

# **CHAPTER 1**

## **INTRODUCTION**

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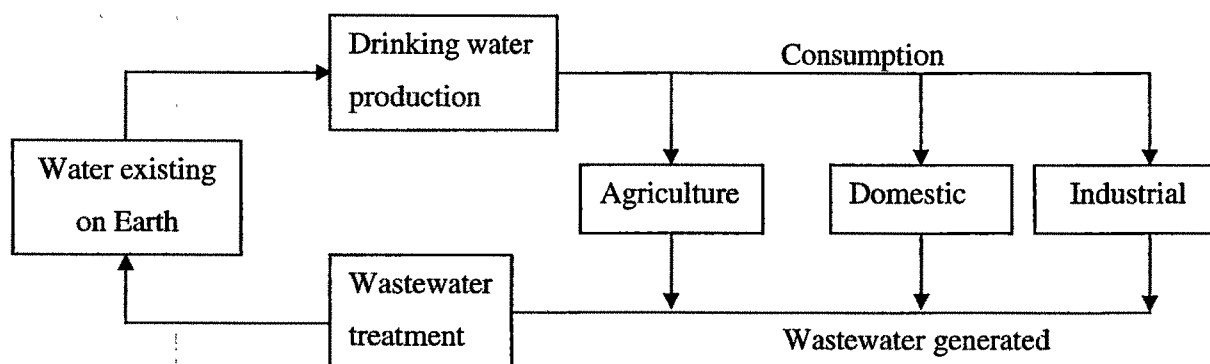
### INTRODUCTION

#### 1.1 GENERAL

The drinking water is not only rare and limited, but the central element of all the vital social and economic processes in the frame of the closed water cycle as shown in Fig. 1.1. This cycle is in crisis because of the development of a consumer society that entails the augmentation of industrial or agro-industrial activities. These activities generate an enormous diversity of commercialized chemical substances that arrive in huge quantities to the water cycle by different ways, endangering the fragile natural equilibrium of which all animals, including humans, are tributary. One of the most alarming phenomena is the growing accumulation of hardly-biodegradable anthropogenic substances under the saturated conditions of such perturbed and overloaded cycle. The situation worsens by the lack, or insufficiency, of adequate water treatment systems capable of diminishing the concentration of toxic substances that represent a chronic chemical risk. It can be said that badly treated wastewaters lead inevitably to a deterioration of quality of water sources and consequently, of drinking water. Two strategies of water treatment have to be enforced in order to counterbalance these growing environmental problems:

- The development of appropriate methods of treatment for contaminated drinking, ground, and surface waters, and mainly
- The development of appropriate methods of treatment for wastewaters containing toxic or non-biodegradable compounds.

The incapability of conventional wastewater treatment methods to remove effectively many bio-recalcitrant pollutants evidences that new efficient treatment systems are needed.



**Figure 1.1.** A simplified view of the water cycle

Wastewaters are examined specifically for substances, which may be lethal to aquatic life because of their toxicity, carcinogenicity, and mutagenesis. These substances are called priority pollutants. Phenols are one of them. The term “phenols” in wastewater includes not only phenol ( $C_6H_5OH$ ) but also an assortment of organic compounds containing one or more hydroxyl (OH) group attached to aromatic ring. These compounds are present in varying concentration in wastewater of synthetic resins, plastics and polymer manufacturing, dyes and dyes intermediate manufacturing and pharmaceutical industries. Disinfectant wastes and cutting oil wastes also contain significant quantities of phenol. Table 1.1 shows levels of phenols in wastewaters of various industries (Patterson 1975, Mahajan 1992).

Phenols impart characteristically, objectionable odor to receiving watercourses at only 2  $\mu g/l$  concentration. These compounds are toxic/lethal to human beings and aquatic life (fish) at 5-25 mg/l. Untreated discharge of such phenolic waste cause a serious problem for the living being on the earth and hence regulatory authority has prescribed the standard norms under the water (Prevention and Control of Pollution) Act 1974 as well as Environment Protection Act 1986, all process Industries shall discharge their waste water after removing the phenolic compounds into the receiving bodies as per prescribed norms given below;

- Public water supply 0.005 mg/l
- Industrial effluents to be discharged to receiving bodies i.e. water, land 1.0 mg/l
- Industrial effluents to be discharged to public sewers 5.0 mg/l

Bureau of Indian standards (IS 2490, IS 10500) has set the limit of 0.002 mg/l as maximum permissible concentration for drinking water.

## 1.2 VARIOUS TREATMENT TECHNOLOGIES FOR PHENOLIC WASTES

Commonly employed methods for the treatment of phenolic wastes are either recovery based or depend on rendering the wastewater harmless, as per the concentration of phenols in the waste. Treatment techniques for phenolic waste include physical (solvent extraction, activated carbon adsorption, ion exchange or membrane processes,), physicochemical (incineration, electrolytic methods and advanced oxidation processes), chemical oxidation (chlorine, chlorine dioxide, ozone, hydrogen peroxide, potassium permanganate and wet air) and biological (activated sludge, trickling filter, oxidation pond, lagoons) treatments using aerobic, anaerobic and anoxic processes (Trivedy and Kaul 1999).

**Table 1.1.** Average levels of phenols in wastewaters of various Industries  
(Patterson 1975, Mahajan 1992)

Industry	Concentration, mg/l
<u>Coking Plant</u>	
Weak ammonia liquor without dephenolization	600-3900
Weak ammonia liquor after dephenolization	4-332
Wash oil still wastes	30-150
<u>Petroleum Refineries</u>	
Sour water	80 – 185
General waste stream	10 - 100
API separator effluent	0.3 – 6.8
<u>Petrochemical</u>	
General petrochemical	50 - 600
Benzene refineries	210
Tar distillation	300
Nitrogen works	250
Plastic factory	600-2000
Phenolic resin production	1600
Fiberboard factory	150
Wood preserving	50-953
Fiberglass manufacturing	40-400
Air craft maintenance	200-400
<u>Coal Carbonization</u>	
Low temperature carbonization	1000 -8000
High temperature carbonization	800-1000
<u>Pharmaceutical Industries</u>	500-6000
<u>Dyes Industries</u>	100-2000
<u>Pesticide Industries</u>	300-4000

All these methods have both merits and demerits and are used according to situation. Table 1.2 shows various treatment technologies for phenolic wastewater and their advantages and limitations.

### **1.2.1 Solvent Extraction**

Recovery is generally applicable when the flow is about 20 l/min or more, with influent concentration of at least 2000 mg/l (Lanouette 1977, Rao 1995). Solvent extraction process can typically reduce phenol concentrations from as high as 17000 mg/l to 900 mg/l (Fedorak and Hruday 1988). Among many benzene and isopropyl ether are extensively used solvents for dephenolization in Benzene-caustic process and Phenolsolvan process respectively (Mahajan 1992). For lower concentration, the recovery of phenol is not feasible (OHEPA 2002). Dephenolised wastewater through extraction will have to be treated by another polishing treatment step (David and Piptak 2002<sup>a</sup>).

### **1.2.2 Steam Stripping/ Hot Gas Stripping**

The liquid waste containing phenols is dephenolated by steam/hot air or gas stripping at around 100 °C. Stripped phenol is then absorbed in a 15% caustic soda solution by chemical reaction (Mahajan 1992). Capital cost of stripper is high, this method is only useful for high concentration (above 1000 mg/l), and residual stream and spent caustic requires polishing step (David and Piptak 2002<sup>b</sup>).

### **1.2.3 Incineration**

Concentrated Phenolic wastes can be handled by incinerating them for complete destruction of phenol to carbon dioxide and water by oxidation reaction. Phenol yields a heat of combustion, which can be utilized in the combustion process (OHEPA 2002). Theoretically a mixture of about 18% phenol and 82% water would be self-sustaining when burnt with 10% excess air at 760°C. However, the solubility of phenol in water at ambient conditions is only about 10% and therefore mechanical mixing is required in order to maintain a combined stream of the two phases; an aqueous phase saturated with phenol and the second heavier liquid phase, which is predominantly phenol. Because phase separation may cause the mixture to fall below the phenol content required to sustain combustion, supplemental fuel may be required (Lanouette 1977).

Table 1.2. Advantages and limitations of different technologies for phenolic waste removal from industrial effluents

Technology	Advantages	Limitations
<b>Solvent Extraction</b>	- Economical recovery	- Require additional treatment before discharge
<b>Steam stripping/ Gas stripping</b>	- Economical recovery	-Applicable for high concentration (>2000 ppm) of effluent
<b>Activated-carbon adsorption</b>	- Good removal up to concentrations less than prescribed limit	-Require additional treatment before discharge
<b>Incineration</b>	- Complete destruction to CO <sub>2</sub> and H <sub>2</sub> O	-Applicable for high concentration (>1000 ppm) of effluent
	- Heat can be utilized in combustion process	-Very expensive
<b>Membrane Processes</b>		-Thermal and chemical regeneration reduces adsorbent life.
- Ion exchange	- Regeneration: Less adsorbent loss	-Air pollution problem
- Membrane filtration	- Good removal	-Supplemental fuel is required
- Liquid membrane	- Good removal	
<b>Electrolytic methods</b>		
- Electrochemical destruction	- Break down compounds are non-hazardous	-Specific, not effective for other constituents in the effluent
- Electro kinetic coagulation	- Economically feasible	-Sludge generation
		-Only at laboratory level
		-High cost of electricity
		-High sludge formation

**Table 1.2.** Advantages and limitations of different technologies for phenolic waste removal from industrial effluents (**Continued**)

<b>Technology</b>	<b>Advantages</b>	<b>Limitations</b>
<b>Chemical Oxidation</b>		
- KMnO <sub>4</sub>	- Good oxidizing capability	- Insoluble MnO is byproduct, hence disposal costs
- Ozone	- Applied in gaseous state: no alteration in volume	- Short half life (~ 20 min)
- Hydrogen peroxide	- Good oxidation, prevents shock loading in biological systems without affecting the performance	- Sludge formation, very much pH sensitive process
- Chlorine dioxide	- No sludge and chlorophenol formation	- pH sensitive, transportation is difficult
- Wet air oxidation	- Complete destruction to CO <sub>2</sub> and H <sub>2</sub> O	- High cost of air, high Temperature and Pressure
<b>Advanced oxidation</b>		
- Photo catalytic	- Break down compounds are non-hazardous, solar spectrum can be used.	- High cost of electricity/energy - Depends strongly on catalyst
- Photo Fenton	- Very fast degradation, complete removal	- pH sensitive
- Photochemical	- Very fast degradation	- Byproduct formation
<b>Biological methods</b>		
- Aerobic	- Efficient for low concentration Phenolic waste	- Air requirement and sludge formation
- Anaerobic	- No sludge formation, convert waste to CH <sub>4</sub> and CO <sub>2</sub>	- Longer start up, sensitive to process parameters, not applicable to all phenols
- Anoxic	- Applicable for nitrogen rich waste water	- Not applicable for high concentration and for all types of phenols

#### 1.2.4 Membrane Processes

Many processes like ion exchange resin beds, membrane filtration and liquid membrane are used for phenol removal (Kunnin 1977). Ion exchange resin beds are used when concentrations of phenols are very less. However, its application up to 20000 mg/l of phenol with polymeric adsorbent like Amberlite XAD and SP1 is reported (Chriswell et. al 1987). Like activated carbon regeneration is essential and after regeneration there is loss in capacity. Common solvents used for regeneration are caustic, acetone, methanol and formaldehyde (Gadekar et. al 1992). Membrane filtration or extraction is based on principle of conversion of phenols into ionic form and concentration on membrane, which can be recovered by pH adjustment (Gonzalez et al. 2002).

Liquid membrane systems are double emulsion drops. Two immiscible phases are separated by a third phase that is immiscible with other two phases. Phenols are generally removed through this dispersed mechanism (Xang 1984). Since phenol is oil soluble, it permeates readily from the outside water phase through the oil membrane phase into the internal receiving phase droplet, which is caustic. In receiving phase, the phenol will be neutralized by the caustic solution and tied up as sodium phenolate that is insoluble in oil phase and consequently cannot diffuse back again. In this removal, the membrane is kerosene containing 5 % v/v of span 80 (surfactant) (Terry et. al. 1982, Nath et. al 2001). A number of other combinations are available for efficient removal. However, this method is very much substance specific and sluggish (Teramoto et. al 1983).

#### 1.2.5 Electrolytic Methods

In electrochemical destruction, an electrochemical cell operating at 50-60°C and atmospheric pressure is used to generate an oxidizing species at the anode in acidic medium. Various materials like titanium dioxide, stainless steel and strontium oxide as anode with lead oxide, strontium oxide, ruthium oxide, and diamond thin film as cathodes are used in phenol removal (Morao and Lopes 2004, Borros et al. 2003, and Fu 2004). Electro-coagulation is a relatively new technique, which was developed in mid 1990s in which a variety of unwanted dissolved particles and suspended matters are effectively removed by electrolysis. In one of the processes, aluminum plates are used as electrodes in which aluminum ions are generated at the anode and hydroxide ion at the cathode. Aluminum ions liberated from the anode interact directly with anions or phenol, which then precipitate out of the solution in the form of an insoluble salt, e.g. aluminium triphenolate (Phutdhawong et al. 2000). This method has some significant advantage of having little or no consumption of chemicals and no sludge build up. However, this process suffers from the drawbacks like high cost of electricity, passivation and destabilization of electrodes (Sires 2004).



### 1.2.6 Chemical Oxidation

Generally in chemical oxidation, phenol oxidizes to hydroquinone and catechol, which are further oxidized to quinines, carboxylic acid and finally to  $\text{CO}_2$ . Requirement of ozone is 7.5 kg per kg of phenol for complete removal (Chakraborty et al. 1998). Hydrogen peroxide is not reactive till  $\text{Fe(II)}$  ions are not present. In presence of ions, it becomes cheapest option in comparison to ozone, chlorine, chlorine dioxide and potassium permanganate. However, it is very sluggish method like permanganate oxidation. Chlorine method is very sensitive to stoichiometric amount otherwise, with phenols, it forms chlorophenols that causes taste and odor problems in drinking water. Chlorine dioxide method can effectively destroy phenols without sludge formation and chlorophenol formation but sensitiveness to pH limits the large-scale application (TES 2003).

### 1.2.7 Wet Air Oxidation (WAO)

In WAO, air or pure oxygen is used to oxidize refractory pollutants either dissolved or suspended in water. However, complete conversion into carbon dioxide and water require severe temperature ( $175\text{-}300^\circ\text{C}$ ) and pressure conditions (200 atm), which penalize the economy of treatment (Mishra et al. 1995). The addition of suitable catalyst can accelerate the oxidation rate, thus severity of the condition needed is lowered, which improves the competitiveness of catalytic wet air oxidation. The lack of mechanically and chemically stable supported catalyst is main reason for less adoption of this technology (Eftaxias et al. 2001). Investigations related to treatment of Phenolic waste using different types of catalyst like  $\text{CuO}$ ,  $\text{CeO}_2$ , Copper/MCM-41, pillared clay containing iron, platinum etc. are conducted either in slurry, rotating basket or trickle bed reactor by various researchers (Lin et al. 2003, Hu et al. 2001, Guelou et al. 2003, Masende et al. 2003, Wu et al. 2001, Alexandre et al. 1998).

### 1.2.8 Activated Carbon Adsorption

It is useful for influent phenol concentration of 400-2500 mg/l and effluent objective of less than 1 mg/l i.e. meeting discharge regulations. It is also less sensitive to fluctuations in environmental conditions such as temperature and pH (Knaebel 1995). The adsorbent becomes saturated after certain period of operation, at that time the adsorbent must be either disposed off as a solid waste, or treated to remove the adsorbed compounds called as regeneration (Schultz and Keinath 1984). The commonly employed regeneration techniques are chemical and thermal. The application of thermal regeneration to exhaust activated carbon in industries is common. In this process of thermal regeneration, controlled oxidation is performed at temperatures typically in the range of  $750\text{-}1000^\circ\text{C}$  in the presence of steam. This is discredited as energy intensive with associated high-

energy costs. Besides, there are losses in total carbon during thermal regeneration due to particle attrition and oxidation of the activated carbon. Approximately 50% loss in surface area after 10 regenerations and total carbon losses of 8% per regeneration have been observed (Fetting 1999, Hutchins 1973).

### 1.2.9 Biological Methods

For the destruction of Phenolic waste, it is applicable for influent level of 7-10 mg/l to several thousand mg/l under properly controlled conditions using biological treatment. However, this option is feasible for influent of up to 1000 ppm (Lanouette 1977). For high concentration waste, most frequently used step is activated sludge process and for low strength waste, aerated lagoons, oxidation ponds, oxidation towers and trickling filters are used (Mahajan 1992). In aerobic degradation, microorganisms utilize phenol as carbon and energy source, due to which, monohydric phenols are converted into dihydric phenols and then ring cleavage converts dihydric phenols to various aliphatic intermediates (Pandey and Kaul 1992). Biological filters, oxidation pond, rotating biological contactor are also used in aerobic processes (Hosseini 2005, Gonzalej et al. 2001, Collins 1997). In absence of oxygen, a different pathway for the phenols degradation leads to methane and CO<sub>2</sub> (Evans 1988). Traditionally anaerobic technology was used for stabilization of sludge generated from aerobic treatment. Now it is used for large-scale industrial and domestic water treatment plants due to the advantage of no sludge generation, no energy requirement by using anaerobic filters and/ or UASB (Up Flow Anaerobic Sludge Blanket) reactor (Duff et al. 1995). In anoxic treatment, nitrate respiration is used in the absence of oxygen by few facultative heterotrophic anaerobic bacteria. Phenol degradation path way is similar to anaerobic process whereas principal biochemical pathways for energy release are similar to aerobic process; hence, this process of denitrification is termed as anoxic. Since for this treatment process nitrogen rich environment is required, several studies on treatment of coke oven wastewater are found feasible (Fedorak and Hrudey 1988). These processes are very sensitive to shock loading and operating parameters (Lin and Weber 1992).

### 1.2.10 Advanced Oxidation Processes (AOPs)

AOPs are defined as near ambient temperature and pressure processes that involve the generation of hydroxyl radicals in sufficient quantity to effect water purification (Andreozzi et al. 1999). The hydroxyl radical (OH·) is a powerful, non-selective chemical oxidant, which acts very rapidly (rate constants usually of the order of  $10^6$ – $10^9$  M<sup>-1</sup> s<sup>-1</sup>) with most organic compounds. AOPs have different variations namely, ozonation, hydrogen peroxide treatment, use of UV radiations

(photochemical), titanium dioxide catalyst with UV radiations (photocatalysis) and by the combination of hydrogen peroxide with ferrous ions as well as UV radiation (photo Fenton) produce  $\text{OH}\cdot$  radicals (Esplugas et al. 2002). These variations are allowing a better application for specific treatment requirements. Almost all the phenolic compounds can be degraded by photocatalytic oxidation (Bhatkhande 2001) and photo-Fenton processes (Wolfgang 2003). Due to UV light, reactivity of ozone and  $\text{H}_2\text{O}_2$  increases for oxidation of phenols. Common problems for all the AOPs are their high cost, fundamentally due to the high demand of electric energy for production of ozone and/or UV lamps.

### **1.2.11 Conclusion**

Treatment technology selection depends on the type and concentration of phenols in wastewater. Wastewater with a phenol concentration of 2000 mg/l or higher would be treated for phenol recovery by solvent extraction. Wastewater with an intermediate or low phenol concentration would not be good for solvent extraction (OHEPA 2002). Biological treatment for the destruction of phenolic waste is applicable to influent with phenol in the range of 1000 ppm to 300 ppm. It can reduce the concentration to 5-10 ppm. For intermediate and dilute solutions of phenols, activated carbon treatment is the best option; it can even reduce the effluent concentration to zero level (Bansal and Rattan 1997). However, activated carbon treatment option is quite expensive because of high cost of regeneration (Lanouette 1977). For complete mineralization of low concentrated (5 ppm) influent phenolic waste, advanced oxidation processes (AOPs) can be used (OHEPA 2002). However, it is noticed that AOPs are not effective for treating concentrated effluents with the concentration of organic compounds greater than 100 mg/l because of high cost (Munter 2001). All the processes described have various imitations. Thus, systematic investigations are required, to make these processes for the treatment of phenolic wastes, economically and ecologically suitable.

## **1.3 TECHNOLOGY SELECTION FOR PHENOLIC WASTE TREATMENT THROUGH “EE” (ECOLOGICAL AND ECONOMICAL) APPROACH**

Based on critical review of techniques available three processes have been selected for further investigations.

### **1.3.1 Studies on Adsorption using Waste Material (Fly Ash) as an Adsorbent**

Activated carbon adsorption is the best option for dilute and low concentration effluent, and currently in use at many treatment plants; however, it has drawback of high cost of regeneration.

The huge deposits of fly ash around the power plants poses environmental problems. At present 100 million tons of fly ash is being generated annually in India and nearly 90000 acres of land is presently occupied by ash pound, which is increasing annually. Indiscriminate disposal of fly ash consumes large volume of land and due to its low density it leads to airborne diseases. As per legislation, its utilization must be at least 25 % of composition in preparing bricks, Portland cement, tiles, road blocks etc. is compulsory within 50 km radii of power plant (MOEF, 1999). In spite of this, utilization is very less (Table 1.3). Numbers of researchers have tried to utilize fly ash in water pollution control (Pandey et al. 1985, Chakradhar et al. 2004, Gupta et al. 2003, Singh et al. 1993, Ramu et al. 1992). For treatment of phenolic compounds work has also been reported by many workers using fly ash as an adsorbent ( Srivastava et al. 1995, Gupta et al. 1998, Singh et al. 1994). Combination of use of fly ash as well as activated carbon for the phenolic wastewater treatment has a potential as eco-friendly technique with sustainable development as per RCRA (Resource Conservation and Recovery Act).

**Table 1.3.** Fly ash generation and utilization in India (Fly ash mission 2004)

Sr. No.	Zone	Fly Ash generation (Metric Ton)	Fly Ash Utilization (Metric Ton)	Fly Ash % Utilization
1.	Southern	13.5	0.8	6.0
2.	Western	16.5	0.8	5.0
3.	Central	18.0	2.8	15.8
4.	Eastern	10.2	2.9	28.8
5.	Northern	15.5	2.3	14.8

In this research program, fly ash from different sources was obtained: fly ash A from lignite based thermal power plant, fly ash B from coal based thermal power plant, fly ash C from the paper and pulp industry and fly ash D from sugar industries and studies on following aspects were carried out:

- i. Batch kinetic studies for adsorption of phenols viz. phenol, catechol, resorcinol, hydroquinone, 2-aminophenol and 3-amino phenol, on fly ash as well as activated carbon.
- ii. Effect of initial conc., initial mass of adsorbent, temperature, presence of salt, contact time and pH.
- iii. Determination of adsorption isotherm parameters for six isotherm models

- iv. Kinetics and thermodynamics of adsorption.
- v. Correlation of the data and statistical analysis.

The above studies were also carried out on activated carbon to compare the adsorption behavior with fly ash.

### 1.3.2 Coupled System of Adsorption and Biodegradation (Bioactive Activated Carbon)

In biological treatment, activated sludge process with their adapted, heterogeneous microbial flora possess the potential of treating aqueous phenolic wastes at reduced capital and operating cost. However, phenol is toxic to most of the microorganisms at high concentration and inhibits growth at even lower concentrations. Even cultures such as *Pseudomonas* reported to have the potential of metabolizing phenol exhibited inhibition kinetics at concentrations above 100 mg/l. (Yang and Humphrey 1975) Further, for maintaining a constant and stable mixed culture, pH, temperature, feed rate and inlet concentrations must be held constant. It has been observed in laboratory studies that because of sudden change in inlet concentration and/or feed rate, washout may occur (Kumar et al. 2004). However, oscillatory but inherent stability observed in real systems may be due to variations in temperature and pH, which overcome unstable transient conditions. An activated sludge process has been found to operate at effluent concentrations nearer 8-10 ppm rather than 1 ppm. In order to bring down the influent concentration to microbially acceptable level and to avoid the possibility of shock loadings, equalization basins are required. Also relatively, long-residence times are required to achieve effluent concentration within acceptable levels. In the event of shock loadings even with the best-designed activated sludge process reactors there are always possibility of rise in phenol concentration well above the allowable discharge level.

The physico-chemical process of activated carbon adsorption can be used to meet increasingly stringent discharge regulations. This treatment option is less sensitive to fluctuations in environmental conditions such as temperature and pH. However, energy intensive thermal regeneration makes it very expensive option.

Some researchers have shown a keen interest in the use of biological methods of regenerating the exhaust carbon, as these methods are less energy intensive and involve less capital and operating costs. Besides, these are capable of transforming toxic organic compounds into innocuous products such as carbon dioxide and water. Therefore, research workers have tried the regeneration of activated carbon biologically. The results were promising (Sontheimer et al. 1979, Lin and Weber 1992, Annadurai et al. 2002). For this purpose, three methods are found in the literature.

In the first method, passing an aerobic microbial culture from a separate fermentor through the carbon column regenerates the exhausted carbon. The function of the culture is (i) to maintain the low concentration at carbon and liquid film interface and (ii) to degrade the desorbed adsorbate to non-toxic entities (Sigurdson and Robinson 1978, Wallis and Bolton 1982, and Hutchinson and Robinson 1990 a,b). While in the second method, the exhausted carbon is regenerated as a result of the microbial growth on the surface of the carbon itself. Third method is just the modification of second method. In this, the microbial growth is encouraged and biodegradation takes place in the same reactor simultaneously. The present work is concerned with the last i.e. third approach of bioregenerating the activated carbon. This coupling of two methods of removal of pollutant is called bioactive activated carbon systems.

#### **1.3.2.1 Bioactive Activated Carbon System**

Sontheimer et al. (1979) was thought to be the first to observe this phenomenon of the beneficial effects of microbial activity on granular activated carbon (GAC) treatment of wastewater. The bioactive activated carbon system is composed of activated carbon and an actively growing biofilm on it (Faust and Aly 1987).

This combination of the two separate modes of removal of impurities has several advantages to it, apart from the regeneration of activated carbon. Bacteria growth is better in presence of activated carbon. Various research works (Nayar and Sylvester 1979, Blanken 1982, and Schultz and Keinath 1984) have been done to study the effect of activated carbon on the bacteria. The beneficial effects include the following:

Biodegradation of slowly biodegradable compounds is enhanced as they are retained for longer times. Enrichment of food and oxygen, and better attachment of microorganisms on activated carbon create conducive environment for the growth of microorganisms. Activated carbon protects the microorganisms from toxic substances by adsorbing these substances. Bad effects on the microbial growth due to fluctuations in concentration and flow rate are either eliminated or dampened ( Nayar and Sylvester 1979). Both the processes, biological and adsorption of removal are operative in the same reactor; the need of two separate reactors is obviated. Volume of the reactor is relatively small owing to less residence time, therefore lower capital investment is required.

Service life of the activated carbon column has been suggested to be extended by biological degradation of the pollutant from liquid phase directly. Secondly pollutants desorbed as a result of negative concentration gradient are degraded as they pass through the microbial films covering these carbon particles; therefore, making active sites available for further adsorption. One school of thought (Perroti and Rodman 1973) proposed that extracellular enzymes excreted from bacteria enter the pores of adsorbent, degrade the biodegradable pollutant adsorbed there and the metabolic products diffuse back to liquid phase, thereby creating active sites for further adsorption. However, Xiaojian et al. (1991) are of view that enzymes are too big in size to enter the carbon micropore, where most of the surface area lie and this active site generation through biological means is bioregeneration of adsorbent.

The present study is mainly concerned with the use of bioactive activated carbon systems for the treatment of industrial wastewaters containing phenol and its derivatives. This has been reported to be viable alternative in treating strong liquor containing high concentration of phenolic compounds by Lin and Weber 1992). They showed that the operation of BAC process was stable and excellent for a period greater than 260 days and no supplemental carbon had to be added to the column for achieving consistent performance.

Further, it may be mentioned that the performance data of such studies are either available in terms of total phenols or in terms of surrogate parameters such as chemical oxygen demand (COD) and total organic carbon (TOC). Also, the phenolic compounds present in effluents may differ in respect of their adsorbability and biodegradability.

In view of the above, the present research program focuses on the need of development of adsorption and biodegradation characteristics of the phenol and some of its derivatives. Combination approach overcomes the drawback of individual methods. Hence the present experimental work would focus on development of biosorption system for the removal of phenol by working on following:

i. Adsorption

- a) Experiments on batch kinetic studies for adsorption of phenols viz. Phenol, catechol and 3-aminophenol in basal salt medium on activated carbon.
- b) Studies on the effect of various parameters such as initial mass of adsorbent, time and initial concentration.

- c) Determination of adsorption isotherm parameters for adsorption of phenols in basal salt medium on activated carbon.
- ii. Biodegradation
  - a) To acclimatize the *Pseudomonas* species to high concentration of phenols.
  - b) To study the degradation of phenols and growth of microorganism.
  - c) To determine the biodegradation kinetic parameters.
- iii. Biosorption
  - a) Batch experiments to study the effect of contact time on immobilization of bacteria on activated carbon.
  - b) To study the degradation of phenols and growth of microorganism on biosorbent.
  - c) Microscopic study of biofilm.
  - d) To study bioregeneration.

### 1.3.3 Advanced Oxidation Processes (AOPs)

These are ecologically best among available methods for treatment of phenolic wastewater. These methods have several advantages over other treatment processes for phenolic wastewater:

- (i) complete mineralization
- (ii) no waste disposal
- (iii) low cost
- (iv) mild temperature and pressure conditions.

AOPs are often employed for treatment of phenolic wastewater that are not amenable to conventional biological methods. The role of AOP depends on the treatment objectives and may vary from partial remediation to complete mineralization. In the case of partial treatment, AOP aims at the selective removal of the more bio-resistant fractions and their conversion to readily biodegradable intermediates that can subsequently be treated biologically. Coupling AOP with biological post treatment is conceptually beneficial as it can lead to increase overall treatment efficiencies compared with the efficiency of each individual stage (Mantzavinos 2004).

Only literature review on AOP is presented in this report. Experimental work could not be carried out beyond making the experimental setup due to resource limitations.



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