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Immobilized Bioreactors for the Treatment of Industrial Wastewater – A Comparative Study

Dr.L.Nageswara Rao
Associate Professor, Department of Chemical Engineering, R.V.R.& J.C. College of Engineering, Chowdavaram, Guntur,Andhra Pradesh, India
lnrao1978@gmail.com

Abstract

The various sources of incidence of various pollutants from major chemical process industries and their dangerous effects have been reported. The various characteristic composition of wastewater from different sources represented. The methods of treatment of wastewater in brief discussed. Special attention has been paid to the biological treatment mentioning the drawbacks of the conventional methods. The relative advantages of various modern bioreactors functioning on immobilization technique have been projected. A comparative representation with respect to various modern bioreactors has been presented and the uniqueness of the fluidized and semi-fluidized bed bioreactors in the treatment of wastewater has been highlighted.

Keywords: Pollution control, water pollution, wastewater, Immobilized cell, semi-fluidized bed, Bioreactor

Introduction

Environmental Pollution is a rising danger and immense disquiet in today's context pertaining to its effect on the ecosystem. The worldwide rise in population and industrialization during the last few decades have resulted in ecological disturb and degradation of the natural property. One of the most vital natural resources which have been the worst victim of population explosion and increasing industrialization is water. In recent years, considerable attention has been paid to industrial wastes discharged to land and surface water. Industrial effluents often contain various several organic and inorganic compounds. Huge amount of wastewater generated from human resolution and industrial sectors accompany the disposal system either as municipal waste water of industrial wastewater. This wastewater is enriched with varied pollutants and harmful both to human being and the aquatic flora and fauna and its successive accumulation in the soil has adverse effect on soil productivity. Over 5 million chemical substances produced by industries have been recognized and about 12000 of these are marketed which amount to around half of the total production.

Due to discharge of contaminated effluents long-term consequences of experience can cause cancer, delayed nervous damage, deformity in urban children, mutagenic charges, neurological disorders etc. various acid manufacturing industries discharge acidic effluent, which not only make the land infertile but make the water of the river acidic also. The high acidity causes stomach diseases and skin ailments in human beings. Alkaline effluents cause infertility of the soil and destroy flora and fauna of the vicinity. Contaminated water by pesticides, such as DDT, aldrin, dieldrin, heptachlor etc is harmful for aquatic life and human beings as well. Discharges of cyanide-contained wastewater to water mass may lead to death of fish and other aquatic life therein. Use of water containing fluoride can causes mental disorders and stomach ailments and can also reduces agricultural production. Characteristics of wastewater from few process industries are shown in table-1(Source: H.M.Jena et al)

Table -1: Characteristics of wastewater from process industries:

Parameter/source &amount range, mg/lt	From steel industry	From petroleum industry	From LT coal carbonization	From milk diary plants
PH	8.5-9.5	-	9.0	7.3-9.5
Total solids	175-1300	-	6720	1690-2730
Dissolved solids	125-800	-	5312	920-1660
Suspended solids	50-500	200-400	1408	690-1810

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Oils and greases	-	2000-3000	-	290-1390
Chlorides as Cl	-	-	Nil	104-190
HS and mercaptans	-	10-220	-	-
Nitrogen	800-1400	-	-	62
Sulphates/sulfides	110-220	09	802	Trace
Cyanides	10-50	-	4576	-
Thiocyanates	50-100	-	2840	-
phenol	500-1000	1500-2000	10240	-
Total alkality	-	-	14670	564-610
Phenolphthalein alkalinity	-	-	Nil	152-185
Turbidity	-	-	-	turbid
BOD	160	100-300	111000ppm	816-3070
COD	790-2450	-	20400ppm	1000-4510

In this way it is very essential to purify and recycle wastewater in vision of reduced availability and deteriorating water quality. Phenol along with other xenobiotic compounds is one of the most common contaminants present in effluents from chemical process industries. Even at lower concentration these compounds harmfully affect aquatic as well as human life. Also these compounds form complexes with metal ions discharged from other industries, which are carcinogenic in nature. It is water soluble and highly mobile. This imparts medicinal taste and odor even at much lower concentration of 2 microgram/liter and it is lethal to fish at concentration of 5-25 microgram/liter. The maximum permitted concentration level of phenol being 0.5-1 mg/l for industrial wastewater and 1 μg/liter for drinking water. So it highly essential to save the water resources and aquatic life by removing these compounds from wastewater before disposal. The main sources of phenolic wastewater are coal chemical plants, oil refineries ,petrochemical industries, fibers glass units, explosive manufacture phenol-based polymerization process, pharmaceuticals, plastic, paints and varnish producing units, textile units making use of organic dyes, anticepticsm antirust products, biocides, photographic chemicals and smelting and related metallurgical operations etc.

Treatment Methods of Industrial Waste Water

The conventional methods of treatment of phenolic and nitrate-nitrogen wastewater are largely physical and chemical processes but these processes led to secondary effluent problems due to configuration of toxic materials such as cyanides, chlorinated phenols, hydrocarbons, etc, these methods are mainly chlorination, ozonation, solvent extraction, incineration ,chemical oxidation, membrane process, coagulation, flocculation, adsorption, ion exchange, reverse osmosis, electrolysis, etc.In solvent extraction there is a danger of infectivity of treated water by the solvent. The solvents used for phenol recovery are benzene, isopropyl ethyl and butyl acetate. In addition to the presence of solvent in treat waters the high cost of solvent is another disadvantage. In adsorption commonly activated carbon is used which is disposed by incineration. The process of incineration generates many furans have very severe consequences on human health. Chemical oxidation requires a reactor, which operates high temperature and high pressure, ultimately huge energy.

Biological treatment is attractive due to the potential to almost degrade phenol and other pollutants while producing innocuous and products, reduced capital and operating costs, maintains phenol concentrations below the toxic limit. However difficulty arises in such treatment due to the toxicity of phenol to the microbial population. In the biological denitification, in the water is converted into gaseous nitrogen. The biological degradation of phenol is accomplished through benzene ring cleavage using the enzyme present in the microorganism. The bacteria express differently when exposed to different initial phenol concentrations and other conditions. The most efficient Pseudonomas Putida is capable of using phenol as the sole source of carbon and energy for cell growth and metabolism degrade phenol via meta-pathway. That is the benzene ring of phenol is dehydroxylated to form catechol derivative and the ring is then opened through meta-oxidation. The final products are molecules that can enter the tri-carboxylic and cycle. The most common Bio-reactors are (1) Aerated lagoon (2) Oxidation Ditch (3) Activated sludge system (4) Anaerobic digestion system (5) Oxidation pond, (6) Trickling filters (7) rotating disc biological reactors (8) Basket type bioreactor (9) Hollow fiber membrane bioreactor and (10) Fluidized bed bioreactor.

Wastewater Treatment Using Bioreactors

Treatment of industrial and /or domestic wastewaters requires a great deal of space when using systems based on activated sludge or aerated lagoons in which retention time is many days. Wastewater having lower phenol concentration in the range 5-500 mg/lt is correctly treated in the bioreactors like Activated sludge, Aerated lagoons, trickling filter, oxidation ponds. The major constraints in using bioreactors with free cells for biodegradation of phenol include maintenance of proper cell concentration, removal of cell sludge, settling and sedimentation of sludge, sludge recycling etc.

A bioreactor integrated to a membrane module is referred as membrane bioreactors. The advantages with MBR s are that they offer long culture retention time and short hydraulic retention time and reduce number of the post treatment processes. The membrane has the intention of removal o particulate substances that replaces the gravitational clarifier to separate the biomass from the treated effluent and retainment of low-growth microbes in the reactor for high cell density operation. The limitation of this reactor is high membrane cost. In Free-Culture bioreactor The microbes suffer from substrate Inhibition, whereby growth (and consequently pollutant degradation) is inhibited at high pollutant concentrations. Biological fixed films exhibit properties that make them preferable to suspended cell systems for a wide variety of wastewater treatment application. These properties include high concentrations, enhanced cell retention due to cell immobilization and an increased resistance to the detriment effects of toxic shock loadings.

Rotating biological contactor give very good phenol removal efficiency at moderate loading rate. It posses high surface area, provide vigorous contact for the biological growth with wastewater and efficiently aerates the wastewater. Two phase partitioning bioreactor(TPPBs) are characterized by a cell –containing aqueous phase and a second immiscible phase that contains toxic and /or hydrophobic substrates that partition to the cells at sub inhibitory levels in response to the metabolic demand of the organisms. This reactor is capable of degrading the highly toxic chemical at very concentration. Hollow-fiber membrane bioreactor (HFMBR) with immobilized culture (biofilm) is an extractive membrane bioreactor, could completely degrade phenol up to 3000 mg/l with moderate hydraulic loading rate. Trickling bed reactors posses a very good biomass concentration show high treatment efficiency at high hydraulic loading rates. But it has limitations like channeling, clogging and high energy consumption

Over the conventional type free-culture bio-reactors the immobilization cell bioreactors like CSTR, PFR, Fluidized bed, air lift type, etc, has the following advantages like continuous reactor operation at any desired liquid throughput without risk of cell washout, protection of cells from toxic substrates, higher growth rate gives high concentration of cells in the reactor, easy cell –treated water separation, enhance gas- liquid mass transfer rate, plug flow operation by maintaining the immobilized ells as a stationary phase. The fluidized bed bioreactors are superior in performance due to immobilization of cells on solid particles reduce the time of treatment, volume of rector is extremely small, lack of clogging of biomass and removal of phenol even at lower concentrations.

Immobilization of Microbial Cells

Cells of mixed culture collected from soils containing pollutants or specific culture (pure) isolated from the pollutant containing soil are immobilized in/on solid matrix. The specific cultures such as Pseudomonas Putida(NICM,SP,MTCC,Q5,DSM,KT etc) either psychotropic or mesophilic type, T cultaneum R57 used for biodegradation of phenol, Catechol, Azo dyes removal of ionic mercury etc, Pseudomonas spp. and Bacillus spp used for denitification, green sulfur bacteria for sulfide removal etc. are used for immobilization. Acclimization of microorganisms is done by increasing the pollutant concentration (say of phenol) gradually during culture preparation. The aclimized culture is used for the immobilization in/on the solid matrix.

Immobilization of cells means that the cells have confined or localized so that it can be reused continuously. These exhibit totally different hydrodynamic characteristics that surrounding environment. Ling cells produce enzyme (biological catalyst) to catalyze cellular reactions vital to the organism, the microorganisms are normally immobilized on natural and synthetic supports. Various types of solid matrices like polyactrylamide gel, Ca alginate, porous glass, plastic beads, activated carbon sand, charcoal, diatomaceous earth, cement balls made of coal ash, cellulose, polymeric materials, polymeric ions, chitosan, lignin's, chitins, coal, collagens etc have been used for immobilization of whole cells. In the recent years, the immobilization of biocatalyst with polyvalent salts of alginic acids has received much attention because of low cost of alginate and the mild conditions of immobilization.

The method of immobilization is broadly classified into four categories namely covalent bonding, cross-linking (chemical methods), entrapment and adsorption (physical methods). Covalent bonding most extensively used technique, where cells or enzymes are covalently linked to the support through the groups in

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them or through the functional groups in the support material. In the cross-linking technique, the cells are immobilized through chemical cross-linking using agents. Adsorption is the simple of all techniques and does not alter the activity of the bound cells. Adsorption involves adhesion or condensation of the cells to the surface of a carrier. The driving force causing immobilization is the combined hydrophobic interactions, hydrogen bonding and salt bridge formation between the adsorbent and cells. Entrapment within the gels or fiber is a convenient method for reactions involving low molecular weight substrates and mainly used for immobilization of whole cells. This method is nothing but the polymerization of the unsaturated monomers in the presence of cells results in the entrapment of cells with in the interstitial spaces of the gel.

Fludized Bed Bioreactor for Wastewater Treatment

This reactor had been successfully applied in the treatment of several kinds of wastewater such as ammonia-nitrogen containing wastewater, photographic processing wastewater, phenolic wastewater, coke oven waster, and other domestic and industrial wastes. Also used successfully for the reductive biotransformation of mercuric ions to elemental mercury present in the effluents from industrial amalgam process, combustors and power stations.

A fluidized bed bioreactor(FBB) is capable of achieving treatment in low retention time because of the high biomass concentration., FBB offers distinct mechanical advantages , which allow small and high surface area media to be used for biomass growth . Fluidization overcomes operating problems such as bed clogging and the high pressure drop , which would occur if small and high surface area media were employed in packed bed operation. Rather than clog with new biomass growth, the fluidized bed simply expands. Thus for a comparable treatment efficiency, the required bioreactor volume is greatly reduced. A further advantage is the possible elimination of the secondary clarifier, although this must be weighed against the medium-biomass separator.

The superior performance of the FBB stems from the very high biomass concentration (up to 30-40 kg/m3) and its ability to produce less amount of excess sludge compared to activate sludge process. The limit on the operating liquid flow rates imposed by the microbial maximum specific growth rate, as encountered in the continuous stirred tank bioreactor, is eliminated due to the decoupling of the residence time of the liquid phase and the growth of the cells. The use of biomass support allows the partial replenishment of the fluidized bed without interrupting the operation in order to maintain high microbial activity. An FBB has attracted considerable interest as an alternative to the conventional suspended growth and fixed film process in wastewater treatment application due to its high efficiency performance. Once fluidized, each particle provides a large surface area for biofilm formation and growth. The support media eventually become covered with biofilm and the vast available growth surface afforded by the media results in a biomass concentration approximately an order of magnitude greated than that maintained in a suspended growth system.A practical approach problem, which occurs in the operation of an FBB, is the excessive growth of biomass on support media. This can lead to the channeling of bio-particles in fluidized beds since biomass loading can increase to such extent that the bio-particle began to be carried over from a bioreactor. The problem of over expansion of fluidized bed due to biomass growth has generally been solved by the removal of heavily biomass-laden particles from bioreactor, followed by the addition of biomass-free particles. However this solution complicates operation of a bioreactor and introduces the need for additional equipment external to the bioreactor, such as a vibrating screen or an incinerator.

One way to achieving the constant biomass loading in an FBB is the regulation of mass of cells grown on surface media so that a steady state is reached where the rate of biomass growth is equal to the rate of biomass attrition. Livingston and Chase have demonstrated that a practically steady biomass loading can be achieved in a draft tube fluidized bed bioreactor where shear forces, occurring between the particles and the liquid, slough off excess biomass from support particles. Another way is the application of a light (matrix particle density smaller than that of liquid) biomass support in a conventional FBB Sokol and Halfani have reported that steady state biomass loading was achieved in a three phase (gas –liquid-solid)fluidized bed bioreactor(TPFBB) with KMT particles (made of poly propylene) for over a 9 month operation. Rusten et al. have demonstrated practically in a bioreactor with a biomass support made of polyethylene.

Conventional FBB are operated in two different ways. In a bioreactor with a heavy (matrix particle density larger than that of liquid) biomass support(e.g. silica sand, coal) , fluidization is commonly conducted with an upward co current flow of gas and liquid through a bed of particle. Under fluidization condition, the bed is fluidized with an upward flow of a liquid counter to the net gravitational force of the particle. Once fluidized, each particle provides a large surface area for biofilm formation and growth. The support media eventually

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become covered with biofilm and the vast available growth surface afforded by the media results in a biomass concentration approximately an order of magnitude greater than that maintained in a suspended growth system. The use of biomass support allows the partial replenishment of the fluidized bed without interrupting the operation in order to maintain high microbial activity. The limit on the operating liquid flow rates imposed by the microbial maximum specific growth rate, as encountered in the continuous stirred tank bioreactor, is eliminated due to the decoupling of the residence time of the liquid phase and of the growth microbial cells.

As a result, loading rates that can be applied in FBBs is greater than those used in the suspended biomass growth systems. Shieh and Keenan have reported that for FBB s a volumetric loading rate of 9.8 x 10^{-4} kg BOD_5 /m^3 can be applied to produce effluent vales of 0.02 kg BOD_5/m^3 and 0.03 kg suspended solids/m3. This value is fairly high than the design value of approximately $1.3x10^{-4}$ kg BOD_5/m^3 s for conventional air activated sludge processes.The degradation of phenolic type liquors, derived from coal processes, in a continuous stirred tank bioreactor CSTR , packed bed bioreactor PBB and FBB shown in table. The degradation rates of 0.087,0.053, and 0.012 kg phenol/m^3 were achieved in the FBB,PBB and CSTR respectively. The effluent concentrations produced by three bioreactors are shown in table-2.

Table-2: Typical assays of feed and effluent compositions for the CSTR, PBR and FBB

Constraints	CSTB		PBR		FBR	
	Concentration mg/l Feed product	Fractional conversion	Concentration mg/l Feed product	Fractional conversion	Concentration mg/l Feed product	Fractional conversion
Phenol	800 0.5	0.99	800 1.0	099	990 <1	0.99
Thiocynate	195 1.0	0.99	250 84	0.66	- -	-
Cyanide	0.4 0.3	0.25	<1 <1	-	- -	-
Sulphate	30 290	-	41 62	-	- -	-
Chloride	115 20	0.76	<10 <10	-	- -	-
Phosphate	125 115	0.08	250 245	0.12	125 115	0.09
Nitrate	554 1019	-	380 1221	-	16 13	0.19
Ammonium-Nitrogen	213 298	-	164 247	-	820 750	0.09
Total carbon	640 96	0.85	1780 496	0.71	750<1	0.99

Table: 3 Comparison of FBB with competing bioreactors in municipal applications

Parameter	Trickling filter (PBB)	Rotating biological contactor	HFMBR	FBB
Specific surface area per bioreactor volume(m^2/m^3)	12-30	40-50	8-10	800-1200
Biomass concentration (kg/m^3)	Upto 170	Upto 6	Upto 22	30-40

The basic nutrients for microbial growth are transported first from bulk phase to the surface of the biofilm, and then transported to the inner regions of the biofilm via diffusion. The limiting mass transport rate controls the presentation of the biofilm reactor. Form the literature it is seen that the external resistance can be neglected in the case of a high fluidization flow rate. In a three-phase fluidized bed bioreactor it is found reaction rate follows first order kinetics with respect to oxygen and zero-order one with respect to phenol. For chemical and bio-chemical process, where mass transfer is the rate-limiting step, it is important to know the gas hold up as this is related directly to mass transfer. the as hold up at high pressure is always larger than that at low pressures, regardless of the liquid velocity and particle size in three- phase fluidization.

Semi-Fluidized Bed Bioreactor for Wastewater Treatment

In this bioreactor, simultaneous formulation of packed bed and fluidized bed is achieved by the prevention of free expansion of a fluidized bed with introduction of an adjustable top screen, which allows the fluid to pass through the bottom portion of the bed will be fluidized condition while the top portion of the bed will be a packed bed. In a fluidized bed the reactor is operated at a liquid or gas velocity fairly less than the washout velocity of the cells. But in semi-fluidized bed higher velocity of fluid is possible which will lessen the external mass transfer resistance. As a top packed bed is formed in such a bioreactor, the reactor pressure drop is high that means it is operated under high pressure condition. Hence the gas hold-up in the fluidizing section of the column will be more this will enhance the mass transfer rate.

If the semi fluidized bed can be used as bioreactor it will overcome the disadvantages of fluidized bed, namely back mixing, attrition and erosion of immobilized solids, reduction of concentration of culture by elutriation, instability due to fluctuation in flow rate of wastewater, avoid agglomeration and also overcome the drawbacks of packed bed such as particles segregation, non-uniformity in temperature and channeling. As the top restraining plate is adjustable slugging by bacterial growth can be prevented. Improved mass transfer in semi-fluidized bed at cost of higher-pressure drop is compensated by lower operation cost through efficient use of oxygen. The top packed bed portion complements the fluidized bed portion by acting as a polishing section, so that the level of contaminants low compared to fluidized bed bioreactor. The parameters, which govern the performance of a semi-fluidized bioreactor are (i) Properties of particles size, shape, and density (ii)Properties of fluid; density, viscosity, and velocity(iii)Dimension of the column and its configurations(iv)Initial static bed height, height of top restraint and ratio of top packed bed (v)To fluidized bed. The comparison of performance of different bioreactors with respect to phenol degradation in wastewater is shown in table-4

Table:4 Comparison of performance of Bioreactors with respect to phenol degradation of wastewater

Condition of fee/effluent	CSTR bioreactor	Packed bed bioreactor	Fluidized bed bioreactor	Semi-fluidized bioreactor
500 gm/lit of phenol	1.0 kg of phenol/day/m3 bioreactor	4.7 kg of phenol/day/m3 bioreactor	8.5 kg of phenol/day/m3 bioreactor	9.1 kg of phenol/day/m3 bioreactor
Treated effluent	0.25-1.0 mg/lit	0.21-1.0 mg/lit	0.01-0.5 mg/lit	0.008-0.45 mg/lit

Conclusions

Immobilized cell bioreactors are superior than free culture bioreactors. Among the immobilized bioreactors, the semi-fluidized bed bioreactor is a novel and efficient one, which can be adopted for the treatment of industrial wastewater containing phenolic compounds and other pollutants even at lower concentrations. A right choice of immobilized culture, careful deliberation of various design parameters for semi-fluidized bed bioreactors will make treatment process cost effective in the long run.

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