CHAPTER 2

LITERATURE REVIEW

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Literature review has been confined to only three types of treatment processes for phenolic wastewater: (i) adsorption (ii) bioactive activated carbon (iii) adavance oxidation processes.

2.1 ADSORPTION FOR PHENOLIC WASTEWATER TREATMENT

The adsorption isotherm constants determined by various workers on different phenolic wastewater and adsorbent systems reported in the literature have been summarized in Table 2.1 and 2.2.

Weber and Moris (1964) investigated the adsorption equilibrium of several organic compounds including phenol on activated carbon. The factors that govern the capacities and positions of adsorption equilibrium were also investigated. The experimental data were correlated well with the Langmuir equation for isotherm. The particle size of the adsorbent, the temperature, pH, molecular weight were reported to affect the adsorption isotherm on activated carbon.

Based on the research studies conducted to evaluate the relative rates and capacities of adsorption of phenolic compounds, Huang and Steffens (1976) noted that the order of rate of adsorption for other phenolic compounds was found to be: o-aminophenol, pyrocatechol and resorcinol. The adsorption capacity was found to increase greatly by the substitution of an amino or hydroxyl group at the ortho position of phenol, with the amino derivative having the most profound effect on increase in capacity. The functional group present at meta position, as in case of resorcinol, did not increase the equilibrium capacity. In all four of the phenolic compounds studied, the data were correlated with the piece-wise Langmuir's Isotherm with good agreement.

Jossens et al. (1978) predicted equilibrium adsorption based on ideal solution theory for the multi-solute aqueous system using only single solute data. They also proposed a three-parameter adsorption isotherm, based on thermodynamic theories, for highly heterogeneous surfaces such as activated carbon.

Table 2.1. Summary of work published on adsorption of phenols (Data correlation by Freundlich and Langmuir isotherms)

Compound	Adsorbent	Conc. range mg/l	Isotherms				Ref.
			Freundlich		Langmuir		
			K_f	1/n	Q	b	
Phenol	Activated Carbon PX-21 [Amoco Research, Illmols] (A-2800-3500)	0.75-846	38.07	0.405	202.48	0.189	Yen and Singer (1984)
	Activated carbon F-400 [Calgon] (A-1050-1200)	8-250*	50.00	0.260	213	0.1	Mckay et al. (1985)
		0-442	47.69	0.27	300.4	0.157	Seidel et al. (1985)
		20-1000	86.7	0.183	-	-	Noll and Gonaris (1988)
		1.18-918	74.00	0.201	-	-	Vidic and Suidan (1991)
		1.4-711	95.94	0.177	-	-	Sorial et al. (1993)
		0-42.3 *	0.313	0.296	2.026	0.021	Yonge et al. (1985)
	Activated carbon AGD3016 [Reidel-de Hean] (A-3000-3500)	47-315	56.54	0.188	180.38	.0376	Khan et al. (1997)
	Activated carbon CZ124 [Prepared in lab.] (A-2450)	0-140*	73.00	0.236	206	0.0527	Hu and Srinivasan (1998)

Table 2.1. Summary of work published on adsorption of phenols (Data correlation by Freundlich and Langmuir isotherms)**(Continued)**

Compound	**Adsorbent**	**Conc. range mg/l**	**Isotherms**				**Ref.**
			Freundlich		**Langmuir**		
			K_f	**1/n**	**Q**	**b**	
Phenol	Activated carbon cloth (A>1500)	0-12*	56.0	0.354	208.0	0.193	Brasquet et al. (1999)
Phenol	Fly ash (A-4.87)	0-450	0.9	0.550	2.35	0.017	Kumar et al. (1986)
Phenol	Saw dust carbon	0-600	5.2	0.652	146.25	4.016	Jadhav et al. (2004)
Phenol	Fly ash (150µm)	0-400	0.1	0.212	0.041	0.0041	Sing et al. (1994)
	Fly ash (100µm)		0.1	0.286	0.049	0.0049	
	Fly ash (45µm)		0.1	0.294	0.069	0.0063	
	Activated carbon [Lurgi] (A-1232)	1-10*	1.7	0.27	2.2	0.178	Costa E et al. (1988)
	Commercial activated carbon		2.1	0.07	-	-	Goto et al. (1996)
	Activated carbon cloth		2.6	0.342	1.84	0.2127	Ayranci (2005)
	Activated carbon ACG40 [Active carbon (I) Ltd.] (A-620)	28-866	37.7	0.228	200	0.014	Singh et al. (1996)
	Actived carbon 60CTC [Active carbon (I) Ltd.] (A-1010)		77.1	0.246	327.27	0.0087	
	Actived carbon 80CTC [Active carbon (I) Ltd.] (A-1260)		89.9	0.254	542.86	0.0033	
	Actived carbon 90CTC [Active carbon (I) Ltd.] (A-1520)		100.8	0.276	571.42	0.0039	

Table 2.1. Summary of work published on adsorption of phenols (Data correlation by Freundlich and Langmuir isotherms)(**Continued**)

Compound	**Adsorbent**	**Conc. range mg/l**	**Isotherms**				**Ref.**
			Freundlich		**Langmuir**		
			K_f	**1/n**	**Q**	**b**	
Phenol	Activated carbon Ceracarbon 208C [Prepared in lab] (A-1141)	1-617	84.6	0.238	-	-	Streat (1995)
	Activated carbon Coconutcell GAC40 [Prepared in lab] (A-1062)		72.1	0.218	-	-	
	Activated carbon Wood-pical03 [Prepared in lab] (A-1699)		99.8	0.246	-	-	
	Activated carbon Coal-Sp-207 [Prepared in lab] (A-865)		69.3	0.225	-	-	
Resorcinol	Activated Carbon [Lab. Grade] (A-492)	3-11*	0.35	0.969	456.6	.00042	Swami et.al (1997)
	Activated carbon,F400 [Calgon, Pittsburg] (A-970)	5.50-27.53*	-	-	125.53	0.615	Huang and Steffens (1976)
Catechol	Activated carbon,F400 [Calgon, Pittsburg] (A-970)	3.67-27.52*	-	-	145.35	145.35	Huang and Steffens (1976)
2-aminophenol	Metal ferrocyanides (CuFc)	11-109*	-	-	16.67	0.0008	Tewari (1997)
	Metal ferrocyanides (ZnFc)		-	-	19.23	0.0006	
	Metal ferrocyanides (MoFc)		-	-	20.00	0.0005	

Table 2.1. Summary of work published on adsorption of phenols (Data correlation by Freundlich and Langmuir isotherms)**(Continued)**

Compound	**Adsorbent**	**Conc. range mg/l**	**Isotherms**				**Ref.**
			Freundlich		**Langmuir**		
			K_f	**1/n**	**Q**	**b**	
3-aminophenol	Activated carbon [Prepared in lab.]	-	0.4	0.680	11.14	0.027	Reddy et al. (1989)
Hydroquinone	Hexadecyl-trimethyl-ammonium-bromide	10-600	-	-	16.64	0.0073	Yıldız (2005)
	Activated carbon cloth	-	3.2	0.371	1.86	0.2765	Ayranci (2005)
4-aminophenol	Metal ferrocyanides (SbFc)	10*	-	-	190.00	0.0180	Tewari (2005)
4-chlorophenol	Activated carbon [Prepared in lab.]	0-12*	131.6	0.206	207.9	2.350	Brasquet et al. (1999)
4-nitrophenol			187.5	0.110	280.9	1.20	
2-tertbutyl-4-methyl phenol			301.0	0.117	427.4	0.549	
2-chlorophenol	Activated carbon AGD3016	0-258	2.1	0.206	2.3474	9.5518	Khan. et al (1997)
3-chlorophenol			2.2	0.184	2.36	12.798	
4-nitrophenol	Fly ash (Bagasse)	0-500	1.2	0.4	8.33	0.0002	Gupta (1998)
2- nitrophenol	Fly Ash	0-350	2.9	0.274	5.795	34.77	Singh et al (1994)
4-nitrophenol			3.5	0.237	7.800	23.40	
2-chlorophenol	Dried activated sludge (A-95)	0-400	13.5	0.483	281.1	0.086	Asku et al (2001)
	Fly ash (A-23)		1.5	1.0	98.7	0.009	
	Granular activated carbon (A-600)		19.2	0.57	380.2	0.114	
4-chlorophenol	Dried activated sludge (A-95)	0-400	16.9	0.47	287.2	0.09	
	Fly ash (A-23)		1.5	0.71	118.6	0.01	
	Granular activated carbon[Prepared in lab.] (A-600)		29.7	0.47	422.1	0.118	

A- Surface area of adsorbent, m^2/g

*** Equilibrium concentration, mg/l**

Mathews and Su (1983) developed adsorption equilibrium and kinetic data of naphthalene and phenol on activated carbon. Homogeneous solid-phase diffusion model was used to predict the kinetic data for both compounds.

Yen and Singer (1984) presented an improved method of calculation procedure to be used with Ideal Adsorbed Solution theory for predicting the adsorption isotherm behavior in binary and ternary systems efficiency. Experimental studies on the adsorption of phenol and substituted phenols on activated carbon were carried out to substantiate the predictions.

Activated carbon (F400) was reported by Mckay et al. (1985) to adsorb various inorganic and organic compounds namely sodium dodecyl sulphate, mercuric ions, chromic ions, phenol and p-chlorophenol. Langmuir and Freundlich isotherm models were used to correlate adsorption data.

Seidel et al (1985) carried out research work for determining the adsorption isotherms of phenol and indol on four different activated carbons from their aqueous solutions in the concentration range 10^{-3}-10^{-2} mmol/l at 20°C. For the calculation of kinetic processes, an isotherm has been proposed by combining Redlich-Peterson equation with elements of Dubnin-Raduskevich analysis.

Kumar et al. (1986) have investigated the adsorption of phenol and cresol and their mixtures from aqueous solutions on activated carbon and fly ash. The effects of contact time and initial solute concentration (50-600 ppm) have been studied and isotherm parameters are evaluated. The Freundlich isotherm has been found to be more suitable for all the systems investigated.

Effects of molecular size, molecular structure, and concentration on the adsorption kinetics have been the focus of research work conducted by Fettig and Sontheimer (1987). Various mass transfer models, namely, film diffusion, surface or pore diffusion, and heterogeneous diffusion model were applied to elucidate the kinetics in fixed-bed adsorption column at low concentrations with an intention of using small number of kinetic parameters.

Noll and Gounaris (1988) adapted the gravimetric method, which is usually used to determine the isotherm in gas / solid adsorbent systems, to the liquid / solid adsorption systems consisting of two adsorbents, activated carbon, and a polymeric resin XAD4, and two adsorbates phenol and p-chlorophenol. The buoyancy force which is almost absent in gas/solid systems was found to pose a problem in liquid / solid system, thus making the interpretation of data difficult. However, an experimental technique was devised by the authors, whereby the buoyancy factor was determined and used in the calculations.

Traegner and Suidan (1989) reported an estimation procedure based on Levenberg-Marquardt numerical algorithm, for determining the parameters of homogeneous surface diffusion model used to describe the dynamics of adsorption of various organic compounds on granular activated carbon (GAC). In order to solve the mathematical model of adsorbent-adsorbate systems, the values of measurable parameters such as particle size, adsorption isotherm parameter, and kinetic parameters such as the liquid film mass transfer coefficient and surface diffusion coefficient must be known.

Vidic and Suidan (1991) conducted batch experiments to investigate the parameters which effect the adsorptive capacity of granular activated carbon (GAC) for several phenolic compounds including phenol and natural organic matter. The results of this research work revealed that the molecular oxygen present in the test environment decreased the adsorption capacity of activated carbon significantly for several phenolic compounds and natural organic matter. Apart form the presence, the quantity of the molecular oxygen present has also been found crucial for determining the adsorption capacity of activated carbon for these compounds. The oxygen may be entrapped inside the carbon pores, sealed in the headspace of isotherm bottles, and dissolved in adsorbate solutions. This oxygen affects the adsorption behaviour differently from the oxygen present in acidic surface oxides.

Sorial et al. (1993) investigated the impact of molecular oxygen on multicomponent adsorption on GAC in aqueous solution at room temperature (23±1°C) in batch reactor. They discovered that discrepancies associated with multicomponent adsorption equilibrium might be the result of monomer transformations occurring in the presence of molecular oxygen. Several models to represent multicomponent equilibrium data were available. Among those, model based on ideal-adsorbed solution theory was thermodynamically the most acceptable.

Vidic et al. (1993) extended the scope of their research on the effect of molecular oxygen on the adsorption capacity of phenolic compounds on activated carbon. This research work tried to offer some explanation for this behaviour also. All the adsorption isotherm data were correlated well with Freundlich type isotherm. Position of functional group showed little effect on the adsorption capacity. Phenolic compounds in their ionic state were found to adsorb on the GAC surface to a lesser extent than neutral molecules. Furthermore, in ionic state the oxidation coupling and irreversible adsorption were much more pronounced.

Singh et al. (1994) investigated that the sorption of toxic phenols, which include phenol, o-cresol, m-cresol, p-cresol, o-nitrophenol, m-nitrophenol and p-nitrophenol on fly ash. The fly ash samples were impregnated with Al^{+3} and Fe^{+3} ions for adsorption studies. The influences of various factors, such as concentration (85-500 ppm), particle size (50-150 µm), impregnation of fly ash, pH (1-10) and temperature (30-60°C) on the sorption capacity have been studied. Equilibrium modeling has been carried out using Langmuir and Freundlich isotherm equations and constants have been calculated under different conditions. Thermodynamic studies have also been carried out and values of standard free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) calculated and adsorption was found to be endothermic.

Streat et al. (1995) compared the performance of activated carbon prepared in laboratory from conventional materials such as coal, coconut shell and wood as well as from nonconventational materials such as straw and rubber tyres using phenol and p-chlorophenol. The findings of this research indicated that straw based activated carbon might be an attractive material for removing the impurities from water. The use of this activated carbon would improve economics.

Singh et al. (1996) conducted batch studies on phenol-water/carbon and oxygen analogue of sulphur mustard-water/carbon systems in order to assess the removal efficiencies of coconut charcoals of different grades. These research studies were undertaken mainly to identify an indigenous (Indian) activated carbon to remove chemical warfare agents from aqueous solutions.

Khan et al. (1997) conducted batch studies to determine the adsorption isotherm of five phenolic compounds, namely, phenol o-chlorophenol, m-chlorophenol, p-chlorophenol, and m-cresol on activated carbon for single and bisolute systems from dilute aqueous solutions. Langmuir, Freundlich and BET isotherms were tried for fitting the data of single solute adsorption isotherm studies. All these phenolic compounds were present in dilute concentrations of below 500 ppm. Molecular size, solubility, and polarity of the compound, all have been found to play a role in competitive adsorption in multi-solute systems.

Table 2.2. Summary of work published on adsorption of phenols (Data correlation by Redlich Peterson, Toth, Radke Prausnitz, and Fritz Schulnder isotherms)

Redlich-Peterson Isotherm : $Q_e = \frac{K_1 C_e}{1+K_2 C_e^{\,m}}$

Compound	**Adsorbent**	**Conc. Range mg/l**	**Parameters**			**Ref.**
			K_1	K_2	m	
Phenol	Activated Carbon F-400 [Calgon] (A=1500)	0-80*	97.5	1.34	0.81	Mathews and Su (1983)
Phenol	Activated Carbon Hydraffin71 [Lurgi]	0.06-442	524	329	0.78	Seidel et al. (1985)
	Activated Carbon TVAx1 [VEBCFW]		1498	866	0.75	
	Activated Carbon F400 [Calgon]		7064	3051	0.8	
	Activated Carbon-AG3 [Technical Product of USSR]		4598	101.3	0.75	
2- chloro phenol	Dried activated sludge (A-95)	0-500	23.37	1.46	0.54	Asku et al. (2001)
	Fly ash (A-23)		1	0.26	0.44	
	Granular activated carbon (A-600)		42.34	0.44	0.69	
4- chloro phenol	Dried activated sludge (A-95)		25.85	1.51	0.58	
	Fly ash (A-23)		1.26	0.15	0.6	
	Granular activated carbon (A-600)		47.8	0.33	0.72	

Table 2.2. Summary of work published on adsorption of phenols (Data correlation by Redlich Peterson, Toth, Radke Prausnitz, and Fritz Schulnder isotherms) **(Continued)**

Toth Isotherm: $Q_e = \frac{TC_e}{\left(a + C_e^{th}\right)^{1/th}}$

Compound	Adsorbent	Conc. Range mg/l	Parameters			Ref.
			T	a	th	
Phenol	Activated carbon B10 [Lurgi] (A=1400-1500)	0.06-813.1	1330.1	0.628	0.148	Jossens et al. (1978)

Radke Prausnitz: $\frac{1}{Q_e} = \frac{1}{KC_e} + \frac{1}{kC_e^{1/p}}$

Compound	Adsorbent	Conc. Range mg/l	Parameters			Ref.
			K	K	1/p	
Phenol	Activated Carbon [Lurgi] (A=1232)	0.188-13.44*	37.33	68.39	0.203	Costa et al. (1988)
Pentachloro-phenol	Activated carbon F-300 [Calgon]	0-200	223	0.14	0.42	Mollah et al. (1996)

Fritz Schulnder: $Q_e = \frac{a_1 C_e^{b_1}}{1 + a_2 C_e^{b_2}}$

Compound	Adsorbent	Conc. Range mg/l	Parameters				Ref.
			a_1	a_2	b_1	b_2	
Phenol	Activated carbon F-300 [Calgon]	-	29.0	0.04	0.46	0.63	Hutchinson and Robinson(1990)
Pentachloro-phenol	Activated carbon F-300 [Calgon]	0-200	580	1.27	2.72	1.12	Mollah et al. (1996)

A- Surface area of adsorbent, m^2/g

*** Equilibrium concentration, mg/l**

Ravi et al. (1998) studied adsorption of phenol, o-, m-, p-cresol and benzyl alcohol from aqueous solutions on activated carbon at 278, 298 and 323 K in their complete solubility range. An anomalous temperature dependence of adsorption of these compounds has been observed. The adsorption and desorption behavior of phenol from water on activated carbon in the lower concentration range is quite different from the higher concentration range. The low concentration behavio is mostly governed by the surface chemical reactions, whereas in the high concentration range, miscibility is playing a more crucial role.

In a study conducted by Swami et al. (1997), resorcinol adsorption on laboratory grade, commercial grade carbon and bagasse fly ash from aqueous solution was compared. Equilibrium data were fitted to Freundlich isotherm well. These research studies showed that break through time increases with the increasing bed height and decreasing flow rate. They concluded that bagasse fly ash as cheap and effective adsorbent comparable with commercial grade activated carbon.

Tewari et al. (1997) studied the removal of 2-aminophenol and 2-nitrophenol from aqueous solution through adsorption on copper, zinc, molybdenum, and chromium ferrocyanides in pH range 2-10 at 277°C.

Edgehill et al. (1998) studied the potential of using carbonized slash pine bark as a substitute for activated carbon in their study. The bark was carbonized by slow heating in nitrogen for 0.5 h to 672°C.

Gupta et al. (1998) investigated that bagasse fly ash, a waste generated in local sugar industries, had been converted into a low cost adsorbent. The product so obtained had been used for the removal of phenol and p-nitrophenol. Investigations included the effect of pH, sorbent dosage, phenol concentration and the effect of surfactant on the uptake of phenol and p-nitrophenol. The adsorption data followed both Langmuir and Freundlich models. For determining the rate controlling step and kinetics, they used models given by Boyd et al. (1947) and Recheinberg (1953). Particle diffusion controlled process was found to be rate controlling step.

Vasudevan and Stone (1998) studied the removal of aromatic ligands possessing three combinations of phenolate and amino groups using adsorption on six hydroxide minerals.

Brasquet et al (1999) investigated that granular activated carbon is easily used in water or wastewater treatment in order to remove organic micro pollutants. Different presentation of activated carbon in the form of clothes had been developed.

Varghese et al. (2003) have explored the use of an aquatic plant material, water hyacinth to prepare a novel activated carbon for the removal of phenol, p-chlorophenol and p-nitrophenol from simulated wastewaters by adsorption process. The effect of pH, contact time, initial concentration of adsorbent and temperature on removal process was investigated. The applicability of the intraparticular mass transfer diffusion kinetic model was studied for phenol, p-chlorophenol and p-nitrophenol separately at different concentrations and temperatures.

Kumar et al. (2003) have studied the adsorption of resorcinol and catechol on granular activated carbon. They have done equilibrium and kinetic studies. Six isotherms have been fitted to coorelate their experimental data. For rate controlling step determination, intra particle diffusion model has been applied.

Jadhav and Vanjara (2004) investigated the possible use of sawdust, polymerized sawdust and sawdust carbon for the adsorption of phenol from phenolic wastewater. The influence of various factors such as initial concentration, agitation speed, and amount of adsorbent, temperature and pH, on the adsorption capacity has been studied. Kinetic data has been correlated using pseudo-second order equation to understand the reaction mechanism. Thermodynamic parameters such as ΔG, ΔH and ΔS for the adsorption process were calculated.

Ayranci et al. (2005) have studied the adsorption of phenol, hydroquinone, *m*-cresol, *p*- cresol and *p*-nitrophenol from aqueous solutions onto high specific area activated carbon cloth. The effect of ionization on adsorption of these ionizable phenolic compounds was examined by studying the adsorption from acidic, basic and natural pH solutions. Kinetics of adsorption was followed by in situ UV spectroscopy over a period of 90 min. First-order rate law was found to be valid for the kinetics of adsorption processes and the rate constants were determined.

Tewari et al. (2005) investigated the p-aminophenol and p-nitrophenol adsorption on antimony, cadmium, and zirconium ferrocyanides.

2.1.1 Summary

Literature survey reveals that enormous information on various aspects of activated carbon adsorption studies is available. Most of the research efforts have been directed towards the removal of phenol. Research work related to adsorption studies on selected substituted phenols such as catechol, resorcinol, hydroquinone, 2-aminophenol and 3-aminophenol using fly ash as an adsorbent has not been reported. Source, composition and characteristic of fly ash determine its usefulness as an adsorbent. No paper was found in which fly ash obtained from different sources for adsorption studies for removal of phenols have been reported. In the present work, it has been proposed to study removal of above mentioned phenols using fly ash collected from different sources.

2.2 BIOACTIVE ACTIVATED CARBON SYSTEM

The review in this section has been divided into the following sections:

(i) conceptual view of bioactive activated carbon
(ii) biodegradation studies
(iii) biological activated carbon system

2.2.1 Conceptual View of Bioactive Activated Carbon System

The conceptual view of the processes occurring in biofilm formation in bioactive activated carbon system has been shown in Fig. 2.1. Diagram shows the elements of the bioactive absorption system. The removal of the pollutant is accomplished through mass transport and reaction/ adsorption mechanisms. Therefore, the rate of removal of pollutant in these systems is influenced by the resistances of biofilm and adsorbent to the mass transport through them, the intrinsic degradation kinetics and adsorption on the surface of the adsorbent (Borja et al. 2003).

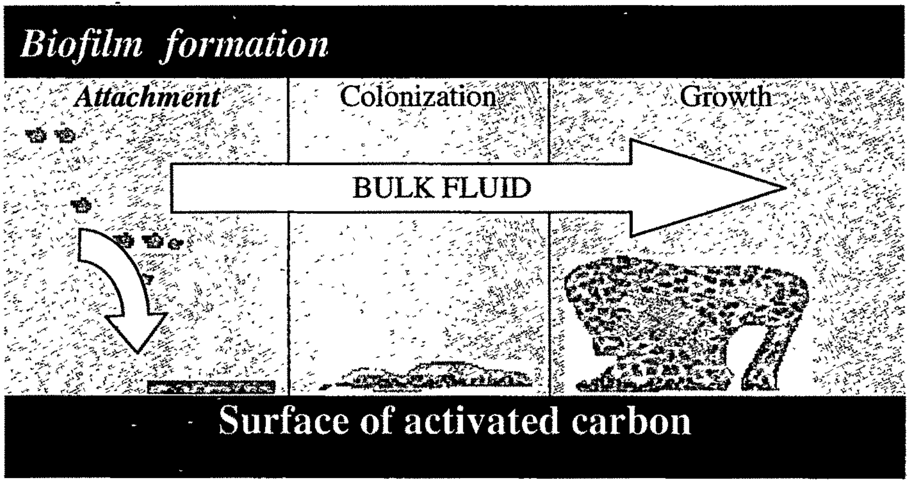


Figure 2.1. Biofilm formation in bioactive activated carbon system (Borja et al. 2003)

2.2.2 Biodegradation Studies

The biological degradation of phenols has been an active area of research for past three decades. These studies have been done by using different microorganisms, in varying concentration ranges of phenols, environmental conditions, various reactor geometries and flow modes. Phenols were considered as non-biodegradable keeping in view the toxic nature of these compounds towards living beings. However, microorganisms with the capability to degrade these phenolic compounds have been isolated (Sastry et al. 1995). These are called phenolytic microorganism and are given in Table 2.3.

The biological degradation is accomplished through benzene ring cleavage using the enzymes present in them. The microorganisms behave differently when exposed to different initial phenol concentrations and other experimental conditions. Therefore, numerous studies have been done to evaluate the behavior of these organisms in different concentrations and environmental conditions, so that outcome could be utilized to design and optimize the biological reactors treating phenolic wastewaters. Both rate and extent of degradation are essential for the understanding of the behavior of microorganisms. Some of the pertinent papers available on these aspects are summarized in Table 2.4., and some of them are reviewed in the following paragraphs.

Pawlowsky and Howell (1973) used two heterogeneous cultures derived from soil and activated sludge to degrade the phenol at higher concentrations. Subsequent to the isolation of these cultures, they were harvested in chemostats operating at residence times of 6 h and 4 h. The culture corresponding to 6 h residence time denoted as "System I' was mainly comprised of spherical and rod shaped bacteria, whereas the culture corresponding to 4 h residence time denoted as "System II " was dominated by filamentous bacteria. The data obtained on these systems were fitted to inhibitory type kinetic models of Haldane and its modifications described by Edwards (1970) in his research paper. The values of kinetics parameters contained in these models were determined by using nonlinear regression technique. To evaluate the goodness of fit of these models, statistical analysis was performed and no model tested could be recommended as best. Any of the models tested could not represent the data satisfactorily near highest growth rates. However, the Haldane type of model was recommended on the basis of its simplicity. It was also observed that "System II" was less affected than "System I" when compared in terms of specific growth rate at higher phenol concentrations. This was attributed to the presence of filamentous type of organism in "System II".

Table 2.3. Phenolytic Microorganisms

Bacteria	*Pseudomonas aeruginosa, Pseudomonas putida, Achromobacter, Alcaligenes, Acinetobacter, Arthrobacter, Azotobacter, Bacillus cereus, Flavobacterium, and Nocardia*
Yeast	*Candida tropicalis, Debaromyces subglobosus, and Trichosporon cutaneoum*
Fungi	*Aspergillus, and Neurospora*

Hill and Robinson (1975) studied in detail the inhibitory growth kinetics of a frequently used aromatic utilizing bacteria, *Pseudomonas putida* with phenol as limiting substrate. *P. putida* was contacted to phenol in both batch and continuous mode. Specific growth rate data were fitted to two substrate inhibition models. Maximum specific growth rate and inhibition coefficients determined by linearizing the Haldane model and fitting the data for high concentration range. To calculate the half-saturation coefficient, the data were fitted to Monod model. Statistical analysis showed that Haldane model gave the best performance. It was concluded that *P. putida* showed a significant tendency for wall growth at high dilution rate, particularly in continuous flow reactors. *P. putida* exhibited the highest phenol degradation rate in batch culture for substrate concentration up to approximately 700 mg/l, in comparison to other phenol utilizing cultures. Despite the fact that *P. putida* has the highest specific growth rate, the heterogeneous microbial population of activated sludge systems may be preferable to these pure cultures for the direct biological waste treatment of phenol because of economy, their sludge setting characteristics and biological adaptability. However, the physical methods such as activated carbon may prove better option for treating reliably effluents containing a high or fluctuating phenol. Subsequently, spent carbon may be regenerated using *P. putida* owing to its high phenol utilization rate and better biofilm forming properties.

Yang and Humphrey (1975) investigated the microbial degradation of phenol using mixed and pure culture of *Pseudomonas putida* in batch and continuous culture systems. The objective of this work was to better understand the mechanism of phenol removal by these microorganisms in wastewater treatment systems. Phenol was used as sole carbon source. The phenol removal kinetics of the two microorganisms, namely bacteria and unicellular yeast was determined in detail. For continuous culture runs, both the modes of operation, steady state as well as transient, were studied. Five inhibitory models were fitted to the data obtained from batch and continuous culture studies. Statistical analysis was also performed for testing fitness of data. No model tested could represent the data well. Therefore, it was not possible to decide the best model out of the five purely on statistical basis. However Haldane's model being a traditional noncompetitive inhibition model was considered for use in further analysis. They concluded that the removal of phenol down to 1-2 ppm is possible in a single stage using *Pseudomonas putida* or *T. Cutaneum.* The inhibitory concentration of phenol for both the species was 100 mg/l.

Chi and Howell (1976) carried out transient experiments on a *Pseudomonas putida* phenol system in a continuous culture to study the behavior of these systems in response to sudden changes in the influent substrate concentration and dilution rate. The growth of the microorganism on the reactor wall was also taken into consideration recognizing its importance especially in operating a laboratory scale biological reactor. Haldane model could not predict the system behavior. Therefore, they modified an existing model as proposed by Powell for non-inhibitory type of waste, and employed it to investigate the systems with substrate inhibition and wall growth. Three types of shock loadings were applied. These are (i) step change in dilution rate (ii) step change in inlet substrate concentration and (iii) finite pulse disturbance in reactor substrate concentration. The shocks were applied over a wide range. For small shocks, the system returned to new high conversion steady state with highly damped oscillations whereas, in response to larger shocks the system returned smoothly (over damped oscillations) to new low conversation state. Powellski bottleneck model was used to predict the system response in the case of small disturbances. Neither model could represent the data obtained for larger disturbance case. The two steady states reached in this research could be directly correlated to the presence of wall growth.

Hutchinson and Robinson (1988) investigated the simultaneous degradation of phenol and p-cresol by pure culture of *Pseudomonas putida* in batch reactor. A relatively simple model proposed in this research gave an excellent prediction of bacterial growth and substrate utilization in this dual substrate system. This research also demonstrated that *Pseudomonas putida* did not utilize preferentially either phenol or p-cresol. This showed that the pathways involved in the degradation of phenol and p-cresol *P.putida* were almost identical and both substrates were metabolized by the same enzymes.

Kotturi et al. (1991) investigated the degradation potential of psychotropic microorganism, *Pseudomonas putida* Q5 for phenol. This was selected because of its ability to grow well in the temperature range 0-30°C and to degrade a wide variety of organic substrates.

Tanyolac and Beyenal (1998) proposed a new approach to evaluate substrate consumption rate, average biofilm density and active thickness of a spherical bioparticle in a completely mixed fluidized bed system. Predictions of substrate consumption rate and average biofilm density were made for a given biofilm surface substrate, concentration and operational biofim thickness. The model developed included the diffusion and reaction inside the biofilm with an effective diffusion coefficient depending on the average film density.

Table 2.4. Comparison of Growth kinetics reported in literature for the Treatment of Phenolic Wastes

Authors	**Bacterial Strain**	**System**	**Conc. Range mg/l**	**Monod's Model**		**Haldane's Model**			**Operating conditions**
				μ_{max} h^{-1}	**K_s mg/l**	**μ_{max} h^{-1}**	**K_s mg/l**	**K_i mg/l**	**Temp °C/pH**
Pawlowsky and Howell (1973)	*Mixed Culture I*	Batch	0-900	-	-	0.260	25.4	173	(28)/ (6.6)
	Mixed culture II (filamentous organism)	Batch	0-1000	-	-	0.223	5.86	934.5	(28)/ (6.6)
Hill and Robinson (1975)	*Pseudomonas putida (ATCC 17484)*	Batch/ Continuous	0-700	-	-	0.534	0.015	470	(30/ (6.2-6.7)
Yang and Humphery (1975)	*Pseudomonas putida (ATCC17514)*	Continuous	0-500	-	-	0.567	2.39	106	(30)/(6.0)
	Trichosporon cutaneum	Continuous	0-900	-	-	0.464	1.66	380	(30)/(4.5)
Chi and Howell (1976)	*Pseudomonas sp.*	Continuous	Up to 700	-	-	0.369	5.94	227	(30)/ (6.8)
Sokol Howel (1981)	*Pseudomonas putida DSM 548*	-	-	-	-	0.26-0.9	0.16-0.62	14.9-19.4	(30)/(6.8)

Table 2.4. Comparison of Growth kinetics reported in literature for the Treatment of Phenolic Wastes **(Continued)**

Authors	**Bacterial Strain**	**System**	**Conc. Range mg/l**	**Monod's Model**		**Haldane's Model**			**Operating conditions**
				μ_{max} h^{-1}	**K_s mg/l**	**μ_{max} h^{-1}**	**K_s mg/l**	**K_i mg/l**	**Temp °C/pH**
D'Adamo et al. (1984)	Mixed culture	-	-	-	-	0.131 - 0.363	5-226	142-1199	(25)/-
Sokol (1987)	*Pseudomonas putida DSM 548*	-	-	-	-	0.33-0.9	0.58-1.25	8.2-19.2	(30)/(6.8)
Lallai et al. (1988)	*Mixed culture*	-	-	-	-	0.318	57.35	1503	-
Tang and Fan (1988)	*Mixed culture*	-	-	-	-	0.365	10.95	113	-
Livingston and Chase (1989)	*NCIB 8250 (Acinetobacter sp.)* + *NCIB10535 (Pseudomonas sp)* + *NCIB1015 (Pseudomonas sp.)*	Batch	0-500	-	-	0.418	2.9	370	(30)/(6.7-6.9)

Table 2.4. Comparison of Growth kinetics reported in literature for the Treatment of Phenolic Wastes **(Continued)**

Authors	**Bacterial Strain**	**System**	**Conc. Range mg/l**	**Monod's Model**		**Haldane's Model**			**Operating conditions**
				μ_{max} h^{-1}	**K_s mg/l**	**μ_{max} h^{-1}**	**K_s mg/l**	**K_i mg/l**	**Temp °C/pH**
Hutchinson & Robinson (1988)	*Pseudomonas putida (ATCC17484)*	Batch	<200	-	-	0.388	1.06	903	(30)/(6.5-6.8)
Kotturi et al.(1991)	*Pseudomonas putida Q5*	Batch	≤200	-	-	0.119	5.27	377	(10)/(7.0)
Okaygun et al. (1992)	Pseudomonas sp.	Batch	0-170	-	-	0.325	8.2	170	(21)/(6.7)
	Klebsiella sp.		0-230	-	-	0.311	3.6	454.8	(21)/(6.7)
Dapaals and Hill(1993)	Pseudomonas putida P71	Batch	50-250	-	-	0.569	18.5	99.4	(25)/(6.8)
Shishido and Toda (1996)	*Phenol-adapted activated sludge.*	Batch	1000	-	-	0.216	5.9	110	(30)

Table 2.4. Comparison of Growth kinetics reported in literature for the Treatment of Phenolic Wastes (**Continued**)

Authors	**Bacterial Strain**	**System**	**Conc. Range mg/l**	**Monod's Model**		**Haldane's Model**			**Operating conditions**
				μ_{max} h^{-1}	**K_s mg/l**	**μ_{max} h^{-1}**	**K_s mg/l**	**K_i mg/l**	**Temp °C/pH**
Kumaran and Paruchuri (1997)	*-Acinetobacter calcoaceticus*	Batch	60-500	0.465	30.96	0.542	36.2	145	Not mentioned
	-Pseudomonas fluorescens 2218	Batch	85-590	0.624	18.66	0.618	71.4	241	Not mentioned
	-Pooled Culture *(P.fluorescens, P.putida, P.cepacia, A.calcoaceticus, Candida tropicalis)*	Batch	300-710	0.463	11.08	0.456	53.9	516	Not mentioned
Diksshitulu et al.(1998)	*Pseudomonas Resinovorans ATCC14235*	Batch-	0-150	-	-	1.007	12	117.7	(28)/ (6.8)
Monteiro (2000)	*Pseudomonas putida DSM 548*	Batch	50-250	-	-	0.436	6.19	54.1	(26)/(6.8)

Table 2.4. Comparison of Growth kinetics reported in literature for the Treatment of Phenolic Wastes **(Continued)**

Authors	**Bacterial Strain**	**System**	**Conc. Range mg/l**	**Monod's Model**		**Haldane's Model**			**Operating conditions**
				μ_{max} h^{-1}	**K_s mg/l**	**μ_{max} h^{-1}**	**K_s** mg/l	**K_i** mg/l	Temp °C/pH
Reardon et al.(2000)	*Pseudomonas putida F1*	Batch	0-54	-	-	0.11	32	0.8	(30)/(7.1)
Sayed-El (2003)	*Burkholderia cepacia PW3*	Batch	3000	-	-	0.321	43.49	1680	(30)/(7)
	Pseudomonas aeruginosa AT2	Batch	3000	-	-	0.253	32	1177	(30)/(7)
Rigo and Alegre (2004)	*Candida tropicalis No.708*	Batch	1000	-	-	0.174	11.2	298	(30-35)/(7)
Kumar et al. (2004)	*Psuedomonas putida MTCC 1194*	Batch-	0-1000	0.26	54	0.305	36.33	129.79	(30)/(7)
Vijayagopal and Viruthagiri (2005)	*Mixed culture*	Batch	50-250	-	-	0.379	18.82	449	(30)/(7)

Research work in batch culture was designed by Rozich et al. (1985) to describe the functional relationship between specific growth rate and the substrate concentration for several types of seed taken from varied sources and to assess the intrinsic variation of the growth model constants for heterogeneous populations metabolizing phenol. The biofilms obtained in this work were highly dense, therefore, offered greater resistance to mass transfer. The mathematical model was developed in this study to investigate the effect of oxygen on biofilm density, which can be solved to evaluate the region of economic operation of the bioreactor.

Shock loads may disturb the proper functioning of the activated sludge plants treating inhibitory waste such as phenol and its derivatives. Most of the studies available in the literature dealt with a single shock load. These studies were extended by Okaygun et al (1992) to consecutive multiple shock load considering it as the worst scenario. These studies were designed to verify experimentally the consequences of microbial activity and population dynamics of exposing activated sludge to multiple shock loads, which might lead to wash out condition. The results indicated that the cell deactivation might also occur if the frequency of the shock loads would be increased.

Various sources of phenols, both anthropogenic and xenobiotic have been reported in a research work by Kumaran and Paruchuri (1997). These compounds have been reported to be toxic to several biochemical reactions. Taking the bacteria from natural sources, which have the capability to transform the phenols to non-toxic entities using enzymes. They carried out batch as well as continuous culture studies. The results indicated that Monod's growth model could not adequately describe the data of degradation of phenol, being an inhibitory substrate. Haldane model was found to describe the growth kinetics well.

Monteiro et al.(2000) studied phenol biodegradation in a batch reactor using a pure culture of *P. putida* DSM 548. The purpose of the experiments was to determine the kinetics of biodegradation by measuring biomass growth rates and phenol concentration as a function of time in a batch reactor. Haldane equation adequately described cell growth.

Reardon et al. (2000) have studied kinetics for benzene, toluene and phenol degradation. Kinetic parameters for phenol biodegradation have been determined for many micro-organisms, including *Pseudomonas*, *Trichosporon*, *Candida* and *Nocardia* species using Monod and Andrews model.

Peyton et al.(2002) studied the biological treatment of high-salinity industrial wastewaters using halophilic bacteria for removing organic compounds without decreasing the salt concentration. Liquid, soil and sediment samples were collected from three distinct saline environments in the western United States. Evaluation of phenol degradation and corresponding cell growth data with Monod and Andrews models indicated that the kinetics were zero-order with respect to phenol.

Kumar et al. (2004) investigated the biological degradation of phenol and catechol by a bacterial strain of *P. putida* (MTCC 1194) in basal salt medium (BSM) in shake-flask experiments at 29.9±0.3 °C at pH of approximately 7.1. The lyophilized cultures of *P. putida* (MTCC 1194) were revived and exposed to increasing concentrations of phenol, and catechol in shake-flasks. This bacterial strain could be acclimatized to the concentrations of 1000 and 500 mg/l for phenol and catechol, respectively. The higher the concentration of phenol or catechol, the longer was the lag period. Haldane's growth kinetics model could be fitted to the growth kinetics data well for the entire concentration range. They also calculated yield and decay coefficients.

2.2.3 Biological Activated Carbon System

Biological activated carbon (BAC) systems invariably employ granular activated carbon (GAC) with a microbial film growing on them. The biological granular activated carbon can be contacted in many ways e.g. packed bed, expanded bed or fluidized bed. In this section research work related to biological activated carbon has been reviewed from experimental as well as modeling point of view.

In a bioactive adsorber column, two mechanisms of substrate removal are operative, namely, adsorption and biodegradation. The rate of these processes is mainly affected by the transport of materials in the liquid phase, microbial growth kinetics, intraparticle transport, and adsorption on the solid phase. Several authors have developed mathematical models considering some or all of the above factors for packed bed, expanded bed and fluidized bed configurations. These models further have been validated taking either one or more specific compounds in wastewaters.

Several modeling efforts incorporate biological activity in activated-carbon adsorber systems. The model proposed by Peel and Benedek (1976) assumed plug-flow conditions, with the carbon particles held in stationery condition in the adsorber column. The salient feature of this model was the fixed film thickness, which did not vary with time and was an externally defined parameter. The model could describe the pilot plant data well for long-term performance, however, could not match the data of initial period, as expected, because of fixed film thickness assumption.

Ying and Weber (1979) proposed a model that incorporated the time and space variant biofilm growth in their model. Liquid film transfer, intraparticle diffusion, substrate utilization by Monod Kinetics and biomass build up were also included in the model. One important feature of their model was the bacterial growth that would reach a certain level where after this would be maintained at that maximum value by washing and air scouring. No provision for additional mass transfer resistance due to biofilm was made, as the maximum allowable biofilm thickness was to be maintained less than that of a monolayer of bacteria. This model was applied to the data from plug flow column and completely mixed fluidized-bed column, and the predictions were in good agreement with data.

Andrews and Tien (1981) gave a general treatment of the growth of bacterial film on adsorbent surface. A model was developed for fluidized bed reactor with a high-circulation rate. In the development of model, following assumptions were made: (i) Mass transfer resistance of the external liquid film and diffusion resistance inside the activated carbon were negligible (ii) The limiting substrate was present in low concentration and degradation kinetics was of first order. Model so developed was solved for a quasi-steady state condition. This model was validated for the removal of valeric acid by adsorption and biodegradation by denitrifying bacteria. Agreement of prediction with experimental data was good in this particular system.

Andrews and Tien (1982) extended the scope of their earlier model by incorporating the effects of uncontrolled active bacterial growth. This growth not only affects bioregeneration, but also changes the settling velocity of the carbon particles. As a result, the settling velocity of the adsorbent changes, which leads to a variable bed height. This poses a difficulty in modeling, which have been reported to be eliminated by the authors by using a variable transformation. Axial dispersion terms have been included to account for the mixing of the liquid phase. A numerical method involving the iterative scheme for solving the resulting second-order, non-linear partial differential equation was proposed. The breakthrough curves were predicted for beds of mono size particles and compared with the published experimental curves for beds of 8 x 35 mesh carbon. These were not matching well. Authors suggested the particle size range to be an important factor in the performance of fluidized bed bacterial carbon treatment units. However, based on this experience, a strategy for operating these beds of mono size particles had been proposed by the authors, whereby heavily coated particles would be removed from the top of the bed, washed to remove the film and put back in the bed for reuse of their adsorptive capacity.

Tien and Wang (1982) applied the simplified version of the Andrews and Tien model for studying the bacterial growth-adsorption interaction in fixed and expanded adsorption beds. Experimental investigations were also conducted in upflow carbon bed for removal of valeric acid from aqueous solutions. Biodegradation was facilitated by a growing film of mixed culture of denitrifying bacteria outside the carbon granules. The agreement between model predictions and experimental data was reported well within the experimental accuracy of the substrate concentration determination. Wang and Tien (1984 a, b) further generalized the diffusion-reaction film model proposed by Andrews and Tien (1981) by allowing the bacterial activity to be, either aerobic or anoxic depending on the film thickness. Simulations were performed to demonstrate the effect of various process variables. Further, removal studies of valeric acid from aqueous solution were conducted in bioactive granular activated carbon columns. This was done in two parts. In the first part, bio-kinetic parameters were determined and then, model developed was solved to predict the performance of carbon column for removing valeric acid.

Andrews and Trapaso (1984) proposed a novel adsorber bioreactor for wastewater treatment. At the core of this unit, a fluidized bed was thought of almost as comprised of monosized granular activated carbon and few bacterial surfaces on the surface. The biofilm would grow into a continuous biofilm with the passage of time. As speculated, this bed should tend to stratify on the basis of settling velocity of the particles. The bio-coated particles would be taken away from the top of the bed and after washing off the biomass, would be returned to the bed. In this research, the preliminary design and feasibility studies were performed using a computer model. On the basis of these computer simulations, this unit has been recommended for the treatment of relatively dilute wastes containing significant amount of refractory organics.

Kim and Pirbazari (1989) developed a mathematical model for a fluidized bed adsorber with recycle. Liquid film transfer, biodegradation and diffusion in the biofim, biofilm growth and adsorption on activated carbon were included in the model. A combinatorial technique comprising of orthogonal collocation and finite differences was employed to solve the model equations. The model was tested on synthetic wastes such as glucose and sucrose and on real wastewaters such as dairy waste and landfill leachate. This research demonstrated that adsorption was the dominant mechanism initially, and in later stages, biodegradation controlled the steady-state effluent concentrations. Sensitivity studies showed that axial diffusivity and recycle ratio were not critical factors at least for the system investigated. It was assumed that the system was well mixed because of high circulation rate maintained.

Andrews and Tien (1974) developed a mathematical model to predict the breakthrough curve of an expanded bed of activated carbon in terms of Total Organic Carbon (TOC). TOC was used as surrogated parameter and included the soluble, colloidal, and suspended organic impurities. However, separate contribution of adsorption, particle deposition and bacterial activity to the overall removal of total organic carbon (TOC) were assumed. The model was simplified by making several assumptions. The model worked well for their particular system and parameter values. The results of this research also showed that the bacterial activity can significantly increase the apparent adsorption capacity of the carbon.

A more complete model accounting for bioregeneration was developed and tested by Speitel et al. (1987). This model had been written for a single substrate. The model incorporated the biofilm growth, liquid film transfer, adsorption on activated carbon, and biodegradation and diffusion in the biofilm. The adsorption isotherm was described by Freundlich isotherm model and the biodegradation was described by Monod kinetics and mass transfer through biofilm was by diffusion. Hydrodynamic shear was considered to cause detachment of biomass from the activated carbon. And this detachment was taken as proportional to the attached biomass and was a function of the shear stress exerted by the fluid. Suspended growth in the liquid phase was assumed to be negligible. The biofilm was considered to consist of a homogeneous matrix of microorganism and exopolymers. The data necessary for the validation of the model were generated in parallel phase of this research. Model performance was compared with these data for both bioregeneration rate and substrate concentration in the liquid phase. The model in its present form was reported to be more of a tool for fitting the data with adjustable parameters rather than for predicting column performance. The biomass loss coefficient had to be increased above its calculated value to predict bioregeneration rate adequately beyond the initial period of microbial acclimatization. However, the model could not match the bioregeneration rate and liquid phase concentration measurements simultaneously. This discrepancy might be attributed to a combination of factors, namely (i) large biomass loss coefficient required to fit the bioregeneration rates, (ii) constant parameter, in the model may actually be time variant, and (iii) numerical method employed.

The experiments were run for 10 days. It was found that model predicted the experimentally observed sharp decrease in liquid phase substrate concentration. However, this model over predicted the concentration during the subsequent steady removal period by about 10 µg/l for the period under study. Though this research demonstrated the feasibility of modeling the compiled interactions involved in such treatment methods, yet additional refinement and testing were required. Further improvement in the predictions may be achieved with the proper understanding of biofilm in respect of their density, diffusional transport resistance, and the loss rate through shearing. Out of the two phenolic compounds tested, predicted bioregeneration was reported more rapid for p-nitrophenol than for phenol. More rapid adsorption due to the larger GAC loading and the larger surface diffusion coefficient for PNP might have been one of the reasons.

Both endogenous decay and biomass shearing constitute the decay coefficient. However, the biomass shearing is poorly understood. It may be concluded that inadequate knowledge of biomass shearing or the basic formulation of the model might have led to the need to adjusting the biomass loss coefficient substantially.

Speitel and Zhu (1990) initiated the research work to refine and to make additional development in the model proposed by Speitel et al. (1987). This model was written to represent the phenomena of simultaneous adsorption and biodegradation in granular activated carbon (GAC) columns treating low concentrations (20-100 µg/l) of synthetic organic chemicals. These concentrations are typically encountered in the treatment of drinking water and clean up of ground water near hazardous waste sites. With earlier model, some problems were encountered in predicting the bioregeneration rate and effluent concentration simultaneously. Also, the value of biomass loss coefficient and adjustable parameter, had to be increased to predict the bioregeneration rate correctly. Two possibilities were postulated by Spietel and Zhu (1990) to account for the above discrepancies. These were inaccurate parameter values and inaccurate description of mass transport resistances. Therefore, these authors responded by performing sensitivity analysis on individual parameter values and by considering several formulations of mass transport resistances within the biofilm and at the biofilm/GAC interface. Three bioregeneration/ adsorption models were compared to examine alternative formulations of mass transport resistances. These were namely, biofilm model, one that by Speitel et al. (1987), one liquid film and two liquid film models. In both one and two liquid film models, it was assumed that biomass growth was scattered on the adsorbent surface and hence did not offer resistance to transport of substrate through it whereas in biofilm model, biomass growth was considered to be grown as a biofilm and there was additional mass transfer resistance to substrate and transport was described by diffusion. In the two liquid film models, a liquid film was assumed to be present between biomass and GAC surface and any substrate molecule had to pass through this film to reach biomass, where these molecules would be biodegraded. The experimental data used to validate the models were taken from the research work done by Speitel et al. (1987). The results of the sensitivity analysis showed that the model was sensitive to the Monod half-saturation coefficient, the surface diffusion coefficient and the initial amount of biomass. The liquid film transfer coefficients, the biofilm diffusion coefficient, and initial thickness at constant amounts of initial biomass have little effect on the response of the model whereas the model was moderately sensitive to the overall biomass loss coefficient. The half-saturation coefficient had impact on biodegradation rate of both sorbed and liquid phase substrate. In order to fit the model predictions of experimental data satisfactorily the smaller values than measured experimentally were required. This result is in line with other researchers who have reported the small half-saturation coefficients for oligotrophic organisms. The results also indicate the need for improved techniques in measuring half saturation coefficient for such microorganisms. The GAC surface diffusion coefficient mainly affected the biodegradation rate of sorbed substrate. Authors also noted some evidence of irreversible adsorption. Hence, they recommended that the adsorption studies be required to describe the observed nonideal behavior in mathematical models. Amount of initial biomass attached to the surface of activated carbon was also reported to have affected biodegradation of substrate from both the adsorbed and liquid phase. However, difficulties were encountered in determining the initial biomass experimentally. Therefore, it was selected a bit arbitrarily. As to the selection of the best model, the one liquid film model performed better in matching the experimental data well. This was expected as the data were collected at low concentrations of a synthetic organic chemical in water, favoring the scattered growth of microbial colonies of the GAC surface. However, the biofilm model was recommended for high concentration wastes, where diffusive transport through biofilm would become important. The results obtained with two liquid film model were not found satisfactory, and this demonstrated that the inclusion of another transport resistance is inappropriate.

Leitao and Rodrigues (1996) developed a mathematical model for a fixed bed biofilm reactor, which had an adsorbent as carrier and a macroporous biofim covering the adsorbent. The simultaneous diffusive and convective transport were considered through adsorbent as well as biofilm. Further, this model was used to evaluate the effect of the adsorptive capacity and of the adsorption isotherm on the amount of substrate removal. Also, the effects of the convective mass transfer through the adsorbent and through the biofilm on substrate removal were studied in detail.

The model was solved for the removal of phenol from the liquid stream passing through a column packed with a granular adsorbent material coated with a biofilm. The biodegradation kinetics within the biofilm was assumed to be linear. The adsorption isotherm was represented by Langmuir model. The thickness of the biofilm coating the adsorbent was assumed to be constant. This was assumed to be balanced by the hydrodynamic shearing of the newly grown biomass. As the biodegradation kinetics had been described by linear model, the value of kinetic constant was used after the approximation of Monod's kinetic model for small liquid substrate concentrations. Also, for small phenol concentrations, the approximated form of Langmuir's model was used.

Ehrhardt and Rehm (1985) investigated adsorption of phenol on activated carbon in the presence of microorganisms namely *Pseudomonas sp.* and *Candida sp.* in batch mode. A comparison of phenol degradation by free cells and that by immobilized cells was made. The activated carbon used in this study had a very good adsorption capacity and this was found suitable as supporting material for microorganisms. After immobilization, the delay in the adsorption was observed and was attributed to the hindrance in diffusion of phenol into the carbon because of the obstruction and narrowing of pores by the bacterial cells. This study also showed that the immobilized cells can tolerate temporarily higher concentrations of phenol up to 15 g/l whereas the free cells could not tolerate more than 1.5 g/l of phenol. The immobilized cells degraded about 90 % of the adsorbed phenol.

The mixed culture of *Pseudomonas putida P8 and Cryptococcus elinovii* H1 was immobilized in research work by Morsen and Rehm (1987) to study the combined effect of adsorption and biodegradation in removing phenol from wastewaters. This integrated entity was called "Biocatalyst" by them. Research work was conducted both with presaturated and without presaturated carbon. The carbon used was of very high adsorption capacity; 1 g carbon could adsorb 0.7 g phenol. Studies with presaturated carbon revealed that microorganisms could utilize the adsorbed phenol. This was in line with a research study by Ehrhardt and Rehm (1985). Difference between the first and the second saturation of activated carbon showed approximately 95% phenol degradation by immobilized bacteria. The phenol removal behaviour was better in case of mixed culture than their pure cultures separately. The immobilized culture could remove the phenol upto 17 g/l and removed it faster than the pure cultures. This was made possible because of the complementary metabolism of the two microorganisms. The activated carbon with adsorbed cells of *pseudomonas putida and C. elinovii Hl* stored for 12 months and it was found that their degrdadation capacity did not decrease in this period. Later, Scanning Electron Micorgraph revealed that *pseudomonas putida* had grown through the pore system of activated carbon. This method of combining the two modes of treatment had been recommended for the treatment of coal conversion industry wastewater, containing phenol concentrations upto 6 g/l. The possibility of storing this biocatalyst for a period as long as 12 months and reuse potential are its attractive features and make the method highly promising in the wastewater treatment field.

Ehrhardt and Rehm (1989) studied the immobilized *pseudomonas putida* adsorbed on activated carbon in semi continuous and continuous culture for degradation of phenol. In fact, authors have extended their earlier work (Ehrhardt and Rehm 1985) to study phenol degradation in continuous cultures of bacteria adsorbed on activated carbon. This work specially addresses the development and effect of the biofilm covering the activated carbon. The amount of bacteria adsorbed on the activated carbon surface depends on the cell concentration in the suspension and on the type of carbon. Twice the numbers of cells were adsorbed from a suspension of 3.0×10^9 cells/ml as compared to those from a suspension containing 0.8×10^9 cells/ml. As to the effect of particle size of activated carbon, small particles adsorbed much more cells than the big particles.

Morsen and Rehm (1990) investigated the properties and limits of activated carbon and sintered glass as carriers for the immobilization of microorganisms. The microorganism immobilized were a mixed culture of the yeast *Cryptococcus elinovii* HI and the bacterium *P. putida* P8. Phenol degradation was used as substrate. The sintered glass used in this research was an opened-pored sintered glass specially developed and tested successfully in earlier investigations on anaerobic wastewater treatment as a carrier for the immobilization of microorganisms. Number of cells of each species attached to activated carbon and sintered glass were different, though the initial concentration of the *pseudomonas putida* P8 and C. *elinovii* HI were same. This work was divided into three parts, namely batch, semi continuous, and continuous. The results of batch studies showed that the activated carbon system could degrade phenol much more quickly and in higher concentrations than the sintered glass system. Also, activated carbon system showed better stability in terms of pH decrease, because of the presence of acidic and basic surface oxides on activated carbon. The O_2 saturation did not decrease appreciably in activated carbon as compared to when using sintered glass system. This was attributed to the enrichment of O_2 on activated carbon surfaces.

Lin and Weber (1992) reported the results of the research studies conducted to assess aerobic Biological Activated Carbon (BAC) process treatment rate and efficiency as a function of organic loading when aeration was supplied by either air or pure oxygen. The wastewater was proposed to be treated using a sequenced anaerobic/aerobic biological activated carbon process. The anaerobic BAC process was designed to achieve significant organic biodegradation under anaerobic conditions, thus reducing ultimate oxygen supply requirement, lowering biological sludge disposal costs and production of methane gas. However, anaerobic process does not produce an affluent suitable for direct discharge. Therefore, the effluent from anaerobic process is polished in aerobic BAC process. The results of this study demonstrated that the aerobic BAC was capable of effectively degrading high phenol content wastewaters. The rate of removal of organics in their BAC system was found comparable to that typically reported for traditional aerobic fixed film systems. At higher loading rate, the optimal performance was affected due to oxygen limitations. In order to overcome oxygen limitations, pure oxygen was supplied as the oxygen source. It was also found that the increased recycle rate was helpful in mitigating oxygen limitations observed during the investigation. It was concluded that a portion of the organic conversion was achieved through anoxic and / or anaerobic biochemical pathways. The start up studies showed that the minimal start-up time would be required to place a BAC system in operation. Also, this system could be operated for more than 260 days under the same conditions, thus showing the long term stability of the operation of the BAC process. During this period, column performance was consistent and the supplemented carbon or carbon regeneration was not required.

Weber et al. (1992) conducted the pilot scale studies on BAC process to assess this treatment option. The results of this investigation demonstrated the feasibility of sequenced anaerobic / aerobic BAC process for treating the strong liquor. As envisaged, a significant organic conversion with minimum solids production and almost stoichiometric methane production in the anaerobic BAC unit. Subsequently, aerobic BAC unit polished excellently from anaerobic BAC process even under variable influent conditions.

Tumbas et al. (1998) have studied the reuse of biologically regenerated activated carbon for phenol removal. Since granular biologically activated carbon (GBAC) is in principle suited for removal of phenolic substrate from wastewater. In this investigation this concept was used. Special attention was paid to the operation of separate aerobic bioregeneration of carbon and reuse of bio regenerated carbon. A 92-100 % efficiency of phenol removal was achieved irrespective of whether the fresh or bio regenerated GBAC was used. The process of bioregeneration for the once used GBAC was faster than for the one that was used several times. It was also faster when phenol alone was used as substrate rather than mixture of phenols. Respirometric measurements indicated that a mixture of substituted phenols showed inhibition effects of microorganisms.

Annadurai et al. (2002) studied the removal of phenol from aqueous solutions using a suspended culture of *Pseudomonas putida* (ATCC 3180) and using the activated carbon on which the microorganisms were immobilized. They studied the effect of pH, temperature, glucose and ammonium sulfate on removal behavior. They used Box-Behnken optimization method to identify the interactions among these factors.

2.2.4 Summary

Literature survey indicates that lot of information on various aspects of bioactive activated carbon for the removal of phenol is available. Investigations reported on adsorption studies of 3-aminophenol and catechol on activated carbon are very few. No publication on biodegradation of 3-aminophenol, catechol using *P. aeruginosa* was found. Also no research work on phenol, 3-aminophenol and catechol removal from aqueous solution using bioactive activated carbon with *P. aeruginosa* was found. Therefore, it was planned to study the removal of these phenols using bioactive activated carbon.

In biosorption experiments, adsorption occurs in presence of basal salt medium. Till todate, there is no method reported to predict the kinetics and adsorption equilibrium of the adsorbate-adsorbent system in presence of salts. These properties change with the change in temperature, pH and composition of the medium. Therefore, the adsorption studies in the presence of basal salt medium at the conditions suitable for biosorption have been planned.

Bacterial film is an active and essential part of this removal system. Maintenance of pH, temperature and supply of nutrients is essential for the proper growth of the bacteria. The literature survey indicates that *pseudomonas sp.* grows best at 30°C and at near neutral pH (Knapp et al. 2002). Therefore, the biodegradation studies at these conditions have been planned for removal of phenol and its derivatives.

2.3 ADVANCED OXIDATION PROCESSES

2.3.1 Introduction

Advanced oxidation process (AOP) aims at the mineralization of the contaminants to carbon dioxide, water and/or at least, at their transformation into harmless products. The classifications of different AOPs are briefly given in Table 2.5. In 1987, Glaze et al. defined AOP as "near ambient temperature and pressure water treatment processes which involve the generation of OH· in sufficient quantity to effect water purification". The main interesting characteristics of OH· are its very high oxidation potential (greater than O_3 and only smaller than F) and the possibility of its generation by different ways. This radical may be produced by combining O_3 with UV light, O_3 with H_2O_2, H_2O_2 with UV light, H_2O_2 with ferrous or ferric ion and by photo catalysis, which uses a semi conductor in combination with visible and UV radiation and molecular O_2 (Prado et al.1994, Duguet et al.1990). All AOPs are characterized by a common chemical feature, the capability of exploiting the high reactivity of OH· in driving oxidation processes, which are suitable for achieving the complete abatement and thorough mineralization of even less reactive pollutants.

AOPs comprise of the combinations of these oxidants and divided into three parts

(i) photochemical (H_2O_2/UV, O_3/UV, H_2O_2/O_3/UV),
(ii) photofenton (Fenton's reagent/UV), and
(iii) photocatalytic processes (semi-conductor/UV).

Table 2.5. Classification of different AOPs

Classification			Process
Reaction Phase	**External Energy**	**OH· Generation**	
Homogeneous	None	Chemical process	O_3 at high pH
	None	Chemical process	H_2O_2/O_3
	Light	Photochemical process	UV/O_3 UV/H_2O_2 UV/H_2O_2/O_3
		Photofenton process	UV/$Fe^{2+}(Fe^{3+})/H_2O_2$
Heterogeneous	Light	Photocatalytic process	UV/TiO_2/O_2 UV/TiO_2/H_2O_2

The potentialities offered by AOPs can be exploited to integrate biological treatment through an oxidative degradation of toxic or refractory substances entering or leaving the biological stage. Energy consumption can be reduced drastically if solar energy is used instead of UV light, which is economical.

2.3.2 Photochemical Degradation

O_3/H_2O_2 at elevated pH have been employed as oxidants in many water and waste water treatment applications. However, for the refractory organics in water, O_3 or H_2O_2 alone without UV radiations reactions exhibited limited selections and lower reaction rates. Andreozzi et al. (1999) and Legrini et al. (1983) have shown that UV-induced chemical oxidation processes utilizing UV radiation with O_3 or H_2O_2 can achieve complete destruction of organic contaminants.

Hoigne and Bader (1998) reported that ozonation is very effective in treating wastewaters containing phenolic compounds. There are differing views about reaction of O_3 with aqueous compounds. Singer and Gurol (1983), Gurol and Vatistas (1987), Trapido et al. (1995) claimed that the indirect radical mechanism might be one of the reaction pathways while Beltran (1995), Beltran and Alvarez (1996) believe that the degradation of phenol by O_3 is the result of direct reaction between the two. The reaction of O_3 with a dissolved compound in wastewater is first-order with respect to O_3 and the compound, respectively.

In O_3/H_2O_2 system, OH· are generated by a radical-chain mechanism by interaction between the O_3 and the H_2O_2 Li, (1996) reported the global reaction showing two O_3 molecules produce two OH radicals through following mechanism

$$H_2O_2 \xrightleftharpoons{H^+} HO_2^-$$

$$OH^- + O_3 \longrightarrow O_2 + HO_2^-$$

$$\cdot HO_2 + O_3 \longrightarrow \cdot HO_2 + O_3\cdot^-$$

$$\cdot HO_2 \rightleftharpoons H^+ + O_2\cdot^-$$

$$O_2\cdot^- + O_3 \longrightarrow O_2 + O_3\cdot^-$$

$$O_3\cdot^- + H^+ \longrightarrow \cdot HO_3$$

$$\cdot HO_3 \longrightarrow OH\cdot + O_2$$

The reaction continues along the indirect pathway described above and OH· are produced. Duguet et al.(1990), Huang et al. (1995) and Glaze and Kang (1989), have extensively studied these mechanisms and supported the advantage of this method in comparison of individual ozonation or peroxide oxidation.

UV/O_3 process is a treatment method in which basically, aqueous systems saturated with O_3 are irradiated with UV light of 254 nm in a reactor convenient for such heterogeneous media. The extinction coefficient of O_3 at 254 nm is 3600 $M^{-1}cm^{-1}$ much higher than that of H_2O_2. Glaze et al.(1987) and Peyton and Glaze(1988) studied the different steps involved in the mechanism of this process.

$O_3 \xrightarrow{hv} O_2 + O$

$O + H_2O \longrightarrow H_2O_2 \xrightarrow{hv} 2\ OH\cdot$

O_3/UV/H_2O_2 is a very powerful method which allows the fast and complete mineralization of pollutants. The addition of H_2O_2 to the O_3/UV process accelerates the decomposition of O_3, which results in an increased rate of OH· generation. In processes involving pollutants that are weak absorbers of UV radiation, it is more cost effective to add H_2O_2 externally at a reduced UV flux. H_2O_2 is catalyzed with UV irradiation and O_3 to create highly reactive radicals which react and cleave a wide variety of organics.The reaction pathways leading to the generation of OH• have been summarized by Legrini et al. (1983)

$O_3 + H_2O \xrightarrow{hv} O_2 + 2\ OH\cdot$

$O_3 + OH\cdot \longrightarrow \cdot HO_2 + O_2$

$O_3 + \cdot HO_2 \longrightarrow OH\cdot + 2O_2$

$H_2O_2 \xrightarrow{hv} 2OH\cdot$

$H_2O_2 + OH\cdot \longrightarrow \cdot HO_2 + H_2O$

$H_2O_2 + \cdot HO_2 \longrightarrow OH\cdot + H_2O + O_2$

$2OH\cdot \longrightarrow H_2O_2$

$2\cdot HO_2 \longrightarrow H_2O_2 + O_2$

$OH\cdot + \cdot HO_2 \longrightarrow H_2O + O_2$

Phenol + $O_3 \longrightarrow$ decomposed products,

Phenol + $OH\cdot \longrightarrow$ decomposed products,

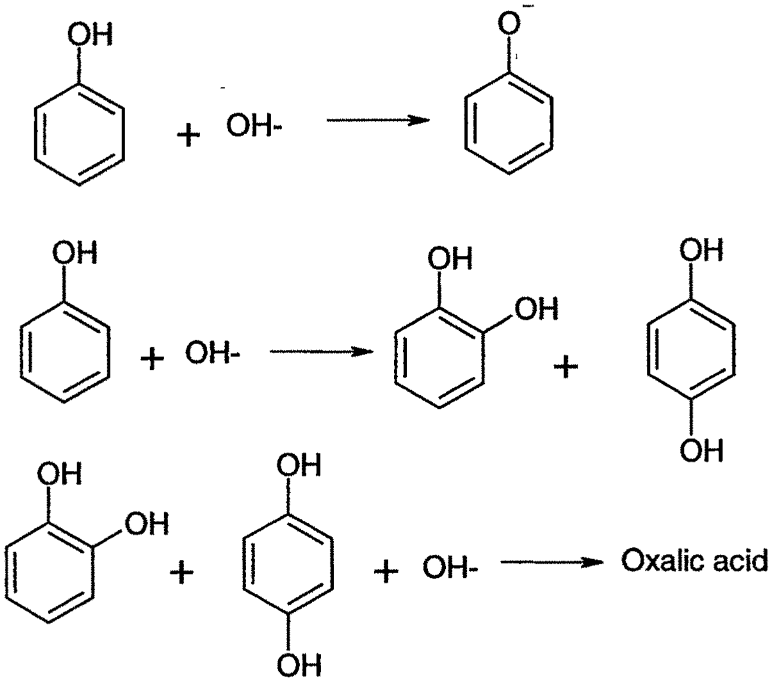
Phenol + $\cdot HO_2 \longrightarrow$ decomposed products.

2.3.2.1 Factors affecting the process

Gurol and Vatistas (1987), and Mokrini et al. (1997) have studied the effect of pH in AOP. It has been found that UV/ O_3 is faster at basic pH, while UV/O_3/ H_2O_2 is faster at low pH. Bicarbonate and carbonate play an important role as scavengers of OH· in natural systems (Bhattacharjee and Shah, 1998). The products of a reaction between OH· and carbonate or bicarbonate ions are passive carbonate radical anions, which do not interact further with O_3 or organic compounds. Munte (2001) has observed that at high dosage, H_2O_2 is a powerful OH· scavenger. However, it is also observed that at pH 5-7, the rate goes through a maximum by increasing the H_2O_2 concentration.

Ollis et al.(1993) reviewed the studies on the effect of light intensity (I) and found that at low intensities the rate increases linearly with I, at intermediate I the rate depends on the $I^{1/2}$, but at high I the rate is independent of I. Baxendale and Wilson (1957) observed that in some cases at wavelength < 250 nm the processes are initiated more efficiently. Hofstadter et al. (1994) reported increase in the percentage degradation with rise in temperature upto 40°C, beyond this temperature (40-50°C) degradation declines. This is attributed to accelerated decomposition of H_2O_2 into O_2 and H_2O.

Huang and Shu (1995) proposed mechanism for phenol decomposition by OH· generated during UV/H_2O_2 and UV/O_3 process is as under:



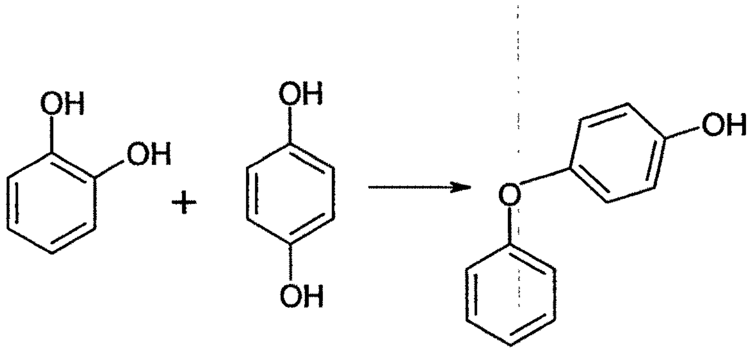


Table 2.6. Summary of compounds degraded by various researchers using Photochemical oxidation

Compound degraded	Method used	Conc. mg/l	Source of light	Reference
4-chlorophenol	O_3/UV	138-177	UV light	Sauleda et al. (2001)
Phenol	O_3/UV	100	Xenon lamp 1500W (Philips)	Canton et al. (2003)
Phenol	UV/H_2O_2	210	Low-pressure Hg vapor lamp	Alnaizy et al. (2000)
2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol	O_3/UV	26, 31, 44, 32, 14	Osram make Hg lamp	Hirvonen et al. (2000)
4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol	UV/H_2O_2, O_3/ UV	39, 49, 59, 70	High pressure Hg lamp (Heraeus TQ150)	Benitez et al. (2000)
Phenol, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,5-dichlorophenol, 2,4,6-trichlorophenol	O_3/H_2O_2	0.1-1	-	Grigoropoulou et al. (1997)
2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol	UV/H_2O_2	39, 50, 61	UV Lamp @ 5.3W	Shen et al. (1995)
Phenol	UV/H_2O_2	100	UV Lamp (Philips, 8W)	Hu et al. (2000)
Phenol	UV/H_2O_2	200	Low pressure Hg lamp of 8W	Han et al. (2004)

Table 2.6. Summary of compounds degraded by various researchers using Photochemical oxidation **(Continued)**

Compound degraded	**Method used**	**Conc. mg/l**	**Source of light**	**Reference**
Phenol	UV/H_2O_2	50	Medium pressure 400W Hg lamp	Colon et al. (2004)
Phenol	UV/H_2O_2	50	Six lamps with 20W power (Philips)	Tryba et al. (2003)
2,4,6-trichlorophenol, 2,3,4,5-phenol, and	UV/H_2O_2, UV/O_3, $UV/H_2O_2/O_3$	64, 47	12W low pressure Hg lamp	Wang et al. (2004a)
Phenol	UV/H_2O_2	95-100	Medium pressue Hg vapour lamp (HPK 125)	Espulgus et al. (2002)
Phenol	UV/H_2O_2	52.2	5000 W low-pressure Hg lamp	Huang et al. (1995)
Phenol	UV/H_2O_2	200	250 W Hg vapour lamp (Phillips)	Azevedo et al. (2004)
2- chlorophenol, 3- chlorophenol	UV/O_3	257	15W six lamps (Phillips)	Boncz et al. (1997)
Metol(N-methyl-p- aminophenol)	UV/H_2O_2	55	Low pressure Hg lamp	Andreozzi et al. (2000)
2,3-dichlorophenol, 2,5- dichlorophenol, 2,6- dichlorophenol, 2,4,5-trichlorophenol	UV/O_3	2-10	10 mW microwave	Utsumi et al. (1998)

2.3.3 Photo-Fenton Degradation

The photo-fenton degradation process (PFDP) is gaining importance in the area of wastewater treatment, especially for wastewater containing small amounts of refractory organic substances viz. phenols, dyes, pesticides and explosives (Feng et al. 2003; Lioua et al. 2003; Kang et al. 2000). Accoring to Acero et al. (2001) the PFDP has several advantages: (i) complete mineralization, (ii) mild temperature & pressure, (iii) odor and color removal, and (iv) utilization of visible light in the solar range, 300-400 nm.

Wolfgang et al. (2003) reviewed the use of PFDP for purification, decontamination, and decolorization of water containing natural phenols. Maletzky et al.(1999) reviewed immobilization of iron ions on Nafion membranes a promising technique to perform the photo-fenton method in a neutral pH range.

In the PFDP, H_2O_2 and Fe^{2+} (catalyst) are added to a solution of organic compound or wastewater and mixture is irradiated.

$$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + 2OH\cdot \qquad (2.1)$$

$$Fe^{3+} + H_2O \xrightarrow{h\nu} Fe^{2+} + 2OH\cdot \qquad (2.2)$$

There are different possibilities for H_2O_2 to react, mainly hydrogen abstraction (eq. 2.3) and electrophilic addition (eq.2.4). Due to the high electron affinity of the OH· it reacts very non-specific with present molecules generating other radicals. The substrate radical is also highly reactive and undergoes further reaction, such as reactions (2.5) and (2.6).

$$R\text{-}H + OH\cdot \longrightarrow H2O + R\cdot \qquad (2.3)$$

$$Ar\text{-}H + OH\cdot \longrightarrow Ar\text{-}OH + H\cdot \qquad (2.4)$$

$$R\cdot + O_2 \longrightarrow \cdot ROO \longrightarrow \text{Product } (CO_2) \qquad (2.5)$$

$$R\cdot + R\cdot \longrightarrow R\text{-}R \qquad (2.6)$$

The increased efficiency of Fenton/Fenton-like reagents with UV/visible irradiation (Grigoropoulou and Philippopoulos, 1997) is attributed to: photo-reduction of ferric ion and efficient use of light quanta.

2.3.3.1 Factors affecting the Process

The optimal efficiency is between pH 2-5. The drop in efficiency on the basic side is attributed to the transition of iron from a hydrated ferrous ion to a colloidal Fe species. There have been some recent developments using non radical scavenging sequestering agents (e.g., Gallic acid) to extend the useful pH range to pH 8-9 (Chan 2003), but no commercial applications are known. According to Kiwi et al. (1994), the inactivity of Fenton's reagent at pH >5 is attributed to faster decomposition of H_2O_2 into water and oxygen. On the other hand Kuo (1999) opines that oxidation of Fe^{2+} by an oxidant other than H_2O_2 or the reaction between Fe^{2+} and H_2O_2 not producing OH· in this pH region is responsible.

The pH shift is observed as the reaction progresses. The pH profile for typical Fenton reactions is shown in Fig. 2.1. with initial wastewater of pH 6.0.

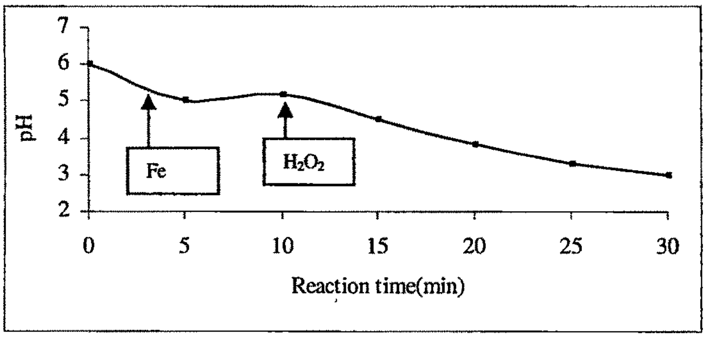


Figure 2.2. pH profile in photo fenton processes

$$OH\cdot + \cdot HO_2 \longrightarrow H_2O + O_2$$

In the photo-Fenton degradation of 2,4-dichlorophenol (2,4-DCP) under 36W light irradiation Ormada et al. (2001) attributed the drop in pH, predominantly to following reaction

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + \cdot HO_2 + H^+ \qquad (2.7)$$

and not to the OH· generation, the Fenton reactions leading the pH of the system in the opposite direction.

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH- + OH\cdot \qquad (2.8)$$

The super-oxide radical $\cdot HO_2$ (Eq. 10) has a considerably lower one-electron standard potential $\cdot HO_2 / O_2-$ $E° = 0.75$ V versus normal hydrogen electrode (NHE) compared to the OH· with $(OH\cdot/OH^-)$ $E° = 1.90$ V versus NHE. The evolution of HCl during the mineralization of 2,4-DCP proceeding according to Eq. (2.9) also important in acidifying the solution

$$HO\text{-}C_6H_3\text{-}Cl_2 + H_2O_2 + \frac{3}{2}O_2 \longrightarrow 6CO2 + 2H_2O + 2HCl \qquad (2.9)$$

But any account of the pH drop in the system would have to take in consideration the sum of all processes occurring during the degradation reaction.

An optimal dose range for iron catalyst is a characteristic of Fenton's Reagent. Safarzadeh et al. (1996) found three factors that typically influence the optimal dose: (i) A minimal threshold concentration of 3-15 mg/l Fe which allows the reaction to proceed within a reasonable period of time regardless of the concentration of organic material, (ii) A constant ratio of Fe/substrate above the minimal threshold, typically 1 part Fe/(10-50) parts substrate, which produces the desired end products. (iii) A supplemental aliquot of Fe, which saturates the chelating properties in the wastewater, thereby availing unsequestered iron to catalyze the formation of OH·.

For most applications, it does not matter whether Fe^{2+} or Fe^{3+} salts are used to catalyze the reaction; the catalytic cycle begins quickly if H_2O_2 and organic material are in abundance.

However, it is preferred to use low doses of Fenton's Reagent (e.g., < 10-25 mg/L H_2O_2). Waite (2002), Wadley and Waite (2000), Chiron et al. (2000), Andreozzi et al.(1999) and Canepa. (2003) suggests use of ferrous iron.

Safarzadeh et al. (1996,1997) found that ferrioxalate can be used as a photoactive catalyst. Irradiation of ferrioxalate in an acidic solution generates Fe (II) and carbon dioxide:

$$[Fe(C_2O_4)_3]^{3-} \xrightarrow{hv} [Fe\,(C_2O_4)_2]^{2-} + C_2O_4^{2-} \qquad (2.10)$$

$$C_2O_4^{2-} + [Fe\,(C_2O_4)_3]^{3-} \longrightarrow [Fe\,(C_2O_4)_2]^{2-} + C_2O_4^{\,2-} + 2CO_2 \qquad (2.11)$$

$$C_2O_4^{2-} + O_2 \longrightarrow O_2^{-} + 2CO_2 \qquad (2.12)$$

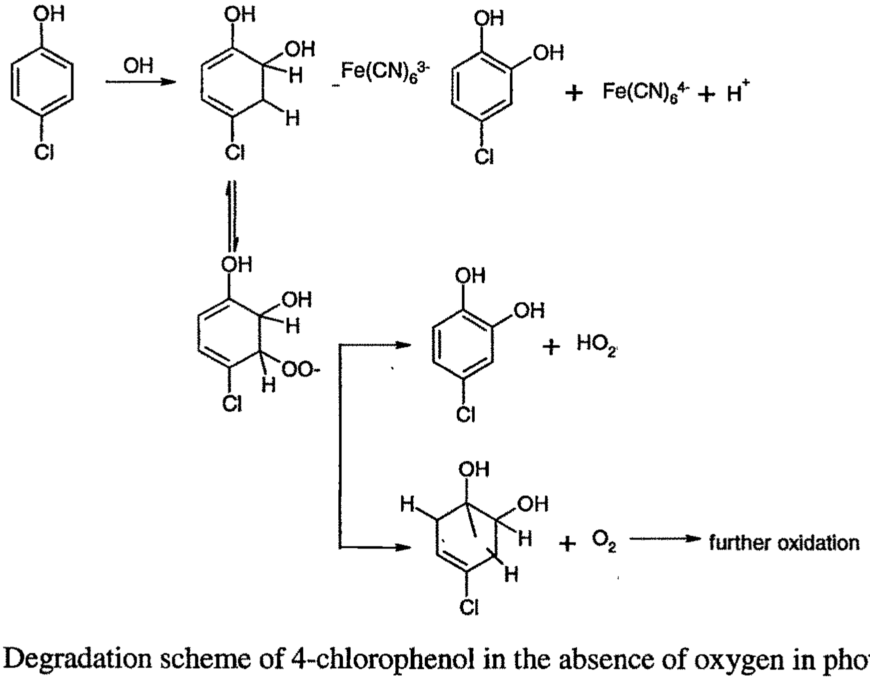
The quantum yield of Fe (II) formation is about 1.0–1.2 times in the range of 250–450 nm wavelength. Whereas Fe(II) formation decreases with further increase in the irradiation wavelength. The photolysis of ferrioxalate produces ferrous (free or complexed with oxalate) ion, which in combination with H_2O_2 provides a continuous source of Fenton's reagent and OH·. The formation of OH· in the photolysis of ferrioxalate/H_2O_2 mixtures was also demonstrated by Raquel et al. (2000).

Rupert et al. (1993) and Chen et al. (1997) observed as the H_2O_2 dose is increased, a steady reduction in COD may occur with little or no change in toxicity until a threshold is attained, whereupon further addition of H_2O_2 results in a rapid decrease in wastewater toxicity.

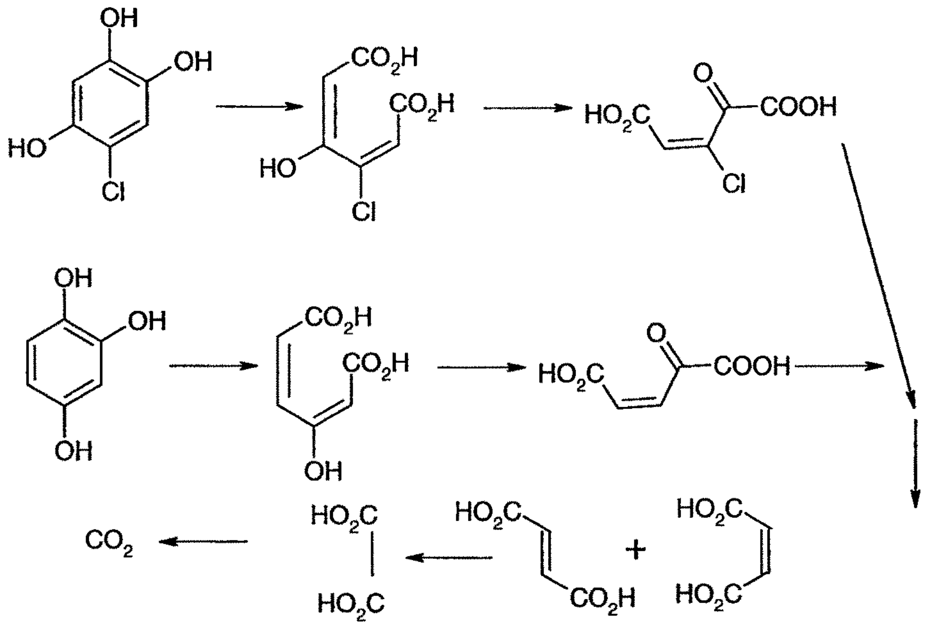
Chan et al. (2003) have shown that at a fixed Fe (II) concentration, generally higher the H_2O_2 concentration or the lower the Fe (II)/H_2O_2 concentration ratio, Atrazine degradation is faster and higher.

Lee et al. (2003) observed similar temperature effect for PFDP as was observed for photochemical oxidations. Moderating the temperature is important not only for economic reasons, but for safety reasons as well.

The time needed to complete a fenton reaction depends on the many variables discussed above, most notably catalyst dose and wastewater strength. For simple phenol oxidation (< 250 mg/L), typical reaction time is 30-60 min. For more complex molecules or more concentrated wastes, the reaction time may be several hours. In such cases, performing the reaction in steps (adding both iron and H_2O_2) is more effective and safer than increasing the initial charges. The presence of residual H_2O_2 will interfere with many wastewater analyses. Residual H_2O_2 is removed by raising the pH to 7-10, or by neutralizing with bisulfite solution (Rupert et al. 1993, Chen et al. 1997).
The studies on photo-fenton degradation of phenolic compounds found in the literature are summarized in Table 2.7. The suggested pathways for 4-chlorophenol degradation in presence of oxygen and absence of oxygen by Schwarz Kathleen (2001) are as below :



Degradation scheme of 4-chlorophenol in the absence of oxygen in photofenton system



Degradation scheme of 4-chlorophenol in presence of oxygen in photofenton system

Table 2.7. Summary of compounds degraded by various researchers using PFDP

Compound degraded	Process	Source of light	Conc., mg/l / Intermediates	Reference
2 and 4-nitrophenols	$Fe(NO_3)_3H_2O$/ H_2O_2	80 mW/cm Hanau suntest lamp	2&4 nitroresocinol	Kiwi et al. (1994)
2,4-dichlorophenol	Fe(II) ammonium sulfate hexahydrate & H_2O_2	Phillips 36W	Large number of intermediates observed	Ormada et al. (2001)
Benzothiazole	Ferric perchlorate/ H_2O_2	125W Hg lamp	Not analyzed	Andreozzi et al. (2000)
2,4-dinitrophenol	$FeSO_4$ / H_2O_2	1010W Osram lamp	Not analyzed	Anna et al. (2003)
4-chlorophenol , 2,4,6-trichlorophenol	Ferrous sulfate/H_2O_2	Heraeus TQ150 Hg vapour lamp	Not analyzed	Benitez et al.(2000)
4-chlorophenol, 4-aminophenol	Ferrous sulfate/ H_2O_2	Osram Ultramed 400 W	Not analyzed	Kohtani et al. (2003)

Table 2.7. Summary of compounds degraded by various researchers using PFDP **(Continued)**

Compound degraded	**Process**	**Source of light**	**Conc., mg/l / Intermediates**	**Reference**
4-chlorophenol	Ferrous sulfate/ H_2O_2	Hg lamp	Not analyzed	Hu et al. (2000)
4-chlorophenol	$Fe^{+3}/H_2O_2/UV$	400W Hg medium pressure lamp	1285	Krutzler et al. (1995)
4-chlorophenol, 4,4dichlorophenol	Fe^{+2}/H_2O_2, Fe^{+3}/H_2O_2	UV light intensity 5 mW/cm^2 .	50	Kuo et al. (1999)
Explosive containing 2,4,6-trinitrophenol	Fe^{+2}/H_2O_2	UV light	550	Lioua et al. (2003)
4-chlorophenol, 4-aminophenol.	Fe^{+2}/H_2O_2	Medium Pressure Hg lamp, Osram Ultratech. 400W	1285, 1090	Krutzler et al. (1999)
Bisphenol A	Fe^{+2}/H_2O_2	Xe lamp (990W, Ushio Electronics Co.)	Phenol, p-hydroquinone	Katsumata et al. (2004)
Phenol	Fe^{+2}/H_2O_2	450 W medium-pressure Hg vapor lamp	550-1000	Will et al. (2004)
Phenol	Fe^{+3}	15W low pressure Hg lamps	100	Rodrýguez et al. (2002)

2.3.4 Photocatalytic Degradation (PCD)

In recent years, there has been growing interest in the use of semiconductors as photo sensitizers for complete oxidative mineralization of pollutants by O_2 (Bhatkhande 2001). For a semiconductor to be photo chemically active as a sensitizer for the reaction, the redox potential of the photo generated valence band hole must be sufficiently positive to generate OH·, which can subsequently oxidize the organic pollutant and the redox potential of the photo-generated conductance band electron must be sufficiently negative to be able to reduce adsorbed O_2 to super oxide as shown in Fig. 2.3. Si, TiO_2, ZnO, WO_3, CdS, ZnS, $SrTiO_3$, SnO_2, WSe_2, Fe_2O_3, etc., are normally used as photocatalysts.

Oxidation of many pollutants, as especially organic species, requires high potential with the result that the valance band location at the semiconductor-electrolyte interface has to be rather positive, Of several different semiconductors tested for PCD, Chatterjee and Bhattachraya (1999) found that TiO_2 and CdS most suitable for pentachlorophenol degradation (Fig.2.4). CdS and ZnO do not have long-term stability in aqueous media. Photo-oxidation kinetics is also poor in n-Si.

Further, though TiO_2 is only an UV absorber (E_{bg} = 3.2eV), it is cheap, insoluble under most conditions, photo stable, and non-toxic.

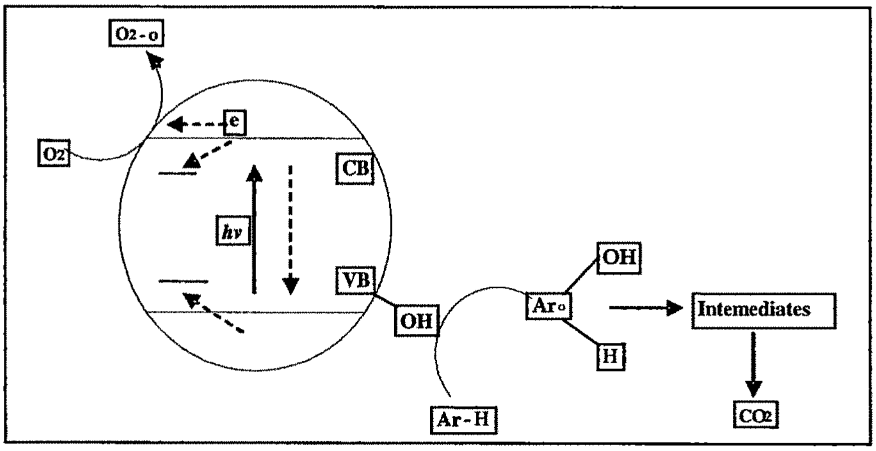


Figure 2.3. Schematic representation of the band energetic model of overall process of semiconductor of photocatalysis for water purification.

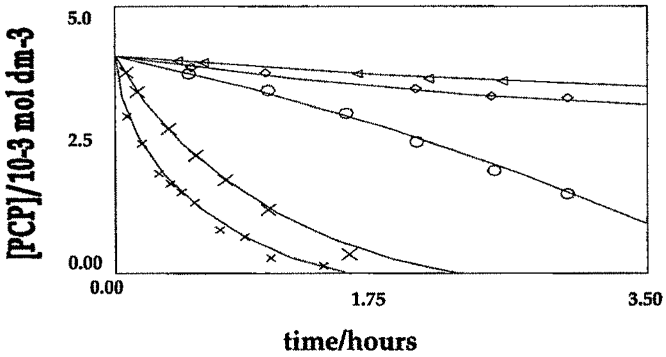


Figure 2.4. Photo-degradation of pentachlorophenol (PCP) sensitized by dispersion of semi-conductors: x- TiO_2, X - ZnO, o - CdS, - WO_3 and ◁ - SnO_2.

Amongst many different sources of TiO_2, Degussa P25 TiO_2 has effectively become a research standard material as it has (i) a reasonably well-defined nature (i.e. typically a 70:30 anatase: rutile mixture, non-porous, BET surface area = 55 ± 15 m^2g^{-1}, average particle size 30 nm) and (ii) a substantially higher photocatalytic activity.

The initiating step in photocatalysis is the excitation of the semiconductor (TiO_2) by radiation sufficiently energetic ($E_{bg} = 1240/\lambda_{min}$) to produce an electron-hole pair (OHEPA 2002). Turchi and Ollis (1990) have shown that when water dissociates on a pure TiO_2 surface, two distinctive hydroxyl groups are formed. The reaction scheme is written as:

Excitation

$$TiO_2 \xrightarrow{h\nu \geq 3.2eV} e^- + h^+ \qquad (2.13)$$

Back reaction

$$e^- + h^+ \longrightarrow \text{Heat} \qquad (2.14)$$

Trapping

$$Ti^{IV}(OH^-/H_2O) + h^+ \longrightarrow Ti^{IV}\text{-}OH\cdot \qquad (2.15)$$

$$Ti^{IV}\text{-}OH\cdot \longrightarrow Ti^{IV}(OH^-/H_2O) + h^+ \qquad (2.16)$$

$$Ti^{IV} + e^- \rightleftarrows Ti^{III} \qquad (2.17)$$

$$Ti^{III} + O_2 \rightleftarrows Ti^{IV}\text{-}O_2\cdot \qquad (2.18)$$

Adsorption of organic pollutant (S) and photo generated intermediates (Q_j)

$$\text{site} + S \rightleftharpoons S_{ads} \tag{2.19}$$

$$\text{site} + Q_j \rightleftharpoons Q_{jads} \tag{2.20}$$

OH· attack on the initial organic pollutant generating inter-mediates

$$Ti^{IV}\text{-}OH\cdot + S_{ads} \longrightarrow Ti^{IV} + Q_{jads} \tag{2.21}$$

$$Ti^{IV}\text{-}OH\cdot + S \longrightarrow Ti^{IV} + Q_j \tag{2.22}$$

OH· attack on intermediates, generating other intermediates

$$Ti^{IV}\text{-}OH\cdot + Q_{jads} \longrightarrow Ti^{IV} + Q_{j+1ads} \tag{2.23}$$

$$Ti^{IV}\text{-}OH\cdot + Q_j \longrightarrow Ti^{IV} + Q_{j+1} \tag{2.24}$$

Where the different intermediates are identified by the different integer values of j. The parameter j will have all values which lie in the range: m (= total number of intermediates generated) $\geq j \geq 1$.

Other reactions:

$$e^- + Ti^{IV}\text{-} O_2\cdot^- + 2H^+ \rightleftharpoons Ti^{IV}(H_2O_2) \tag{2.25}$$

$$Ti^{IV}\text{-}O_2\cdot^- + H^+ \rightleftharpoons Ti^{IV}(\cdot HO_2) \tag{2.26}$$

$$Ti^{IV}(H_2O_2) + Ti^{IV}\text{-}OH\cdot \rightleftharpoons Ti^{IV}(\cdot HO_2) + Ti^{IV}(H_2O) \tag{2.27}$$

Reactions (2.24-2.27) indicate that the reduction of O_2 by e^- can lead to the formation of radicals, such as $Ti^{IV}(\cdot HO_2)$, which may be capable of oxidizing the organic pollutants.

It was shown by Okamoto *et al* (1985a and b) that OH· are formed not only via holes but also via H_2O_2 from the super oxide ion O_2^-. Fujishima and Rao(1987) reported the reduction of oxygen in aerated aqueous solution to form O_2 and H_2O_2 enables charge neutrality to be maintained and drive the photocatalytic reaction. H_2O_2 may also be produced and is photo decomposed to OH· which reacts with the substrates (Tuneshi and Anderson 1991).

The photo-catalytic degradation for some phenolic compounds investigated is given in Table 2.8.

Table 2.8. Summary of compounds degraded by various researchers using PCD

Compound degradation	**Photocatalyst used**	**Conc. mg/l**	**Source of light / Intermediates**	**Reference**
Phenol	TiO_2-SiO_2	500	125 W UV lamp (Silvania) / Catechol, acetic and formic acids	Almeny et al. (1997)
Phenol	TiO_2 with Activated carbon	94	125W UV lamp (Phillips)/ Hydroquinone Benzoquinone	Matos et al. (1998)
Phenol	TiO_2 (Degussa P25)	10	UV lamp in quartz tube 0.35 mW/cm^2	Wanga et al. (1999)
Phenol, 4-chlorophenol, 4-nitrophenol.	TiO_2 (Degussa P25)	20	125W High-pressure Hg vapour lamp(Phillips)	Chen et al. (1999)
Phenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-richlorophenol, 2,3,6-trichlorophenol, 2,3,5-trichlorophenol	TiO_2 Catalyst Pellets	250	UV tube having UV-365 nm(Spectronics)	Dionysious et al. (2000)
Phenol	TiO_2 Thin Film	250	Phillips HPK 125W UV-lamp	Dumitriu et al. (2000)
Phenol, guaiacol, 2-chlorophenol, catechol.	TiO_2 (Degussa P25)	10	125W medium pressure Hg vapour lamp (Philips HPK) / Catechol, Napthol, Resorcinol, Benzoquinol	Peiro et al. (2001)
4-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol	TiO_2	10	Philips HPK 125W Lamp	Ksibi et al. (2003)
Phenol, chlorophenol, trichlorophenol	Pt/TiO_2 (Degussa P25)	94	50W tungsten lamp (Philips)	Chatterjee et al. (1999)
Phenol	TiO_2 (anastase and rutile)	94	100W high-pressure Hd lamp	Okamoto et al. (1985)

Table 2.8. Summary of compounds degraded by various researchers using PCD **(Continued)**

Compound degradation	**Photocatalyst used**	**Conc. mg/l**	**Source of light / Intermediates**	**Reference**
Phenol	TiO_2 and activated carbon	50	six lamps with 20W	Tryba et al. (2003)
Phenol	Sulphated TiO_2 (Degussa P25)	50	400W medium pressure Hg lamp supplied	Colon et al. (2003)
Phenol, catechol, resorcinol, hydroquinone	TiO_2 (Degussa P25))	440	xenon lamp, radiant flux (40mW/cm^2)	Parra et al. (2000)
Phenol	TiO_2	100	500 W high-pressure mercury lamp	Preis et al. (1997)
4-chlorophenol	TiO_2	65	UV light at 365 nm /hydroquinone, benzoquinone & 4-chlorocatechol	Waldner et al. (2003)
2-chlorophenol	TiO_2	10	Blue-blackfluorescent UV Lamp	Ku et al. (1996)
2-, 3-, 4-chlorophenol, pentachlorophenol, 4-fluorophenol	TiO_2 (Degussa P25)	-	125 W lamp (Philips HPK)	Herrmann (1999)
3-nitrophenol, 4-nitrocatechol, 2-nitroresorcinol, 4-nitrophenol, 2-nitrophenol	TiO_2 (Degussa P25)	200	125W UV lamp (Phillips)	Bhatkhande et al. (2004)
Phenol	TiO_2 (Degussa P25) and ZnO	50	125 W medium-pressure Hg lamp (Phillips HPK)	Hadjsalah et al. (2004)
4-chlorophenol	TiO_2 (Degussa P25)	-	- /Hydroquinone, benzoquinone etc	Sayyed et al. (1991)

Table 2.8. Summary of compounds degraded by various researchers using PCD **(Continued)**

Compound degradation	**Photocatalyst used**	**Conc. mg/l**	**Source of light / Intermediates**	**Reference**
Phenol	TiO_2 powders	50	125W Hg lamp (Philips HPK)	Boujday et al. (2004)
4-chlorophenol, hydroquinone, 4-nitrophenol	TiO_2 (Degussa P25)	10	Two sources of low pressure Hg lamp- UV 254 nm and Vacuum UV-185 nm	Han et al. (2004)
Phenol	TiO_2 (Degussa P25)	50	125W Hg lamp (Philips HPK)	Chhor et al. (2004)
Phenol	Silver ion doped ZnO nanocrystallites	20	Lamp having illumination >254 nm	Wang et al. (2004b)
Phenol	TiO_2 (Degussa P25)	10	high pressure mercury lamp	Noorjahan et al. (2003)
4-chlorophenol, 4-nitrophenol	TiO_2 (Degussa P25), TiO2–SiO2 aerogels	60	Xenon and Hg lamp	Malinowska et al. (2003)
Phenol	TiO_2 (Degussa P25)	50	medium pressure 400W Hg lamp	Colon et al. (2003)
2-chlorophenol	TiO2/UV	100	A medium pressure mercury vapor lamp 400W	Rao et al. (2003)
Phenols	TiO_2 (Degussa P25)	50	6W low pressure mercury lamp.	Lathasree et al. (2004)
Phenol	TiO_2 (Degussa P25)	100	8W low pressure mercury lamp. lamps	Li et al. (2004)
2- chlorophenol, 3- chlorophenol	TiO_2 (Degussa P25)	20	105W high-pressure Hg lamp(Philips)	Ollveria (1990)
Phenol, 4-chlorophenol, 2-chlorophenol	TiO_2 (Degussa P25) attached to glass mesh	-	20W black light fluorescent tube(NEC)	Matthews et al. (1987)

Table 2.8. Summary of compounds degraded by various researchers using PCD **(Continued)**

Compound degradation	**Photocatalyst used**	**Conc. mg/l**	**Source of light / Intermediates**	**Reference**
Phenol	TiO_2 (Degussa P25)	-	15 W UV lamp	Matthews & McEvoy (1992)
4-nitrophenol	TiO_2 (Degussa P25)	20	125W high-pressure Hg lamp(Philips) / Mineral acid	Chen et al. (1998)
2,4,6-trichlorophenol	Anatase TiO2	-	Low pressure Hg lamp	Tanaka et al. (1994)
2,3,5-trichlorophenol, Pentachlorophenol	TiO_2 (Degussa P25)	-	High pressure Hg lamp / Trichloro hydroquinone	Jardim et al. (1997)

2.3.4.1 Factors Effecting Rate of PCD

The effect of both intensity and wavelength of radiation are important. Okamoto et al (1985) found in the PCD of phenol over anatase powder that both initial PCD rate and apparent rate constant were proportional to *I* (Intensity of light) below PCD rate of 1 x 10^{-5} mol $m^{-2}s^{-1}$ and $I^{1/2}$ above a PCD rate of 2 x 10^{-5} mol m^{-2} s^{-1}. Matthews and McEvoy (1992) showed that shorter wavelength (254 nm) radiation is considerably more effective in promoting degradation then radiation centered at 350 nm and the optimum rate occurred with a lower catalyst loading than required at 350 nm. Subramaniam et al. (2000) showed that the adsorption and PCD rates bear a direct relationship and as adsorption increased the PCD rate also increased.

Matthews and McEvoy (1992) observed a negligible pH effect on the PCD of phenol in the pH range 3.5-8.5 with the rate increasing marginally with increasing pH. This was attributed to the increase in concentration of OH^- ions. Ku and Hsich(1992) studied the effect of pH on the degradation of 2,4-DCP over anatase TiO_2 and showed that in alkaline solutions the PCD rate was slightly greater than that at neutral and acidic pH with less intermediates being formed.

In general, adsorption is maximum near the zero point charge pH, at which the PCD rate is also maximum. In the case of substances, which are weakly, acidic, the PCD increases at lower pH because of an increase in the adsorption. Some substances undergo hydrolysis at alkaline pH, which is one of the reasons for the increase in the PCD at alkaline pH values. Also at alkaline pH values, the concentration OH· are relatively higher and this may also be another reason for the increase in the PCD rate. Andreozzi et al. (2000) studied the effect of temperature on the PCD of 4-nitrophenol at pH 3 and 8.5. The rate constant k_o is linear with the temperature in the range of 20-50°C. A negative temperature dependence observed in the acidic pH was attributed to exothermic adsorption.

Brezova and Blazkova (1995) found that presence of anions (such as chloride, sulfate, carbonate, and bicarbonate) in industrial effluents affect the adsorption of the degrading species, act as hydroxyl ion scavengers and may absorb UV light as well. Yawalkar *et* al. (2001) studied the degradation of phenol in the presence of various anions. They observed that detrimental effect on the PCD of phenol follows the sequence: $SO_4^{2-} < CO_3^{2-} < Cl^- < HCO_3^-$

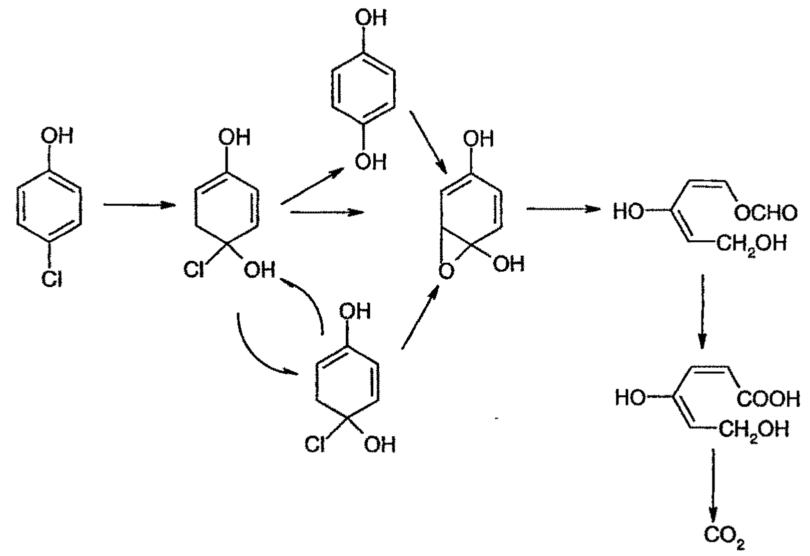
Wei et al. (1991) studied the effect of transition metal ions, such as Fe^{3+} and Cu^{2+} on the PCD of phenol. They found that phenol removal increased rapidly as the concentration of the ferric ion was gradually increased. It reached a maximum value in the neighborhood of 4.8 mmol dm^{-3}. However, excessive ferric ions retarded the catalytic effect. The phenol removal decreases from 26 to 15% as 20 mmol dm^{-3} cupric ions were added.

Prairie et al. (1993) investigated the effect of the presence of dissolved metals (Ag, Au, Cd, Cr, Cu, Hg, Ni, and Pt) on the PCD of phenol. They found that only those metals with standard reduction potentials more positive than 0.3 V can be treated using TiO_2 as the photocatalyst.

No aliphatic acids/compounds have been detected (Yawalkar et al. 2000) which indicates that after loading of the ring by two to three hydroxyl groups, the ring opens up. The intermediates detected by in the case of phenol confirm the degradation scheme suggested by Turchi and Ollis(1990) that opened ring is rapidly converted to CO_2, H_2O, etc.

Chen and Ray (1998, 1999) and Chen and Rulkens (1997) studied the kinetics of degradation reactions using Langmuir Hinshelwood kinetic schemes.

Mills et al. (1999) has proposed following reaction pathway in the PCD of 4-chlorophenol in the presence of ClO_3.



Gogate and Pandit (2004) show the limitation of PCD, an ecological technique to process industries as per Indian perspective:

- Engineering design and operation strategies required for an efficient design of reactors at large scale are not readily available.
- Compared to conventional chemical reaction rate, the reaction rate of photo-catalytic processes is usually slow and there is a need to provide larger amounts of active catalyst in the reactor.
- For reactors with catalyst in suspended form, ultrafine separation is an inconvenient, expensive and timeconsuming process.
- Very few examples of application to real industrial effluents with higher destruction efficiency of photocatalytic oxidation alone are available.

2.3.5 Feasible Routes

Although AOPs are attractive ecologically, a serious drawback of AOP is their relatively high operational costs in terms of catalyst/chemical and energy. Investment costs for biological processes may range from 5 to 20 times less than those of advanced processes such as ozonation or H_2O_2 oxidation, while treatment costs may range from 3 to 10 times less. (Mantzavinos et al. 2004). Economic feasibility can be enhanced by following two modes:

- Integration of biological treatment with AOPs
- Use of sun light as source of energy in AOP

2.3.5.1 Integration of Biological Treatment with AOP

Given the specific treatment objective, the effluent characteristics(e.g. composition and concentration) and the oxidation potential of the oxidant in question, advanced oxidation technologies may be used either for the complete mineralization of all to carbon dioxide, water and mineral salts or for the partial removal of certain target pollutants and their conversion to intermediates. In general, advanced oxidation method aiming at complete mineralization might become very cost intensive since highly oxidized end products that are formed during oxidation tend to be refractory to total oxidation. Biological oxidation is generally thought to increase with decreasing molecular size. Conversely, total chemical oxidation of intermediates to carbon oxide and water may be difficult and require severe oxidative conditions, since the rate of chemical C-C bond scission seems to decrease with decreasing molecular size. Putting these two separate observations together in a qualitative sense, the concept of an integrated advanced oxidation and biological treatment process can be illustrated schematically in Fig. 2.5. As seen, there appears to be a breakpoint beyond which biological treatment becomes more attractive than advanced oxidation in terms of rate. Therefore, combinations of AOP as preliminary treatments with inexpensive biological processes seem very promising from economic point of view (Mantazavinos and Psillakis 2004).

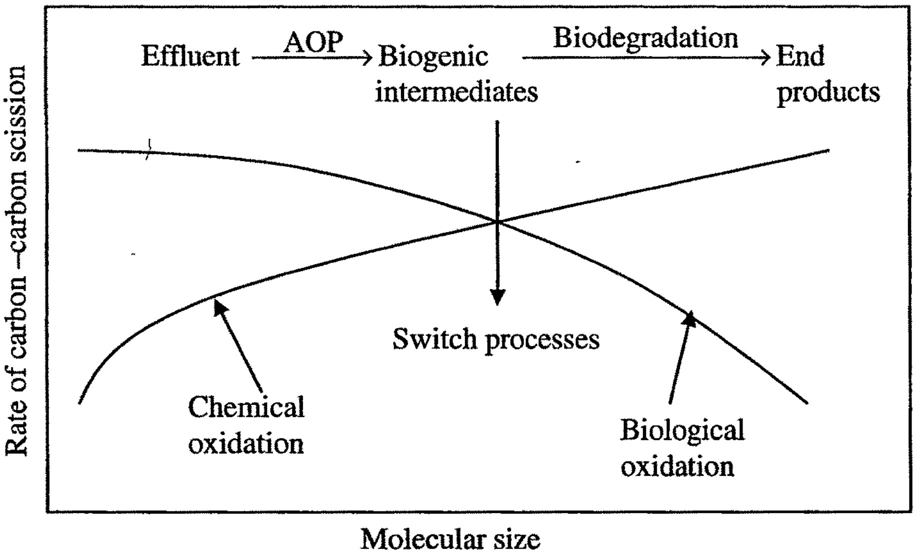


Figure 2.5. The concept of integrated chemical and biological treatment

A great deal of research into chemical oxidation pretreatment has been undertaken over the past 20-25 years. Review of studies upto 1995 has been given by Scott and Ollis (1995) while Mantazavinos and Psillakis (2004) provided a review account upto 2004. Work on phenolic waste with integration concept is summarized in Table 2.9.

2.3.5.2 Use of Sunlight in AOP

The work reported on solar detoxification of phenols in literature is represented in Table 2.10. Solar detoxification is non-selective and can be employed with complex mixtures of contaminants. Application of solar irradiation to the photo processes reduces cost but this is only possible for catalyzed homogeneous and heterogeneous reaction using ferrous ions and titanium dioxides, respectively. These catalysts absorb at wavelength of the solar spectrum while O_3 and H_2O_2 donot above 300 nm, which is the most important condition for the use of sunlight (Parra et al. 2000).

Though, in some cases, the photo-Fenton process has demonstrated higher degradation efficiencies than heterogeneous TiO_2 photocatalysis, but the Fe cycle is found to be affected by the contaminants and photo-fenton does not work at all in many cases.

2.3.6 Photochemical Reactors

The adoption of photo-oxidation treatment requires the use of suitable UV sources and of appropriate photochemical reactors. In the photo reactor design a careful attention must be paid to proper sizing of the path length between quartz sleeve (housing the lamp) and the reactor walls. The rule generally adopted is that more than 90% of emitted light must be absorbed by the solution. A proper sizing of the path length renders useless the adoption of reflective reactor walls. The use of special reflective materials is a controversial point since they are expensive and the benefits of the reflectors can be easily reduced or erased by the fouling in the case of wastewaters containing suspended particles. The problem of fouling is more relevant for the quartz sleeve. It is essential that it remains clean during the operation. For this purpose the reactor is generally provided with a quartz sleeve cleaning device.

When O_3 is admitted (O_3/UV), a gas–liquid contactor is required (i.e. a sparging device) (Prado et al. 1994). Rodrýguez et al. (2002) used continuous tubular reactor whereas Chen and Chan (1997) used stirred tank photochemical reactors. Ray et al. (1998) proposed the flow reactor for PCD process, in which TiO_2 was fixed on reactor wall and the contaminated water was flowed over it, this eliminated the need for filtration or settling the suspension of the photo catalyst.

For integral system involving combination of biological and PCD processes, the photochemical reactors described above are used(Mazenonions 2004). Parra et al. (2000) used Heliomann type and compound parabolic collectors for solar reactors.

Table 2.9. Effect of AOP pretreatment on biological properties (+ positive effect, - negative effect, 0 insignificant effect)

Compound degraded /type of effluent	AOP used	Biological degradation	Effect on different parameters	Conc. range mg/l	Reference
Olive mill effluent (diluted 10 times)	O_3	Active sludge respirometry	BOD/COD ratio (+)	COD =250-1400	Amat et al. (2003)
Coke processing effluent	O_3 at 5.4 pH	BOD, acclimated activated sludge in aerated reaction	BOD/COD ratio, removal of COD and total phenols (+)	COD =2000 BOD_5 =2000 Phenol=300	Benitez et al. (2003)
Industrial effluents with various chlorocarbons, phenols & aniline	$Fe^{+2}/H_2O_2/UV$, $Fe^{+3}/H_2O_2/UV$	BOD	BOD_5/TOC ratio (0)	COD =1300 TOC =500	Bozzi et al. (2003)
2, 4-dichlorophenol	O_3	BOD, acclimated and non acclimated activated sludge in aerated reactors	BOD/COD ratio TOC removal (+)	C= 100	Contreras et al.(2003)
2- nitrophenol, 4-nitrophenol, 2,4 dinitrophenol,2-methyl-4,6 dinitrophenol (either in mixture or alone	O_3 at 2.5 and 9 pH	BOD, incubation for 24 h with Daphnia magna	BOD/COD ratio Toxicity (+)	C= 70 for each compound in mixture and C= 75 for single solution	Goi et al. (2004)
4-chlorophenol, 2,4-dichlorophenol	$Fe^{+2}/H_2O_2/UV$	BOD	BOD/COD ratio (+)	C = 300	Chamarro et al. (2001)
2,4,5-trichlorophenol	$FeCl_3$, $Fe(ClO_4)_3$	BOD	Toxicity (+)	C=160	Georgiy et al. 1997
Phenol	O_3 at 4,7 and 10 pH	Incubation for 15 min. with photobacterius phosphreum	Toxicity (-/+)	C=150-800	Shang et al. 2002
2-chlorphenol, 3-chlorphenol, 4-chlorphenol,	O_3 at 7 pH	Incubation for 15 min. with photobacterius phosphreum	Toxicity (-/+)	C=100-200	Shang et al. 2002
Olive mill effluent	O_3, Fe^{+2}/H_2O_2	Aerated microorganisms in batch reactors	COD and total phenols (+)	COD= 95000 BOD= 5200	Beltran et al. 2001

Table 2.10. Summary of compounds degraded by various researchers using Solar Energy

Compound degraded	Method used	Mode of light	Intermediates Detected/Conc. mg/l	References
Phenol, aminophenols, mono-hydroxy phenols	TiO_2 (Degussa P25), Photo-fenton	Sunlgiht	-	Parra et al. (2001)
Phenol	TiO_2 (Degussa P25)	Sunlight	Benzoquinone, hydroquinone, resorcinol, pyrocatechol	Yawalkar et al. (2001)
Phenol	TiO_2 (Degussa P25) as freely suspended	Natural sunlight	Not analyzed	Matthews & McEvoy (1992)
Phenol, 2-chorophenol	TiO_2 (Degussa P25) attached to glass mesh	Parabolic trough solar	Not analyzed	Matthews et al. (1987)
Phenol, 2,4-dichlorophenol	TiO_2 (Degussa P25)	Solar light using flat and cpc collector	500	Gimenez et al.(1999)

2.3.7 Economic Considerations

There are only few papers published in the literature reporting the economical consideration for the treatment of phenolic wastewater. The methods cannot be compared directly. The cost factor depends on the type of phenolic compound, its concentration in wastewater, presence of other dissolved impurities, quality of the wastewater to be treated to government limits set for disposal, etc. (Espulgus et al. 2002, Andreozzi et al. 1999).

Bhatkhande et al. (2001) gave a rough estimate of operating costs of the two processes i.e. photochemical and photocatalytic degradation using solar radiation in place artificial UV light. As per their calculations the cost of photo catalytic process is $20 Rs.h^{-1}$ and for the photochemical process is $90 Rs.h^{-1.}$

2.3.8 Summary

AOP is ecologically promising technology for treating the phenolic waste. However, AOPs cannot be applied economically at present due to very high cost of UV radiation. Use of sunlight as light source can reduce the cost of treatment. Only photocatalytic degradation process using titanium dioxide can utilize the solar light for detoxification.

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