



Review

Technologies for the removal of phenol from fluid streams: A short review of recent developments

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ARTICLE INFO

Article history:

Received 2 November 2007

Received in revised form 26 February 2008

Accepted 11 March 2008

Available online 20 March 2008

Keywords:

Phenol

Water purification

Wastewater treatment

Pollution abatement

Air purification

VOC abatement

Technologies for phenol abatement

Adsorption of phenol

Absorption of phenol

Extraction of phenol

Combustion of phenol

Photocatalytic oxidation

Catalytic oxidation

ABSTRACT

The available technologies for the abatement of phenol from water and gaseous streams are briefly reviewed, and the recent advancements summarized. Separation technologies such as distillation, liquid–liquid extraction with different solvents, adsorption over activated carbons and polymeric and inorganic adsorbents, membrane pervaporation and membrane–solvent extraction, have been discussed. Destruction technologies such as non-catalytic, supercritical and catalytic wet air oxidation, ozonation, non-catalytic, catalytic and enzymatic peroxide wet oxidation, electrochemical and photocatalytic oxidation, supercritical wet gasification, destruction with electron discharges as well as biochemical treatments have been considered. As for the abatement of phenol from gases, condensation, absorption in liquids, adsorption on solids, membrane separation, thermal, catalytic, photocatalytic and biological oxidation have also been considered. The experimental conditions and the performances of the different techniques have been compared.

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1. Introduction

Industrial processes generate a variety of molecules that may pollute air and waters due to negative impacts for ecosystems and humans (toxicity, carcinogenic and mutagenic properties). Phenol is one of the most common organic water pollutants, because it is toxic even at low concentrations, and also its presence in natural waters can lead further to the formation of substituted compounds during disinfection and oxidation processes. Phenol is also relevant in the field of environmental research, because it has been chosen frequently as a model pollutant and many data are available on its removal and destruction in particular with respect to wastewater treatments. In this review some recent advances in the methods for phenol removal from fluid streams will be shortly reviewed. The idea is to summarize all possible techniques to remove phenols from fluid streams, considering the most recent literature data. This work is expected to be useful to support the choice of the best technique to treat phenol emissions in practical cases.

2. Phenol properties and pollution sources

2.1. Phenol chemical and physical properties [1,2]

Some chemical and physical properties of phenol (also called phenic acid or carboic acid) are reported in Table 1. Phenol was first isolated from coal tar in 1834 by the German chemist Runge. It is an aromatic compound. At ambient temperature and pressure it is a hygroscopic crystalline solid. When pure, solid phenol is white but is mostly colored due to the presence of impurities. Phenol is very soluble in ethyl alcohol, in ether and in several polar solvents, as well as in hydrocarbons such as benzene. In water it has a limited solubility and behaves as a weak acid. As a liquid phenol attacks rubber, coatings, and some forms of plastic. Hot liquid phenol attacks aluminum, magnesium, lead, and zinc metals. It is characterized by a typical pungent sweet, medicinal, or tar-like odour [3]. It is a combustible compound.

2.2. Phenol industrial syntheses and sources

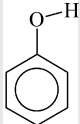
Currently, phenol is produced at a rate of about 6 million ton/yr worldwide, with a significantly increasing trend [2]. The so called

Hock processes, i.e., the three-step cumene synthesis and oxidation processes (such as the Sunoco-UOP, the KBR and the GE-Lummus processes), consisting in the simultaneous syntheses of phenol and acetone from benzene, propylene and oxygen, produces about 95% of the phenol used in the world. These processes [4] involve: (i) alkylation of benzene with propene to form cumene, catalyzed by phosphoric acid, aluminum chloride or, recently, by beta or MCM22 zeolite [5]; (ii) oxidation of cumene to cumene hydroperoxide (CHP) with air proceeding via a free-radical mechanism that is essentially auto-catalyzed by CHP; (iii) cleavage of cumene hydroperoxide to phenol and acetone, catalyzed by sulphuric acid.

Several alternative industrial syntheses of phenol exist [2,6–8], i.e., through chlorobenzene (reaction with caustic soda at 350 °C) or by sodic benzenesulfonate alkaline fusion or by oxidation of toluene via benzoic acid. Phenol is also present in benzole and coal tar produced during coal coking. It may be separated from these by-products by extraction with caustic solutions as sodium phenate. It is shipped in the molten state at elevated temperatures or in the solid or crystalline form; it is also available as an aqueous solution.

Phenol and many substituted phenols are natural components of many substances (e.g., tea, wine and smoked foods), and phenol is also emitted from the combustion of fossil fuels and tobacco. It is also present in animal wastes and decomposing organic material

Table 1
Chemical and physical properties of phenol

Formula	C_6H_5OH 
Molecular weight (g/mol)	94.11
T_{melt} (°C)	40.9
T_{eb} (°C)	181.75
Water solubility (r.t.)	9.3 g _{phenol} /100 ml _{H₂O}
pK _a	9.89
Flammability limits in air (vol%)	1.7 (lower) 8.6 (higher)
Flash point (°C)	79 (closed cup)
Autoignition temperature (°C)	715

and may be formed in air as a product of benzene photooxidation. Bacteria in the environment quickly break down phenol, and so levels in air (1–2 days), water (9 days) and soil (2–5 days) are generally quite low.

2.3. Phenol industrial applications

As a pure substance, phenol is used as a disinfectant, for the preparation of some cream and shaving soap for its germicidal and local anesthetic properties, in veterinary medicine as an internal antiseptic and gastric anesthetic, as a peptizing agent in glue, as an extracting solvent in refinery and lubricant production, as a blocking agent for blocked isocyanate monomers, as a reagent in chemical analysis and as a primary petrochemical intermediate. Its largest use (35%) is to produce phenolic resins like phenol–formaldehyde resins (Bakelite) which are low-cost thermosetting resins applied as plywood adhesive, construction, automotive and appliance industries. By reaction with acetone it may also be converted into bisphenol A, a monomer for epoxy-resins (28%). It is also used to produce cyclohexanone and cyclohexanone–cyclohexanol mixtures by selective catalytic hydrogenation. Cyclohexanone is later converted into its oxime and further to ϵ -caprolactame, the monomer for nylon 6 (16% of phenol applications). The mixture cyclohexanone–cyclohexanol is oxidized by nitric acid to adipic acid, one of the monomers for the production of nylon-6,6. Phenol is also used to produce polyphenoxy and polysulphone polymers, corrosion-resistant polyester and polyester polyols.

Phenol may be converted into xlenols, alkylphenols, chlorophenols, aniline, and other secondary intermediates in the production of surfactants, fertilizers, explosives, paints and paint removers, textiles, rubber and plastic plasticizers and antioxidants, and curing agents and so on. Phenol is also a building block for the synthesis of pharmaceuticals, such as, e.g., aspirin.

2.4. Phenol and health

The sterilizing activity of phenol was discovered by the English surgeon Joseph Lister in 1865. The germicidal activity of phenol appears associated to its protein denaturing ability. It has lipophile properties, so it binds itself to the batteric proteine by hydrogen bonds.

On the other hand, phenol has relevant health effects for humans [9]. The manufacture and transportation of phenol as well as its many uses may lead to worker exposures to this substance, through inhalation, ingestion, eye or skin contact, and absorption through the skin. Phenol is rapidly absorbed through the skin and can cause skin and eye burns upon contact. Comas, convulsions, cyanosis and death can result from overexposure to it. Internally, phenol affects the liver, kidneys, lungs, and vascular system. The ingestion of 1 g of phenol is deadly for man.

The Nazi used phenol toxicity for refining extermination techniques, making phenol injections for killing the prisoners. Death was coming up in a few seconds and the method was considered to efficacious and economic [10]. No evidence exists to indicate that phenol has any carcinogenic potential.

3. Abatement technologies for phenol in wastewaters

Phenols are present in wastewater of various industries, such as refineries (6–500 mg/l), coking operations (28–3900 mg/l), coal processing (9–6800 mg/l), and manufacture of petrochemicals (2.8–1220 mg/l). Phenols are also the main organic constituents present in condensate streams in coal gasification and liquefaction processes. Other sources of waste streamwater containing

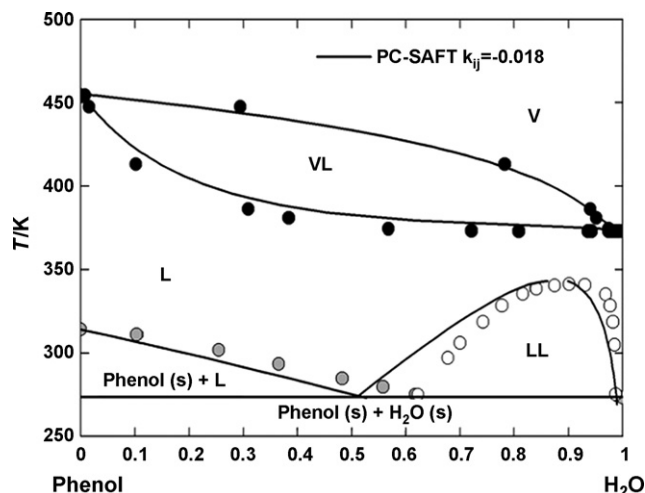


Fig. 1. Phase diagram of phenol–water system showing vapor–liquid, liquid–liquid, solid–liquid, and solid–liquid–liquid equilibria. Experimental data were taken from Ref. [12]. Lines are modeling results with PC-SAFT equation of state using $k_{ij} = -0.018$. Reprinted with permission from Ref. [11].

phenols are pharmaceutical, plastics, wood products, paint, and pulp and paper industries (0.1–1600 mg/l). As a particular case we can cite olive oil mill wastewaters, rich in phenol and polyphenol derivatives that give rise to relevant phytotoxicity. They represent a significant problem in the Mediterranean area.

Phenol-containing wastewater may not be conducted into open water without treatment because of the toxicity of phenol. It also contributes to off-flavours in drinking and food processing waters. Due to the toxic nature of some of these compounds the Environmental Protection Agency has set a water purification standard of less than 1 part per billion (ppb) of phenol in surface waters. In Italy, in agreement with the recommendations of the European Union, the limit for phenols in potable and mineral waters is 0.5 $\mu\text{g/l}$ (0.5 ppb), while the limits for wastewater emissions are 0.5 mg/l (0.5 ppm) for surface waters and 1 mg/l for the sewerage system (law no. 152/2006).

In this review, the abatement technologies for phenol from wastewaters will be considered. A comparison of the experimental condition for most of these techniques is given, with some comments, in Table 2. Actually, several phenol derivatives are also possible water contaminants. The data concerning phenol abatement could be also taken as references for the treatment of waters polluted by phenol derivatives.

3.1. Separation of phenol from water solutions

3.1.1. Separation by steam distillation

In Fig. 1 the solid–liquid–vapor state diagram for the water–phenol system as reported recently by Tumakaka et al. [11] is shown. The origin of the experimental data is from Ref. [12]. In the liquid state phenol has a limited miscibility with water (near 10–70% (w/w) phenol are approximately the limits at room temperature) but this immiscibility fully vanishes above 68 °C [2,13]. On the other hand, the miscibility gap increases with increasing salt concentration, as shown in Fig. 2 for the phenol–water–NaCl system [13].

Phenol–water solutions have a minimum azeotrope, at 9.21% phenol (w/w), corresponding to a molar fraction of 0.019, T_{eb} 94.5 °C at 1 atm [2,14,15]. The removal of phenol from organic media is frequently carried out by steam distillation processes, just based on the steam volatility of phenol. On the other hand, distillation may allow the drying of phenol from rich phenol–water mixtures. This is

Table 2
Summary of experimental conditions for technology for the treatment of phenol–water mixtures

Technique	Temperature range (°C)	Pressure	pH	Reactor	Additional chemicals	Additional energy supply	Performances (ex.)	Ref	Comments
Distillation	95–180	~1 atm	As such	Distillation column	No	No	Complete separation possible	[12,22]	Commercial; recovery of phenol; costly
Liquid–liquid extraction	I 20–50; II 60–180 (regeneration)	~1 atm	As such	I washing column; II distillation column	DIPE or MIBK (recycled)	No	$K_d (W_{ph} \text{ in MIBK}/W_{ph} \text{ in H}_2\text{O}) \sim 100$ at 30 °C	[6,18,22]	Commercial; recovery of phenol; costly
Adsorption (AC)	20–50	~1 atm	~Neutral	Fixed bed column	AC	No	Adsorption capacity 200–400 mg _{ph} /g _{AC}	[23,24]	Commercial, secondary pollution (disposal or burning of the spent AC adsorbent)
Adsorption (resins, inorganics)	I 20–50; II 20–50 (regeneration)	~1 atm	~Neutral	Fixed bed column	PV-PDS resin; regeneration solution	No	Adsorption capacity 80–100 mg _{ph} /g _{AC} (resins); adsorption capacity <200 mg _{ph} /g _{AC} (silicalite)	[34,36,41,42]	Commercial, secondary pollution (regeneration solution); possible recovery of phenol
Enzymatic oligomerization/adsorption	20–50	~1 atm	Slightly acidic	Fixed enzyme bed on support; adsorption bed	Enzyme/support; Chitosan	No	C_{ph}^0 0.02 g/l; tyrosinase 46 U/ml; chitosan 50 g/l; >phenol removal 90%	[64]	Secondary pollution (spent enzyme, support, adsorbent)
Pervaporation	20–50	~1 atm/1–20 Torr	As such	Membrane module	Membrane	Vacuum production	PEBA: enrichment factor 4–60 permeate flux 0–0.3 kg _{ph} /(m ² h)	[34]	Commercial, recovery of phenol
Membrane extraction (ex. MTBE)	20–50	~1 atm	as such	Membrane module	Membrane Solvent	Solvent regeneration	C_{ph}^0 0–5 g/l; feed flow 1–8 cm ³ /s; depletion degree 50–100% (MTBE)	[34]	Commercial, recovery of phenol
WAO	180–315	20–160 Atm	Slightly acidic	Bubble column, stirred reactor, jet-agitated reactor	Air, an acid	No (stirring)	COD° 10–100 g/l, τ 15–120 min, COD conv 75–90%	[57,69]	Commercial, further treatment needed
SWAO	400–650	250–350 Atm	As such	Bubble column, stirred or jet-agitated reactor	Air	No	TOC conv 99.99%; residual TOC < 3.5 ppm	[60]	Commercial, total combustion possible
CWAO	100–200	3–35 Atm	As such	Pressurized slurry TR; fixed trickle bed	Air/catalyst	No	Noble metal or metal oxide cat.; COD° 10–100 g/l, TOC conv > 80–99%; $t > 20$ min	[69,57]	Commercial; Total combustion possible (?); Catalyst leaching?
Ozonation	20–50	~1 atm	Basic	Bubble column, ejector	O ₃ , a base (a catalyst)	No (or ozone production)	Liquid flow 0.8 m ³ /h, O ₃ -O ₂ gas flow 0.5 Nm ³ /h, C_{ph}^0 6 10 ⁻⁵ g/l; phenol conv 100% after 30–80 min, ejector, semi-batch.	[73]	Commercial. In case, pollution by the catalyst or catalyst removal
CWPO-Fenton oxidation	20–50	~1 atm	Acidic	Stirred slurry reactor, fixed bed reactor	H ₂ O ₂ , FeSO ₄ , an acid	No	C_{ph}^0 s 0.1 g/l; $C_{H_2O_2}^0$ 10 ⁻² ml/l; $C_{Fe^{2+}}^0$ 2.5 10 ⁻⁴ ml/l, 5 h, TOC conv. >90%.	[85]	Commercial; recovery of the catalyst or secondary pollution (the catalyst)

Enzymatic peroxidation	20–50	~1 atm	As such	Supported enzyme in a fixed or fluid bed, fixed bed for polymer separation	Enzyme, support, H ₂ O ₂ , an acid	No	C _{ph} ^o 0.1 g/l; C ^o _{H2O2} 0.034 g/l; flow rate 5–10 ml/min; phenol conversion 50–80%	[98]	Recovery of the enzyme; secondary pollution (spent enzyme, polyphenols, additives to limit enzyme inhibition)
Indirect electro-oxidation (electro-fenton)	20–50	~1 atm	Acidic	Electrochemical cell	O ₂ , catalyst (e.g., FeSO ₄), an acid	≤1 V	COD ^o < 1000 ppm; COD _{final} < 10 ppm	[85]	Recovery of the catalyst or secondary pollution (the catalyst)
Anodic oxidation	20–50	~1 atm	As such	Electrochemical cell	Expensive electrodes (BDD)	4–15 V	TOC ^o 0.02 g/l; TOC conv 60–100%, t 10–20 h	[106]	
Photocatalytic oxidation (UV)	20–50	~1 atm	As such	Photochemical cell (slurry or fixed bed)	TiO ₂	hν (λ < 400 nm)	C _{ph} ^o 0.04 g/l; t 300 min; TOC conv > 90%	[115–119]	Commercial, recovery and/or leaching of the photocatalyst
Photocatalytic oxidation (vis)	20–50	~1 atm	As such	Photochemical cell (slurry or fixed bed)	N-doped TiO ₂ ; TiO ₂ -carbon	Solar light	N-TiO ₂ , C _{ph} ^o 0.06 g/l; t 120 min, phenol conv 27%	[121,122]	Recovery and/or leaching of the photocatalyst; Catalyst stability?
SCWG	~600	250–350 Atm	As such	Pressurized stirred tank reactor	No	No	C _{ph} ^o 5%; in the presence of Ni, t 45 min; phenol conv 100% (H ₂ , CH ₄ , CO ₂ , benzene)	[125]	
PCD	20–50	~1 atm	Basic	Discharge reactor	Soda	30 kV	C _{ph} ^o 0.05 g/l; NaOH 210 mmol/l; t 40 min; phenol conv 100%	[126]	Difficulties with salt water
GDE	20–50	~1 atm	Slightly acidic	Discharge reactor	An acid, Pt electrodes	900 V	C _{ph} ^o 0.3 g/l; C _{ph} 100 and TOC conv 60% t 80 min	[128]	
Biological degradation	20–50	~1 atm	As such	Slurry or fixed bed reactor	Microbial cultures, fungi (support)	No	C _{ph} ^o 0.4 g/l; removal rate 1.30 g _{ph} /l d	[133–135]	Commercial, Secondary pollution (spent microbial system)

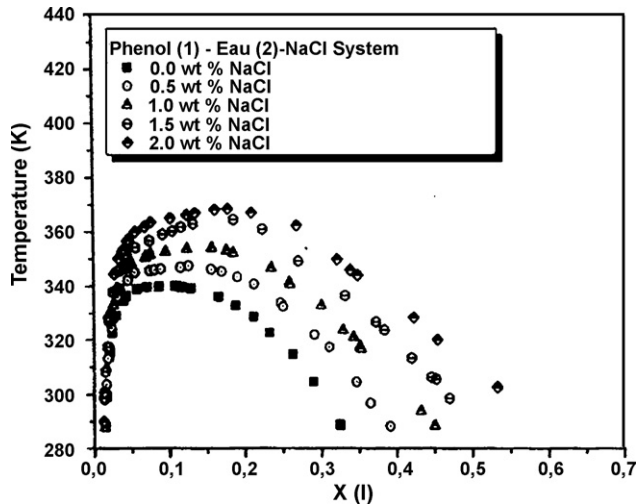


Fig. 2. Comparison of the influence of NaCl on the miscibility of phenol–water: (a) NaCl; phenol(1)–water(2)–NaCl system: 0.0 wt% NaCl, 0.5 wt% NaCl, 1.0 wt% NaCl, 1.5 wt% NaCl, 2.0 wt% NaCl. Reprinted with permission from Ref. [13].

done for example in the dewatering columns of the Monsanto process for the synthesis of phenol via soda fusion of benzenesulphonic acid: the azeotrope, or a water rich fraction, is distilled and recycled to previous steps while crude phenol is distilled later from heavies [6]. Similarly, in the phenol alkylation processes with alcohols, the water containing reaction product is dewatered by distillation: a water rich fraction is formed at the head of the column and splits in the condenser, allowing recycle of phenol [6]. Azeotropic distillation and/or steam stripping should also allow the purification of water from phenol impurities. The azeotrope, recovered as the head fraction, should split and the phenol-rich phase may be recovered, while the water rich phase may be refluxed to the column. This is what happens in the K3 stripping/distillation column of the extraction process shown in Fig. 3, where water is purified by stripping of the azeotrope. These procedures are quite energy demanding.

3.1.2. Separation by extraction

Several organic solvents, such as hydrocarbons and oxygenated compounds, may allow the extraction of phenol from water. Among others, *n*-hexane and cyclohexane, benzene, toluene, ethylbenzene, cumene, acetate esters (ethyl acetate, isopropyl acetate, *n*-butyl acetate, *n*-pentyl-acetate, *iso*-pentyl-acetate, *n*-hexyl acetate, and *cyclo*-hexyl acetate), di-isopropyl ether, methyl-*iso*-butyl ketone [16–18], as well as more complex molecules such as *n*-octyl-pyrrolidone [19].

Phenol-containing water from the production of phenol by the cumene process, i.e., the liquid arising from caustic washing and distillation of crude acetone and that arises from caustic washing of cumene to be recycled [2,4], which can contain 1–3% phenol, are mixed and freed by extraction from most of their phenol content. Cumene produced by the process is used as extracting agent in a counter-current extraction column. The cumene solvent from the top of the extraction column is then scrubbed of phenol in a counter-current caustic scrubbing column. The resulting sodium phenate solution then flows to the sodium phenate tank. The lean cumene is recycled to the extraction column. The extraction column bottom is one of the net wastewater streams from the phenol unit. In this way phenol is removed, depending on the process, down to a residual concentration of 20–500 mg/l. The remaining phenol is removed in the biological purification stage in a sewage treatment plant.

The so-called “Phenosovan” extraction process, from Lurgi, is used to remove phenol from waters in gasification plants [20], as well as in coke oven and carbonization plants, in the phenol industry, and in coal hydrogenation plants [21]. The filtered and cooled phenolic effluent is treated counter-currently with a suitable solvent, usually diisopropylether (DIPE) in a multistage extractor. The extract is separated by fractional distillation into pure DIPE solvent (overhead product, $T_{eb} = 69^\circ\text{C}$) and crude phenol (bottom product), while a water-containing azeotrope can also be recovered as a lateral stream and recycled back. The solvent is recycled to the extractor. The raffinate still contains a small amount of solvent which is recovered by stripping with recycled gas. The solvent is then removed from the gas by absorption in cooled and recycled crude phenols, from which it is subsequently recovered in the stripping section of the fraction-

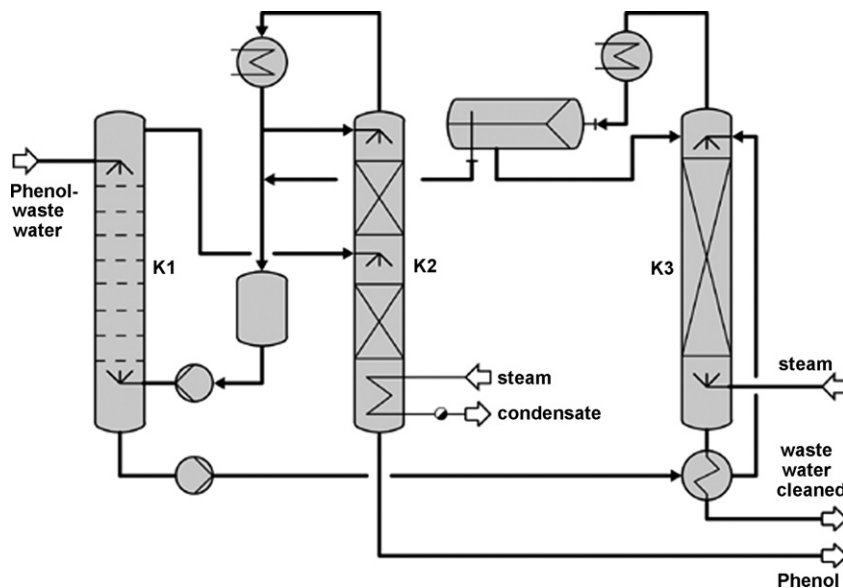


Fig. 3. Schematics of a process for the removal of phenol from wastewater using methyl-isobutylketone (MIBK). K1: extraction column; K2: distillation column; K3: stripping column. Reprinted with permission from Ref. [22].

ator. The Phenosolvan process can be operated with different feedstocks, different solvents or solvent mixtures (e.g., benzene and DIPE or DIPE plus methyl-isobutylketone, MIBK), and different solvent recovery systems (e.g., steam, gas, or ammonia stripping). All steam volatile phenols and neutral oils can be recovered almost completely, but only partial recovery of dihydric phenols is possible. If large gas condensate flows must be dephenolized, extraction must be performed in mixer settlers, exhibiting high stage efficiencies. Lower flow rates can be treated in extraction columns by using many stages to compensate for low efficiency.

In Fig. 3 the scheme of a commercial process for phenol extraction from water using MIBK is reported [22], similar to that described in Ref. [18]. In the K1 contactor MIBK extracts phenol from water, in the K2 distillation tower MIBK is regenerated as the head fraction ($T_{eb} = 117^\circ\text{C}$), while in the K3 column water is azeotropically purified by stripping the azeotrope with steam. The azeotrope splits in the condenser, the phenol-rich fraction being recycled to the contactor.

3.1.3. Separation by adsorption

Adsorptive processes are widely used in the purification of polluted streams and diluted wastewaters. Conventional fixed bed processes involve a saturation, adsorption or loading step, followed by desorption, elution or regeneration steps. However, regeneration may be not possible or not convenient: in this case the saturated adsorbent bed is removed and disposed or, in case, destroyed by burning in appropriate furnaces.

The most usual adsorbents for water treatment are activated carbons (ACs) [23]. The application of ACs to phenolics adsorption has been reviewed recently [24]. In liquid-phase adsorption, the adsorption capacity of AC for aromatic compounds depends on a number of factors such as the physical nature of the adsorbent (pore structure, ash content, functional groups, depending on its precursor material and preparation method), the nature of the adsorbate (its solubility, pK_a , functional groups present, polarity, molecular weight, size) and the solution conditions (pH, ionic strength, adsorbate concentration, oxygen availability). Therefore, two different procedures, denoted as “oxic” and “anoxic” are employed in conducting adsorption isotherm tests.

The following possible interactions between the carbon surface and the phenols have been proposed by Laszlo et al. [25]: (a) electron donor–acceptor interactions between the aromatic phenolic ring and the basic surface oxygens, such as carbonyl groups; (b) dispersion effect between the aromatic phenolic ring and the π electrons of the graphitic structure; (c) electrostatic attraction and repulsion when ions are present. On the other hand, Terzyk et al. [26,27] distinguished the following three stages of the mechanism of phenol adsorption on ACs: adsorption at the infinite dilution, micropore filling, and adsorption in larger micropores and mesopores.

Owing to the amphoteric character of a carbon surface its adsorption properties may be influenced by the pH value of the solution. If adsorption takes place from unbuffered solutions, nearly neutral or weakly acidic, all three types of surface-phenol interactions may occur simultaneously. Instead, dispersion effects are predominant at low pH (≤ 3), when the phenolic compounds are in the non-ionized forms, and the surface groups are either neutral or positively charged. In these conditions the more polar the surface of carbon, the lower the adsorbability of phenol, the adsorption of water and phenol being competitive.

For $\text{pH} > pK_a$ (e.g., at pH 11), the phenols dissociate, forming phenolate anions, while the surface functional groups are either neutral or negatively charged. The electrostatic repulsion between the identical charges lowers the adsorption capacities. Besides, the

phenolate anions are more soluble in the aqueous solution, and stronger adsorbate–water bonds must be broken before adsorption can take place.

In the range of adsorption in micropores, competition exists between micropore filling of the smallest micropores and the adsorption on active sites located in larger micropores. A temperature increase leads to vanishing of the effect of surface-chemical composition of ACs on phenol adsorption. In consequence, at higher temperatures, the porous structure of carbon determines the mechanism of phenol adsorption.

Fierro et al. [28] recently investigated the adsorption of phenol on commercial ACs and on highly microporous ACs prepared from chemical activation of Kraft lignin with sodium hydroxide (AC–Na), potassium hydroxide (AC–K) or phosphoric acid (apparent surface areas 940–2340 m^2/g). When soaked into an aqueous solution of phenol, all the tested ACs reached their maximum adsorption capacities in approximately 2 h. In all cases, the adsorption kinetics could be very satisfactorily fitted by a pseudo second-order equation. The transport of phenol from the solution to the surface of the adsorbents was shown to occur according to two steps, the first one corresponding to macropore and mesopore diffusion, and the second one being related to micropore diffusion. All the adsorption isotherms could be very well adjusted by Langmuir’s equation, and the highest phenol adsorption capacities were obtained with AC–Na and AC–K: 238.10 and 212.77 mg/g , respectively. The phenol uptake was found to depend not only on the micropore volume, but also on the total number of basic and carbonyl groups, and on the ratio of acid to basic groups.

Stavropoulos et al. [29] examined recently modified activated carbons with tailored adsorption capacity properties towards phenol. Oxygen gasification resulted in samples with surface area slightly lower than the raw activated carbon; the introduction of surface functional groups depended upon the severity of the treatment: carbonylic and phenolic type groups were introduced in all partially gasified samples, while low temperatures and short reaction times enhanced the basic character of the carbon. However, nitric acid treatment resulted in the introduction of high nitrogen amounts in the samples, the reduction of surface area and the development of a surface containing carboxylic, lactonic, phenolic and carbonylic groups with negligible HCl neutralization capacity. Treatment of activated carbon by urea supported the formation of basic groups and carbonyls. The presence of surface functional groups affected the adsorption capacity of the produced samples for the removal of specific pollutants such as phenols. Urea treated samples with a basic character and high nitrogen content presented the highest phenol uptake capacity; nitric acid treated carbons and oxygen gasified samples presented an acidic surface functionality and a low phenol adsorption capacity. The beneficial role of nitrogen on phenol adsorption was attributed to adsorbate–adsorbent interactions. The interaction of phenol with activated carbons has also been the object of a theoretical study [30].

It has been known for a long time that some of the phenols and its derivatives can adsorb on carbon irreversibly, that is, the irreversibly adsorbed phenol cannot be desorbed in water or by heating to the temperatures as high as 800°C . Phenol adsorption depends on the presence of oxygen in solutions (oxic or anoxic conditions) [31]. Here two important effects occur, i.e., chemisorption and so called “oxidative coupling”. The former leads to the creation of covalent bonds between phenol and carbon surface, while the latter yields to reaction products, i.e., phenol dimers, trimers, and multimers. The major factor responsible for the differences recorded in phenol adsorption under the oxic and anoxic conditions is the oxidative coupling. The differences between adsorption determined under the oxic and anoxic conditions are the parabolic-like function decreasing in the range of primary micro-

pore filling and increasing in the range of adsorption in larger pores.

Regeneration of AC, which is made difficult by irreversible adsorption of phenols, is crucial to ensuring that the adsorption process will be economically attractive. There are many methods used today to regenerate ACs. The most extensively used technique is thermal regeneration. Hot water [32], steam or heated nitrogen is used to destroy organic contaminants and recycle the carbon for reuse. Unfortunately, this process is time-consuming and expensive, and after a series of regenerations involving repetitive heating and cooling, AC becomes damaged with loss of carbon (5–10% per cycle) due to oxidation and attrition. Thermal regeneration of the exhausted AC is favoured under CO₂ atmosphere, compared to inert atmosphere. This is due to partial gasification of the sample, that contributes to preserve the porous structure. Decomposition of phenol at high temperature blocks the pore structure of the adsorbent due to coke deposited inside the AC. However, this deposited products might react with CO₂ so that the effect of blocking the texture would be lessened [33]. Alternatively, chemical methods (pH-swing or extraction with solvents) may be applied.

Recently, the efficiency of applying microwave heating technology to regenerate industrial waste activated carbon has been investigated. The results are very promising due to the rapid heating of the AC by microwave energy. In addition, microwave technology allowed the carbon to be recycled and reused a large number of times. This technique does not damage the carbon; rather, it increases the surface area allowing more contaminants to adhere, thereby increasing the value [idem].

Polymeric resins represent an alternative to activated carbons for adsorption of phenols. A significant aspect of the resin adsorption is that the bonding forces between the adsorbent and the adsorbate are usually weaker than those encountered in activated carbon adsorption. Regeneration of the resin can be accomplished by simple, non-destructive means, such as solvent washing, thus providing the potential for solute recovery.

Kujawski et al. [34,35] et al investigated the removal of phenol from water on different resins of the Amberlite family (Rohm and Haas). The Amberlite XAD-4 (polystyrene-divinylbenzene, PS-DVB) had better properties than acrylate-divinylbenzene resins in decontamination of aqueous phenol solutions. It was shown that regeneration of the adsorbent bed could be effectively performed with sodium hydroxide solution. The adsorption capacity of PS-DVB resins is in the range 80–100 mg/g [36].

The use of PS-DVB copolymer Amberlite XAD-16 resin as an adsorbent for the removal of phenol and *p*-chlorophenol from single and bisolute aqueous solutions under equilibrium and dynamic column experimental conditions has been the object of another study [37]. The loaded adsorbent with the phenols is regenerated with solvent washing technique using methanol as an eluent.

Different studies show that ACs have definitely higher capacities than the PS-DVB polymeric and polyacrylamide adsorbents for phenol adsorption from water [38,39], although it is also relevant that ACs have definitely lower apparent densities than resins. On the other hand, resins may be more sensitive to temperature effect than ACs [40].

In the work published by Roostaei and Handan Tezel [41] experiments have been conducted to examine the liquid-phase adsorption of phenol from water by silica gel, two kinds of activated alumina, one basic and the other acidic, two kinds of activated carbons, two hydrophobic/organophilic zeolitic adsorbents HiSiv 3000 (ZSM-5-type structure), and HiSiv 1000 (Y-Faujasite-type structure), both from UOP. There was no significant phenol adsorption by silica gel and activated alumina. The results showed that adsorption capacity of HiSiv 1000 (Y-Faujasite) decreased with increasing temperature. But did not change after 14 regeneration

cycles at 360 °C. However, equilibrium experiments showed that the adsorption capacities of activated carbons were several times higher than that of HiSiv 1000. The adsorption isotherm model of the Langmuir–Freundlich type was the best to describe adsorption equilibrium data for phenol for the adsorbents studied.

According to the producers [42] HiSiv adsorbents are a unique line of hydrophobic (organophilic) molecular sieves, specially designed to be effective in high-humidity air vent streams, more than for wastewaters. However, the robust inert nature of HiSiv adsorbents offers added benefit of oxidative stability versus activated carbon. HiSiv adsorbents are typically regenerated by using hot air. In any case, the use of siliceous zeolites (silicalites) for the removal of organics from water is well known. In fact, according to Shu et al. [43] the adsorption of phenol on silicalite and zeolite beta is enhanced by a high silicon-to aluminum ratio, which gives the zeolites a more hydrophobic character. The capacities of these materials are comparable to but slightly lower (by a factor of two) than the capacities of the organic resins XAD-2, XAD-4 and XAD-7 [44], which are designed for the adsorption of organics from aqueous solution. The isotherms for the silicalites are steeper at low phenol concentrations than for the other adsorbents, indicating that although the capacities of the silicalites are lower, their efficiency at low phenol concentrations may indicate a possible application of the silicalites for polishing dilute phenol solutions. Similarly, Khalid et al. [45] found that purely siliceous BEA zeolite can be used with success for phenol removal; the adsorption capacity was slightly higher at low phenol concentration (<1.6 g/l) than the one of activated carbon (surface area close to 1150 m²/g).

In a recent paper the application of arylene- and ethylene-bridged polysilsesquioxane to adsorption of different phenols has been reported [46]. The efficient removal of adsorbed phenols by a simple ethanol wash led to sorbent regeneration and separation of the aromatic species.

A variety of other adsorbents have been proposed for removal of phenols from single solute aqueous solutions, including bentonite and perlite, rubber seed coat, hydrotalcite and its calcined product acid-activated bituminous shale, zirconium(IV) arsenate–vanadate ion-exchanger, cross-linked polyvinylpyrrolidone, activated natural zeolites, and water-insoluble cationic starch.

On the whole, wastewater purification by means of conventional fixed bed comprise two drawbacks, one is the low efficiency of the fixed bed operation, since only a fraction of the adsorbent is used and the other is the use of a chemical regenerant to get an operative bed, with the associate waste disposal and a new pollution problem. Parametric pumping is a cyclic separation process in which a mobile phase percolates through a fixed bed upwards and downwards alternatively; a change in the temperature (or in another thermodynamic variables such as pressure, pH, etc.) occurring simultaneously with the change in the flow direction. Otero et al. [40] tested two polymeric resins and an activated charcoal in order to find out their adsorptive performance when removing phenol from wastewater. Both batch equilibrium and fixed bed tests were carried out at three different temperatures (293, 310 and 333 K) for each of the adsorbents. Polymeric resins, whose behavior is more sensitive to temperature than ACs, were found to allow high level of purification by applying thermal parametric pumping.

3.1.4. Separation by membrane pervaporation

Pervaporation is a quite recent technology applied to the removal of organics from water [47]. Pervaporation membranes separate water at the feed side and a vapor at the permeate side, simultaneously evaporating the permeating compound. Polyether–polyamide block copolymer (PEBA) membrane, which is particularly useful for the separation of aromatics, was also found performant to separate phenol from water in an earlier study [48].

The separation of a phenol–water mixture using a polyurethane membrane by a pervaporation method was investigated by Hoshi et al. [49]. The polyurethane layer was sandwiched with a porous polypropylene membrane (Celgard® 2500). Pervaporation measurement was carried out under vacuum on the permeate side, and the permeate vapor was collected with a liquid nitrogen trap. The phenol concentration in the permeate solution increased from 0 to 65 wt% with increasing feed concentration of phenol from 0 to 7 wt%. The total flux also increased up to 930 g/(m² h) with increasing phenol partial flux. In the sorption measurement at 60 °C, the concentration of phenol in the membrane was 68 wt%, which was higher than that of the permeate solution. Therefore, it was considered that the phenol selectivity was based on high solubility in the polyurethane membranes.

Application of pervaporation to the removal of phenol from water solutions modeling wastewater was investigated by Kujawski et al. [34,35] using composite membranes based on PEBA, polydimethylsiloxane (PDMS) and zeolite-filled PDMS pervaporation. The PEBA membrane showed the best selectivity. The use of cellulose acetate for separation of phenol from water through membrane pervaporation has also been reported recently [50]. As reported by Field and Lobo [51], to achieve pollution control and waste minimization, pervaporation (when applied to sparingly soluble organics such as phenol) is more viable when operated as a pervaporation–decanter hybrid process than in a stand-alone mode.

3.1.5. Separation by membrane-based solvent extraction

The membrane separation of water–phenol mixture has been the object of several recent studies mostly using hollow-fiber modules. Polypropylene membranes were applied by Kujawski et al. [34,35] using organic extraction solvent such as methyl-terbutyl ether (MTBE), cumene and a mixture of hydrocarbons and an overpressure of 31–38 kPa in the shell side. MTBE, probably due to its higher polarity and the possibility of establishing H-bonds with phenol, was found to be largely superior than hydrocarbons as extracting agent. Similar experiments have been performed using other solvents such as alkylamines (e.g., Amberlite LA-2 based on *N*-dodecyl-*N*-hexamethylhexyl-amine), tributylphosphate trialkylphosphine oxides and trialkylphosphine sulphide. Cichy and Szymanowski [52] used hollow fiber modules for investigating the separation of phenol–water solutions using Amberlite LA-2, troctylamine (TOA) and Cyanex 923 (a mixture of trialkylphosphine oxides). Cyanex 923 was found to allow the best performances in terms of mass transfer coefficients and times of extraction. The same solvent Cyanex 923 has also been investigated by Reis et al. in polypropylene hollow fiber modules [53]. Ninety-eight percent recovery of phenol with 39-fold increase in concentration were obtained. Re-extraction can be obtained by stripping with 0.2 M soda solution.

Xiao et al. [54] compared the ability of poly (dimethylsiloxane), i.e., PDMS and poly (methyl vinyl) siloxane (PVMS) in the membrane extraction of water–phenol mixtures with a sodium hydroxide solution. It was found that PDMS was more suitable for the operation under strong base condition. The effects of feed flow rate, phenol concentration, temperature and pH in the stripping solution and ionic strength on the process were studied. The effects of liquid flow status and system temperature on the membrane surface on the overall mass transfer coefficient (OMTC) and the permeability for phenol through the membrane were also discussed. The experimental results showed that the phenol removal efficiency was over 95% under the conditions of a flow rate 2.01/d, phenol > 5000 mg/l, at 323.2 K and pH 13.0. OMTCs increased with increasing salt concentration. The order of OMTC was 10⁻⁷ m/s, and the experimental data was agreement with the Arrhenius relation-

ship for the temperature dependence of the permeability of phenol through the polymer.

Emulsion liquid membranes (ELMs), which is an alternative liquid membrane technique, consist of an aqueous phase (internal receptor phase) stabilized by oil soluble surfactants and dispersed as very fine droplets (1–10 μm) inside an oil phase (membrane phase). The resulting liquid membrane, or water-in-oil emulsion, is further dispersed as emulsion globules (0.1–2 mm) in another aqueous solution (external donor phase). Target solutes in the external donor phase (e.g., contaminants in industrial wastewater) are transferred across the membrane phase into the internal receptor phase during an extraction process. In this water-oil-water ELM (i.e., in contrast to an oil-water-oil type ELM), the oil phase functions as a selective barrier, or membrane. The solute mass transfer is driven by the concentration difference between the external donor phase and the internal receptor phase. Activity of target solutes in the internal phase is typically kept at near zero by using a trapping agent in order to maintain the concentration gradient, although it gradually decreases, until most of target solutes are extracted from the external phase. After a desired level of extraction is achieved, the external phase and the ELMs are gravimetrically separated.

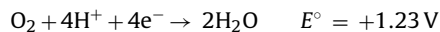
The ELMs are further demulsified for separation of the internal phase from the membrane phase which is typically regenerated and reused for successive extraction processes. A separation process employing ELMs is characterized by: (1) relatively low-energy consumption especially compared to other separation processes such as thermal evaporation, electrodialysis and pressure-driven membrane processes, (2) rapid extraction with relatively high efficiency. widespread use of the ELM processes has been limited due to instability of emulsion globules against fluid shear. Breakup of emulsions and subsequent release of the internal receptor phase to the external donor phase would nullify the extraction process.

A novel ELM process that combined these two innovative modifications has been proven highly successful for the treatment of model industrial wastewaters containing phenols and selected substituted phenols (hydroquinone, three chlorophenols and two nitrophenols) at relatively high concentrations. Under optimized operating conditions, all the compounds except hydroquinone were extracted with the maximum extraction efficiency of over 96% and the time to reach maximum extraction ranged from 2 to 30 min [55].

3.2. Destruction of phenol in water solution

3.2.1. Total oxidation of phenol by air or oxygen in water solution

3.2.1.1. *Non catalytic wet air oxidation (WAO)*. Wet air oxidation (WAO) is based on the oxidizing properties of air's oxygen



WAO was first developed and applied as a commercial process by Zimmerman [56]. Nowadays, WAO is a well-established technique of importance for wastewater treatment, especially when these are too dilute to incinerate and too toxic to biotreat. Several reviews have been published on this subject, including a very recent one [57].

According to Luck [58] typical conditions for wet oxidation range from 180 °C and 2 MPa to 315 °C and 15 MPa. Residence times may range from 15 to 120 min, and the chemical oxygen demand (COD) and total organic carbon (TOC) removal may typically be about 75–90%. Insoluble organic matter is converted to simpler soluble organic compounds without emissions of NO_x, SO₂, HCl, dioxins, furans, fly ash, etc.

In non-catalyzed wet oxidation, the mass transfer of oxygen from the gas phase to the liquid phase and the reaction rate in the liquid phase control the overall reaction. For gases that are only slightly soluble, such as oxygen, gas-phase mass-transfer resistance is negligible, compared to the resistance in the liquid layer; the mass transfer is effectively controlled by liquid-film resistance. Consequently, phenol WAO is significantly influenced by reaction temperature and oxygen partial pressure, and by solution pH as well. At 130 °C and $P_{O_2} = 0.5$ MPa, ~5% TOC conversion occurs after 2 h, whereas at 220 °C and $P_{O_2} = 3$ MPa ~88% TOC conversion occurs after 2 h.

Solution pH has a significant influence on the rate/extent of phenol WO. Kolarczkowski et al. [59] observed that, at pH < 2 and 7–10, no WO of phenol occurred at 200 °C and a total pressure of 3 MPa, whereas at pH 2–7 and > 10, significant phenol destruction occurred. The influence of solution pH on the rate/extent of the WO of phenol can be attributed to the following: (i) the different reactions that occur for some key free-radical species with changing pH; (ii) the influence of solution pH on oxygen solubility (and, hence, the initiation reaction in WO of phenol); and (iii) the effect of solution pH on the chemical structure of the phenol (i.e., the conversion of phenol to the phenolate ion at high pH). Solution pH has also been shown to have a strong influence on the intermediates/products involved in the WO of phenol. This is due to some of these compounds, such as acetic acid and oxalic acid, being more or less resistant to WO at varying pH, and also because H^+ and/or OH^- can react with certain intermediates, hence altering the reaction pathway.

Among the numerous studies on WO of phenol, only very few have involved a thorough investigation of the reaction mechanism and pathway. The intermediates/products identified by different authors were formic acid, acetic acid, maleic acid, oxalic acid, succinic acid, acetone, and acetaldehyde. The ortho and para dihydroxy-benzenes (catechol and hydroquinone) and ortho and para benzoquinones are supposed to act as precursors for aromatic ring opening.

A complete mineralization of the waste stream is impossible by WAO, since some low molecular weight oxygenated compounds (especially acetic and propionic acids, methanol, ethanol, and acetaldehyde) are resistant to oxidation. For instance, removal of acetic acid is usually negligible at temperatures lower than 300 °C. Therefore, WAO is a pre-treatment of liquid wastes which requires additional treatment of the process liquid and gas streams.

Aqueous oxidation at high pressure and temperature can be operated also above the critical point of water (374.2 °C and 22.1 MPa), usually ranging from 400 to 650 °C and from 25 to 35 MPa, respectively often referred to as super critical water oxidation (SCWO) [60]. SCWO takes advantage of the miscibility of organics, water, and oxygen to rapidly oxidize the organics in the single-phase mixture. Organic feed destruction rates are usually better than 99.99% producing CO_2 and water. Liquid effluent total organic carbon (TOC) levels are consistently below 3.5 ppm. Because of the lower than incineration operating temperatures and high concentration of supercritical water, priority air pollutants NO_x and CO are below 25 and 100 ppm, respectively.

According to Portela et al. [61] simple kinetic equations (based on pseudo-first-order assumption) for WAO and SCWO of phenol predict reasonably well the conversions observed experimentally. In the supercritical region, the rate law from Gopalan and Savage [62] provided the best match with their experimental results. Observing the kinetic parameters obtained in this work and those present in the literature, it is not possible to predict the real behaviour of phenol oxidation under hydrothermal conditions. There are many aspects, like oxygen/phenol ratio, different geometry and material of the reactor, operating proce-

dures, etc., that affects the reaction mechanism and, consequently, the resulting rate law expression. Global rate laws obtained in WAO and SCWO environments are mainly useful for the operating conditions where they were obtained, and many times only applicable to the reactor system in which experimental data were obtained. At near critical operating conditions, experimental data are scattered and difficult to predict from WAO or SCWO rate law expressions. Furthermore, predicted reaction rates from WAO studies are always higher than those predicted by SCWO studies and any coincidence observed must be considered fortuitous.

3.2.1.2. Catalytic wet air oxidation (CWAO). Considerable amount of research has been performed on WO catalysts to overcome the aforementioned costly, high-pressure, energy-intensive conditions. The number of different industrial waste/process streams requiring organics removal and the diversity of organic and inorganic compounds present in these streams has resulted in the investigation of a wide range of homogeneous and heterogeneous catalysts over the last three decades.

Catalytic wet air oxidation of phenol has been the object of many investigations in recent years. These studies have also been reviewed recently [57,58,63]. Homogeneous catalysts for CWAO are usually transition metal cations, such as Cu and Fe ions. Industrial homogenous CWAO processes have been developed such as the Ciba-Geigy/Garnit process working at high temperature (300 °C), and the LOPROX Bayer process working with oxygen below 200 °C in the presence of iron ions. Common two-phase reactor types used in homogeneous CWO include bubble columns, jet-agitated reactors, and mechanically stirred reactor vessels [58].

For practical reasons, solid catalysts are more useful to avoid the need of a separation step of the catalyst, and pollution of the waste. Most of the active catalysts proposed for CWAO or phenol are solids containing either noble metals (Pt, Ru) or transition metal cations (Cu, Co, Mn, Fe) as the active redox phases. Frequently, such active phases are supported on alumina or carbon carriers and may contain ceria additives. Activated carbon may also act as a catalyst although it may be consumed by oxidation. Typical reaction conditions allowing phenol conversion >90–95% and TOC or COD removal >80–90% are $T = 100–200$ °C and $P_{O_2} = 0.3–3.5$ MPa, $t = 1–3$ h.

One of the most active catalysts that have been developed for CWO of phenol, in terms of TOC removal, is a $Pt_xAg_{1-x}-MnO_2/CeO_2$ catalyst that was developed by Hamoudi et al. [64]. This catalyst achieved 80% TOC removal in 1 h at 80 °C, using an oxygen partial pressure of 0.5 MPa. However, the actual TOC conversion (to CO_2) achieved under the same conditions was only 40%. The difference in TOC removal and conversion is due to deposition of polymeric products on the catalyst, which contributes to an approximately 40% increase in TOC removal. Polymeric products deposited on the catalyst were found to deactivate this and several other catalysts.

Catalysts containing Mn and Ce were also found very active by Chen et al. [65], who reported that the high activity of this Mn-Ce-O catalyst is presumably due to the following: (i) improved oxygen storage capacity, (ii) improved oxygen mobility on the surface of the catalyst, and (iii) an electron-rich surface, which may be very important in the activation of adsorbed oxygen. Solid compounds containing manganese, such as the commercial perovskite lanthanum strontium manganite (LSM) also show interesting properties in phenol CWO [66].

Reaction pathways for the CWO of phenol have been studied by several researchers. Many different intermediates form from the CWO of phenol on various catalysts. These intermediates can have a significant effect on phenol TOC conversion. In recent studies, attention has been paid in the evolution of ecotoxicity during WAO and CWAO of phenol and of other water pollutants. A significant

increase of toxicity has been observed during the early stages of phenol oxidation [67] caused by the formation of hydroquinone and *p*-benzoquinone as intermediates, the former showing the highest toxicity. Furthermore, synergistic effects, giving rise to a significant increase of toxicity, have been observed. These effects derive from the interactions among copper leached from the catalyst (a commercial copper-based catalyst in this case) and catechol, hydroquinone, and *p*-benzoquinone and demand that close attention be paid to this potential problem in catalytic wet oxidation. Acetic acid is formed as a final intermediate during CWO of phenol using several different catalysts. Because acetic acid is a difficult compound to remove via CWO, it has a negative impact on phenol TOC conversions. First order in phenol has usually been obtained together with 0.5 order in oxygen.

A relevant problem in heterogeneous CWO is associated to the leaching of the active metal species, that can produce a heterogeneous/homogeneous catalysis. Leaching, however, pollutes the wastewater and results in the progressive loss of catalytic activity of the solid catalyst. This phenomenon is evident mostly for supported transition metal catalysts.

The kinetics of phenol wet oxidation over noble metal catalysts has been investigated by Cybulski and Trawczyński [68]. According to this study, oxidation of phenol proceeds substantially via two routes: (1) directly to carbon dioxide, and (2) through intermediates which are difficult to oxidize over the catalysts studied.

According to Levec and Pintar [69], that reviewed very recently process conditions for industrial CWO processes, the catalyst must be tailored for each particular application and made of inexpensive materials. Oxides of Zr, Ce, and Ti may be used as stable supports. Metal oxide catalysts are very active but unstable (dissolution). In order to reduce leaching, the catalytically active compounds have to be incorporated into a lattice of catalyst support. If this is not feasible, the catalytic active phase should consist of precious metals. In fact, existing commercial processes (see Ref. [69]) employ supported noble metal catalysts. It would be advantageous to design a catalyst that can be employed for the treatment in single-pass

reactors with a minimum lifetime over 500 h. To improve the performances, a step constituted by a AC adsorbing bed, where the organics are removed from the wastewater stream and pre-concentrated, may be useful, as in the CALIPHOX process, as shown in Fig. 4. In any case, the primary goal of CWO should be to convert organics into products more amenable to biological treatment; complete oxidation may be too expensive.

Although several academic investigations are performed in Slurry Stirred Tank Reactors, industrial application should need trickle bed (Fig. 4), bubble slurry column, and bubble fixed bed (monolith) or three-phase fluidised bed reactors, to allow easy separation of the catalyst and continuous operation.

3.2.1.3. Oxidative polymerization with oxygen in the presence of enzymes. Enzymes called tyrosinase (also known as polyphenol oxidase) and laccase convert phenols using oxygen into *o*-quinones. These compounds are further converted into heavier oligomeric species that may be more easily filtered and/or adsorbed on a solid [70]. Chitosan is apparently particularly active useful in the absorption of these compounds [71,72].

3.2.2. Wet oxidation with chemical oxidants

Different chemical oxidants have been reported to be active in the wet total oxidation of phenol in water solution. The most used are: ozone and hydrogen peroxide.

3.2.2.1. Oxidation with ozone. Ozonation consists in molecular ozone acting directly on the nucleophilic sites and unsaturated bonds of the organic compounds. Ozone is one of the strongest oxidants technically applied [73], according to its high reduction potentials in principle both at acid and basic pHs:

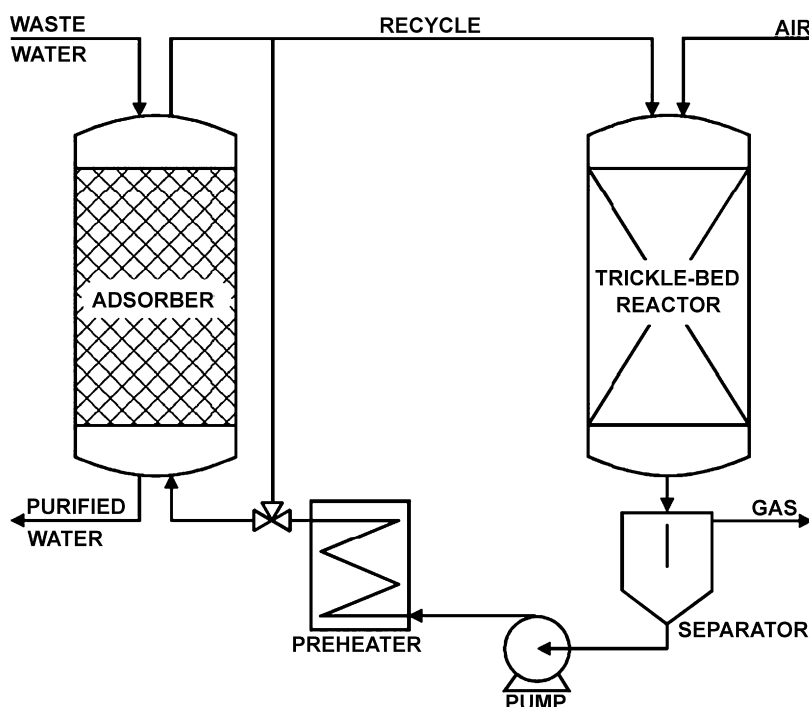
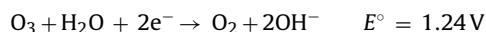
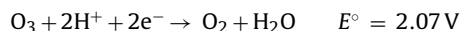


Fig. 4. Schematic drawing of the CALIPHOX process for catalytic liquid-phase oxidation of organic pollutants with an adsorber unit for pre-concentration. Reprinted with permission from Ref. [69].

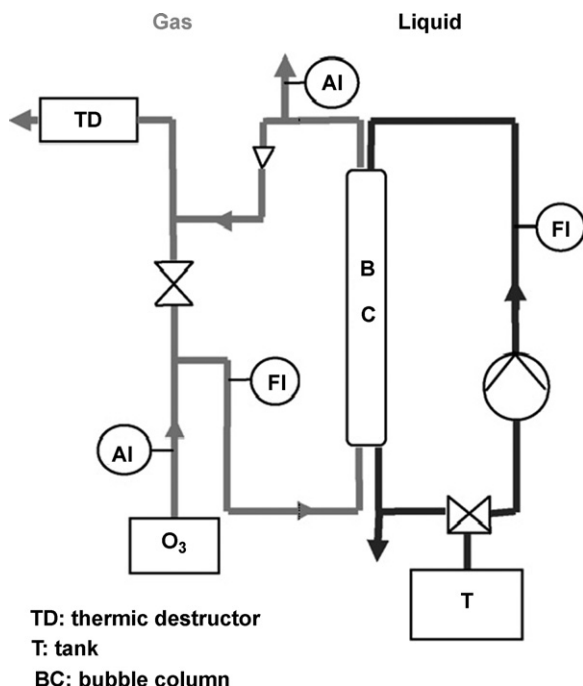


Fig. 5. Schematics of a bubble column reactor for ozonation. Reprinted with permission from Ref. [73].

Its action is selective, and the kinetics of reaction depends on the nature of the organic compounds. For dissociating organic compounds, second order rate constants vary from 10^{-1} to $10^9 \text{ M}^{-1} \text{ s}^{-1}$ according to the degree of dissociation of the species.

The kinetics of the reaction between ozone and phenol is fast: the rate of phenol degradation observes a pseudo-first order kinetics with regard to phenol concentration, and the kinetic constant increases with the pH, phenoxide ion being much more reactive than phenol [74]. In Fig. 5 a typical bubble column reaction for ozonation is schematised. Working at sufficiently high pH the reaction occurs in diffusion-controlled regime. In this case the use of an ejector for the introduction of ozone may accelerate the reaction, due to a faster ozone mass transfer [73].

Hoigné [75] showed that the ozone decomposition in aqueous solution develops through the formation of $\cdot\text{OH}$ radicals. In the reaction mechanism OH^- ion has the role of initiator. The relevant influence of pH may also be due to the fact that in the ozone decomposition mechanism the active species is the conjugate base of hydrogen peroxide, HO_2^- , which is formed from ozone and whose concentration is strictly dependent upon pH [76]. The increase of pH to the aqueous O_3 solution will thus result into higher rates of $\cdot\text{OH}$ radicals production and the attainment of higher steady-state concentrations of $\cdot\text{OH}$ radicals in the radical chain decomposition process.

According to Gimeno et al. [77] ozone (C_{O_3} 10^{-4} mol/l) allows the almost complete conversion of 200 mg/l phenol in 2 h at 20°C without any buffer. However, the removal of COD is only 35% and that of TOC is less than 20%. Hydroquinone, benzoquinone and catechol are main intermediates, but at higher conversion oxalic acid is the main product. The conversion of phenol is only slightly increased if pH 10 is produced due to the addition of soda [78]. A further increase in phenol conversion may be obtained by the use of ultrasound, but this effect is more relevant at neutral than at basic pH [79]. The use of Differential Neural Network Observers to the products formation during phenol ozonation has been the object of a recent paper [79].

The presence of catalysts may enhance the conversion of ozone and of COD and TOC. Typical homogeneous catalysts for ozona-

tion are transition metal ions such as Mn^{2+} [76], Fe^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Cu^{2+} and Ag^+ . The presence of these metals increases the TOC removal efficiency as compared to ozonation alone. Matheswaran et al. [80] reported recently a relevant effect of Ce^{3+} in phenol oxidation, allowing 100% TOC removal after 200 min.

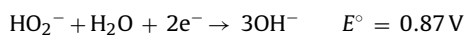
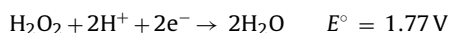
Also in this case, heterogeneous catalysis could be better than homogeneous one, to avoid further separation. Beltran et al. [81] compared the effect an homogeneous and an heterogeneous iron catalysts (Fe(III) and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$) in the ozonation of oxalic acid in water at pH 2.5. Percentage removals of oxalic acid were 1.8%, 7% and 30% corresponding to the non-catalytic, homogeneous and heterogeneous catalytic ozonations, respectively. Catalytic oxalic acid ozonation led in all cases to total mineralization. The mechanism of ozonation likely develops through formation of iron-oxalate complexes that further react with ozone without the participation of hydroxyl radicals. Because of the stringent acidic conditions, some metal leaching has been observed.

According to Carbajo et al. [82] the perovskite catalyst $\text{LaTi}_{0.15}\text{Cu}_{0.85}\text{O}_3$ is an active and stable catalyst in ozonation processes provided that the effluent treated shows some refractory nature towards the non-catalytic ozonation. If the wastewater to be cleaned contains compounds readily attacked by molecular ozone, like phenol, there is no need of using heterogeneous catalysts.

While Gimeno et al. [77] found a slight inhibiting effect of TiO_2 on ozonation of phenol, Sano et al. [83] found a remarkable catalytic effect of Al_2O_3 -loaded silica-gel, TiO_2 -loaded silica-gel as well as of zeolites such as NaX and NaA on TOC conversion during phenol ozonation. TOC may be totally converted in 30 min in the presence of the zeolites.

3.2.2.2. Oxidation with hydrogen peroxide (wet peroxide oxidation, WPO).

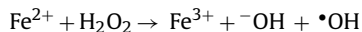
3.2.2.2.1. Non catalytic oxidation with hydrogen peroxide. Hydrogen peroxide (H_2O_2) has effective oxygen content, low cost, safe storage and operation methods, and above all, an environmentally friendly nature. The standard reduction potentials of hydrogen peroxide



imply that it is a strong oxidant in both acidic and basic solutions. The reactivity of hydrogen peroxide is generally low and largely incomplete [84] due to kinetics, in particular in acidic media, while being much enhanced by homogeneous and/or heterogeneous catalysts.

3.2.2.2.2. Homogeneous catalysis in the oxidation with hydrogen peroxide: conventional homogeneous Fenton reaction. The conventional Fenton reaction [85] uses hydrogen peroxide in conjunction with an iron(II) salt to produce high fluxes of hydroxyl radicals which can oxidise organic compounds in solution.

Use of Fenton's reagent is one of the most effective ways for $\cdot\text{OH}$ radical generation. In addition, due to the simplicity of equipment and mild operation conditions (atmospheric pressure and room temperature) it has been postulated as the most economic oxidation alternative. The mechanism of $\cdot\text{OH}$ generation, which has been well established in the literature, is quite complex. Briefly, H_2O_2 decomposes catalytically by means of Fe^{2+} at acid pH giving rise to hydroxyl radicals.



Fe^{3+} can react, at acid pH, with H_2O_2 in the so-called Fenton-like reaction, regenerating the catalyst and producing the $\text{HO}_2\cdot$ radical, thus sustaining the process. This reactant is an attractive oxidative

system for wastewater treatment due to the fact that iron is very abundant and non toxic element and hydrogen peroxide is easy to handle and environmentally safe. The organics may be completely mineralized.

However, for efficient reaction, acidic pH and stoichiometric excess of hydrogen peroxide are required and this usually means that significant quantities of ferric salts need to be disposed off after the reaction is complete. Additionally, technical requirements for optimization or monitoring of the Fenton's reaction efficiency are complex and costly (e.g., GC–MS), which inhibits its common usage. Even with optimization of the reaction efficiency this treatment technique implies significant costs, which can be an important limitation in the choice of treatment. For this reason, Fenton's reaction may be recommended as a pre-treatment process to enhance later microbial transformation, lowering the operational costs.

Kang et al. [86] performed a kinetic modelling of Fenton oxidation of phenol and mono-chlorophenols, consisting of 28 reactions, that reasonably predicts decomposition kinetics and by-product formation. Actually, according to Zazo et al. [87] the pathway may be much more complex than expected. The same research group [88] recently measured the evolution of ecotoxicity upon the Fenton's oxidation of phenol in water. As already observed, some intermediates such as hydroquinone and *p*-benzoquinone show toxicity levels much higher than phenol itself. However, depending on the operating conditions, these intermediates could be completely transformed into organic acids, mainly oxalic and formic.

In spite of the drawbacks it has been reported that industrial processes based on the application of Fenton's reagent for purification of wastewaters have been developed and demonstrated. The IDE-NSA process demonstrated high oxidation efficiency (up to 98%, COD removal up to 95%) in mild conditions (90–130 °C, 0.1–0.5 MPa at pH 3) [58]. More complex homogeneous catalysts may also be used, based on Fe–Cu–Mn, and be recovered by precipitation at pH 9. A new process is cited as under development, using air and minor amounts of iron peroxide in the presence of Fe²⁺, working at 120–150 °C.

Recently, the use of ferrous waste metals as a source of iron ions to be used as catalysts for WPO has been proposed [89]. In acidic conditions, the surface of iron corrodes giving rise to ferrous ions and hydrogen gas. The former, in the presence of hydrogen peroxide, reacts rapidly to produce hydroxyl radicals in the normal Fenton reaction and leads to the formation of ferric ions. The zero-valent iron metal surface can then reduce the ferric ions down to ferrous (so increasing the reaction rate) or indeed may interact with hydroxyl radicals resulting in oxidation to hydroxide ions, so limiting the reaction rate.

3.2.2.2.3. Catalytic wet peroxide oxidation (CWPO): heterogeneous Fenton reaction. The application of conventional homogeneous Fenton reaction is complicated by the problems typical of homogeneous catalysis, such as catalyst separation, regeneration, etc. Moreover, it is necessary to control pH carefully to prevent precipitation of iron hydroxide. Thus, Fenton like heterogeneous catalysts, i.e., solids containing transition metal cations (mostly iron ions) have been developed and tested.

Typically, the activity of microporous catalysts in phenol oxidation with H₂O₂ is maximal at pH 3–4 and is accompanied with substantial iron leaching. Particular interest has been devoted to microporous catalysts. One of the most popular is Fe–ZSM-5 zeolite [90], which has been found to be very active but may suffer from diffusion limitation due to relatively small size of its pores.

Calleja et al. [91] evaluated activity and stability of iron-containing materials, prepared following several strategies of synthesis, and using different silica supports (amorphous, zeolitic and mesostructured materials) on the wet peroxide oxidation of phenol under mild reaction conditions (100 °C, air pressure of 1 MPa

and stoichiometric amount of hydrogen peroxide for the complete mineralization of phenol). Crystalline iron oxide species supported over mesostructured SBA-15 materials was found to be the most interesting catalyst in terms of phenol and total organic carbon (TOC) conversions according to its high organic mineralization, low sensitivity to leaching out and good oxidant efficiency.

Transition metal- containing mesoporous materials, like those of the MCM-41 and HMS type, are viewed as perspective catalysts due to a larger pore size that is expected to enhance diffusion of reagents as compared to microporous materials used as catalysts for wet phenol oxidation with H₂O₂ under mild reaction conditions (pH 3.5, P 1 atm, 353 K). It was demonstrated that after 15 min the phenol conversion in the first cycle attained 100% and the removal of the total pollution was 55–85%. However, these materials suffered from destruction of the mesopores order, iron agglomeration, and leaching (from 6 to 100 wt%). Timofeeva et al. [92] tested iron-containing mesoporous mesophase materials (denoted as Fe-MMM-2) and found that isolated iron species predominate in silica framework under Fe < 2 wt% and pH < 1.0 or Fe < 1 wt% and pH < 2.0. These species are stable to leaching and highly active in full H₂O₂-based phenol oxidation. The increase in iron loading and pH of the synthesis solution lead to the agglomeration and formation of oligomeric iron species, which, in turn, results in the reduction of the catalytic activity of Fe-MMM-2 and the increase of iron leaching. Several other iron containing solids, such clays, pillared clays, minerals, resins have also been tested and found interesting heterogeneous Fenton-type WPO catalysts.

3.2.2.2.4. CWPO: non iron heterogeneous catalysts. Non-iron catalysts may also work to enhance water peroxide oxidation reaction rate. In particular, copper containing microporous or mesoporous materials such as Cu–Al pillared clays [93] and Cu–ZSM-5 zeolite [94]. In a recent paper Zrncevic and Gomzi reported interesting data on the use of Cu–Y zeolite [95]. The process was carried out within the temperature range from 323 to 353 K and at atmospheric total pressure. Other operating variables were stirrer speeds (200–800 min⁻¹), hydrogen peroxide concentrations (0.008–0.254 mol dm⁻³), and catalyst loadings (0.05–0.4 g). The initial phenol concentration was 0.01 mol dm⁻³. The results show that the used catalyst entirely eliminated phenol and could be reused in successive runs, without significant loss of activity.

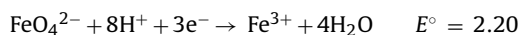
3.2.2.2.5. Oxidative polymerization with hydrogen peroxide catalyzed by peroxidases. Peroxidase enzymes may be used in waste treatment in order to remove phenols from aqueous solutions in the presence of hydrogen peroxide. In this treatment, phenolic compounds are polymerized through a radical oxidation–reduction mechanism. High molecular weight polymers are insoluble and non-toxic and can be easily separated by filtration. It has been indicated that by using enzymes, treatment costs would be less than those in the conventional processes.

Horseradish peroxidase is, by far, the most commonly used peroxidase and catalyzes the oxidation of aromatic hydrogen donors by hydrogen peroxide through a two-electron transfer pathway [96]. However, due to high cost of the enzyme, efforts have been devoted to find an alternative source of peroxidases, such as enzymes from tomato hairy roots [97] and soybean peroxidase immobilized in a fluid bed [98]. Treatment costs are significant not only due to the price of the purified enzyme but, also, because peroxidase is susceptible to permanent inactivation by various undesirable side reactions of the treatment process. In order to minimise such inactivation, some researchers have suggested the addition of compounds such as polyethylene glycol (PEG) to decrease the adsorption of polymers onto the enzyme's active site. According to Nazari et al. [99] Ni²⁺ protects the horseradish peroxidase enzyme against suicide-peroxide inactivation, which is the main mechanism of enzyme inactivation at low phenol concentration.

Obviously, the addition of both PEG and Ni ions decreases significantly the environmental friendliness of the process.

3.2.2.3. Oxidation with other chemical oxidants. In the early report of Throop [100] alternative oxidation procedures for phenol removal were reported, including oxidation chlorine and chlorine dioxide, as well as with potassium permanganate. These methods are certainly not environmentally friendly, due in particular to the formation of chlorinated organic compounds and the dispersion of Mn compounds. Also they are expensive due to the cost of the reagents, as well as the need for quite precise control of pH.

In recent years increasing interest has been devoted to ferrate (VI) ion as environmentally friendly oxidant [101–103]. The ferrate ion, whose reduced form is ferric ions, is in fact a strong oxidant



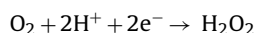
but its redox potential strongly decreases by increasing pH. The oxidation of phenol by ferrate ions has been the object of some studies. Graham et al. [104] reported that the maximum phenol degradation (80% at ferrate:phenol 5:1) occurs at a pH ~ 9.2. At this pH a proportion (17%) of the phenol is dissociated, which may be the reason for the maximum degradation. The extent of degradation at pH 10 was of a similar magnitude to that at pH ~ 9.2, which may be explained by the increased extent of phenol dissociation, and therefore greater reactivity, compensating for the reduced oxidation potential of ferrate at the higher pH. Phenol degradation was substantially lower at pH 11 owing to the relatively low oxidation potential of ferrate under these conditions. Some kinetic parameters concerning phenols oxidation by ferrate ions have been determined in a more recent paper [105].

3.2.3. Electrochemical oxidation

As reviewed by Chen [106], electro-oxidation of water pollutants can be fulfilled through different ways.

3.2.3.1. Indirect electro-oxidation processes including “electrofenton” process. Use of the chlorine and hypochlorite generated anodically to destroy pollutants is well known. This technique can effectively oxidize many inorganic and organic pollutants at high chloride concentration, typically larger than 3 g/l. The possible formation of chlorinated organic compounds intermediates or final products hinders the wide application of this technique. Moreover, if the chloride content in the raw wastewater is low, a large amount of salt must be added to increase the process efficiency.

Hydrogen peroxide can be produced by a two-electron reduction of oxygen at appropriate cathodic potential on certain electrodes such as reticulated vitreous carbon, graphite and gas diffusion electrode



Thus, the strong oxidant hydroxyl radical can be generated in the solution with the addition of Fe^{2+} as catalyst, like for Fenton reagent, and this active species can attack and initiate the oxidation of pollutant. H_2O_2 is generated electrically from dissolved oxygen in aqueous solution in a continuous mode, which may be more efficient and cost-effective than conventional chemical dosing methods. The electrofenton process has the advantage of allowing a better control of hydroxyl radical production. Several reports on electrofenton process application for the degradation of organic pollutants such as benzene ring compounds, including phenol [107], have been reported.

A kinetic model for the electrofenton reaction, considering both the H_2O_2 generation rate and the H_2O_2 consumption rate, and the

three key factors of current density, dissolved oxygen concentration and ferrous ion concentration has been reported recently [108].

Electrically generated ozone is also reported for wastewater treatment. Farmer et al. [109] proposed another kind of electro-oxidation, mediated electro-oxidation, in treating mixed and hazardous wastes. In this process, metal ions, usually called mediators, are oxidized on an anode from a stable, low valence state to a reactive, high valence state, which in turn attack organic pollutants directly, and may also produce hydroxyl free radicals that promote destruction of the organic pollutants. Subsequently, the mediators are regenerated on the anode, forming a closed cycle. The typical mediators include Ag^{2+} , Co^{3+} , Fe^{3+} , Ce^{4+} and Ni^{2+} .

Mediated electro-oxidation as well as electrofenton usually need to operate in acidic media to avoid precipitation of metal hydroxides. In addition, there exists the secondary pollution from the heavy metals added. These disadvantages limit the application of these processes.

3.2.3.2. Direct anodic oxidation. Electro-oxidation of pollutants can also occur directly on anodes by generating physically adsorbed “active oxygen” (adsorbed hydroxyl radicals, $\cdot\text{OH}$) or chemisorbed “active oxygen” (oxygen in the oxide lattice, MO_{x+1}). These processes are usually called anodic oxidation or direct oxidation. The physically adsorbed “active oxygen” may cause the complete combustion of organic compounds (R), while the chemisorbed “active oxygen” (MO_{x+1}) may participate in the formation of selective oxidation products:

In general, $\cdot\text{OH}$ is more effective for pollutant oxidation than O in MO_{x+1} . Because O_2 evolution can also take place at the anode, high over-potentials for O_2 evolution is required in order total oxidation of the organic can proceed with high current efficiency. Otherwise, most of the current supplied will be wasted to split water. The anodic oxidation does not need to add a large amount of chemicals to wastewater or to feed O_2 to cathodes, with no tendency of producing secondary pollution and fewer accessories required. These advantages make anodic oxidation more attractive than other electro-oxidation processes. The important part of an anodic oxidation process is obviously the anode material. Anode materials investigated include Ti/RuO₂, Ti/Pt-Ir, fiber carbon, MnO₂, Pt-carbon black, porous carbon felt, stainless steel, and reticulated vitreous carbon. However, none of them have sufficient activity and at the same time stability. Graphite, Pt, PbO₂, IrO₂, TiO₂, SnO₂, and diamond film have been the object of recent investigation.

The application of boron-doped diamond (BDD) electrodes has been reviewed by Panizza and Cerisola [110]. These materials exhibit activity in the oxidation of aromatic compounds not only in the potential region of oxygen evolution, with the electrogeneration of hydroxy radicals, but also in the potential region before oxygen evolution (water stability). In the latter case, direct electron transfer from the anode to the molecule occurs but fast deactivation of the anode is observed, due to deposition of a carbonaceous film. On the contrary, at high anodic potentials total mineralization of phenol may occur with no anode deactivation. The reaction is controlled by the diffusion of phenol towards the anode surface, the current efficiency being favoured by a high mass-transport coefficient, high organic concentration and low current density. In optimised conditions, the current efficiency approaches 100%. In contrast, according to Pacheco et al. [111] phenol combustion efficiency on BDD electrodes is independent of the concentration, pointing out that combustion and current efficiencies are independent quantities.

Most authors find for phenol mineralization better performances of BDD electrodes with respect to SnO₂, PbO₂ and IrO₂ based electrodes. Ti/SnO₂-Sb anodes are also reported to allow the

complete mineralization of phenol without relevant deactivation problems [112].

3.2.4. Photocatalytic oxidation

Working with: $T_0 = 20^\circ\text{C}$, $Q_g = 50\text{ l/h}$, $C_{\text{TiO}_2} = 1.5\text{ g/l}$, $C_{\text{phenol}} = 2.1 \times 10^{-3}\text{ M}$, $\text{pH}_0 = 6.2$, Gimeno et al. [77] found a significant phenol conversion by UV alone. A similar result has been reported by Kamenev et al. [84]. However, activity in phenol oxidation upon UV irradiation may be strongly enhanced in the presence of photocatalysts. Among several materials which find some photocatalytic activity, TiO_2 photocatalysis has been intensively investigated for its application to the destruction of environmental toxic pollutants [113]. TiO_2 -anatase is inexpensive, non-toxic, resistant to photo-corrosion, and has high oxidative power. On the other hand, TiO_2 -anatase has a moderate Lewis-type acid–base character [114], allowing the adsorption of pollutants but also the desorption of intermediates and products. However, an important drawback of TiO_2 for photocatalysis is that its band-gap is rather large, 3.0–3.2 eV, and thus only a small fraction of the solar spectrum ($\lambda < 380\text{ nm}$, corresponding to the UV region) is absorbed.

The primary event occurring on the UV-illuminated TiO_2 is the generation of photo-induced electron/hole ($e^- - h^+$) pairs. These charge carriers can rapidly migrate to the surface where they are captured by a suitable electron donor and acceptor, initiating an oxidation and reduction reaction, and/or they are recombined, dissipating the input light energy onto heat. The strong oxidizing ability of TiO_2 photocatalysts has been ascribed to highly oxidative valence band holes and various oxygen-containing radical species (e.g., $\cdot\text{OH}$, $\text{O}_2^{\cdot-}$, HO_2^{\cdot}). Among these species, holes and $\cdot\text{OH}$ radicals play the most important roles in the photodegradation of organic pollutants. The overall quantum efficiency depends from the competition between charge-carrier recombination, trapping, and interfacial charge transfer.

Colon et al. [115] found complete conversion of phenol (50 ppm) with TiO_2 (1 g/l) using a medium pressure 400 WHg lamp (270 nm) after 90 min illumination. These authors found a decrease in activity by increasing calcination temperature and, consequently, surface area of the photocatalyst. However, deactivation is limited by sulphuric acid treatment.

Improving photocatalytic efficiency requires primarily a decreased $e^- - h^+$ recombination rate, which is generally achieved by increase of the rate of photogenerated electrons transfer to the oxidant at the interface and/or the capture of holes via oxidation process.

Among various efforts for enhancing photocatalytic efficiency, the surface modification of TiO_2 seems mostly interesting. The surface modification of TiO_2 can be performed by depositing noble metal clusters on the surface of TiO_2 . For example, platinumized- TiO_2 photocatalysts may show higher photoactivity towards phenol, with an optimal Pt particle size obtained by calcination at 300°C [116]. Also copper may favour photoactivity of TiO_2 towards phenol degradation in particular in conjunction with sulphation [117]. Vione et al. have observed that the degradation of phenol may depend inversely on the radiation scattering from the photocatalyst, depending on its particle size, and is enhanced by using surface fluorinated- TiO_2 [118]. The surface fluoride-enhanced effect is ascribed to accelerating generation of mobile $\cdot\text{OH}$ radicals, due to enhanced holes availability for water oxidation through the displacement of $\equiv\text{Ti}-\text{OH}$ by $\equiv\text{Ti}-\text{F}$. The copresence of Cu and fluorine show synergistic effects enhancing reciprocally the photocatalytic activity in phenol oxidation [119].

N-doped anatase TiO_2 [120] is also the object of recent investigations for its increased range of radiation absorption. It contains thermally stable single N-atom impurities either as charged dia-

magnetic centers or as neutral paramagnetic centers (N_b). The N-atoms can occupy both interstitial or substitutional positions in the solid, with some evidence for a preference for interstitial sites. All types of N_b centers give rise to localized states in the band-gap of the oxide, thus accounting for the related reduction of absorption band edge. The relative abundance of these species depends on the oxidation state of the solid. N-doped anatase exhibits high ultra-violet and visible light photocatalytic activity in degrading phenol [121,122]. An alternative mode to make TiO_2 -anatase to be photocatalytically active under visible light for phenol conversion is to combine it with carbon [123].

Reactors operating photocatalytically [124] use semiconductors such as TiO_2 in different ways, e.g., in suspension as a fluidised bed, or internally supported as a fixed bed. In the aqueous phase, the inconvenience of using TiO_2 in the form of slurry is due to the need of recovering the semiconductor powder in an additional treatment, which may turn the process more time consuming in terms of energy and labour and therefore more expensive. When the catalyst is used as a fixed bed, the procedures normally used to support it are based on sol–gel methods, or catalyst dilution in solvents, followed by deposition on the internal reactor walls, and subsequent solvent elimination. Some disadvantages of these methods are: (a) the possibility of catalyst leaching into the effluent when working in the aqueous phase, causing loss of activity during reuse, and (b) the necessity of heating at high temperatures, which can cause changes in the crystallographic of TiO_2 from anatase to the less photoactive rutile.

3.2.5. Supercritical water gasification of phenol

SCWG is the conversion of organic material into gaseous products (H_2 , CO , CO_2 , CH_4) via reactions in and with water at a temperature and pressure exceeding the thermodynamic critical point ($T_c = 374^\circ\text{C}$, $P_c = 22.1\text{ MPa}$). Under these conditions [125] phenol is mainly gasified into hydrogen, carbon dioxide, and methane. Hydrogen was the most abundant product at high phenol conversions. The gas compositions measured experimentally were largely consistent with those anticipated from chemical equilibrium calculations. In the absence of nickel, phenol conversions up to 68% were reached after 1 h. In the presence of Ni wire, complete conversion was obtained within 10 min. These results show that homogeneous, uncatalyzed gasification in supercritical water is slow, but rates are greatly increased by added Ni.

3.2.6. Application of electrical discharges to degradation of phenol

Interest in the application of electrical discharges for the degradation of organic pollutants in aqueous solution has grown enormously, mainly because of high removal efficiency and environmental compatibility of these techniques. Several different processes, such as electro-hydraulic discharge (EHD), pulsed corona discharge (PCD), and glow discharge electrolysis (GDE) are being developed. Among them, PCD has received the most extensive investigations because it can directly inject the electrical energy into an aqueous solution through plasma channels. A corona discharge occurs at a high voltage (25–40 kV), and has a very short pulse width (approximately 200–1000 ns). One very important consequence of the very short duration of the pulse is that it minimizes the power normally wasted on ionic migration because the mobility of ions is much less than that of electrons. In a pulsed corona discharge process a non-thermal plasma is produced in which various active species exist such as $\cdot\text{OH}$, $\cdot\text{H}$, $\cdot\text{O}$, $^1\text{O}_2$, $\cdot\text{HO}_2$, H_2O_2 , O_3 , etc. In addition, thermal oxidation within the plasma channel, and vacuum UV photolysis at the surface of the plasma channel, and supercritical oxidation with the subsequent bubble occur in the immediate vicinity of the plasma channel. All of these species and effects can oxidize organic pollutants effectively. This can be

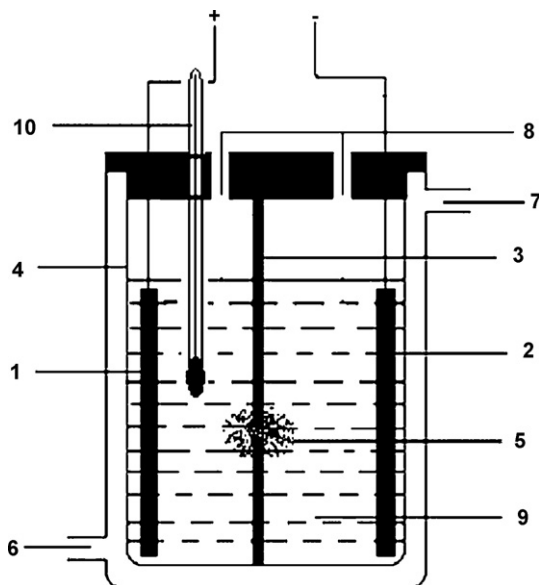


Fig. 6. Experimental setup of the diaphragm glow discharge reactor: (1 and 2) graphite electrodes; (3) dielectric diaphragm with small hole; (4) reaction vessel; (5) glow discharge; (6) cooling water in; (7) cooling water out; (8) gas outlet; (9) electrolytic solution; (10) thermometer. Reprinted with permission from Ref. [128].

performed with two basic types of electrode configurations, either with electrodes which are fully submerged within the liquid phase or with point electrodes in the gas phase above the water surface, and the ground electrode either submerged in the liquid or placed below the liquid phase. Using multi-point-disk electrodes reactor He et al. [126] investigated to identify the important role of $\cdot\text{OH}$ in phenol removal and the degradation mechanism. The removal efficiency of phenol was highest at about 150 rpm of the disk electrode. Decreasing the gap of electrodes or increasing the repetition rate of pulse could benefit to the phenol removal. Reactive species could be produced not only from dissociation of water vapor and O_2 but also from N_2 . The formation of HNO_3 mainly resulted in the decrease in pH, and the decrease in pH in return resulted in the decrease of phenol removal rate. The ozone was formed from radical reactions, then diffused into solution and oxidized the phenols. The radicals very near the solution surface could also have the possibility to diffuse into solution and oxidize the phenols in the liquid–gas interface. The basic media could improve the ozone oxidation processes, but the acidic media could worsen them. According to Shen et al. [127] the effect of various gases bubbling on phenol degradation rate ranked in the following order: oxygen-containing ozone > oxygen > argon > nitrogen. The high gas bubbling flow rate was beneficial to the removal of phenol.

Glow discharge electrolysis (GDE) has the advantage of working also with salt solutions but with the drawback of using very expensive Pt electrodes. Diaphragm Glow Discharge technique has been proposed as an optimal solution applicable to salt-containing wastewater (see Fig. 6). With this technique phenol degradation depends on voltage and on pH. Using 900 V and 110 mA discharge and pH 4.2 almost complete phenol removal is obtained at r.t. after 40 min (C_{phenol}^0 300 mg/l) [128].

The study reported by Grymonpré et al. [129] combined the advantages of gas-phase discharge (i.e., for ozone and oxygen radical formation in the gas phase and at the interface) and liquid-phase discharge (i.e., for hydroxyl radical and hydrogen peroxide formation) through the use of a hybrid gas–liquid corona discharge reactor whereby the high voltage electrode is placed in the liquid phase and the ground electrode is placed in the gas phase. This elec-

trode configuration led to simultaneous formation of ozone and other gas-phase reactive species as well as hydrogen peroxide and other liquid-phase reactive species.

3.2.7. Other techniques for providing energy to destroy phenol in water solutions

Other systems to provide energy to phenol water solutions to achieve phenol destruction have been proposed. Among them we can cite sonication [130,131] and hydrodynamic cavitation [132]. Both have been found to be poorly efficient if carried out alone, without the co-presence of chemical oxidants. However, when combined with other oxidation procedures they can improve the performances in phenol destruction.

3.2.8. Biochemical abatement

Aerobic biodegradation of many classes of aromatic compounds is common and proceeds through the key intermediate, catechol. Many microbial strains capable of degrading phenol have been cited such as *Pseudomonas putida*, *Pseudomonas fluorescens*, *Acinetobacter*, *Trichosporon cutaneum* and *Candida tropicalis*. Most of the cultures tested are capable of degrading phenol at low concentrations. However phenol is toxic to most types of microorganisms at sufficiently high concentration and can be a growth rate inhibitory to even those species, which have the metabolic capability of using it as a substrate for growth. So, for achieving satisfactory performance, phenol concentration needs to be maintained below toxic limits and acclimatization of organism to the wastewater environment is required.

Most of these studies have involved single microbial species which may have limitations in field application due to the presence of different contaminants in the waste. The physical contact among co-aggregative cells can lead to a combined metabolic advantage over single cells, favour mutualistic relationships for biofilm growth, and facilitate the flow of diffusible signals. Therefore, co-aggregates may enable the proper spatial location of different species and facilitate the opportunity to form essential partnerships within the growing biofilms, thus influencing the overall development of the complex microbial community. The effect of co-aggregation of two bacterial strains, *Propioniferax*-like PG-02 and *Comamonas* sp. PG-08 on phenol degradation and aerobic granulation was investigated by Lond Jang et al. [133]. In batch, the coculture degraded phenol at an initial concentration of 250 mg/l, faster than each strain separately. The biodegradation of phenol by a mixed microbial culture, isolated from a sewage treatment plant, was investigated recently by Saravanan et al. [134].

Also fungi strains have been reported to be active in phenol biodegradation. *Nocardia hydrocarbonoxydans*, an actinomycetes, was found to effectively degrade phenol, to be resistant to contamination and to have higher inhibitory concentration level, as compared to many microbial species degrading phenol. The continuous aerobic biodegradation of phenol in synthetic wastewater was carried out using *N. hydrocarbonoxydans* immobilized over glass beads packed between the plates in a pulsed plate bioreactor at a frequency of pulsation of 0.5 s^{-1} and amplitude of 4.7 cm [135]. The time taken to reach steady state has increased with increase in dilution rate and influent phenol concentration. It was found that, as the dilution rate is increased, the percentage degradation has decreased. Steady state percentage degradation was also reduced with increased influent phenol concentration. Almost 100% degradation of 300 and 500 ppm influent phenol could be achieved at a dilution rate of 0.4094 h^{-1} and more than 99% degradation could be achieved with higher dilution rates. At a higher dilution rate of 1.0235 h^{-1} and at concentrations of 800 and 900 ppm the percentage degradation has reduced to around 94% and 93%, respectively. The attached biomass dry weight, biofilm thickness and biofilm

density at steady state were influenced by influent phenol concentration and dilution rate.

A recent study took into consideration the behavior of *Fusarium* sp. in the detoxification of phenol in the effluents [136]. It was found active and retained catalytic activity in a wide range of pH (3–8.8) and temperature (30–50 °C), although the activity is decreased by the presence of mineral salts.

Most of the studies have involved single microbial or fungi species. The activated sludge is considered as a natural microbial consortium and appears as a more attractive solution because of its various advantages [137,138], and is largely used in wastewater purification processes. Activated sludge acclimatized to 400 ppm phenol was used for the biodegradation of phenol in a batch reactor system and a Rotating Biological Contactor (RBC). Phenol degradation in the batch reactor was studied in relation to supply of oxygen, in addition to the effect of biomass concentration. An aeration pump and oxygen concentrator were used to supply oxygen. It was confirmed that the performance of system improved with increased availability of oxygen, as determined from the phenol degradation rate. Alternatively increasing stirring speed proportionally, increased the mass transfer coefficient of oxygen and also resulted in improved phenol degradation. However, in all the above cases the dissolved oxygen (DO) was zero in the presence of phenol. Studies using the RBC led to amelioration/improvement in DO levels, thus overcoming the limitations of oxygen supply to the process during phenol degradation in the batch mode

3.2.9. Combined and sequential processes

The combination of different techniques has been found frequently very useful to improve the performances in phenol degradation processes. Many different solutions are reported in the literature. The coupling of UV irradiation with chemical oxidation with ozone or/and hydrogen peroxide has been found to be convenient [84] and seem to have already industrial application in water treatment [139]. According to Gimeno et al. [77] the coupling of ozonation with photochemical and/or photocatalytic oxidation are the most attractive technologies. Commercial Sonoperoxone® Clearwater System and Sonoperoxone® Blackwater System are processes developed by Furness-Newburge, Inc. [140] to treat different wastewaters with high-powered acoustics, ozone and hydrogen peroxide without and with an additional solids separation system. According to the producers, these systems effectively reduce pollutants and remove odors, no other technology providing similar energy and environmental benefits,

The Fenton-type CWPO of phenol is made more efficient by coupling with sonication [79,90] and hydrodynamic cavitation [132]. On the other hand also the coupling of adsorption on alumina with electrical discharges [141] as well as of adsorption on ACs and polymeric materials with sonication [130] have been reported as very efficient methods to remove phenol. In a recent study the coupling of activated sludge treatment with photocatalysis in phenol destruction has been investigated [142]. The CALIPHOX process couples adsorption with wet catalytic oxidation (see Fig. 4 [69]). Sequential extraction–oxidation–adsorption processes have also been proposed for treatment of industrial effluents [143]. Oxidation processes are considered to be optimal pretreatments for a successive biological degradation step, to limit toxicity of the solution with respect to the microbial cultures. A comprehensive review of hybrid methods for wastewater treatments has been published a few years ago [144].

4. Abatement of phenol from gaseous streams

The vapor pressure for phenol is 0.3513 mmHg at 25 °C, corresponding to 462.5 mg/m³. The odor threshold for phenol is 0.04

parts per million (ppm), which corresponds to 0.154 mg/m³, with a very sweet “medicinal” odor reported. The US National Institute of Occupational Safety and Health (NIOSH) fixed the concentration immediately dangerous to life or health at 960 mg/m³ (NIOSH IDLH), the recommend exposure limit ceiling (i.e., the concentration that should not be exceeded at any time) of 60 mg/m³ (NIOSH ceiling), and a recommended exposure limit for an 8- or 10-h time-weighted-average exposure and/or ceiling at 19 mg/m³ (NIOSH REL), the same of OSHA PEL, i.e., the US Occupational Safety and Health Administration’s permissible exposure limit. The European Community Directive 2000/39/CE indicates 7.8 mg/m³ (2 ppm) as the limit value for professional exposition to phenol vapor.

Actually, due to the relatively low vapor pressure of phenol, its absolute amount in vent air is generally relatively low, and this makes removal techniques usually less interesting than destruction techniques. Although many studies have been undertaken concerning the purification of air from volatile organic compounds (VOCs), very few data can be found in the literature concerning the treatment of phenol-containing gaseous streams.

4.1. Techniques allowing phenol recovery or concentration

4.1.1. Condensation

Phenol can be separated as a liquid after compression and cooling gaseous streams that contain it. Part of the cost of compression can be recovered by applying a turbine to the final tail gas. The efficiency strongly depends on phenol starting concentration and the total applied pressure. This procedure may be useful when its concentration is very high.

4.1.2. Absorption in liquids

According to the polarity of phenol and their partial reciprocal solubility, water can be chosen to remove phenol from gaseous streams. However, according to the weak acidity of phenol and the large solubility of sodium phenate in water, 3–20% sodium hydroxide is mostly used as the scrubbing agent [2,6]. These procedures are effective in the purification of the gaseous streams but produce a phenol- or phenate-containing wastewater that should be later disposed or treated according to the previously described technologies.

Alternatively, several different organic liquids, as those already cited in Section 3.1.2, may be used to remove phenol from gaseous streams. Regeneration of the organic solvents may be obtained by distillation or by re-extraction with water or soda solutions. With the former procedure, quite expensive, pure phenol can be recovered, in the latter case a phenol-containing wastewater is produced again.

4.1.3. Adsorption on solids

This is perhaps the most common technology to recover VOCs from contaminated air. Packed columns are mostly used, the adsorbent regeneration being mostly obtained at higher temperature (temperature swing adsorption, TSA), or by purging or stripping with a gas (commonly steam or nitrogen). Rotor adsorption can be applied at high flowrates and low concentrations, by using a rotor concentrator (Fig. 7 [145]), i.e., a device constituted by a rotating wheel made from a honeycomb lattice containing the adsorbent: any segment of the wheel adsorbs the contaminant(s) from the gas in a low temperature position and, after rotation, desorbs it in an higher temperature position giving rise to a more concentrated stream. This can be feed, e.g., to a incinerator or to a condenser.

Activated carbons [146], carbon molecular sieves [147] and carbon fibers [148] are largely applied to this purpose, although they are quite delicate and only allow small VOC loadings to have acceptable lifetime. The regeneration can be performed by temperature

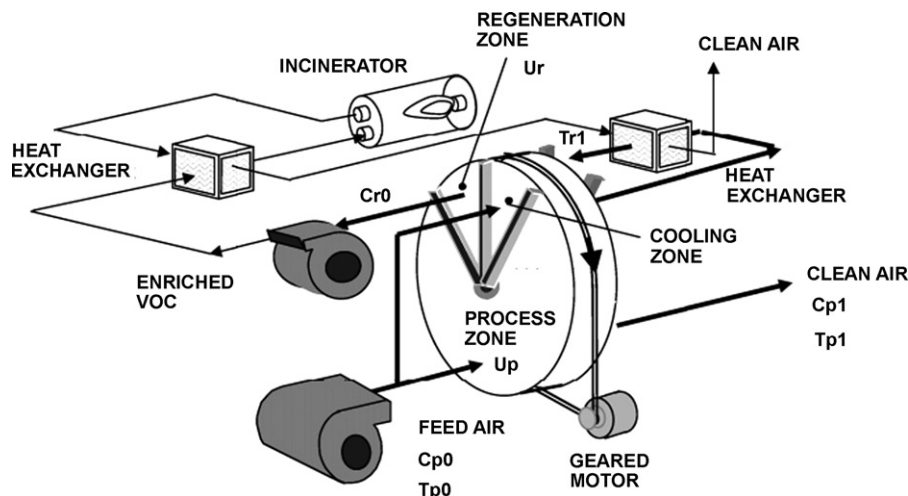


Fig. 7. Integrated system of VOC abatement with a thermal swing honeycomb rotor incorporated. Reprinted with permission from Ref. [145].

and vacuum pressure swing adsorption of combinations of them [149]. The regeneration, however, is frequently difficult and incomplete. Consequently, saturated AC's are frequently removed and disposed or burnt in appropriate furnaces. The use of ACs for removal of phenol from waste gases is cited in the literature [2], and some data can be found in Ref. [150].

Alternatives to carbonaceous sorbents for air purification are inorganic or polymeric sorbents. Most of inorganics, such as zeolites, silica and activated alumina, although quite efficient in adsorbing organics [151], preferentially adsorb water and therefore waste most of their capacity in wet streams. High-silica hydrophobic zeolites (silicalites) are proposed by UOP as HiSiv adsorbents line [42] as most effective in high-humidity air vent streams. In fact, the internal pore surface of these solids is constituted by a highly covalent silica framework, polar groups (silanol OH's) being only located at the external surface [152,153], where water may adsorb. The adsorption of VOC's on these solids is very weak, thus they regenerated easily using hot air (TSA), or by varying the pressure (PSA—pressure swing adsorption), as shown, e.g., for the adsorption of acetonitrile [154]. Yamauchi et al. [145] measured the performances of a rotor concentrator using hydrophobic high-silica zeolite deposited on a ceramic honeycomb structure for the abatement of different VOCs. To perform in wet atmospheres, hydrophobic silicas have also been developed either by inertizing the external surface or by producing materials free from surface hydroxy groups, and some of these materials adsorb VOCs more selectively than usual silica [155]. However, according to Das et al. [148], the commercially obtained AC fibers exhibit greater adsorption for VOC than most of the other adsorbents available in pellets or powders form, including granular activated carbon, zeolites, and silica gel, under identical operating conditions.

Dow proposes macroporous PS-DVB resins (DOWEX OPTIPORE) for the concentration and removal of VOC from gases [156]. Desorption can be done with steam, hot air or microwave energy. According to the producers they are more effective than activated carbon for styrene and formaldehyde vapor removal. This agrees with data published by Lu and Zellers [147].

4.1.4. Membrane separation

In contrast to adsorption processes in which the absorbent must be regenerated periodically, a thin porous membrane can be used to separate gaseous mixtures in an efficient and continuous manner. Silicon-based [157–160], polyether-imide based [161], and fluorinated elastomer-based [162] polymeric membranes can

be applied to separate organic vapors (to which the membranes are permeable) from air. Over pressure is needed to obtain permeation, and the selectivity is not complete. Highly concentrated VOC's-containing streams can be obtained, with more than 90% of organics recovery. Later, the VOC-containing stream can be recycled to the plant, or condensation of organics can be easily obtained. Unfortunately, the membrane lifetime is generally not very high.

Although their selectivities are relatively high, the permeabilities of polymeric membranes for solvents are very small. Moreover, polymeric membranes cannot withstand high temperature and harsh chemical environments.

Ceramic porous membranes not only have adequate thermal and chemical resistance but also have higher permeabilities. Vycor glass was applied successfully to separation of some VOCs from air [163]. MFI-type zeolite membranes prepared by liquid phase hydrothermal synthesis on tubular commercial supports were used to remove model pollutants *n*-hexane, formaldehyde and benzene present at very low concentration levels (2–230 ppmv) in indoor air. Depending on the operation conditions, permeation fluxes of the organic compound up to 3300, 130 and 30 mg/(m² h) and organic/air separation factors of 250, 6.3 and 38 were achieved for *n*-hexane, formaldehyde and benzene, respectively. [164]. Similarly, La₂O₃-modified γ -Al₂O₃ membrane appears to be the most effective for use in the VOC recovery process as compared to polymeric, Vycor glass, and unmodified γ -Al₂O₃ membranes [165].

4.2. Phenol destruction techniques

4.2.1. Thermal oxidation

Thermal incineration is typically applied to gaseous wastes highly concentrated in low value hydrocarbon or oxygenated vapors, and in plants needing additional energy supply in the form of heat or steam. In this case in fact no additional fuel has to be added and the energy obtained is utilised either by producing steam (regenerative burners) or by preheating the gas (recuperative burners). This is the case of several wastes from refinery or petrochemical plants. If concentration of VOC is low, additional fuel is to be added, and this strongly lowers the economicity of the process. On the other hand, thermal incineration is applied if the waste VOC is harmful and does not give rise by combustion to other noxious compounds. One of the main drawbacks of this technology is the production of NO_x, due to the high temperature combustion in air. This technique may be applied to phenol-containing waste gases, in particular when in combination with other organic pollutants.

4.2.2. Catalytic oxidation

Catalytic combustion [166] represents the alternative to thermal incineration to destroy highly concentrated VOC-containing streams, allowing heat recovery. The advantages are represented by the lower NO_x emissions and the lower amount of fuel needed, both associated with the lower combustion temperature obtained in the presence of catalysts, i.e., 300–500 °C. However, also in this case the heat can be recovered and utilized, but is obviously at lower temperature. The drawbacks are represented by a more complex reactor design, by the cost of the catalyst and sometimes by the relatively low catalyst lifetime. In fact combustion catalysts can be deactivated in particular when the feed contains sulphur, nitrogen and chlorine. In this case either regeneration procedures are needed, or the lifetime of the catalyst is low. Moreover, partial oxidation of the organic contaminants can occur and this can give rise to low concentration of partially oxidized species in the out-stream that can be even more toxic than the original contaminant [167]. Catalyst producers propose different catalyst formulations for combustion of different contaminants [168].

Typical VOC combustion catalysts are constituted by noble metals supported on thermally stable ceramic supports. Among noble metals, palladium and platinum are very active. Among supports, aluminas appear to be sufficiently stable at the needed temperatures of at least 500 °C. The thermal stability of aluminas is increased by doping with large cations such as, e.g., Lanthanum [169]. Ozawa et al. [170] reported on the catalytic activity of Pd/ Al_2O_3 in adsorption and combustion of phenol in a catalytic sensor, with very high sensitivity. According to this study, the combustion of phenol is similar to that of benzene. Total combustion of benzene can be performed in the 230–330 °C range over Pt/ Al_2O_3 [171] and on supported Pd [172], but also on non-noble metal catalysts like Co/ Al_2O_3 [173]. Transition metal based compounds such as spinels [174] and perovskites [169,175–177] give also rise to very efficient combustion catalysts. In particular manganese oxide based materials find excellent activity for catalytic combustion of hydrocarbons oxygenated compounds [178,179] with high selectivity to CO_2 . Chromium containing materials also very active [180], but the high toxicity of chromium causes serious disposal problems with this system.

However, also transition metal-based catalysts may undergo poisoning. This is the case, e.g., of Mn catalysts in the presence of chlorine [181]. Highly active combustion catalysts which are stable in the presence of chlorine are those based on $\text{V}_2\text{O}_5\text{-WO}_3\text{-TiO}_2$ and $\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2$ which are also applied in the processes for the simultaneous removal of dioxins and NO_x [182]. These materials have also been found to allow complete combustion of aromatic compounds.

4.2.3. Photocatalytic destruction

Photocatalytic treatment of gaseous wastes is possible but still in the experimental stage of evolution. This method can avoid the need of additional fuel and the emission of NO_x , but requires energy consumption in the form of UV light. The catalysts are based on TiO_2 materials and are not very expensive. Commercial application is already available, e.g., for air purification in the car's climatization devices. Application to larger scales will possibly become commercial in the near future. Interesting potential large scale applications imply the deposition of photocatalytically active TiO_2 layers on lightened surfaces such as skyscraper windows, traffic lights, road sign reflectors and also computer and TV screens, to apply sunlight or artificial light to photo-catalyze the decomposition of outdoor and indoor air pollutants [183].

The photocatalytic abatement of phenol vapors on anatase TiO_2 has been the object of a study by Palmisano et al. [184]. The phenol photodegradation rate follows pseudo-first order kinetics with an

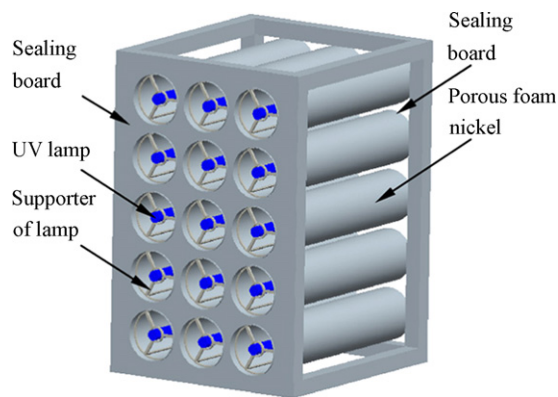


Fig. 8. Schematic diagram of a new PCO reactor. Reprinted with permission from Ref. [187].

observed rate constant, $K_b = 1.69 \text{ h}^{-1}$. The mineralization process is complete in about 3–4 h while accumulation of organic intermediate compounds in the first 30 min of the reaction was observed. Spectroscopic measurements suggest that pyrocatechol is an intermediate in the reaction, while hydroquinone was not observed, although it was found that hydroquinone, if formed, converts very rapidly into carbon oxides. The same research groups [185] found the occurrence of different photodegradation pathways in the case of liquid–solid and gas–solid photocatalysis, not only depending on the interfaces and on the presence of water, but also on the kind of photocatalyst, different anatase preparations behaving in different ways. Deveau et al. [186] showed that, in the case of gas/solid photocatalysis, one of the most important steps in the photodegradation is the VOC and photoproduct adsorption and desorption from the photocatalyst. This study highlights that it is not possible to conclude on pollutant degradation and mineralization without taking in account the adsorbed photoproducts; their desorption and then their photodegradation depend on the relative humidity in the gaseous phase and on the activation energy of desorption.

In a recent paper [187], based on theoretical analyses, a novel photocatalytic oxidation (PCO) reactor for air deodorization (Fig. 8), containing 15 parallel-connected cells was designed. Each reaction cell was composed of an UV lamp and a TiO_2 -coated tubular foam nickel. The performance of the reactor was tested by degrading gaseous formaldehyde at an indoor concentration level. The results showed that the reactor had low-pressure loss and good degradation capability.

4.2.4. Biofiltration

Bio-filtration consists in the treatment of the waste, usually prehumidified, by passing it at room or slightly higher temperature through a wet bed of organic materials which is populated by micro-organisms [188–190]. Odorous contaminants are aerobically degraded to various end products and/or incorporated in the bio-mass. Different bacteria can be responsible for the organic carbon oxidation to carbon dioxide, for the conversion of nitrogen compounds to nitrate ion and for the oxidation of sulphur to sulphate ions. Mixed micro-organisms cultures naturally grow on appropriate natural biofilter beds, that can be maintained in a wet environment by appropriated humidification and ventilation procedures (Fig. 9), and abatement of all volatile compounds can be obtained simultaneously. This technique is becoming widely applied due to its efficiency (in particular for sulphur compounds if the feed is not excessively concentrated), to the moderate capital costs, and to the very low maintenance costs. In particular biofiltration seems to be the choice technique for the treatment of the odorous emissions arising from wastewater treatments [191–194]

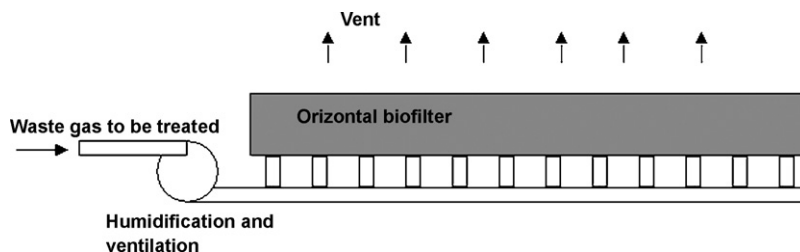


Fig. 9. Schematics of a horizontal biofilter.

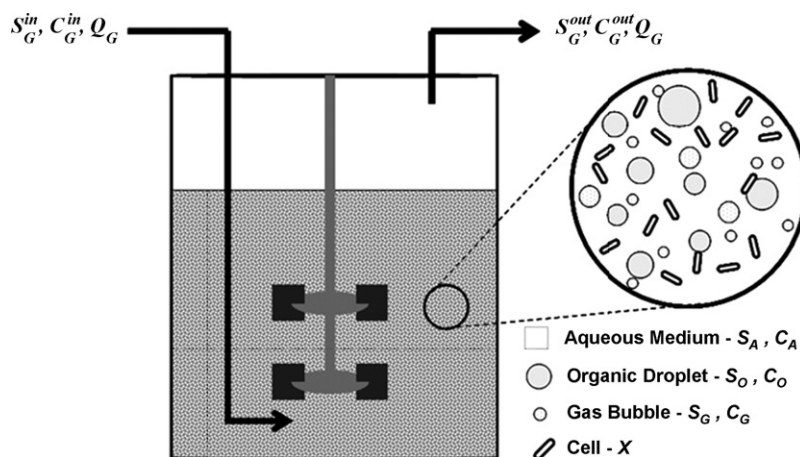


Fig. 10. Illustration of the two-phase partitioning bioscrubber (TPPB). Reprinted with permission from Ref. [201].

and from the bio-industry due to (i) the chemical complexity of the wastes; (ii) the low concentration of the contaminants; (iii) the high flow rates to be handled [195]. On the other hand this technology is quite versatile, being applied to waste gases of very different origins and containing any quality of pollutants.

The application of a pure strain of *P. putida* and a mixed culture of *Pseudomonas* sp. for phenol biofiltration from waste gases has been the object of studies by Zilli et al. [196,197]. More commonly, mixed strains culture are spontaneously formed or inoculated on biofilters over soil, organic, inorganic, and inert matter. Natural materials such as peat, compost, soil, activated carbon have been mostly used as filter media. The nature of biofilter medium is a key factor for a successful application of biofilters, affecting both, the removal performance related to bacterial activity, and the cost related to pressure drop and bed material replacement [198].

As reviewed by Kennes and Veiga [199], recently isolated new fungal strains are able to degrade alkylbenzenes and other related volatile organic pollutants, including phenol, for air pollution control. In biofiltration, the most extensively studied organism belongs to the genus *Exophiala*, although strains of *Scedosporium*, *Paezilomyces*, *Cladosporium*, *Cladophialophora*, and white-rot fungi are all potential candidates for use in biofilters. Encouraging results were obtained in most of the cases in which some of those organisms were present in gas-phase biofilters. They allow reaching high elimination capacities and are resistant to low pH values and to reduce moisture content.

The performance of biofilters can be improved by adopting design and operational strategies to manage transients which may occur during normal operation [200].

The two-phase partitioning bioscrubber (TPPB) is an emerging biotechnology developed to treat waste gases that has shown promise for removing toxic VOCs, such as benzene [201]. The TPPB is essentially operated as a liquid–liquid partitioning bioreactor into which the VOC substrate and oxygen are both continuously and

solely introduced through absorption from the gas stream while the liquid contents effectively remain as a closed system (Fig. 10). The high performance potential of TPPBs is due to enhanced rates of absorption of hydrophobic VOCs and dissolved oxygen, as well as biodegradation by their ability to maintain sub-inhibitory conditions when treating toxic compounds. The TPPB and its primary physical and biological constituents are illustrated in Fig. 10. Two-phase partitioning bioscrubbers are characterized by a cell-containing aqueous phase, as well as an immiscible, biocompatible, non-bioavailable organic phase that serves as a reservoir to buffer the cells against high concentrations of toxic substrates. VOC substrates are captured in the TPPB through absorption as the waste gas passes through the liquid phases, preferentially accumulating in the organic phase. Substrate then partitions into the aqueous phase at greatly reduced concentrations, being delivered at rates which are dictated by the metabolism of the cells. Microbial strains like *P. putida* can be used to degrade phenol from waste gases with this system.

4.2.5. Combined processes for removal of phenol from gaseous streams

Also in the case of the treatment of gaseous streams, many of the previously cited procedures may be combined to obtain better performances. As for example the coupling of adsorption, to concentrate the pollutant, with abatement technologies are very useful. The coupling of rotor concentrators with thermal [202] or catalytic oxidizers are available commercially, while the coupling of rotor concentrator with photochemical oxidizer has also been proposed [203].

5. Conclusive comments

The data summarized in this review (Table 2) provide evidence for the strong research efforts carried out in recent time to develop

new and improved technologies for the purification of water and air effluents from VOC contaminants. In particular, much attention is focused today to the abatement of phenol and phenols from wastewaters. The best technology to be applied strongly depends on single cases, in particular from the concentration of phenol in the stream, the copresence of other contaminants, the nature of the plant where this problem is found. Technologically quite simple methods are available, such as, e.g., the adsorption on activated carbons without any regeneration; however the expense for activated carbon to replace the spent beds may be significant. Much more complex technologies, where advanced apparatus are needed, such as, e.g., catalytic combustion or high-voltage discharge methods, make certainly more expensive the plant and more complex its operation, but might result very successful in the future to abate small concentration of pollutants in small plants. However, according to the opinion of the present authors, when the concentration of phenol in wastes is small, abatement techniques that can be performed without the addition of other reactants (in particular bases or acids) nor of much energy supply should be the preferred choices from the environmental point of view. This makes, in perspective, fixed bed solar photocatalysis a very interesting field to be further investigated, due to the still poor performances. Adsorption on activated carbon with burning of the spent adsorbent and heat recovery is also a quite satisfactory technique at least for small plants.

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