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An Analysis on the Removal Process of Organic Pollutants in Water: A Review

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Abstract – Wastewater from manufacturing or chemical industries constitutes a very important source of water pollution. Industrial wastewater usually contains specific and readily identifiable chemical compounds. These include a variety of organic compounds. Many of these compounds, particularly the aromatic organic compounds are either carcinogenic or mutagenic in nature, which resist biological oxidation processes normally used by the industries for treating wastewater. These compounds are stable and persistent in nature with long-lasting adverse effects and they get dispersed over large areas before undergoing transformation into some other compounds. Many of these organic compounds are synthesized in the laboratory and even in very low concentration, they present a long term hazard as they are likely to accumulate either in food chain or in water sediment.

The halogenated aromatic hydrocarbons are particularly stable and their solubility in fat aids accumulation in living beings. The majority of well-known persistent organic pollutants belong to the category of halogenated aromatic hydrocarbons. These compounds are not natural and are products or byproducts of various industrial processes, particularly the petroleum industry. Many of these compounds, like trihalomethanes (THM), chlorinated alkanes and alkenes, halogenated acetonitriles, chlorophenols, chlorinated humic acids, aminoacids and benzoquinone appear as chlorination byproducts in drinking water treatment.

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INTRODUCTION

Water is the most precious natural resource that exists on our planet as over 70% of the Earth's surface is covered by water. When Neil Armstrong saw the Earth from the Moon, it appeared blue! This is because water covers more than two-thirds of the Earth's surface. But fresh water represents less than 0.5 **%** of the total water on Earth (Zacharia, 2004). Surface water is the resource for the provision of drinking water, irrigation water for agricultural activities, and process water for industrial activities.

Every human activity affecting watershed components can have a strong impact on the surface water pollution. Water pollution occurs when water is adversely affected due to the addition of large amounts of materials to the water. The principal sources of water pollution are:

- Industrial discharge of chemical wastes and byproducts.
- Discharge of poorly treated or untreated sewage.
- Surface runoff containing pesticides.
- Surface runoff containing spilled petroleum products.
- Discharge of contaminated and/or heated water used for industrial processes
- Excess nutrients added by runoff containing detergents or fertilizers
- Acid rain caused by industrial discharge of sulfur dioxide (SEPA 2005).

The sources of water pollution are categorized as point sources and non-point sources of pollution. Point sources of pollution occur when the polluting substance is emitted directly into the waterway. A pipe spewing toxic chemicals directly into a river is an example. A non-point source occurs when there is runoff of pollutants into a waterway, for instance when fertilizer from an agricultural field is carried into a stream by surface runoff. The point sources include effluent outfalls from factories, refineries, and waste treatment plants, etc., that emit fluids of varying quality directly into water bodies. Non-point sources include contaminants that enter the water supply from soils/groundwater systems and from the atmosphere via rain water.

Wastewater from manufacturing or chemical processes in industries contributes to water pollution. Industrial wastewater usually contains specific and readily identifiable chemical compounds. During the last fifty years, the number of industries in India has grown rapidly. But water pollution is concentrated within a few sub-sectors, mainly in the form of toxic wastes and organic pollutants. Out of this a large portion can be traced to the processing industries.

The wastewater from various industries contains a high concentration of organic compounds. Many of these compounds, particularly the aromatic organic compounds are either carcinogenic or mutagenic in nature and they resist biological oxidation processes normally used by the industries for treating wastewater.

All toxins entering the environment can be. regarded as environmental poisons. Certain pollutants can, acting over long periods, harm living organisms even in low concentrations. This means that pollutants that are stable and thus persistent have a great ability to act as environmental poisons. Their stability means not only that their effects are long-lasting, but also that they are dispersed over large areas before being broken. Many areas of surface water are now contaminated with heavy metals, POPs (persistent organic pollutants), and nutrients that have an adverse effect on health.

ORGANIC POLLUTANTS IN WATER

The source of organic matter in water is industrial effluents and domestic sewage. The organic matter is mainly responsible for depleting oxygen in the water column as it decomposes, stressing or suffocating aquatic life in the process. Water contains aliphatic-, cycloaliphatic-, aromatic and polycyclic aromatic hydrocarbons. Small quantities of these compounds cause taste and odor problems in drinking water. Aromatic hydrocarbons, particularly the polyaromatic hydrocarbons (PAH) are generally carcinogenic in nature and have harmful health effects.

Many synthetic organic compounds can be found as trace contaminants in surface water. Even if they are present in very low concentration they can represent a long term hazard due to accumulation process either in food chain or in water sediment. Source of these organic compounds can be the agricultural activities (e.g. pesticide use), accidents (like spillage from oil pipeline) and the industrial discharges. Wastewater deriving from chemical industries is the main source of surface water contamination with synthetic organic compounds, the type of pollution varying according to the type of processed material.

Natural Organic Matter-

The decomposition of plant, animal and microbial material in soil and water produces a variety of complex organic molecules, collectively called natural organic matter. These compounds include carbohydrates, amino acids, proteins, fats and humic acids. Amino acids and proteins provide utility nitrogen for microorganisms in soil and water. Natural organic matter (NOM) occurs in all natural water sources and water high in NOM may be more costly to treat.

The variety of the components in NOM changes from water to water (seasonal changes, climate effects and drought) which leads to variation in the reactivity with chemical disinfectants such as chlorine, ozone and chlorine dioxide. Many of the disinfection by-products (DBPs) formed by the reaction of NOM with disinfectants, usually chlorine, are reported to be toxic, carcinogenic and mutagenic to humans if ingested over an extended period of time. Thus, natural organic matter creates problems in water disinfection and supply, requiring their removal to minimize color and odour in water, and also to prevent formation of potentially harmful chemical byproducts during chlorination. Through a process called "bio-fouling", natural organic matter is also a major culprit in degrading the performance of membrane filtration systems used for water purification and desalination.

Organic matter in groundwater plays important roles in controlling geochemical processes by acting as proton donors/aeceptors and as pH buffers, by affecting the transport and degradation of pollutants, and by participating in mineral dissolution/ precipitation reactions. Dissolved and particulate organic matter may also influence the availability of nutrients and serve as a carbon substrate for microbially mediated reactions. Numerous studies have recognized the importance of natural organic matter in the mobilization of hydrophobic organic species, viz., the metals (e.g. Pb, Cd, Cu, Zn, Hg, and Cr), and radionuclides (e.g. Pu, Am, U, and Co). Many contaminants that scientists view as virtually immobile in aqueous systems can interact with dissolved organic carbon or colloidal organic matter, resulting in migration of hydrophobic chemicals far beyond distances predicted by strueture/activity relationships. Although organic matter is often present in low concentrations in subsurface systems, this organic matter can exhibit significant reactivity with contaminants. In addition, these compounds are reactive substances that are potential precursors for the formation of disinfection by-products resulting from water treatment practices.

Organic matter in surface and groundwater is a diverse mixture of organic compounds ranging from macromolecules to low molecular weight compounds such as simple organic acids and short-chained hydrocarbons. Historically, organic matter in natural waters has been arbitrarily divided into dissolved

(DOC) and particulate organic carbon (POC), based on filtration through a 0.45 pm filter. No natural cutoff exists between these two fractions and the distinction is arbitrary, based on the filtration of the sample. Overlapping the dissolved and particulate fractions is the colloidal fraction, which consists of suspended solids that are operationally considered solutes. Colloidal organic matter in natural waters is composed of living and senescent organisms, cellular exudates, and partially-to-extensively degraded detrital material, all of which may be associated with mineral phases. Generally, DOC is in greater abundance than POC, accounting for approximately 90 % of the total organic carbon of most waters.

Microbial degradation of organic matter results in the formation of many of the compounds that comprise DOC, especially non-volatile organic acids that dominate the DOC in most aquatic environments. Many of these organic acids are considered refractory because the rates of subsequent biodegradation are slower than for other fractions or classes of organic matter. Organic matter derived from different source materials has distinctive chemical characteristics associated with those source materials. Organic matter derived from higher plants, for instance, has been found to have relatively large amounts of aromatic carbon, is high in phenolic content, and low in nitrogen content. Microbially-derived organic matter (from algae and bacteria), on the other hand, has greater nitrogen content, and low aromatic-C and phenolic content.

In ground water, there are 3 main natural sources of organic matter: organic matter deposits such as buried peat, kerogen and coal; soil and sediment organic matter, and organic matter present in waters infiltrating into the subsurface from rivers, lakes and marine systems. The relative contributions of these sources of organic matter varies between different water bodies, but there is presently no way to quantify this variation based on chemical characterization of the organic matter. Once in the system, microbial processes continue to slowly alter the structure and chemical reactivity of the organic matter.

A number of significant mechanisms can be responsible for the transport or retention of organic molecules in the subsurface. Once in the system, organic compounds, whether they can be anthropogenic or naturally derived, can be truly dissolved, associated with immobile particles or associated with mobile particles. Mobile particles include DOC, DOC-iron complexes and colloids. For an organic compound, each state is related to the other states through equilibrium partitioning and air/water exchange.

The magnitude of the partitioning coefficients and the abundance of sorbents determine the mechanisms and enhancement of transport for a particular organic compound. Regardless of environment, chemical reactivity and speciation will be controlled by thermodynamics and reaction kinetics.

Organic particles in the water may harbor harmful bacteria and pathogens. Infection by the microorganisms may occur if the water is used for primary contact or as a raw drinking water source. Treated drinking water will not present the same health risks. In a potable drinking water plant, all organics should be removed from the water before distribution.

High organic inputs trigger deoxygenation. If excess organics are introduced to the system, there is potential for complete depletion of dissolved oxygen. Without oxygen, the entire aquatic community is threatened. The only organisms present will be airbreathing insects and anaerobic bacteria. If all oxygen is depleted, aerobic decomposition ceases and further organic breakdown is accomplished anaerobically. Anaerobic microbes obtain energy from oxygen bound to other molecules such as sulfate compounds. Thus, anoxic conditions result in the mobilization of many otherwise insoluble compounds.

Five-day Biochemical Oxygen Demand (BODS) is defined as the amount of oxygen required by bacteria to decompose organic matter for a specified time (usually 5 days) under aerobic conditions. The amount of oxygen reported with this method represents only the carbonaceous oxygen demand (CBOD) or the easily decomposed organic matter. BOD5 is commonly used to measure natural organic pollution. Chemical Oxygen Demand (COD) is defined as the oxygen equivalent of the organic portion of the sample that is susceptible to oxidation by a strong chemical oxidant, COD does not distinguish between refractory or "inert" organic matter.

Biodegradable organic matter-

Biodegradable organic matter in water is broken down by the activity of microorganisms and the decomposition products enter into the biogeochemical cycles. They act as pollutants only when their quantity is large and they are not degraded at the right time. Examples of such pollutants are domestic waste products, urine and faecal matter, sewage, agricultural residue, paper, wood, cloth, etc.

Untreated or inadequately treated municipal sewage is a major source of biodegradable organic matter in surface and ground water in the developing and the under-developed countries where scientific treatment of sewage is almost absent The biodegradable organic matter uses up substantial amounts of oxygen as the organics are being used by micro-organisms as food and in the process, upset the ecological balance of rivers and lakes.

Non-biodegradable Organic matter-

Many aromatic hydrocarbons are both fat-soluble and persistent. If these compounds become halogenated (i.e. if their hydrogen atoms are replaced by chlorine, bromine or other halogens), their stability and their solubility in fat both tend to increase further. In some cases toxicity also increases. The majority of well-known persistent organic pollutants thus belong to the category of halogenated aromatic hydrocarbons (EPA, 2006). Clorinated organic compounds are not natural.

Tap water contains halogenated organic compounds, polychlorinated biphenyls and chlorinated pesticides. These compounds are toxic to human health. POPs or persistent organic pollutants represent the most harmful substances for the ecosystem and human health. These chemicals can accumulate in fish and cause serious damage to human health. Where pesticides are used on a large-scale, groundwater gets contaminated and this leads to the chemical contamination of drinking water.

The POPs are considered as hazardous because of four characteristics:

(i) they are toxic;

(ii) they are persistent, they resist normal processes that break down contaminants;

(iii) they accumulate in the body fat of people, marine mammals, and other animals and are passed from mother to fetus; and

(iv) they can travel great distances with wind and water currents (Zacharia et al, 2004). POPs have been linked to adverse effects on human health and animals, such as cancer, damage to the nervous system, reproductive disorders, and disruption of the immune system. Because they circulate globally via the atmosphere, oceans, and other pathways, POPs released in one part of the world can travel to regions far from their source of origin.

Another group of POPs is the pesticides, which were originally invented and used effectively to better the human environment by controlling undesirable life forms such as bacteria, pests, and foraging insects. Their effectiveness, however, has caused considerable pollution. The persistent, or hard, pesticides, which are relatively inert and non-degradable by chemical or biologic activity, are also bio accumulative; that is, they are retained within the body of the consuming organism and are concentrated with each ensuing level of the biologic food chain.

Runoffs from farms, backyards, and golf courses contain pesticides such as DDT that in turn contaminate the water. Leachates from landfill sites are another major contaminating source. Their main effects on the ecosystem and health are endocrine and reproductive damage in wildlife. Groundwater is susceptible to contamination, as pesticides are mobile in the soil. It is a matter of concern as these chemicals are persistent in the soil and water.

Water disinfection byproducts-

Chlorine is added to the drinking water by municipal authorities to destroy diseasecausing bacteria. The following chlorination by-products are found in drinking water trihalomethanes (THM), chlorinated alkanes and alkenes, halogenated acetonitriles, chlorophenols, chlorinated humic acids, aminoacids and benzoquinone. Of these, the trihalomethanes are the most frequent chlorinated side products, deriving from methane, where three hydrogen atoms are exchanged for three halogen atoms. Many trihalomethanes have mutagenic and carcinogenic effects.

EFFECTS OF ORGANIC POLLUTANTS

The effects of water pollution are not only devastating to people but also to animals, fish, and birds. Polluted water is unsuitable for drinking, recreation, agriculture, and industry. It diminishes the aesthetic quality of lakes and rivers. More seriously, contaminated water destroys aquatic life and reduces its reproductive ability. Eventually, it is a hazard to human health. Nobody can escape the effects of water pollution. Toxicity of an organic pollutant is defined as its inherent ability to cause an adverse health effect, such as the ability to induce cancer, birth defects and other illnesses in animals and humans.

Among the many organic chemicals that exhibit acute toxicity are: polychlorinated and polybrominated biphenyls (PCBs and PBBs), a group of chemicals that are used in paints, electrical transformers, and insulators; and the pesticides aldicarb, paraquat, and DDT. Some of the acute effects from exposure to low doses of these compounds include diarrhea, nausea, respiratory distress, vomiting, convulsions, and blurred vision (ATSDR, 1999).

These and other POPs remain intact in the environment for long periods, become widely distributed geographically, and accumulate in the fatty tissue of living organisms and are toxic to humans and wildlife. The compounds circulate globally and can cause damage wherever they travel.

Chlorophenols with at least two chlorines either have been used directly as pesticides or converted into pesticides. Also, chlorophenols, especially 4-chlorophenol, have been used as antiseptics. In addition to being produced commercially, small amounts of some chlorophenols, especially the mono- and dichlorophenols, may be produced when waste water or drinking water is disinfected with chlorine, if certain contaminants are present in the raw water.

They are also produced during the bleaching of wood pulp with chlorine when paper is being produced (ATSDR, 1999).

Chlorophenols can enter the environment while they are being made or used as pesticides. Most of the chlorophenols released into the environment go into water, with very little entering the air. Chlorophenols also rapidly enter the body through the skin. The monochlorophenols do not slay inside the body very long. They are changed to less harmful products, and most leave through the urine within 24 hours. The other chlorophenols (dichlorophenol, trichlorophenols, tetrachlorophenols), which also leave through the urine as less harmful chemicals, can stay in the body for several days.

Phenols can cause damage to the cells of the living organisms. It has been shown that a long-time intake of phenols by experimental animals leads to changes in the skin, lungs, liver, mucous membranes, oesophagus and in the kidneys (Bruce et al, 1987). As a result of phenol penetration through the man's skin, its darkening and weakening of the muscles are observed. Lethal doses cause structural and functional changes in the brain, necrosis of the liver, and emphysema (Roy et al, 1998). Poisoning caused by phenol compounds provoke such symptoms as headaches, diyness of the throat, dyspnoea, nausea, vomiting, diarrhoea, (Juhl et al, 2003). According to other reports phenols have cytotoxic effect on skeletal muscle and neurotoxic effect on pyramidal neurones (Nikonorow, 1979). Phenol and its derivatives also show mutagenic effect by unbinding of the DNA helix, inhibition of DNA synthesis in the human cells, and induction of gene mutations.

The chlorinated phenols like 4-chlorophenol (4-CP), 2,4-diehlorophenol (2,4-DCP), etc., are found in waste effluents of iron and steel manufacturing industries, electrical component manufacturing units, photographic equipments, pharmaceuticals, pesticide industries, and paper and pulp manufacture (EPA, 1987). Other releases of 4-CP to water come from leather tanning and textile factories. Also, common pesticides such as lindane and hexachlorobenzene are metabolized to 4-CP by plants, animals and microorganisms. Some current research shows that 4-CP is carcinogenic in rodents, can induce chromosomal aberrations, and is associated with leukemia, malignant lymphoma and soft tissue sarcoma in humans (Exon, 1983). 4-CP is listed as hazardous for landfill disposal (Freedman et al., 1989).

2,4-dichlorophenol (2,4-DCP) has been reported to cause lethargy, tremors and convulsions in mice while workers who made pesticides or were exposed to chlorophenols developed acne and mild liver injuries (EPA,2006). 2,4-dichlorophenol is a key intermediate in the synthesis of chloride-based herbicides, such as 2,4-dichlorophenoxyacetic acid (2,4-D) and 2-(2,4-dichlorophenoxy) propionic acid (2,4- DP) (Mark,1992). Not only the inhalation of dust containing 2,4-DCP can irritate the respiratory tract but the detrimental effects on kidneys, liver and blood-forming organs are known.

Physical, chemical and biological methods, including incineration, adsorption on activated carbon, chemical or enzymatic oxidation, solvent extraction, microbial degradation, incubation in the presence of microorganisms, etc., have been proposed for removing or degrading several chlorophenols from waste water (Debtainel996, Tong 1997, Polcaro 2001).

Factors affecting the toxicity of synthetic organic compound are molecular structure, water solubility, biodegradability, photodegradability and volatility. Halogen containing compound are considered as the most dangerous ones due to their persistence (resistance to biodegradation) and to their accumulation. Hazardousness of halogenated compounds seems to increase with the increase of the number of halogen atoms in the molecule.

Soluble chemicals are generally less dangerous than insoluble or fatty soluble substances as they scarcely accumulate in organisms, being removed by the regular turnover mechanisms. Also their accumulation in water sediments and on water particles is reduced. Biodegradable organic chemicals like detergents and surfactant show a low toxicity risk as they are decomposed by water microorganism and are therefore less susceptible to the accumulation process.

The EPA recommends that drinking water concentrations of 2-chlorophenol should not be more than 0.04 parts per million (ppm), and concentrations of 2,4-diehlorophenol should not be more than 0.02 ppm; these are levels that can be tested (EPA, 2006). In order for chlorophenols to be lower than levels that can be tested, the EPA recommends levels of 0.1 parts per billion (ppb; the amount of chlorophenols per billion parts of water) for monoehlorophenols, 0.3 ppb for 2,4-dichlorophenols, and 1 ppb for 2,4,5-trichlorophenol and 2,3,4,6-tetrachlorophenol.

A wide range of adverse effects has been reported well documented human exposure to phenol by the dermal, oral or intravenous routes. Gastrointestinal irritation has been reported following ingestion. Local effects following dermal exposure range from painless blanching or erythema to corrosion and deep necrosis. Systemic effects include cardiac dysrhythmias, metabolic acidosis, hyperventilation, respiratory distress, acute renal failure, renal damage, dark urine, methaemoglobinaemia, neurological effects (including convulsions), cardiovascular shock, coma and death. The lowest reported dose resulting in a human death was 4.8 g by ingestion; death occurred within 10 min.

The potential for poisoning through inhalation of phenol vapours has long been recognized, but no cases of death following this route of exposure have been reported.

Symptoms associated with inhalation of phenol included anorexia, weight loss, headache, vertigo, salivation and dark urine.

TECHNIQUES OF REMOVAL

It is therefore very important to develop suitable techniques for treatment of water contaminated with the toxic and the persistent phenolic compounds. A few methods in use are described here.

Wet air oxidation (WAO)-

Wet air oxidation (WAO) is the process of oxidizing organic matter in the presence of liquid water. Theoretically, any substance that is capable of burning can be wet oxidized in water.

Oxidation reactions take place in the aqueous environment where the water is an integral part of the reaction. Water provides a medium for the dissolved oxygen to react with the organics and can also react in part with the organics. It is theorized that the chemistry of wet oxidation involves free radical formation with oxygen derived radicals attacking the organic compounds and resulting in the formation of organic radicals (Teletzke 1966, Li 1991). Catalysts, such as homogeneous Cu2+ and Fe3+, their heterogeneous counterparts, or precious metal catalysts can be used to enhance the effectiveness of the WAO reaction. (Fortuny 1999, Ohta 1980, Maugans 1997, Sadana 1979).

It is an ideal process for pretreatment of wastes that are problematic to conventional biological facilities. The WAO process is suited to the oxidation of concentrated waste liquors, slurries, and sludge's where the oxygen demanding organic matter is only a few percent of the predominantly water stream (Eletzke 1966).

Oxidation reactions take place in the aqueous environment where the water behaves much like a catalyst and is an integral part of the reaction. It is theorized that the chemistry of WAO involves free radical formation with the oxygen and/or water derived radicals attacking the organic compounds and encouraging the formation of organic radicals (Birchmeier 2000).

Wet oxidation processes can be carried out at conditions below or above the vapourliquid critical point of water (374oC and 22.1 MPa). While a high temperature is required to attain a rapid rate of reaction, an increase in temperature will also increase the saturated water vapour pressure, which means that a higher pressure is required to maintain the liquid phase. Wet air oxidation (WAO) is carried out below the critical point of water, typically at 200 - 320oC and 2.0 - 20.0 MPa (Mishra et al., 1995). When compared to incineration, the WAO process creates minimal air pollution problems as the contaminants remain in the aqueous phase. The WAO process generally produces low molecular weight oxygenated compounds, like acetic and propionic acids, ethanol, etc. (Luck,1999). Supercritical water oxidation (SCWO) processes are carried out at supercritical conditions. A recent review (Savage, 1999) on SCWO processes shows that complete and rapid oxidation of phenol as well as other organics can be achieved.

Although higher efficiency for destruction of organic contaminants may be achieved in SCWO than in WAO, SCWO is usually an expensive process to install and operate.

Wet-air oxidation process is known to have a great potential for the treatment of effluents containing a high content of organic matter (chemical oxygen demand, COD 10-100 g/L), or toxic contaminants for which direct biological purification is unfeasible (Mishra et al., 1995). The WAO process has well-known capacities for breaking down biologically refractory compounds to simpler, easily treated materials before they are released into the environment. In general, this aqueous phase flameless combustion process takes place at severe reaction temperatures (473-593 K) and pressures (20-200 bar) by means of active oxygen species, such as hydroxyl radicals. Residence times of the liquid-phase in a three-phase reactor may range from 15 to 120 min, and the extent of COD removal may typically be about 75-90% (Luck 1999).

In the WAO processes, the organic contaminants dissolved in water are either partially degraded by means of an oxidizing agent into biodegradable intermediates or mineralized into innocuous inorganic compounds such as CO2, H20 and inorganic salts, which remain in the aqueous phase.

In contrast to other thermal processes, WAO produces no NOx. S02, HC1, dioxins, fiirans, fly ash, etc. (Luck 1999).One of the main drawbacks of the WAO process is its inability to achieve complete mineralization of organics, since some low molecular weight oxygenated compounds (especially acetic and propionic acids as well as methanol, ethanol, and acetaldehyde), originally present in a wastewater or accumulated in the liquid-phase during the oxidation process, are resistant to further transformation to carbon dioxide. For example, removal of acetic acid is usually negligible at temperatures lower than 573K (Mishra et al„ 1995). Furthermore, organic nitrogen compounds are mostly transformed to ammonia, which is also stable in WAO operating conditions. Hence, the WAO process is considered as a pre-treatment step of wastewaters, which requires additional treatment, typically in a conventional biological treatment plant. WAO is not a new process. Its origins can be traced to the Strehlenert process of wood technology patented in 1911 and to the zinc sulfide oxidation process of hydrometallurgy patented in 1927 (Strehlenert, 1911). Nevertheless, the WAO process may be prohibitively expensive when used to achieve deep oxidation of all organic material present to carbon dioxide. Consequently, it is considered as one of the most promising and simplest techniques for partial oxidation of parent pollutants into more biologically amenable intermediates. The efficiency of aqueous phase oxidation can be largely improved by the use of catalysts, either in the form of solids or as homogeneous catalysts.

Biological treatment-

The aerobic genus *pseudomonas* is an attractive organism for use in wastewater treatment applications. Several types of phenol-degrading microorganisms, which have been isolated, harvested and tested on the substrates showed biodegradable efficiency comparable to Pseudomonas. This includes the fungi *phanerochaete chrysoporium.*

cryptococcus elinovii yeasts, bacteria of genera *alcaligenes*, *bacillus, micrococcus, rhodotorulas,* and others. A biological method for removal of chlorophenols in drinking water and wastewater is enzymatic detoxification using the horse radish peroxidase enzyme. The addition of this enzyme with hydrogen peroxide to solution causes enzymatic cross-linking of the substrate forming insoluble polymers, which then precipitate out of solution. This enzyme isolated from the roots of horseradishes, has been shown to be applicable for the treatment of several industrial wastewaters (Klibanov 1980, Klibanov 1983, Cooper 1996).

One-electron oxidation of aromatic substrates (AH**2**) catalyzed by peroxidases is depicted by the Chance-George mechanism (Nicell 1994) as the following:

E + H2O2 — * Ei + H2O (1)

Ei + AH2 —» Eii + AH- (2)

Eii + AH2 —> E + AH- (3)

The native enzyme (E) is oxidized by peroxide (H**2**O**2**) to an active intermediate enzymatic form called compound I (Ei). Compound I accept an aromatic compound (AH2) into its active site and carries out its oxidation. A free radical (AH-) is produced and released into solution leaving the enzyme in the compound 0 (Eii) state. Compound II oxidizes a second aromatic molecule, releasing another free radical product and returning the enzyme to its native state, thereby completing the cycle. The overall peroxidase reaction consists of the reactions described by Equations (1), (2) and (3). (Nicell 1994).

Photo-Fenton reaction-

The treatment of industrial wastewater, which contains organic wastes, by biological processes, is often unsuitable due to their inherent toxicity to micro-organism. The use of traditional non-catalytic chemical processes or incineration may be too costly and energy intensive. Conventional wet air oxidation (WAO) processes usually require higher pressures (0.5-20 M Pa) and temperatures (423-598 K), which result in a high capital investment and a high energy consumption for operation. The application of homogenous and heterogeneous catalyst can improve the oxidation efficiency of organic wastes in water and reaction temperature can be reduced (Mishra 1995. Matatov-Meytal 1998). Homogeneous catalysts are reported to be more effective in increasing the rate of oxidation, but heterogeneous catalysts are preferred because the catalyst is present as a separate phase and therefore easier to separate.

The photo-Fenton reaction is also well-known in the literature (Kiwi 1993, Ruppert 1993) which is an efficient and inexpensive method for wastewater and soil treatment (Bauer 1997, Chen 1997, Kim 1996). Photo-Fenton is known to be able to improve the efficiency of dark Fenton or Fenton-like reagents, respectively, by means of the interaction of radiation (UV or Visible) with Fenton's reagent (Hislop 1999.

Pignatellol992). This technique has been suggested to be a feasible and promising process to remove pollutants from natural and industrial waters by increasing the biodegradability of chlorophenols and could be used as a pre-treatment method to decrease the toxicity of water (Fallmann et al., 1999a, 1999b).

In presence of Fenton reagent, photochemical reactions can be driven with photons of low energy, photons that belong to the visible part of the spectrum. Thus. photo- Fenton processes can be considered as low-cost techniques that can be run under solar irradiation (Klibanov 1983).

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH. + OH- \qquad (5)$$

$$Fe3+ + H2O + hv \rightarrow Fe2+ + H+ + OH. \qquad (6)$$

Nevertheless applying Fenton's method has some drawbacks. The regeneration of ferric iron is slow. By applying irradiation the photo-Fenton reaction takes place, which accelerates the overall reaction rate by closing the catalytic cycle of Fenton and photo-Fenton reaction faster (Equations 5 and 6). This results in the advantage that another highly reactive hydroxyl radical is produced without consumption of hydrogen peroxide.

The photo-Fenton method has the advantage that it has high reaction rates and can be powered by sunlight. Furthermore hydrogen peroxide is a cheap oxidant compared for example to persulphate. The commonly mentioned disadvantage of the photo-Fenton method is the necessity to work at low pH (in literature normally a pH below 4 is considered to be necessaiy), because at higher pH ferric ions would begin to precipitate as hydroxide. Furthermore, the added iron has to be removed after the treatment (Klibanov 1980).

Adsorption of organic compounds onto activated carbon-

Carbon adsorption is an advanced wastewater treatment method used for the removal of recalcitrant organic compounds as well as residual amounts of inorganic compounds such as nitrogen, sulfides, and heavy metals. This is a separation method in which the contaminant is transferred from a water phase, where it is dissolved, to the surface of active carbon where is accumulated for its subsequent extraction or destruction. The adsorption onto activated carbon is widely used for wastewater treatment. Thus, it is used in the control of color and odors, in the removal of organic compounds or trihalomethanes precursors, to remove chlorine and in general to remove toxic compounds.

The adsorption of nitrobenzene (NB) and phenol onto activated carbon has been widely studied. Both (NB and phenol) showed to be well adsorbable compounds onto activated carbon but in low concentration (Canizares *et al,* 1999; Sacher *et al,* 2001). This method has also been combined with others and a significant improvement has been obtained (Canizares *et al,* 1999). Many studies have been found in the literature regarding the treatment of textile wastewater by means of activated carbon (Roy and Volesky, 1977; Lin and Lai, 2000; Yeh *et al.,* 2002). Most of them showed the high effectiveness of carbon activated adsorption process in the reduction of COD (Chemical Oxidation Demand) and color removal from textile wastewater.

CONCLUSION

The present work demonstrated that phenol, 4-chlorophenol and 2,4-dichlorophenol could be oxidized to harmless end products at room temperature with the help of the catalysts used and further that use of an external oxidant such as H20 2 could be avoided. The cost of water treatment can be considerably reduced since there is no need for using H20 2 as an oxidizing agent and the oxidation could be ensured by simply agitating the reaction mixture in air such that the dissolved oxygen was utilized for the oxidative destruction of the pollutant The catalysts used in the work were cheap and commercially available material. Therefore, the treatment of water contaminated with the organic pollutants by wet oxidation is an affordable technique for water purification particularly for relevant industrial effluents.

REFERENCES

1. Ammann, Lars (2003) Cation exchange and adsorption on clays and clay minerals, *Dissertation,* Christian-Albrechts-University, Kiel.

2. APHA-AWWA-WEF (1985) oxygen demand (chemical).In standard Methods for the Examination of Water and Wastewater,id *th ed.American Public Health Association,*American Water work Association and Water Pollution Control Fedration, Washington, DC, pp.533-534.

3. Debtaine H., Chakehouk M., Foussard J.N., Tissot D. and Striolo P. (1996) *Environ. Pollution,* 92, pp. 155.

4. Eletzke G. H. (1966) Wet Air Oxidation - Industrial Waste Applications, *39th Annual Conference,* Water Pollution Control Federation.

5. Fortuny A. et. al, (1999) Water pollution abatement by Catalytic Wet Air Oxidation in a Trickle Bed Reactor, *Catalysis Today,* Vol 53, pp. 107-44.

6. Teletzke G. H, (1966) Wet Air Oxidation - Industrial Waste Applications, *39th Annual Conferenc,* Water Pollution Control Federation.

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