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A Novel Technique for Phenolic Wastewater Treatment

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ABSTRACT

Fresh water crisis and its degradation due to contamination by industrial and municipal waste highlighted. Phenol is one of the most common contaminant, the methods of treatment of phenolic wastewater discussed emphasis given on the aerobic biological treatment. Special attention has been paid to the biological treatment mentioning the drawbacks of the traditional methods. The relative advantages of various modern bioreactors working on immobilization technique have been projected. The uniqueness of the fluidized and semi-fluidized bed bioreactors in the treatment of wastewater has been emphasized.

Keywords: Pollution control; water pollution; Wastewater; phenol; Semi-fluidized bed; Bioreactor

Introduction

Water is, literally, the source of life on earth. About 70 percent of the earth is water, but only one percent is accessible surface freshwater. The one percent surface fresh water is regularly renewed by rainfall and other means and thus available on a sustainable basis and easily considered accessible for human use.

Water is the biggest crisis facing the world today. In India the crisis in terms spread and severity affects one in three people. As per an estimate in 2000, there were 7,800 cubic meters of fresh water available per person annually. It will be 5,100 cubic meters (51,00,000 liters) by 2025. Even this amount is sufficient for human needs, if it were properly distributed. But, equitable distribution is not possible

India, which has 16 percent of world’s population, 2.45 percent of world’s land area and 4 percent of the world’s water resources, has already faced with grave drinking water crisis. Water is the single largest problem facing India today. Years of rapid population growth and increasing water consumption for agriculture, industry and municipalities and other areas have strained Indian fresh water resources. In many parts of our country chronic water shortages, loss of arable land, destruction of natural habitats, degradation of environment, and widespread pollution undermine public health and threaten economic and social progress. By 2050 more than 50 percent of population is expected to shift to the cities and the drinking water scarcity will be acute.

In the developed world, for example, the United Kingdom must spend close to $ 60 billion building wastewater treatment plants over the next decade to meet the new European water quality standards. The World Bank has estimated that over the next decade between US $ 600 to 800 billion will be required to meet the total demand for fresh water, including that for sanitation, irrigation and power generation. A water short world is inherently unstable world. Now the world needs another revolution, i.e., a Blue Revolution for conservation and proper maintenance of freshwater.

Environmental pollution is an emerging threat and of great concern in today's context pertaining to its effect on the ecosystem. Water pollution is one of the greatest concerns now a day. Industrial effluents often contain various toxic metals, harmful gases, and several organic and inorganic compounds.

The worldwide rise in population and the industrialization during the last few decades have resulted in ecological unbalance and degradation of the natural resources. One of the most essential natural resources, which have been the worst victim of population explosion and growing industrialization, is water. Huge quantity of wastewater generated from human settlement and industrial sectors accompany the disposal system either as municipal wastewater or industrial wastewater.

Over 5 million chemical substances produced by industries have been identified and about 12000 of these are marketed which amount to around half of the total production. Due to discharge of toxic effluents long-term consequence of exposure can cause cancer, delayed nervous damage, malformation in urban children, mutagenic changes, 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 [1,5]. Alkaline effluents cause infertility of the soil and destroy the flora and fauna of the vicinity. Contaminated water by pesticides, such as DDT, aldrin, dieldrin, heptachlor etc is harm full for aquatic life and human beings as well. Discharge 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 [1-7]. Characteristics of wastewater from few process industries are shown in table-1.

Thus it is imperative to purify and recycle wastewater in view 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 adversely affect aquatic as well as human life [1-4,8-13]. 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 odour even at much lower concentration of 2 μg/l and it is lethal to fish at concentrations of 5-25 mg/l [10]. The maximum permitted concentration level of phenol being 0.5-1 mg/l for industrial wastewater and 1μg/l for drinking water [15,17]. So it is 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, fibre glass units, explosive manufacture, phenol-based polymerization process, pharmaceuticals, plastic, paints and varnish producing units, textile units making use of organic dyes, anticeptics, antirust products, biocides, photographic chemicals and smelting and related metallurgical operations, etc [2,8-10, 17,20].

Table 1: Characteristics of wastewater from process industries

Parameter / Source & amount range, mg/l	From steel industry	From petroleum refinery	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
Oils and grease	-	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 alkalinity	-	-	14670	564-610
Phenolphthalein alkalinity	-	-	Nil	152-185
Turbidity	-	-	-	Turbid
BOD	160	100-300	11100ppm	816-3070
COD	790-2450	-	20400ppm	1000-4510

Treatment Methods

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 formation of toxic materials such as cyanates, 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 [2,8,9,19].

In solvent extraction there is a danger of contamination 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 treated water, 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 new compounds such as dioxins and furans have very severe consequences on human health. Chemical oxidation requires a reactor, which operates at high temperature and high pressure, ultimately huge energy [2,30]. Aerobic and anaerobic biochemical treatment techniques are replacing these methods because of their inherent advantages.

Biological treatment is attractive due to the potential to almost degrade phenol and other pollutats while producing innocuous end 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 [30]. In the biological dentrification, in the water is converted into gaseous nitrogen (N_2) [7]. 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 [10]. The most efficient *Pseudomonas 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 tricarboxylic acid cycle [24].

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 discs biological reactors, (8) Basket type bioreactors, (9) Hollow fiber membrane bioreactor, and (10) Fluidized bed bioreactors [1,2,4-24].

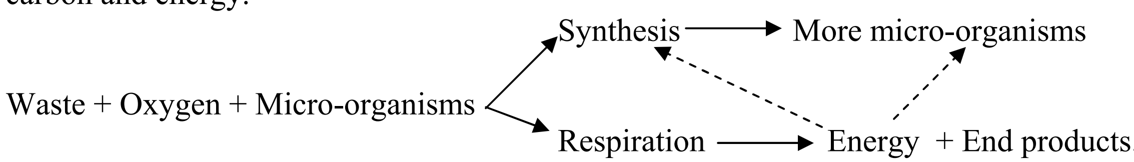
Aerobic processes have several advantages, including a large range of wastewater that can be treated, high degree of BOD removal, acceptability of toxic conditions, simultaneous nitrogen and phosphorous removal, better chlorinated organic contaminants degradation, low solids retention time, and feasible small plants.

Aerobic Degradation

The aerobic biodegradation process is represented by the following equation $C_xH_y + O_2$ + (microorganisms / nutrient) ----------→ $H_2O + CO_2$ + biomass. Aerobic treatment of waste is the degradation and purification process in which bacteria that thrive in oxygen-rich environments break down and digest the waste. The mixed aerobic microbial consortium uses the organic carbon present in the effluent as their carbon and energy source. The complex organics finally get converted to microbial biomass (sludge) and carbon dioxide.

Digestion Pathway

During this oxidation process, contaminants and pollutants are broken down into end products such as carbon dioxide, water, nitrates, sulphates and biomass (microorganisms). In the conventional aerobic system, the substrate is used as a source of carbon and energy.



It serves as an electron donor, resulting in bacterial growth. The extent of degradation is correlated with the rate of oxygen consumption in the same substrate. Two enzymes primarily involved in the process are di and mono-oxygenases. The latter enzyme can act both aromatic and aliphatic compounds, while the former can act only on aromatic compounds. Another class of enzymes involved in aerobic condition is peroxidases, which are receiving attention recently for their ability to degrade lignin.

Characteristics of aerobic bioreactors.

A large range of waste water can be treated. Purification and resettling required. Can handle low to high CODs. Suitable for both cold and warm effluent. Acceptable to toxic presence of toxic materials to certain extent. Neutralization of alkaline wastewater required. Operated in continuous mode with less stability and control. High oxygen requirement. Degree of BOD removal is also high. Simultaneous nitrogen and phosphorous(nutrients) removal is possible. Posses high degradation rate to Chlorinated organic contaminants. When carrier material is used leads to clogging danger. Volumetric loading rates and solids retention time is low. Maintenance required for aeration systems, sludge treatment. Has odour problems if open systems used. Sludge production is high. Investment cost low to medium. High costs for aeration (power), nutrients, sludge disposal. Small plants are possible.

Aerobic treatment produces greater amount of CO_2 which is let out in the environment to increase the atmospheric green house gas (GHG) content. For aerobic treatment the total, the total output is 2.4 kg CO_2/ kg COD (1.4 kg CO_2/ kg COD due to oxidation of hydrocarbons and rest due to degradation of the pollutants in the wastewater). CIS 1, 2 Dichloroethene (DCE) and vinyl chloride concentrations reduced by an average of 80% in aerobic bioreactor. From the study of the effect of toxic chemicals (inhibitory compounds), namely $CrCl_3$, $FeCl_3$, $NaBO_3$, NaCl, $NaNO_2$, $NaNO_3$, and $CHCl_3$, it is found that the oxygen utilization reduced by the biomass during the metabolism in the aerobic bioreactors. In dye wastewater treatment azo dyes are cleaved to aromatic amines. These amines mineralized by means of aerobic treatment by non-specific enzymes through hydroxylation and ring opening giving rise to CO_2, H_2O and NH_3 under aerobic conditions. For treatment of tannery water aerobic bioreactors superior in terms of loading and presence of toxic chemicals and sludge produced contaminated only to a small fraction with chromium. Studies carried out with wastewater from a poultry slaughterhouse showed that COD removal ratio was generally higher in the aerobic bioreactor. Successfully treats the Ploychlorinated Dibenzo Dioxin (PCDD) and Ploychlorinated Dibenzofuran (PCDF). A large number microorganisms that includes Pseudomonas sp., degrade alkanes; mono and poly aromatics, benzene, toluene etc. a part of petroleum hydrocarbon pollution.

The drawbacks are huge amounts of sludge and carbon dioxide production, less stability and control of process, maintenance of aeration and sludge disposal systems, high costs for aeration and sludge disposal, clogging danger when carrer material is used and odour problem in open system.

Advancement of Aerobic Bioreactors in Wastewater Treatment

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, enhanced gas-liquid mass transfer rate, plug flow operation by maintaining the immobilized cells as a stationary phase [1,2,8-10,14,15,17,24]. The fluidized bed bioreactors are superior in performance due to immobilization of cells on solid particles reduce the time of treatment, volume of reactor is extremely small, lack of clogging of bio-mass and removal of phenol even at lower concentrations [1,2,4-6,9-19].

Fluidized 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 waste water, coke oven wastewater, 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 [1,2,4-6,9,11-15,18,19].

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 [1,2,9,13-15]. 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 [13,15,25].

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 particles. Under fluidization conditions, the bed is fluidized with an upward flow of a liquid counter to the net gravitational force of the particles. 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 greater than that maintained in a suspended growth system [13,15,25].

A practical 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 bioparticles in fluidized beds since biomass loading can increase to such extent that the bioparticles 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 [13-15,25,26].

The degradation of phenolic type liquors, derived from coal processes, in a continuous stirred-tank bioreactor (CSTB), packed-bed bioreactor (PBB) and FBB shown in [15]. The degradation rates of 0.087, 0.053 and 0.012 kg phenol/m^3 were achieved in the FBB, PBB and CSTB respectively.

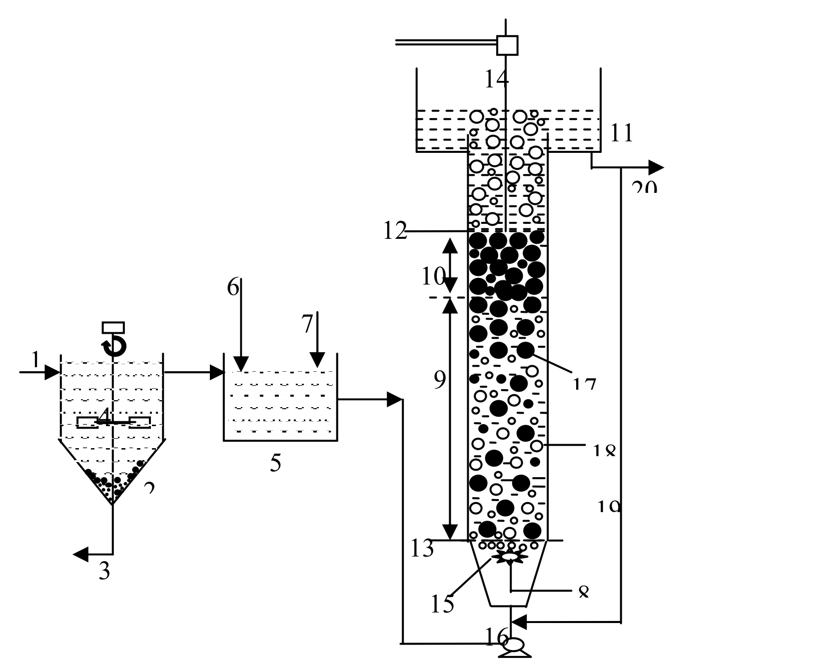
The nutrients for microbial growth are transported first from bulk phase to the surface of the biofilm, and then transported to the inner regions of the biofilm via diffusion. The limiting mass transport rate controls the performance of the biofilm reactor [12,15,32]. From literature it is seen that the external resistance can be neglected in the case of a high fluidization flow rate [12]. 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 [33]. 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 [34]. The gas hold up at high pressures is always larger than that at low pressures, regardless of the liquid velocity and particle size in three-phase fluidization [35].

Semi-fluidized bed bioreactor for wastewater treatment

Semi-fluidization is a novel technique in this direction by the simultaneous formation of a packed bed and a fluidized bed by prevention of the free expansion of a fluidized bed with the introduction of a top adjustable screen, which allows only the fluid to pass through. This overcomes the disadvantages of fluidized bed, namely backmixing, attrition and erosion of immobilized solids, reduction of concentration of culture by elutriation, instability due to fluctuation in flow rate of waste water, avoid agglomeration and also overcomes the drawbacks of packed bed such as particle segregation , non-uniformity in temperature and channeling. The top packed bed portion complements the fluidized bed portion by acting as a polishing section, so that the level of contaminants is low compared to fluidized bed bioreactor. Moreover the semi-fluidized bed is self regulatory, the amount of particles in the fluidized and packed portions being directly related to effluent flow rate.

The parameters, which govern the performance of a semi-fluidized bioreactor, are: (i) Properties of particle; size, shape and density. (ii) Properties of fluid; density, viscosity and velocity. (iii) Dimensions of the column and its configuration. (iv) Initial static bed height, height of top restraint and ratio of top packed bed.

Figure-1 shows the schematic diagram of a fluidized bed bioreactor.



1-Phenolic wastewater
2-Primery clarifier
3-Excess sludge
4-Agitator
5-Diluton tank
6-Fresh water
7-Nutrient
8-Air
9-Fluidized bed section
10-Packed bed section
11-Disengagement section
12-Top screen
13-Bottom grid
14–Clam holder to freely adjust the top screen level
15-Air sparger
16-Pump
17-Immobilized culture on solid matrix
18-Air bubbles
19-Recycle
20-Treated effluent

Conclusion

Immobilized cell bioreactors are better than free culture bioreactors. Among the immobilized cell bioreactors, no doubt 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 concentration. A proper choice of immobilized culture, careful consideration of various design parameters for semi-fluidized bed bioreactors will make treatment process cost effective in the long run.

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