is diluted to a level such that overall concentration is reduced to about 200mg/lit. The diluted waste-water passes through the semifluidized bed bioreactor containing immobilized culture on cellulosic triacetate polymer and the outlet treated waste water is recycled continuosly. BOD is measured with time. As in fluidized bed bioreactors, the semifluidized bed bioreactor is initially seeded by introducing microorganisms and nutrients and waste water is admitted to the bed at flowrate slightly greater than the minium fluidization velocity. The microorganisms will first grow in the suspended phase and then attach themselvs to the available surface area i.e., the column wall and the fluidizing particles. The particles may consist of sand, activated carbon or coal particles. Once the particles are covered with microbes, the semifluidized bed reactor immediately becomes operational. With the microbical growth on the bed internals, the phenolicc removal efficiency of the bioreactor will not be adversely affected by changes in the temperature, flow and/or concentration flux. The fluidized portion of the bed will carry the main load of digestion with the thin packed portion of the bed acting as a polishing section. The fluid reaching the latter section will be lean in phenolic concentration, and thus will not excessively contribute to increase in cell mass that can clog the bed.

If the packed portion of the bed become plugged by excess cells or by suspended solids, the clogging can be cleared by raising the upper porous screen and completely fluidizing the bed. To control the microbial population, the entries bed should periodically be fully fluidized. During fluidization, excess cell mass is removed from the particles by shearing.

The comparison of performance of different bioreactors with respect to phenol degradation in waste water have been given in table-2

Table 2.

**Comparison of performance of bio-reactors with respect to phenoldegradation of waste water.**

| | Performance data at Max. phenol degradation | | | |
|---|---|---|---|---|
| **Condition of feed/ effluent** | **CSTR bioreactor** | **Packed bed bioreactor** | **Fluidized bed bioreactor** | **Semifluidized bed bioreactor** |
| 500 mg/ lit. of phenol | 1.0 gm. of PhoH day/m3 bioreactor | 4.7 gm. of PhoH/day/m3 bioreactor volume | 8.5 gm. of PhoH/day/m3 bioreactor volume | 9.1 gm. of PhoH/day/m3 bioreactor volume |
| Treated effluent | 0.25-1.0mg/lit | 0.21-1.0 mg/lit | 0.01-0.5 mg/lit | 0.008-0.45 mg/lit |

### 5.2 Various Design Aspects Of A Semifluidized Bed Bioreactor (SFBBR)

The height of the packed and fluidized bed portions of a SFBBR can be found out the following experssion

$$H_{pa} = (H - H_f) \frac{1 - C_f}{C_f - C_{pa}} \quad (1)$$

The hegiht of the fluidized portion ($H_f$) is $H-H_{pa}$.

From the volumetric flow rate ($Q_v$) and the kinetic rate equation of microbial reaction, the corresponding volume, height and the diameter of the reactor can be found out.

The relationship can be expressed as

$$\tau = \frac{V}{Q_v} = C_{Ao} \int_0^{X_A} \frac{dx_A}{-r_A} \quad (2)$$

The pressure drop through a semifluidized bed is the sum of pressure drop through the fluidized and packed bed sections (2)

$$\Delta P = \frac{\Delta P}{L} (H - H_{pa}) + \frac{\Delta P}{L} H_{pa} \quad (3)$$

By substituing the effective weight of the particles into the first term in the right hand side of eqn. (3), the Ergun equation for packed bed into the second term of equation (1), and combining the resultant expression with eqn. (1), the overall pressure drop is obtained as

(4)

The parameters which govern the performance of a semi-fluidized bio-reactor are:

(i) Properties of particle; size, shape and density

(ii) Properties of fluid; density, viscosity and velocity

(iii) Initial static bed height

(iv) Height of top restraint.

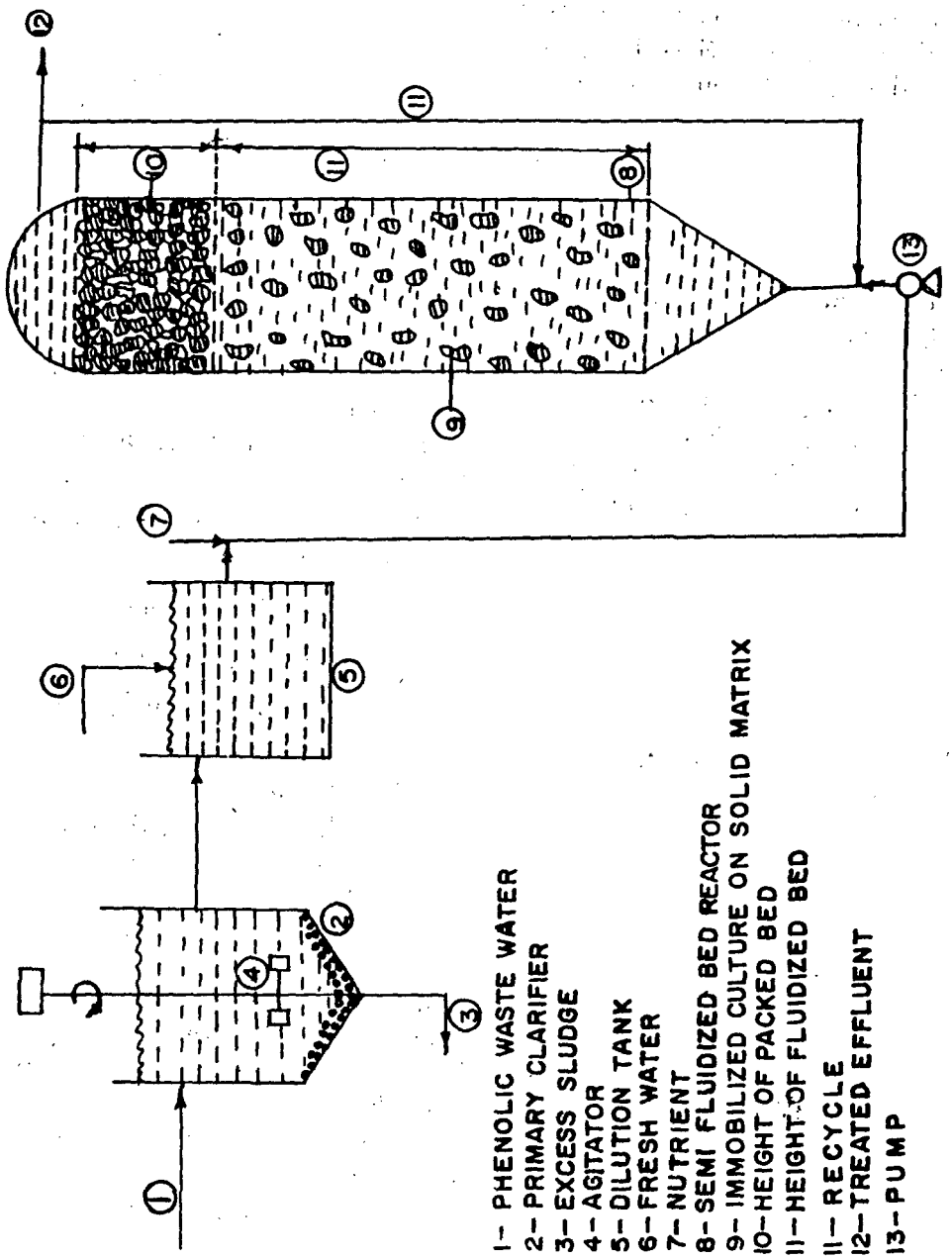
(v) Dimensions of column and its configuration.

### 6.0 Conclusion

The immobilized semifluidized bed bioreactor is, no doubt, a novel and efficient appliance, which can be adopted for the treatment of industrial wastewater cotaining phenolic compounds even at lower concentration. A proper choice of immobilized culture, careful consideration of various design parameters for a semifluidized bed bioreactor will make treatment process cost effective in the long run.

Fig : 1

**PROPOSED PILOT PLANT FOR DEGRADATION OF PHENOLIC WASTE WATER**



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## Nomenclature :

- $C_{AO}$ - initial phenol concentration, kg.mole/$m^3$
- $d_p$ - diameter of particle, m
- G - mass velocity, kg/$m^2$. sec.
- H - height of semi-fluidized bed reactor, m
- $H_f$ - Height of fluidized bed portion, m
- $H_{pa}$ - height of packed bed portion, m
- $P_t$ - total pressure drop through the semifluidized bed bio-reactor, N/$m^2$
- $Q_v$ - flow rate of phenolic waste water, $m^3$/sec.
- $-r_A$ - kinetic rate equation of phenol degradation
- T - residence time, sec.
- U - Superficial velocity, m/sec.
- V - volume of the SFBBR, $m^3$
- $X_A$ - fractional degradation of phenol
- $C_f$ - porosity of fluidized section of the bed
- $C_{pa}$ - porosity of packed section of the bed
- $P_{s,f}$ - density of solid & fluid respectively, kg/$m^3$
- $\mu$ - viscosity of fuid, kg/m. sec.