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Removal of Phenolic Compounds from Water by Adsorption and Photocatalysis

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Additional information is available at the end of the chapter

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Abstract

Phenolic compounds are important industrial wastes, and are classified as hazardous substances contaminating groundwater resources. Therefore, the removal or diminish of these organics compounds in order to reach the permitted levels before discharging becomes a challenging. Several processes have been developed to remove phenolic compounds from waters, including electrochemical oxidation, redox reactions, membrane separation and photocatalytic degradation. Recently, tendency of phenolic compounds removal involves adsorption and photocatalytic process, using synthetic or natural particles, such as carbon materials and clays. Actually, materials in nanometric scale play an important role in the processes previously mention due to their unique chemical and physical properties. In this book chapter, the first part shows the chemical properties of phenolic compounds that play an important role in the removal process. In the second part, different materials in macro, micro and nanosize used as adsorbents or photocatalysts are reviewed. In addition, other removal processes of phenolic compounds as electrochemistry and redox reactions are included. The removal conditions in these process, such as pH, adsorbate and adsorbent concentration are analyzed and discussed. Furthermore, special emphasis is included in micro and nanocarbon materials, used as adsorbents or photocatalyst to remove phenol from water in recently researches.

Keywords: phenolic compounds, water pollution, removal methods, adsorption, photocatalysis

1. Introduction

Water pollution is one of the most important problems in the world, which represents a risk to the human and environment. The increasing industrial and human activities have caused an increase on the discharge of wastewater into the water resources. Phenolic compounds from different industrial activities such as refineries, pesticides, insecticides, pharmaceutical, etc., are found among the main pollutants of water. These compounds are toxic and their degradation is difficult; thus, it is important the development of materials and effective methods that allow the removal of these pollutants from water.

Different methods have been used to assist with this problem. The adsorption and photocatalysis are two promising technologies related to the removal of phenol from the water. In the adsorption process, the molecules of the contaminant are retained on the surface of the adsorbent material and then these can be separated from the water. In the photocatalysis process, a semiconductor material is used to produce chemical species with high reactivity and it is possible degrading the molecules of the contaminant.

Some materials commonly used on the removal of phenolic compounds by adsorption are activated carbon, clays, zeolites, membranes and recently has emerged a new class of adsorbents, the nanomaterials. These materials are very promising in this area. On the other hand, the size reduction in the semiconductors particles increases the degradation of phenolic compounds due to the increments on their surface area. In addition, carbon nanomaterials as graphene and graphene-based materials have demonstrated an important performance on the degradation of phenolic compounds.

Thus, this chapter presents a review of researches where the adsorbents before mentioned have been used on the removal of different phenolic compounds. Phenolic compounds degraded by photocatalysis are also reviewed and presented. The influence of some parameters such as temperature, pH solution, dosage of photocatalyst/adsorbent, solution concentration on the process of adsorption and photocatalysis are also analyzed.

2. Phenolic compounds

In the last times, phenolic compounds have attracted a great interest, because they have several applications indispensable in our daily life. The phenolic compounds are present in adhesives, foams, emulsifiers and detergents, insecticides, dyes, explosives, flavors and rubber chemicals, self-assembly to nanomaterials, resins and so on, in other different applications. All these products have great economic importance in many industries such as food, medicine, petrochemical, agriculture, chemical synthesis and polymer chemistry, among others [1]. Thus, there is a great environmental interest in the removal of phenolic compounds. Phenolic compounds are among the most important contaminants present in the environment. On the other hand, phenolic compounds are not only generated by human activity, but they are also formed naturally, the phenols are present in soils and sediments and therefore these compounds produce the contamination of groundwater. Some organizations such as

the European Union and the US Environmental Protection Agency (EPA) have included as priority contaminants, some of the phenolic compounds due to their high toxicity and persistence in the environment [2]. The structures of eleven phenols considered priority pollutants by the EPA are shown in **Figure 1**.

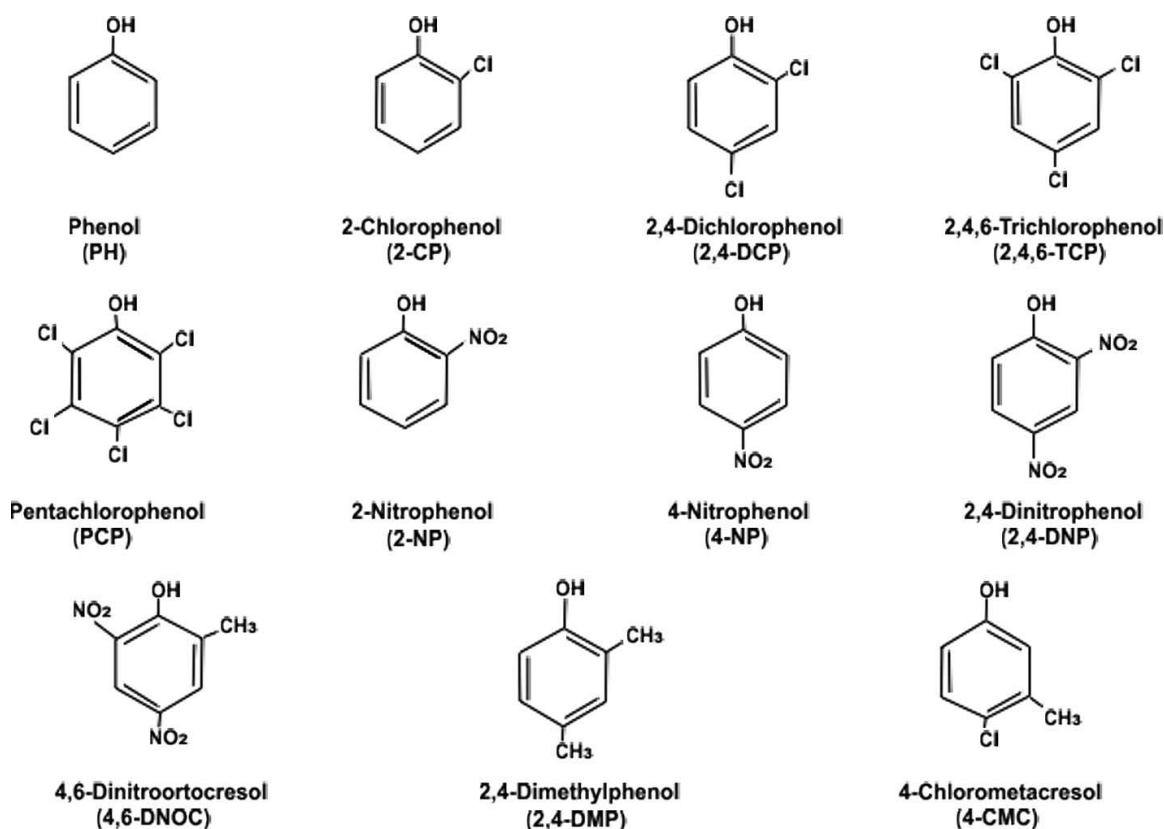


Figure 1. Phenolic compounds structures considered priority contaminants by US EPA. Reprinted with permission from Mahugo-Santana et al. [2]. Used under Creative Commons Attribution 3.0 Unported (CC BY 3.0) (<https://creativecommons.org/licenses/by/3.0/>).

2.1. Generalities

Industries generate large annual volumes of wastewater containing hazardous compounds to the environment, including natural water resources. Many of these compounds are in concentrations that are too low for recovery but high enough to act as contaminants; usually, they are nonbiodegradable substances. Therefore, conventional biological processes do not have the ability to remove all contaminants that are present in the industrial wastewater. Some organic compounds are hardy to biological degradation such as phenols, tannic acids, lignine, cellulose, chlorinated compounds, pesticides, aromatic hydrocarbons and so on; all of them are examples of nonbiodegradable organic compounds that are extensively employed in the chemical industry and, therefore, are common contaminants found in industrial wastewater discharges. In recent years, phenolic compounds have warranted more attention in the field of industrial wastewaters, because of their toxicity and the frequency of industrial processes producing waters contaminated by phenols [3].

Pollution of environment is one of the main problems facing humans today. Recently, the problem of environmental pollution has increased exponentially and reached worrying level in terms of its impact on the life of human beings. Among the contaminants that have harmful effects in animals and humans are considered the toxic organic compounds. As mentioned earlier, dissolved phenolic compounds that are present in industrial wastewater cause pollution of ground-water and owing to its harmful effect these compounds generate a serious problem in this type of water resources. Exposure to this type of chemical reagents, once they enter into human body can cause damage to the nervous and respiratory systems, kidney and blood system. Phenolic compounds have been classified as the top 45th in the list of priority hazardous substances by the Agency for Toxic substances and Disease Registry, USA, which require immediate treatment before disposal in the environment [4]. Consequently, removing organic compounds or reducing their concentrations to the permitted levels by environmental standards represents a big challenge.

2.2. Chemistry of phenolic compounds

The approach of this section is to present a summary of physicochemical properties of phenolic compounds.

2.2.1. Physical properties of phenols

Phenols are in some respects as alcohols, due to the presence of hydroxyl groups in their structures. They have the ability to form strong hydrogen bonds. Moreover, these compounds present higher boiling points than hydrocarbons of the same molecular weight. Phenols are also slightly soluble in water because of their ability to form strong hydrogen bonds with water molecules [5]. Phenols are stronger acids than alcohols. They react with bases like sodium hydroxide to form phenoxide ions. However, they are weaker acids than carboxylic acids and do not react with sodium hydrogen carbonate [6].

2.2.2. Reactions of phenols

Phenolic compounds behave as nucleophiles in most of their reactions and also the reagents that interact on them behave as electrophiles. In phenolic compounds, the site of nucleophilic reactivity may occur at the hydroxyl group or the aromatic ring. The reactions are carried out on the aromatic ring results in electrophilic aromatic substitution [7].

Halogenation: Bromination and chlorination of phenols occur easily even in the absence of a catalyst. Substitution occurs primarily at the para position to the hydroxyl group. When the para position is blocked, ortho-substitution is carried out.

Nitration: Phenol reacts with dilute nitric acid in either water or acetic acid. It is not necessary to use mixtures of nitric and sulfuric acids, due to the high reactivity of phenolic compounds. The o-nitrophenol is a phenolic compound ortho-substituted and therefore, this compound has considerably lower boiling point than the meta and para isomers. This is due to the hydrogen bond that is produced between the hydroxyl group and the substituent partially compensates for the energy required to go from the liquid to the vapor phase.

Nitrosation: The nitrosonium ion $[N \equiv O^+]$ is obtained during the acidification of sodium nitrite, which is a weak electrophile and reacts with the strongly activated ring of a phenol. The resulting product is a nitrosophenol.

Sulfonation: The sulfonation of the ring can be carried out by reacting phenol with concentrated sulfuric acid.

Friedel-Crafts alkylation: Alcohols in combination with acids serve as sources of carbocations. Attack of a carbocation on the electron ring of a phenol results in the alkylation.

Oxidation of phenols: quinones: Phenols do not undergo oxidation in the same way that alcohols do because they do not have a hydrogen atom on the hydroxyl-bearing carbon. Instead, oxidation of a phenol yields a cyclohexa-2,5-diene-1,4-dione, or quinone [8].

3. Removal methods of phenolic compounds from water

Phenolic compounds are priority contaminants with high toxicity even at low concentrations. These compounds are present in industrial effluents, where increase biochemical and chemical oxygen demands resulting in detrimental effects on the environment. Some of them are highly toxic as well as carcinogenic and can remain in the environment for a long time due to their stability and bioaccumulation. Owing to the high toxicity of phenolic compounds, treatment of the organic wastewater has an important effect on the lives of human beings [9].

Many phenolic compounds can be removed efficiently by conventional treatments such as extraction, distillation, chemical oxidation, electrochemical oxidation and adsorption among others. On the other hand, some advanced treatments use less chemical reagents compared to the conventional processes, but they have the disadvantage of having high energy costs. Within the advanced treatments are as follows: Fenton, ozonation, wet air oxidation and photochemical method. Biological treatments have certain advantages compared to physicochemical treatments; among these advantages may be mentioned: environmentally friendly and energy saving. However, it has the disadvantage that cannot treat high concentration of contaminants. One of the best ways to treat phenolic compounds under mild conditions is the enzymatic treatment, which uses different enzymes such as peroxidases, laccases and tyrosinases [10]. Thus, there is a need to treat waste contaminated with phenolic compounds at low and high concentrations before discharge. Some methods used today are described below:

Adsorption: Adsorption method for removal of phenols from water is effective from low concentrations to high concentrations, depending on the economics and recycling the required secondary material, adsorbent. Activated carbon (AC) is the most used in industry as adsorbent. It is expensive but has been shown to be effective for removal of trace organic compounds. Therefore, new options are being developed including impregnation with nanoparticles, different sources of carbon, different activation methods, carbon nanotubes (CNTs), graphene-based materials, as well as substitution with low cost biosorbents, such as chitin/chitosan which are promising alternatives to remove phenolic compounds [11–13].

Membrane processes: Membrane processes are applied in water and wastewater treatment to remove organic contaminants. At present, this technology has been investigated for the phenolic compounds removal. Low energy consumption, low operating cost and easy scale up by membrane modules are the main advantages of these technologies. Today, separation membranes have many uses with a growing potential for industrial applications in biotechnology, nanotechnology and purification processes.

Reverse osmosis and nanofiltration: Reverse osmosis (RO) is a membrane-based demineralization technique that is used to separate dissolved solids, especially ions, mainly from aqueous solutions. On the other hand, nanofiltration (NF) is widely used for removing organic pollutants, inorganic salts, color and hardness from aqueous solutions. NF is useful to use prior to an RO unit in order to decrease the pressures associated with organic matter [14].

Chemical oxidation: Chemical oxidants provide destructive methods of phenolic compounds. The processes have low consumption of reagents and energy costs, operating under mild conditions (temperature and pH). Ozone, chlorine, chlorine dioxide, chloramines, ferrate [Fe (VI)] and permanganate [Mn (VII)] are the most common chemicals applied in oxidative treatment of contaminated water.

Electrochemical oxidation: This technique can effectively oxidize many organic contaminants at high chloride concentration, usually larger than 3 g/L. Electrochemical oxidation is an alternative destructive of phenols which does not require addition of reagents. This technique is divided into direct and indirect oxidation. Direct or anodic treatment occurs through adsorption of the contaminants on the anode surface. Various anode materials are used with Pt, PbO₂, SnO₂, IrO₂ and BDD (boron-doped diamond) being the most investigated ones. Parameters such as current density, pH, anode material and electrolytes used have significant impact on process efficiency.

Advanced oxidation processes: Advanced oxidation processes (AOP) are techniques that present the common feature that they form hydroxyl radical (OH•) in situ and this free radical is capable of mineralizing most organics, including phenolics compounds. AOP are used mainly for the treatment of contaminated waters that contain recalcitrant organics (e.g., pesticides, surfactants, coloring matters, pharmaceuticals) [10].

Fenton and fenton-like treatment: An AOP with the capability to oxidize aromatic compounds is the Fenton reagent, which consists of hydrogen peroxide (H₂O₂) and ferrous ion at low pH. The iron (II) reacts with H₂O₂ to produce iron (III) and hydroxyl radicals. Then, Iron (III) is regenerated to Fe (II) by H₂O₂ in acid medium. Some of the variants of the Fenton process are as follows: Fenton-like, photo-Fenton and electro-Fenton [15].

Biological treatment: Biological treatment is the most commonly applied treatment for aqueous phenols. The treatment is an inexpensive method, simple design and maintenance, for transforming phenolic solutions into simple end products.

Wide research is carried out daily on phenolic compounds removal from water, from conventional methods to new technologies. Optimization and modification of conventional processes provide attractive alternatives on contaminants removal. Some other methods used in the

removal of phenol are as follows: wet air oxidation (WAO), catalytic wet air oxidation (CWAO), solvent extraction, extractive membrane bioreactors (EMBR), photocatalytic membrane reactors (PMR), UV/H₂O₂ treatment with microwave, etc.

3.1. Adsorption

Adsorption process is preferred over all methods because it is nondestructive and with this method is possible recover the organics pollutants through regeneration, relatively simple. Due to the high adsorption capacity of adsorbents, adsorption seems to be the best process, especially for the removal of moderate and low concentration phenolic compounds from an effluent [9].

The most common method for the removal of dissolved organic material is the adsorption with activated carbon, a product that is produced from a variety of carbonaceous materials, including wood, pulp mill char, peat, lignite, etc. Adsorption is the physical and/or chemical process in which a substance is accumulated at an interface between phases. The substance which is being removed from the liquid phase to the interface is called as adsorbate and the solid phase in the process is known as adsorbent. Physical adsorption (physisorption) is relatively nonspecific and is due to the operation of weak forces between molecules. Chemical adsorption (chemisorption) is also based on electrostatic forces, but much stronger forces act a major role on this process. In chemisorption, the attraction between adsorbent and adsorbate is due to a covalent bond or electrostatic forces among atoms [16].

3.1.1. Zeolites and clays

Zeolites and clays are two adsorbent materials commonly used on the adsorption process. Different investigations have shown interesting results on the phenolic compound removal.

Khalid [17] has carried out a research on phenol removal using four kinds of zeolites as adsorbents and adsorption properties were compared to those of an activated carbon. In this investigation, phenol diluted in water was used as contaminant and adsorption was carried out in batch and continuous flow. Siliceous BEA zeolite was successfully used; the adsorption capacity was slightly higher at low phenol concentration (1.6 g/L) than the one of activated carbon. Siliceous BEA zeolite showed to be efficient as adsorbent able to be easily regenerated.

Investigation of removal of 3-nitrophenol isomers (ortho, meta and para) was studied by Huong [18]. They used nano zeolite (NZ) as adsorbents. The adsorption of nitrophenols onto NZ reached equilibrium within 150 min at pH 6.0. The maximum adsorption capacities of NZ for meta-, ortho- and para-nitrophenols were 125.7, 143.8 and 156.7 mg/g, respectively. The removal percentages of nitrophenols were maintained at more than 70% of the initial values. The regeneration process showed that desorption efficiency of nitrophenols remained above 70% even after five adsorption-desorption cycles.

Adsorption capacity of a modified zeolite was evaluated by Xie [19] for the removal of ionizable phenolic compounds (phenol, p-chlorophenol and bisphenol A) and nonionizable organic compounds (aniline, nitrobenzene and naphthalene). The isotherm data of ionizable compounds fitted well to the Langmuir model but those of non-ionizable chemicals followed

a linear equation. Adsorption capacity of ionizable compounds depended greatly on pH, increasing at alkaline pH conditions. On the other hand, adsorption of non-ionizable compounds was practically the same at all pH levels studied.

Djebbar et al. [20] employed as adsorbent, a natural clay, for the removal of phenol from aqueous solutions. This clay was easily activated. Some parameters such as pH solution, temperature, contact time and initial phenol concentration were studied. The adsorption experiments were carried out employing 100 mg of adsorbent and 100 mL of phenol solution at different initial concentrations of phenol at 23°C. The results indicated that up to 60 and 70% of phenol was removed by activated and natural clay after of 5 h of contact time. The activated process improved the adsorption of phenol onto natural clay. The adsorption capacity of phenol decreased when the temperature was increasing. The best results were obtained at pH 5. Adsorption equilibrium data were well fitted to both Freundlich and Langmuir isotherm indicating that the adsorption was favorable. The adsorption of phenol onto activated natural clay was exothermic.

Other investigation of phenol removal from water with clay of low cost was investigated by Nayak and Singh [21]. The influence of pH phenol solution, temperature and particles size was studied. Results indicated that the higher adsorption capacity of phenol was achieved when the particle size decreased from 140 to 50 μm , the pH decreased from 10 to 2 and the temperature increased from 30 to 50°C. The adsorption process was found to be spontaneous.

The removal of p-chlorophenol (PCP) and p-nitrophenol (PNP) from water with two types of organoclays prepared from different surfactants such as dodecyltrimethylammonium bromide (DDTMA) and didodecyldimethylammonium bromide (DDDMA) was investigated by Park [22]. In the experiments, 200 mg of adsorbents were dispersed into 30 mL of PNP and PCP solutions at initial concentration of 100 mg/L and pH 5–6. In the isotherm studies, the initial concentration of PNP and PCP was studied in the range of 5–250 g/L. The best adsorption results were found on the organoclays where DDDMA surfactant was used. The adsorption of PNP and PCP onto organoclays was more efficient than in unmodified clay which was attributed to hydrophobic behavior. The adsorption equilibrium data were well fitted to Freundlich isotherm, indicating the presence of multilayer sorption.

3.1.2. Membranes

Membranes are considered a process to separate two streams, a barrier to facilitate the selective mass transport between fluids; feed and permeate [23]. Before to select the optimal membrane to remove or recover a specific compound, it is important to know the macro and molecular separation level. Munirasu et al. [24], divided into two categories, inorganic; anion and cation and organic compounds; these later compounds are quite complex and due to its nature, they can be classified such as oil, grease, dissolved, disperse and emulsified organic forms, solids and/or particles, such as clays, waxes, bacteria, sand or any solids based on chemical productions. Membranes separation efficiency depends on diverse factors including physic-chemical composition; as type, weight, polarity and solute charge, operat-

ing parameters; as feed flow rate, transmembrane pressure, temperature, permeate flux; also it is important to contemplate the membrane characteristics, for example, membrane material, porous size and configuration of membranes (modules). On the other hand, these aspects play an important key role on specific phenomena related to the concentration polarization and membrane fouling, contributing directly to the solute retention and hydrophobic interactions between the solute and membrane surface [25].

The application of a driven force, measure as transmembrane pressure (TPM), divided the conventional membrane separation in microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) processes (**Figure 2**), the membranes separate the feed solution into permeate and retentate. The permeate stream contains the solvent passing through the membrane, this stream is rich in solutes with a nominal weight cut-off (NMWCO) below the porous size of membranes and the retentate stream are particles and dissolved compounds which are kept inside membrane. When a pressure force is applied, the membrane operation and the hydrodynamic resistance fluctuate, depending on the pore size; thus, the operating pressure increases while the pore size of the membrane decreases [24, 25]. Pressure driven force is a strategy to improve low weight molecules removal, for example, salt or organic compounds; however, despite the excellent rejection of salts, the process frequently present low rejection levels to organic molecules, which include aliphatic or aromatic chemical structures; with polar or nonpolar properties, as well as different kinds of alcoholic, amino, carboxyl, phenol, or hydroxyl functional groups, just to mention some examples [24, 26]. Bellona et al. [27] reported the factors affecting the permeation of solutes in high-pressure membrane and

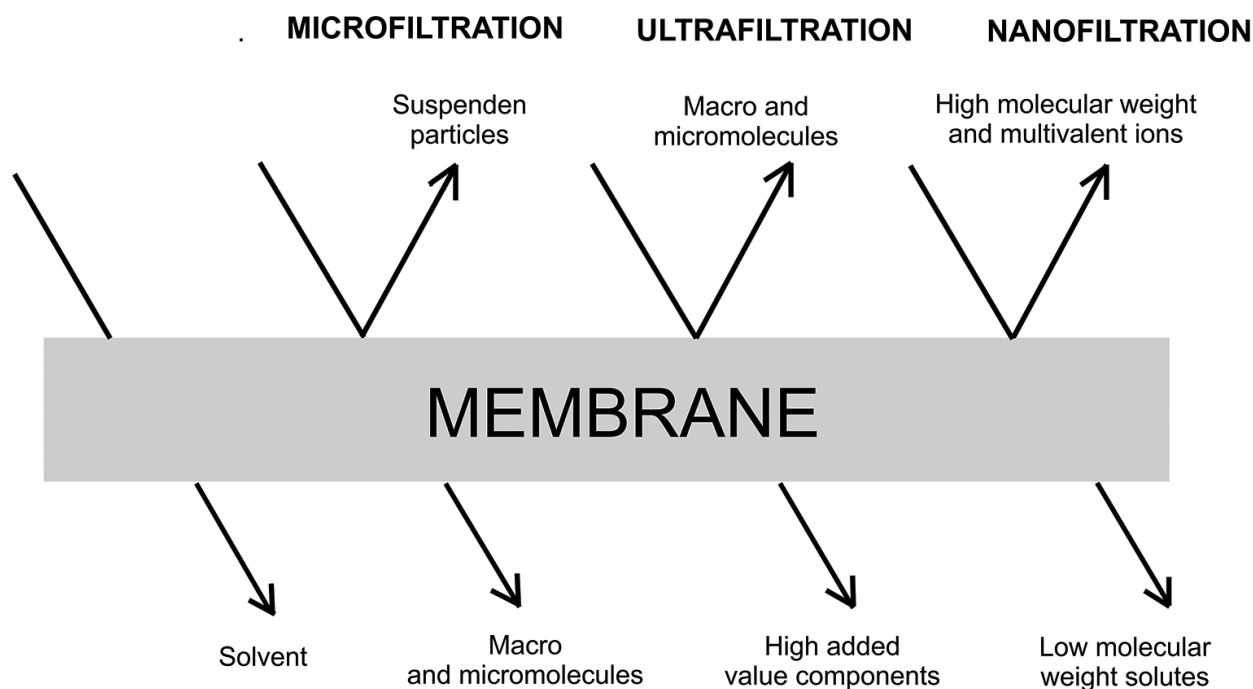


Figure 2. Scheme for microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) technologies. Adapted from Castro-Muñoz et al. [25].

some important solute parameters were identified to those that affect mainly solute rejection: molecular weight, molecular size (length and width), acid disassociation constant (pKa), hydrophobicity/hydrophilicity character and diffusion coefficient. Besides, membrane properties play an important role on the separation process: molecular weight cut-off, pore size, surface charge (zeta potential), hydrophobicity/hydrophilicity (contact angle) and surface morphology (roughness). Furthermore, water composition, such as pH, ionic strength, hardness and the presence of organic matter, was also associated to influence on the solute rejection.

Membrane process has been used to remove organic pollutants, among these technologies the liquid, anion exchange, nanofiltration, reverse osmosis and pervaporation membranes are precedents of this technology [28]. Hybrid processes is a recent tendency to get better removal of these compounds. These procedures are based on combination of diverse techniques, such as adsorption pretreatment process accomplish with reverse osmosis [29] and pervaporation with reverse osmosis [30], forward osmosis (FO) and reverse osmosis (RO) [31], NF/RO membranes [32], polymerization of phenolic compounds and UF/MF removal membranes [33].

Therefore, there is still a necessity to find advanced techniques to remove nonbiodegradable, high concentration organic substances from wastewater, not only those come from refineries but all complex wastewater from industry. In this sense, researchers are trying to design a combination of treatment methods for a complete and successful removal of such pollutants, due to variability of wastewater composition, the traditional methods become inadequate and could not be used individually in full scale [34]. Phenol and phenol stability usually offers difficulties to remove them, some of the main advantages of applying advanced techniques are the interfacial area; lower solvent losses, downstream phase separation and easy scale up. In the case of membrane process, the higher interfacial mass transfer, overcome the lower mass transfer rate in this kind of systems [25, 35–37].

In recent years, also composite membranes have been investigated to remove phenol compounds. In these materials, surface properties are controlled during membrane synthesis. Membrane aromatic recovery system (MARS) is a promising technology to recover phenol and aromatic amines. Composite membranes including poly(dimethylsiloxane) (PDMS) are commonly investigated to control porosity and the operational stability by synthesizing nonporous selective layer coated on a microporous support layer cast; reinforcement polymers could be poly(vinylidene fluoride), polyethersulfones, polyetherimides, polyacrylonitrile, polyester, polyphenylenesulphones. Xiao et al. [38] developed a pertraction membrane (pervaporation and extraction combine process), through plate composite polydimethylsiloxane/polyvinylidene fluoride polymers to recover phenol compound. Results show that mass transfer coefficient is five times higher compared to silicon rubber membranes nonreinforced (from 15×10^{-7} to 3.5×10^{-7} m/s), another property improved was the mass flux (2.38×10^{-2} kg/m² h), however, diminish the activation energy of permeation (9.7 kJ/mol), permeability (5.9×10^{-12} m²/s) and diffusion coefficient (2.4×10^{-11} m²/s). Lee et al. [39] also found a higher permeate flux using a wet phase inversion process polydimethylsiloxane/polysulfone (PDMS/PS) composite. Permeate flux is influenced by controlling the skin layer thickness of the asymmetric membrane during formation reaction, phenol concentration and recirculation rate. Additionally, the relatively

hydrophilic nature of phenol and specificity of membranes are related to chemical moieties, both point of views allow making highly flexible polymer, with hydrophobicity and organophilicity properties and controlled free volume; this is the case of the poly(dimethylsiloxane) (PDMS) and poly(vinylmethylsiloxane) (PVMS) to synthesize extractive membrane bioreactor (EMBR). Main characteristic to the EMBR system is to permeate organic compounds, meaning it should have a high organic flux while being effectively impermeable to inorganic and water, such as silicon-based rubbers [40].

Due to complexity of phenol and phenolic compounds, researchers are focused on to develop new technologies to improve efficiency removal, mainly on the size/steric exclusion, electrostatic repulsion, fouling and energy consumption. Hybrid or combine process involving two or more steps, previously mention, could be the answer to the problem. Heo et al. [41] suggest that forward osmosis/reverse osmosis (FO/RO) provide the advantage to enhance the driven pressure force, diminishing the fouling property and making it less energy costly process. Due to, FO depends on the molar concentration of the solution instead of the nature of the solutes and RO offers higher selectivity characteristics, internal concentration polarization and low flux; the efficiency of both membranes (FO/RO) was attributed to porous, mesh fabric, hydrophobicity and steric hindrance. Surface fouling is one of the issues to overcome on the wastewater treatment; thus, forward osmosis alleviated the reverse osmosis membrane fouling as demonstrated by Choi et al. [31], after repeated cleaning membrane process where the permeate flux was recovered. Biopolymer-like substances were persistently accumulated on the membrane surface as seen in **Figure 3**.

Some authors have paid attention on the porosity as main property to develop integrated systems on phenol removal and/or recovery, taking into account the molecular weight (MW) of the species, such as the case of the combined nanofiltration and reverse osmosis [32, 42]. However, in case that a specific compound is desired to isolate, the complexity of the system could include more than two combine steps, for example, an innovative integrated process to recover an important food polyphenol, such as the Gallic acid. The proposal consisting of purification steps based on the MW of the specific molecule with UF-NF-RO and their further separation with an adsorption/desorption resins, where the final product had a phenol concentration of 378 g/L in Gallic acid equivalents and the initial quantity was 2.64 g/L [43].

The membranes contactor is an alternative technology, based on solvent extraction using hollow fiber membranes (membrane-based extraction method), to recover or remove low concentration of aromatic compounds. Two fluid phases flow in adjacent channels with the interface maintained in the intermediate membranes pores; in other words, the process involves extraction of the compound to a second phase stabilizing the aqueous and organic phases within the pores of the polymeric membrane. If compared to the conventional solvent extraction, membrane contactors offer a large interfacial area, a reduction in solvent by-products and lower solvent losses. Nevertheless, the operational pressure range limits the applications of the process. Research challenger is the interface stabilization of fluids in the membrane pores, which affect the operational conditions and the properties of both, membrane materials and fluids [44, 45]. Diverse factors to the design of this kind of membranes include modified surface properties. It can improve the gradual erosion caused by the shear forces generated by the aqueous phase

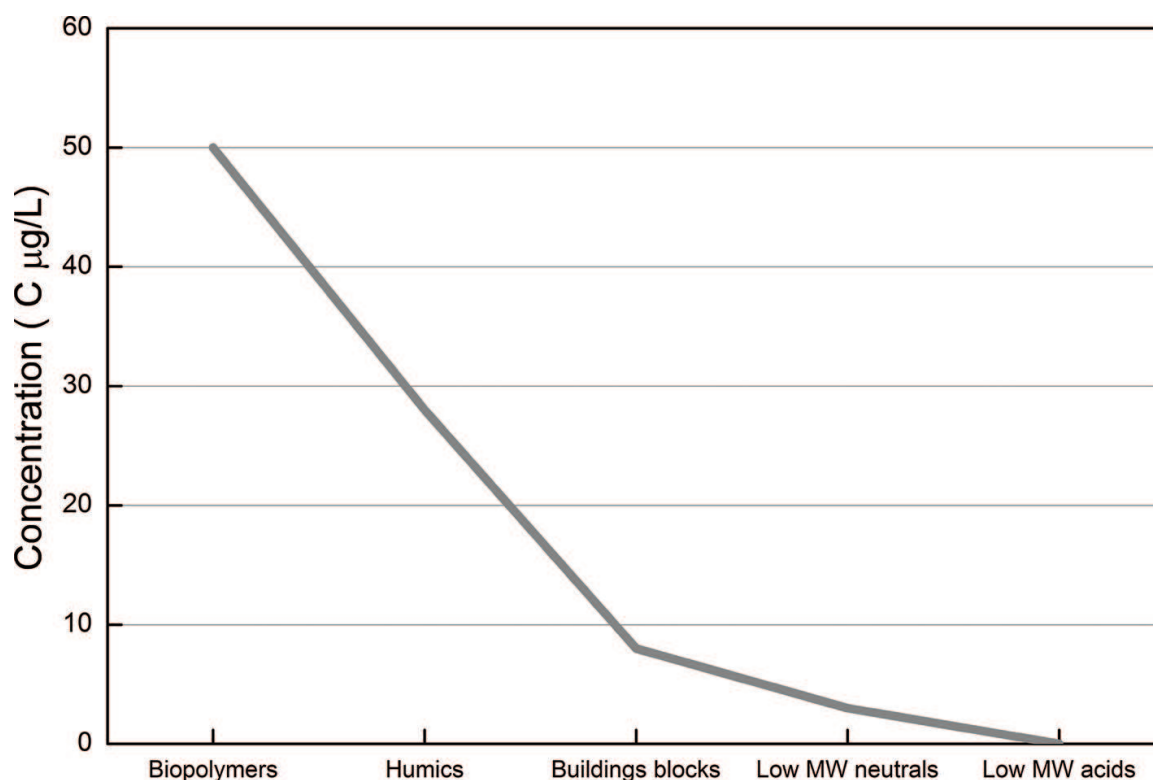


Figure 3. Concentration of DOMs (byopolymers, humic, buildings blocks, low-MW neutrals and low-MW acids) on the fouled membranes surface. Adapted from Choi et al. [31].

flowing over the liquid membrane. Alternatives, such as hollow fiber, supported liquid membrane (HFSLM), with solids-extractants immobilized on the pores of the hydrophobic surface, serve to dissolve a nonvolatile carrier solvent to maintain a high distribution coefficient for the solute. Trioctylphosphine oxide (TOPO) act as extractants in the liquid membranes; due to in solid crystalline powder can be impregnated on a polypropylene membrane, changing from a conventional liquid-liquid extraction into a solvent extraction liquid membrane of aromatic compounds; to study model molecules [46] or applied as osmotic membranes bioreactor (TPPOMBR) [47]. A variant of liquid-liquid phenol extraction and hollow fiber contactor membranes are the liquid membrane processes. Mainly, the process combines liquid-liquid extraction and stripping operations in a single unit operation; pertraction. In a pertraction system, the liquid membrane phase (organic solution phase) separates into two additional liquid phases (feed and stripping phase) which are immiscible (aqueous solution phase). There exist different types of liquid membranes, bulk liquid membranes (BLM), supported liquid membranes (SLM) and emulsion liquid membranes (ELM). The bulk liquid membrane is considering one of the simplest arrangements of liquid membrane systems. Mass transfer, solvent extractants, pH, temperature and rate migration are the foremost drawbacks to study [48–50].

3.1.3. Carbon-based materials (activated carbon and nanomaterials)

Due to structural and surface properties, carbon materials as activated carbon obtained of different sources have been used as effective adsorbents of pollutants from water. However, in

addition to the structural and surface properties, the size of the adsorbents is an important factor that can improve the efficiency of the process, therefore, carbon nanomaterials as carbon nanotubes and graphene have been used as adsorbents of pollutants from water obtaining good results. Thus, investigations related to carbon activated, carbon nanotubes and graphene-based materials used as adsorbents of phenolic compounds from water are reviewed in this section.

Activate carbon (AC) is a carbon material very effective in the removal of pollutants from water. Its effectivity was probed on the removal of bisphenol A (BA). Liu et al. [51] investigated the effect of modification treatments of two AC (W20 and F20) onto removal of BA. The ACs treated with nitric acid were labeled as W20A and F20A and the AC modified with thermal treatment under a flow of N_2 was labeled as W20N and F20N. The highest adsorption capacities of BA were found on W20 (382.12 mg/g) and W20N (432.34 mg/g) samples. The thermal treatment favored more the BA adsorption on AC than the acid treatment. The surface charge density of the different ACs and their content of oxygenated groups are factors very important that affect the BA adsorption. Similarly than other experiments with phenolic compounds, the adsorption of BA onto ACs decreased when the temperature was increasing. The removal by adsorption of Bisphenol A also has been investigated with AC derivatives of coconut and coal with good results [52]. The best results were found in the pH range from 3 to 9. The adsorption capacity of both ACs decreased in pH range (>10), it was attributed to the electrostatic repulsion between the negative charge surface of the ACs and the bisphenolate anion from the ionization of bisphenol A. Factors as surface area and pore volume were determinants for the good adsorption of BA onto ACs; however, surface polarity also played an important role in this adsorption process.

Fasfous et al. [53] studied the adsorption of tetrabromobisphenol (TBBPA) on multiwalled carbon nanotubes (MWCNTs). The results showed that MWCNTs have a high potential for removal of TBBPA from water. The removal of TBBPA after of 60 min was 90%. The adsorption capacity was increasing when the initial TBBPA concentration and contact time were increased. Oppositely, the adsorption capacity of TBBPA decreased when the temperature and pH ($pH > 7$) were increased. The experimental kinetic data were well adjusted to the pseudo-second-order model and the Freundlich and Langmuir models described well the experimental equilibrium data. The adsorption of TBBPA on MWCNTs was spontaneous with exothermic nature. In other investigation for TBBPA removal, Zhang et al. [54] employed graphene oxide (GO) as adsorbent. The experiments were conducted modifying the pH of TBBPA solution in the range from 2 to 12 and the temperature from 288 to 318 K. The results indicated that at 0.3 and 1 mg/L TBBPA concentrations, the maximum adsorption capacities were of 70–90% after of 120 min, indicating an influence of the initial concentration of TBBPA. The adsorption capacity of TBBPA on GO decreased when the temperature of the solutions was increased. The adsorption process of TBBPA on GO was exothermic. These effect of the temperature and type of process were similar when were used MWCNTs. The main interaction mechanisms between TBBPA and GO were π - π interaction and hydrogen bonding. Ji et al. [55] also investigated the removal of TBBPA but using Fe_3O_4 nanoparticles loaded on MWCNTs (MWCNTs- Fe_3O_4) composite and MWCNTs- Fe_3O_4 modified with 3-aminopropyltriethoxysilane (APTS) (MWCNTs/ Fe_3O_4 - NH_2). The solution concentration of the TBBPA was 10 mg/L and the adsorbent dosage was 0.5 g/L for all experiments. The solution pH was adjusted from 1.4 to 9 in order to

optimize the pH for the maximum adsorption capacity of TBBPA on the composites. The results showed that the adsorption capacity of TBBPA on the two composites was increasing when the pH increasing from 1.5 to about 5.5, where the TBBPA is not dissociated. The donor-acceptor interactions between TBBPA and the magnetic nanocomposites through the graphene sheets of MWCNTs, the aromatic structure of TBBPA and π - π interactions between the benzene-ring structure on both of TBBPA and MWCNTs and Hydrogen bonding are the main possible adsorption mechanism of TBBPA on the two nanocomposites. The functionalization of the MWCNTs/ Fe_3O_4 with amine groups improved the adsorption of TBBPA. The maximum adsorption capacity of TBBPA was found on MWCNTs/ Fe_3O_4 nanocomposite (33.72 mg/g). The experimental kinetic data were well adjusted to the pseudo-second-order model.

The removal of phenol, 2-chlorophenol and 4-chlorophenol from aqueous solutions using as adsorbents activated carbon, multiwalled carbon nanotubes and carbon-encapsulated iron nanoparticles (CEINs) was investigated by Strachowski and Bystrzejewski [56]. The surface area of the different materials was found to be 1187, 156 and 36 m^2/g for AC, MWCNTs and CEINs, respectively. All adsorption kinetic experiments were carried out with a 150 mg/L initial concentration of the phenolic compounds and the relation of adsorbent mass and solution volume was 0.5 g/L. The results showed that the maximum adsorption capacity of the phenolic compounds was obtained for AC followed of activated carbon nanotubes (act-MWCNTs), MWCNTs and CEINs in this order. However, the maximum adsorption kinetic rate of the studied adsorbates was found in MWCNTs followed of act-MWCNTs = CEINs and AC, in this order. The highest adsorption capacity was found for 2-chlorophenol (549.5 mg/g). MWCNTs showed a rapid adsorption kinetic and the equilibrium concentration was achieved around of 5 min. The adsorption kinetic data were well fitted to the pseudo-second-order model.

Different studies have investigated the removal of phenol from water employing different carbon materials. de la Luz-Asunción et al. [13] realized the removal of phenol from aqueous solutions with carbon nanomaterials of 1D and 2D. The adsorbents used were MWCNTs and oxidized MWCNTs (O-MWCNTs), pristine single-walled carbon nanotubes (SWCNTs) and oxidized SWCNTs (O-SWCNTs), GO and reduced graphene oxide (rGO). The oxidation of the carbon nanotubes was carried out in microwave using H_2O_2 as oxidant agent. This method reduced the time of oxidation. GO and rGO were obtained by Hummer's method. The results showed that the pristine 1D nanomaterials (MWCNTs and SWCNTs) have a better adsorption capacity than rGO, however, GO presents a higher adsorption capacity than O-MWCNTs and O-SWCNTs. The best adsorption capacities of phenol were obtained by GO and O-SWCNTs. Oxygenated functional groups play an important role in the removal of phenol with carbon nanomaterials of 1D and 2D. The kinetic adsorption data and the adsorption equilibrium data were well fitted to the pseudo-second-order model and the Freundlich model, respectively. **Figure 4** shows the fit of Freundlich isotherms on the adsorption of phenol onto carbon nanomaterials. The main mechanism of adsorption of phenol onto the different carbon structure was due to π - π interactions between the aromatic structure of the graphitic layers and aromatic rings of the phenol structure. Other mechanism proposed in the adsorption of phenol onto carbon nanomaterials was hydrogen bonding. Li et al. [57] also studied the removal of phenol from aqueous solutions onto rGO. The effect of phenol solutions pH on the adsorption capacity of rGO was analyzed

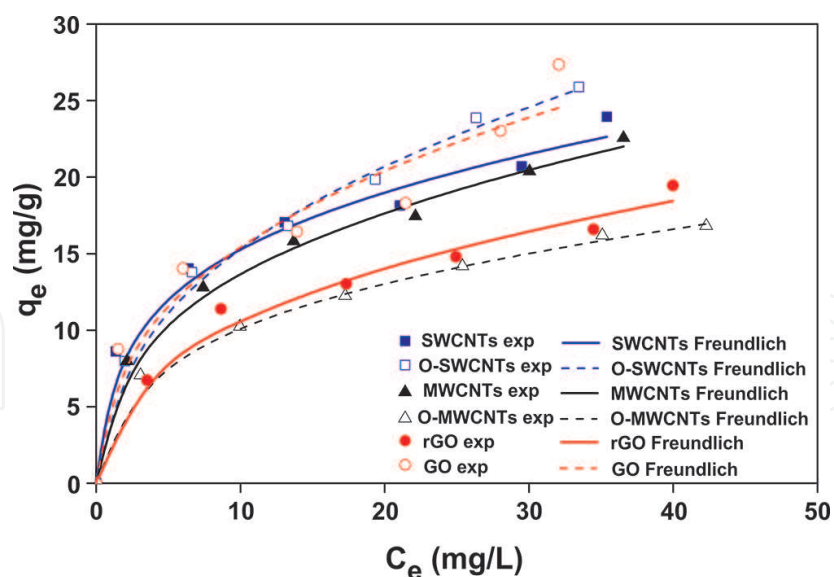


Figure 4. Freundlich isotherms of phenol adsorption onto carbon nanomaterials. Reprinted and adapted with permission from de la Luz-Asunción et al. [13]. Copyright © 2015, Hindawi Publishing Corporation.

when the pH increased from 2.3 to 11.5. The highest rGO adsorption capacities were found when the pH of phenol solutions was adjusted between 4 and 6.6. In this pH range, the complexation capability of the oxygenated groups present on the surface of rGO increased. Besides, the graphitic structure of rGO and the aromatic ring of phenol interact through of π - π interactions. The phenol removal increased when the rGO concentration was increasing gradually in the range from 0.5 to 1.7 g/L. Thermodynamic study revealed that the adsorption process of phenol onto rGO was endothermic and spontaneous.

Others phenolic compounds have been studied through of the adsorption process with carbon materials. Mehrizad and Gharbani [58] used rGO as adsorbent for the removal of 4-Chloro-2-nitrophenol (4C2NP) from aqueous solutions. The adsorption capacity of rGO onto 4C2NP removal decreased with increasing dosage of adsorbent from 0.2 to 0.8 g/L but in all cases the adsorption velocity was rapid (10 min) reaching the equilibrium at about 60 min. The best results of adsorption were found in the pH range from 3 to 7, 298 K and initial concentration of 10 mg/L. The pseudo-second-order model described well the adsorption kinetic data and the equilibrium adsorption data were well fitted to the Freundlich model. The adsorption of 4C2NP was found to be spontaneous and exothermic process in the temperature range from 298 to 328 K.

The adsorption of other phenol chloride compound onto carbon materials was studied by Pei et al. [59]. For the adsorption of 2,4,6-trichlorophenol (246TCP) from aqueous solutions were used rGO and GO as adsorbents. The adsorption of 246TCP onto rGO and GO was favored to pH range from 2.0 to 6.0. After of pH 6.0, the fraction of negatively charged 246TCP species increase in the solution causing electrostatic repulsion with negatively charged surfaces of rGO and GO. The adsorption capacity of rGO was higher than GO. The adsorption experimental data of 246TCP onto rGO and GO were well fitted to Freundlich equation.

Definitely, the application of carbon materials on the removal of phenolic compounds by adsorption process is a good alternative for the remediation of the contamination problem of water by this kind of compounds.

3.2. Photocatalysis

In advanced oxidation process, heterogeneous photocatalysis is a process with important potential for the degradation of recalcitrant organic contaminants in water. In this process, the use of a radiation source that generally is UV light and a semiconductor material as catalyst is necessary. The photon energy is converted into chemical energy which is capable of to degrade the organic pollutants. The photogenerated holes in the valence band diffuse to particle semiconductor surface and react with organic molecules present in aqueous solution forming hydroxyl radical ($\text{OH}\cdot$). Meanwhile, electrons in the conduction band participate in reduction processes, reacting with molecular oxygen in the air to produce superoxide radical anions ($\text{O}_2\cdot^-$). Titanium dioxide (TiO_2) is the most important semiconductor used in the heterogeneous photocatalysis due to different properties such as superhydrophilicity, chemical stability, long durability, nontoxicity, low cost and transparency to visible light; however, other semiconductor materials have been used also in this process with good performance in the contaminants degradation from water. The size of the semiconductors particles is an important factor that has influence on the efficiency of the photocatalytic process. Others important factors in the photocatalysis are the specific surface area, pore volume, pore structure, crystalline phase and the exposed surface. On the other hand, the charge separation is a problem that affects the efficiency of the photocatalytic process and whereby the improving of photocatalysts is a challenge. Thus, in this section, it is reviewed different works related to semiconductor particles and nanoparticles in the photocatalytic degradation of phenolic compounds. Also, we present some investigations associated with graphene nanomaterials focused to reduce the charges recombination in the photocatalytic degradation of phenolic compounds.

3.2.1. Semiconductor particles and nanoparticles

Although TiO_2 is the semiconductor more employed as catalyst in the heterogeneous photocatalysis, at present, there exist others semiconductor materials that have been developed and employed in the degradation of pollutants from water obtaining good results. The reduction in the particle size is an important factor that can improve the photocatalytic performance due to an increase in the surface area. With the aim to improve the results on the degradation of contaminants from water, also, the combination of semiconductor particles has been developed, obtaining composites and hybrids materials. A review of investigations about the degradation of phenolic compounds using semiconductor particles is presented.

Phenol is the phenolic compound more studied in the photocatalysis. Different semiconductor materials have been used in its degradation, but TiO_2 is the semiconductor more used in the photocatalytic process. Ye and Lu [60] synthesized anatase TiO_2 nanocrystals with exposed $\{0\ 0\ 1\}$ facets; these materials were obtained in the presence of fluoride ions. The photocatalytic results indicated that the oxidation of phenol increased with the rise

in the percentage of {0 0 1} facets of TiO_2 . The main intermediates produced during the photocatalytic degradation of phenol were catechol and hydroquinone. The improving in the photocatalytic performance of TiO_2 nanocrystallites was attributed to the synergistic effects of the exposed {0 0 1} facets and surface fluorination. The TiO_2 doped have been used to improve the photocatalytic activity on the phenol degradation [61]. An important efficiency in the degradation of phenol was found. Best results of phenol degradation were found at high pH values. Composites of $\text{V}_2\text{O}_5/\text{N,S-TiO}_2$ were used as photocatalyst for phenol degradation under direct solar light [62]. The sample of $\text{V}_2\text{O}_5/\text{N,S-TiO}_2$ activated at 500°C showed the best photocatalytic performance, reaching a degradation of 88% of phenol solution (100 mg/L) in 4 h. The V_2O_5 component played a key role for the visible light activity of the composite system at longer wavelengths. The photocatalytic activity of the composite was mainly attributed to the acid sites present on the surface; however, other factors such as the surface area, anatase/rutile ratio and the absorption at longer wavelengths were important.

The phenol degradation also was investigated by Liu et al. [63]. In this investigation, BiPO_4 synthesized through hydrothermal process was used as photocatalyst and the process was assisted with H_2O_2 . The initial concentration of phenol solution was 50 mg/L and the catalyst concentration was 0.5 g/L. The results indicated that the phenol could be mineralized after of 4 h with BiPO_4 but not by H_2O_2 . The efficiency of BiPO_4 was attributed to the high potential photogenerated holes in the valence band and the high separation efficiency of electron hole pairs.

ZnO , other important semiconductor also have been used in the phenol degradation. Europium-doped flower like ZnO hierarchical [64], Ni-loaded ZnO nanorods [65], cerium-doped ZnO hierarchical micro/nanospheres [66] and ZnO nanosheets immobilized on montmorillonite [67] are some of the ZnO -based catalysts that have been employed successfully on the phenol degradation.

Although Al_2O_3 is known as insulator material, Tzompantzi et al. [68] synthesized an Al_2O_3 by the sol-gel method. The Al_2O_3 was dried and annealed at 400, 500, 600 and 700°C . The samples were tested in the degradation of phenol from water. The best results of degradation were obtained with the sample calcinated at 400°C . The photocatalytic activity of the Al_2O_3 can be due to the modification in the Al-O bonds distances and hydroxyl groups present in the Al_2O_3 structure, delaying the recombination process. The sample annealed to 400°C also was tested in the p-cresol and 4-chlorophenol degradation. The major degradation was obtained on 4-chlorophenol, followed by phenol and p-cresol, in this order.

The degradation of 4-chlorophenol also have been studied by different investigation groups. A composite of anatase/titanate nanosheet was employed by Liu et al. [69] for phenol degradation from water. Titanate acted as the main adsorption site. The phenol degradation was carried out in a binary system. About of 99% of phenol was degraded within 120 min. The important photocatalytic efficiency was attributed to the synergetic effect on the photo-oxidation of 4-chlorophenol and photoreduction in Cr (VI) due to the efficient separation of electron-hole pairs. In other investigation of phenol degradation, Naeem and Ouyang [70] investigated the degradation of 4-chlorophenol on TiO_2 supported on materials as activated carbon, silica

Proposal system	Type of photocatalytic material	Degraded component	References
One photocatalytic step	Bismute vanadate, BiV ₄	Phenol	[71]
	Ag/ZnO	Nitrophenol	[72]
Photocatalytic-UV-C irradiation	BiPO ₄ photocatalytic activity degradation under UV-C irradiation	Phenol	[73]
Heterogeneous photocatalytic-UV-laser irradiation	ZnO nanoparticles coupled under UV-laser irradiation	Phenol	[74]
Solar light photocatalytic degradation	Ag-core TiO ₂ nanoparticles under solar light irradiation	Phenol	[75]

Table 1. Photocatalytic materials used on the removal of phenolic compounds.

(SiO₂) and zeolite (ZSM-5). All materials TiO₂-supported reached a better photocatalytic performance on the 4-chlorophenol degradation than TiO₂ alone. AC was found to be the best support followed by ZSM-5 and SiO₂. The maximum degradation of 4-chlorophenol using TiO₂-AC as photocatalyst was 89.7%. Others photocatalytic materials that have been studied on phenols degradation in water are shown in **Table 1**.

3.2.2. Graphene materials and graphene-based materials

Graphene materials have the capacity to transfer the charges rapidly which is very important to reduce the charge recombination. Besides this, the photocatalytic activity of graphene oxide, a functional form of graphene, has been proved [76]. Therefore, a review of the investigations where graphene materials have been used individually and in combination with others compounds for the removal of phenolic compounds is presented.

Bustos-Ramirez et al. [77] investigated the removal of phenol by photocatalysis using as photocatalyst GO synthesized under different conditions. The time of oxidation (2, 4 and 6 h) and the degassing units (55 and 65) were modified. The samples were labeled as GEO-2-55, GEO-2-65, GEO-4-55, GEO-4-65, GEO-6-55 and GEO-6-65. The experiment was carried out in a batch photoreactor containing 100 mL of initial concentration of 100 mg/L. The time of reaction was 2 h and as radiation source an UV lamp of 254 nm was used. The band gap obtained by all samples indicated that these materials could act as photocatalysts. The best results of phenol removal were found with the sample GO-2-55 (38.62%), followed by GO-6-55 (14.96%) and GO-4-55 (12.29%). **Figure 5** shows the absorption spectra of phenol before and after of the photocatalysis process using the GO-2-55 sample as photocatalyst. The degassing units and the oxygen functional groups played an important role in the preparation of GO and its photocatalytic activity, respectively. The obtained results indicated that GO under specific synthesis conditions is a very viable material for its use in photocatalytic processes for the contaminants degradation.

A better photocatalytic activity of GO was found on the degradation of 4-clorophenol (4-CP) [78]. The photocatalytic experiments were carried out using 30 mL of phenol solution with initial concentration of 30 mg/L, pH 7 and GO dosage of 0.8 g/L. As irradiation source was

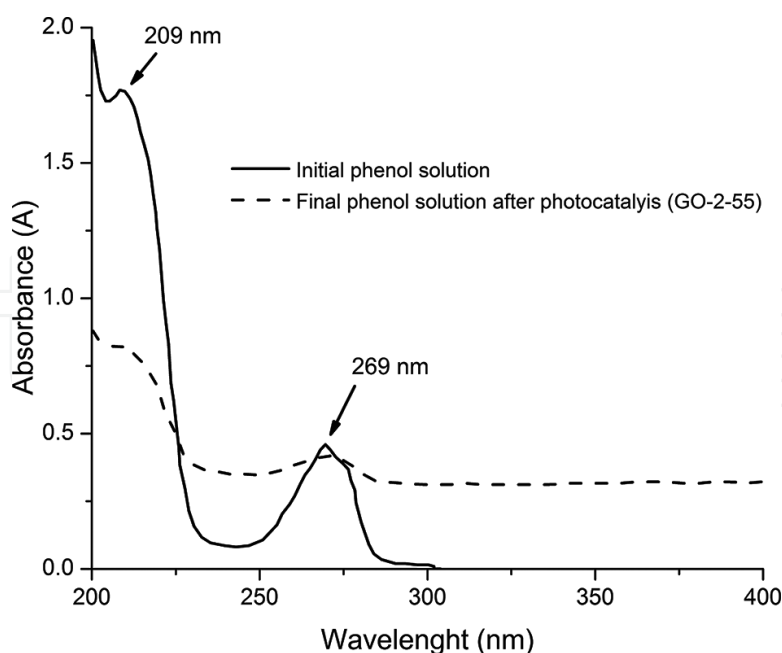


Figure 5. Phenol absorption spectra at initial and after of 2 h of photocatalytic reaction (reprinted with permission of Karina Bustos-Ramirez et al. [77]. Copyright © 2015, used under the Creative Commons Attribution License).

used an UV lamp (Pencil UV lamp, 254 nm and 5.5 W), which was introduced in the phenol solution. The photocatalytic results indicated that about of 80% of phenol was removed of the solution in a time of 100 min. About of 50% of removal was obtained in the first 20 min. The results of the chemical oxygen demand (COD) tests indicated that 97% of the organic matter was removed (**Figure 6**). Aromatic compounds and carboxylic acids are the main by-products generated in this photocatalytic process. The high efficiency of GO on the 4-CP degradation indicated that graphene materials have an important future in the photocatalysis area.

On the other hand, some investigations have studied the degradation of phenolic compounds employing composites of graphene and semiconductors particles. Some composites of graphene/TiO₂ have been synthesized by different routes for the degradation of phenol from water [79–81]. In all cases, the combination of graphene materials and TiO₂ particles improve the performance obtained with only TiO₂. This was attributed to an increase in the adsorption of phenol molecules, a better and more efficient charge separation and the improvement light absorption. The degradation of phenol was so well studied using other composites of graphene-based materials with good results [82–86].

Other phenolic compound that has been investigated was Bisphenol A. Wang et al. [87] synthesized a GO/Ag₃PO₄ composite and proved its efficiency on the BA degradation. The degradation of BA was carried out using 75 mL of a solution of BA with initial concentration of 20 mg/L and 75 mg of catalyst. A 300 W Xe lamp with a 400 nm cutoff filter was used as irradiation source. The results indicated that the GO/Ag₃PO₄ (6 wt%) composite improved the degradation of BA with respect to the pure Ag₃PO₄. This enhancing of the photocatalytic activity of GO/Ag₃PO₄ was attributed to the presence of GO, which contributed to the separation electron-hole pairs in the composite. Similar results were found by Chen [88] on the

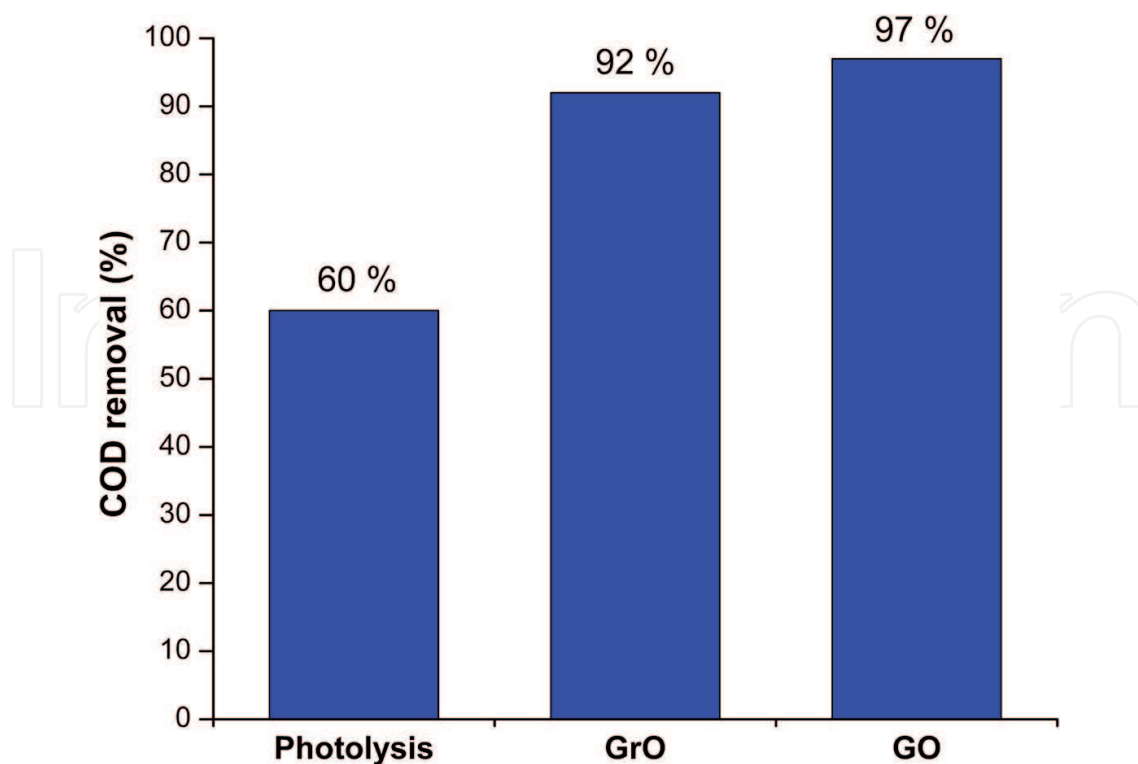


Figure 6. COD removal percentage obtained at the end of photolysis and photocatalysis tests using as catalysts (graphite oxide) GrO and GO on the 4-CP degradation. Adapted from Bustos-Ramírez et al. [78]; BioMed Central. 2015.

2,4-dichlorophenol degradation using as photocatalyst a $\text{GO}/\text{Ag}_3\text{PO}_4$ (5 wt%) composite. It is important to note that in both investigations was used visible light which is one of the most important challenges in the photocatalysis process.

In general, the revised investigations revealed that the combination of graphene materials with different semiconductors particles improve the degradation efficiency of the different phenolic compounds from water with respect to the individual particles. Besides, the graphene oxide showed an important photocatalytic activity capable of degrading the phenolic compounds.

3.3. Others

3.3.1. Electrochemistry

Currently, efforts have been made at developing more effective technologies to remove persistent organic pollutants. Advanced oxidation processes are based on the in situ production of reactive hydroxyl radicals ($\text{OH}\cdot$) which non-selectively react with most organics, being able to degrade even resistant compounds. Although, $\text{OH}\cdot$ radicals are extremely reactive and cannot exist for a longtime, they can be used to decompose almost all organic to inorganic compounds [89, 90]. Combination process such as ozone, ultraviolet (UV) light, a semiconductor photocatalyst, hydrogen peroxide, ultrasound, Fenton reagent, photo-Fenton are widely studied to generate hydroxyl radicals ($\text{OH}\cdot$). Recently, electrochemical advanced oxidation processes (EAOPs) are a promising derivative strategy that comes from AOPs. The easiest EAOPs method is the anodic oxidation (AO), where the organics can be directly oxidized

at the anode surface by electron transfer and/or indirectly oxidized by $\text{OH}\cdot$ barely physisorbed at the anode surface with the presence of agents at the bulk solution such as oxidizing reagents, O_3 , chlorine species, persulfates or H_2O_2 . On the other hand, when AO accomplish with cathodic electrogeneration of H_2O_2 , the process is a cathodic oxidation. When H_2O_2 is electrochemically produced in the presence of Fe^{2+} at the bulk of reactions, as well as the $\text{OH}\cdot$, it brings about the electro-Fenton process (EF). The phenomena originate a variety of techniques, for example, peroxi-coagulation (PC), Fered-Fenton, electrochemical peroxidation and sonoelectro-Fenton, or combine systems which include biological, chemical coagulation, electrocoagulation (EC) and membrane processes [90].

Phenol belongs to the recalcitrant pollutants commonly treated by conventional physico-chemical and biological methods, so advanced oxidation (AO) represents an actual process for treatment of wastewater containing toxic persistent organic compounds. Pimentel et al. [91] applied a variant of advanced oxidation techniques to remove phenolic pollutants. They studied the oxidative degradation of aqueous phenol solutions in acidic medium by electro-Fenton technique using a carbon felt cathode and platinum anode in order to evaluate the mineralization efficiency, results evidenced that pH 3 enhance hydrogen peroxide electrochemical production, the most effective catalysts was ferrous iron ion at optimal concentration of 0.1 mM. Phenol oxidation by hydroxyl radical follows a pseudo-first-order kinetic with a rate constant of 0.037 min^{-1} . Additionally, phenol hydroxylation generate maleic, fumaric, succinic and glycolic acids in the beginning of the reaction; benzoquinone, catechol and hydroquinone as intermediate and oxalic and formic acids as final products. The total mineralization of phenol and its reactions intermediates put in context the effectiveness of the electro-Fenton process. If the process is combined, it could arises higher efficiencies as demonstrated Wang et al. [92], when combining electrocatalytic process and membrane bioreactor (MEBR), increases 11% the quality of the phenol removal, compared to the conventional and sum of the two individual processes; as result of the synergetic enhancement effect in one reactor. Also it was found that one of the degradation products is the benzoquinone (2,6-di.tert-butyl-p-benzoquinone).

Following with the electrochemical tendency process, Vasudevan [93] studied the peroxi-electrocoagulation method using mild steel as anode and graphite as cathode, obtaining 92% of removal from an initial phenol concentration of 2.5 mg/L and pH 2. The electro-coagulation (oxidation of sacrificial anode), amalgamates advantages from the separate procedures. Coagulants introduced without corresponding sulfate or chloride ions are more efficient to remove contaminants from waste, mainly when eliminate competitive anions and use a highly pure coagulant, it can be obtained lower metals residuals and less sludge as by-products if used metal salts. Moreover, when electrochemical reactors operate at high cell potential under acidic pH, the anodic process occurs in the potential region of water discharge and consequently hydroxyl radicals ($\text{OH}\cdot$) are produced. This confirms that, ferrous ion generated in electrocoagulation function as coagulation materials and catalytically creates $\text{OH}\cdot$ radicals according to the conditions. Therefore, EAOPs can be even more effective than their chemical analogous, showing higher removal rates and greater reductions in organic toxic wastewater. EAOPs offer, the availability of higher amounts of H_2O_2 at the reaction beginning in the chemical processes; mainly in the presence of aromatic compounds; which is the case of phenol and phenolic molecules, demonstrated to induce faster initial removal

rates for organic pollutants. Additionally, while increases the efficiency of the process the waste by-products diminish during the oxidation reaction to remove phenol compounds. Thus, EAOPs challenge needs to consider the implementation of high H_2O_2 quantities since the reaction initiation, as well as take into account aspects related to the investment costs, design of electrochemical cell; meaning less expensive hardware and electrodes materials and more versatile systems. In case of the light-assisted source, also should be considered, the UV lamps or photoreactors for natural sunlight capture. Even more, the operational costs include electrical energy for the electrochemical cell, plant operation, reagents and maintenance [90].

Nowadays, there is a growing interest to establish a great deal of attention to develop new strategies based on nanomaterials in conjunction with single and/or hybrid AOPs to remove or recover phenol species. One of the advantages of nanomaterial is the high surface area, where the volume/mass ratio will significantly improve the adsorption properties. Some nanomaterials studied are semiconductors, nanoclays, nanocatalyst, nanoclusters, nanorods, nanocomposites; for example, TiO_2 , palladium, Fe_3O_4 , Cerium oxide and magnetic chitosan, along or combined, $\text{CoFe}_3\text{-xO}_4$, CoFe_2O_4 magnetic nanoparticles, BiAg_xO_y . From this point, can be synthesized nanoparticles, nanomembranes and nanopowders able to apply on the AOP technology [94].

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