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**MARMARA UNIVERSITY**

**INSTITUTE FOR GRADUATE STUDIES IN**

**PURE AND APPLIED SCIENCES**

# DEVELOPING A COST EFFECTIVE TECHNOLOGY FOR THE REUSE OF SEWAGE TREATMENT PLANT EFFLUENT

**Çiĵ dem DEMIķRCIķOĴ LU KUķ**

## THESIS

**FOR THE DEGREE OF MASTER OF SCIENCE**

**IN**

**ENVIRONMENTAL ENGINEERING**

**SUPERVISOR**

**Assoc. Prof. Zehra Semra CAN**

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# ACCEPTANCE AND APPROVAL DOCUMENT

The jury established by the Executive Board of the *INSTITUTE FOR GRADUATE STUDIES IN PURE AND APPLIED SCIENCES* on 05/07/2010 (Resolution no: 2010/13-47) has accepted ~~Mr~~/Ms Çiğdem Demircioğlu Kuş's thesis titled "**Developing a Cost Effective Technology for the Reuse of Sewage Treatment Plant Effluent**" as Master of Science / ~~Doctor of Philosophy~~ thesis in Environmental Engineering.

Advisor : Doç. Dr. Zehra S. CAN, Marmara University.............

1. Member of the jury: Yrd. Doç. Dr. Kozet YAPSAKLI, Marmara University.....
2. Member of the jury: Yrd. Doç. Dr. Seval GENÇ, Marmara University...

Date : 12.07.2010

## APPROVAL

Mr/Ms. Çiğdem Demircioğlu Kuş has satisfactorily completed the requirements for the degree of Master of Science / ~~Doctor of Philosophy~~ in Environmental Engineering at Marmara University. The Executive Commitee approves that he/she be granted the degree of Master of Science / ~~Doctor of Philosophy~~ on 20.07.2010 (Resolution no: 2010/14-56.

**DIRECTOR OF THE INSTITUTE**

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**July, 2010** **Çiĝdem DEMĶRCĶOĜLU KUĶ**

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# ABSTRACT

## DEVELOPING A COST EFFECTIVE TECHNOLOGY FOR THE REUSE OF SEWAGE TREATMENT PLANT EFFLUENT

Adding powdered activated carbon to activated sludge is demonstrated to improve biological treatment and remove refractory organic compounds of treated wastewater. On the other hand, ozonation of refractory organic compounds in wastewater usually produces more biodegradable organics, thus, it improves the removal of the organics biologically.

The purpose of this study was to develop a cost effective technology for further treatment of Paкaköy Advanced Biological Treatment Plant (PABTP) effluent for reuse purposes. To serve this purpose, powdered activated carbon (PAC) treatment process based on adsorption capacity of PAC in activated sludge (AS) and the effect of dissolved organic substances in activated sludge on the adsorption capacity of PAC were investigated in this context. Ozone was used as a pretreatment process to increase the biodegradability of effluent.

The 50 mg/L of applied ozone dosage was found to be optimum for efficient biodegradability increment for PABTP effluent. Both for K and 1/n values showed that the organic matter in raw effluent was more adsorbable onto activated carbon. Steam activated peat/wood based Norit SAE Super had shown the best adsorption intensity and strongest adsorption bond. DOC, $BOD_5$ and $UV_{254}$ absorbance reductions were nearly the same for both raw and preozonated effluents in the PAC and PAC+AS systems. The results suggest that the most cost effective treatment option for the reuse of PABTP effluent is powdered activated carbon adsorption without preozonation.

**July, 2010** **Çiĵ dem DEMĶRCĶOĴ LU KUķ**

# ÖZET

## ATIKSU ARITMA TESİSİ ÇIKIŞ SUYU YENİDEN KULLANIMI İÇİN UYGUN MALİYETLİ TEKNOLOJİ GELİŞTİRİLMESİ

Aktif çamura toz aktif karbonun ilave edilmesi sonucunda biyolojik arıtmanın veriminin arttığı ve arıtılmış atıksudaki refrakter organik bileşiklerin giderildiği gözlemlenmiştir. Diğer yandan, atıksudaki refrakter organik bileşiklerin ozonlanması ile daha fazla biyolojik olarak ayrışabilen organikler oluşturulmakta ve böylece organiklerin biyolojik olarak giderimi sağlanmaktadır.

Bu çalışmanın amacı Paşaköy İleri Biyolojik Arıtma Tesisi çıkış suyunun yeniden kullanım amacıyla uygun maliyetli arıtma teknolojisinin geliştirilmesi idi. Bu amaç doğrultusunda, aktif çamurdaki toz aktif karbonun (PAC) adsorpsiyon kapasitesine dayalı toz aktif karbon (PAC) arıtma prosesi ve aktif çamurdaki çözünmüş organik maddelerin PAC'ın adsorpsiyon kapasitesi üzerine etkisi incelenmiştir. Çıkış suyunun biyolojik olarak ayrıştırılabilirliğini artırmak için ozon bir ön arıtma prosesi olarak kullanılmıştır.

Paşaköy İleri Biyolojik Arıtma Tesisi çıkış suyunun biyolojik olarak ayrıştırılabilmesi için en uygun ozon dozu 50 mg/L olarak bulunmuştur. Hem K hem de 1/n değerleri, organik maddenin aktif karbona ozonlanmamış suda daha kuvvetli tutunduğunu göstermiştir. Buharla aktive edilmiş odun kömürü temelli Norit SAE Süper toz aktif karbonun, en iyi adsorpsiyon yoğunluğuna ve en kuvvetli adsorpsiyon bağına sahip olduğu bulunmuştur. Toz aktif karbon ve toz aktif karbon+aktif çamur sistemleri için hem ham çıkış suyunda hem de ön ozonlanmış çıkış suyunda benzer DOC, $BOD_5$ ve $UV_{254}$ absorbans giderimleri elde edilmiştir. Bu sonuçlar Paşaköy İleri Biyolojik Arıtma Tesisi çıkış suyunun yeniden kullanımı için en uygun maliyetli arıtma yönteminin ön ozonlama yapmadan toz aktif karbon adsorpsiyonu prosesi olduğunu göstermiştir.

**Temmuz, 2010** **Çiğdem DEMİRCİOĞLU KUŞ**

# SYMBOLS

**1/n** : Function of the Strength of Adsorption

**$C_e$** : Equilibrium Solution Concentration

**$E^0$** **:** Oxidation Potential

**K** : Capacity of the Adsorbent for the Adsorbate

**$q_e$** : Equilibrium Surface Concentrations

**v** **:** Volt

**V** **:** Volume of Sample Inside

**w/w** **:** By Weight

# ABBREVIATIONS

**AOX** **:** Adsorbable Organic Halogens
**A2/O** : Anaerobic zone followed by anoxic zone then oxic zones aeration
**AS** **:** Activated Sludge
**BAC** **:** Biological Activated Carbon
**B.E.T** **:** Total Surface Area
**BDOC** **:** Biodegradable Dissolved Organic Carbon
**BOD** **:** Biochemical Oxygen Demand
**BPA** **:** Aromatic Compound Including Phenol and Bis-phenol A
**CF** **:** Continues-Flow
**COD** **:** Chemical Oxygen Demand
**DOC** **:** Dissolved Organic Carbon
**DALY** **:** Disability Adjusted Life Years
**DBP** **:** Disinfection ByProduct
**DOX** **:** Dissolved Organic Halogen
**DPT** **:** Devlet Planlama Teĸkilatē
**DSĶ** **:** General Directorate of State Hydraulic Works
**EfOM** **:** Effluent Organic Matter
**EDCs** : Endocrine Disrupting Chemicals
**EPA** **:** Environmental Protection Agency
**EUR** **:** Molasses number
**GAC** **:** Granular Activated Carbon
**GEC** **:** Global Environment Centre
**GESAP** **:** GEC Sanitation Programme
**ISKI** **:** Istanbul Water and Sewerage Administration
**KHP** **:** Potassium Hydrogen Phthalate
**MEP** **:** Metabolic End Product
**NSA** **:** Naphthalene Sulfonic Acids
**NOM** **:** Natural Organic Matter
**NOSB TAP:** National Organic Standards Board Technical Advisory Panel

**PABTP** **:** Paкaköy Advanced Biological Treatment Plant
**PAC** **:** Powdered Activated Carbon
**PACT** **:** Powdered Activated Carbon Treatment
**PAC+AS** **:** Powdered Activated Carbon + Activated Sludge System
**PAHs** : Poly Aromatic Hydrocarbons
**PCE** : Tetrachloroethylene
**ppm** : parts per million by volume
**SCFB** **:** Semi-Continuously Fed Batch
**SCFH** **:** Cubic feet per hour at specific standard conditions
**TOC** **:** Total Organic Carbon
**TSS** **:** Total Suspended Solids
**UNEP** **:** United Nation Environmental Programme
**US** **:** United States
**USEPA** **:** U.S. Environmental Protection Agency
**UV** **:** Ultraviolet
**$UV_{254}$** **:** Ultraviolet at 254 nm absorbance
**UV-VIS** **:** Ultraviolet Visible Spectrophotometer
**WHO** **:** World Health Organization

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# CHAPTER I

## INTRODUCTION AND AIM

Water is becoming an increasingly scarce resource in many populated areas of the world. Therefore, there is an increasing trend to require more efficient use of water resources, both in urban and rural environment. Under the given circumstances, reclamation and reuse of wastewater seems to be an attractive option to cope with the water resources shortage (Toze, 2006).

Several advanced wastewater treatment technologies for the production of high quality effluents have been put forward, the quality of which complies with the specific applications of wastewater reclamation and reuse. The level of treatment is defined first and foremost by the required use of reclaimed water (Asano and Levine, 1996). As a result of the high concentrations and complex nature of pollutants in the environment, it proves more demanding to remove by more traditional techniques, either physical or chemical. Existing physicochemical technologies are costly, and therefore, commercially less appealing. Oxidation processes, be they biological, chemical or physical, are crucial steps in water treatment. Biological oxidation is considered to be economically feasible and thus it is more widely applicable (Muruganandham et al., 2007). Since the 1970s, ozonation has been employed to meet discharge requirements for coliform and virus inactivation (Rice et al., 1981), to effectively eliminate the recalcitrant organic pollutants in wastewater (Kuo and Huang, 1998).

The most widespread processes used in advanced treatment of activated sludge effluents include filtration (depth, surface or membrane filtration), adsorption, reverse osmosis, ion exchange and others, followed by disinfection using chlorine or ozone (Metcalf and Eddy, 2003). Nevertheless, filtration does not remove refractory organics and volatile organic compounds, even if coupled with chemical coagulation. The residual dissolved organic matter of treated wastewaters may effectively be removed by applying carbon adsorption, while ozonation, due to its high oxidative potential, contributes to the general improvement of the effluent quality (Weber and LeBoeuf, 1999, http://www.norit-ac.com). Adding powdered activated carbon to activated sludge was demonstrated to improve biological treatment and remove refractory organic compounds (Aktaк and Çeçen, 2001) in the co-treatment of leachate. A number of researchers (Orshansky and Narkis, 1997; Costa and M´arquez, 1998) have studied the effect of incorporating powdered activated carbon to activated sludge systems for the treatment of complex liquid waste, containing non-biodegradable compounds and toxic or inhibitory matter, in order to improve the treatment process (Orozco et al., 2008).

Activated sludge system is a common and economical process for the treatment of organic matter in wastewater. However, nonbiodegradable or slowly biodegradable compounds pass through the process without any removal. Adding activated carbon to an activated sludge system can help removing such persistent organic compounds by adsorption. As a result, the treatment efficiency of the activated sludge system is increased (Çeçen, 1994; Sublette et al., 1982; Kang et al., 1990; Specchia and Gianetto, 1984). Several researchers have suggested the existence of a synergy between activated carbon and microorganisms, which further improves organic matter removal by biodegradation in the activated sludge system (Orshansky and Narkis, 1997; Sublette et al., 1982; Marquez and Costa, 1996). According to these researches nonbiodegradable or toxic organics and some heavy metals could be removed from wastewater by activated carbon and this causes biological activities to achieve higher organic matter removal efficiencies (Çeçen and Aktaк, 2001b). For that reason, in this study treatment of preozonated Paкaköy Advanced Biological Wastewater Treatment Plant effluent by activated carbon + activated sludge process will be investigated as a means for producing high quality reclaimed water.

The main goal of this study is to develop a cost effective technology for the treatment of Paкaköy Advanced Biological Treatment Plant effluent for reuse purposes. To achieve this goal, firstly ozone will be applied to the effluent to convert nonbiodegradable organics to biodegradable organic matter. Then, the ozonated effluent will be treated by powdered activated carbon + activated sludge system. The removal efficiencies of activated carbon, activated sludge and activated carbon + activated sludge systems will be compared with each other to design the most cost effective treatment option.

# CHAPTER II

## GENERAL BACKGROUND

### II. 1 WASTEWATER REUSE

The worldés population is expected to increase dramatically between now and the year 2020- and with this growth will come an increased need for water to meet various needs, as well as an increased production of water. Many communities throughout the world are approaching, or have already reached, the limits of their available water supplies; water reclamation and reuse have almost become necessary for conserving and extending available water supplies. Water reuse may also present communities with an alternate wastewater disposal method as well as provide pollution abatement by diverting effluent discharge away from sensitive surface waters. Already accepted and endorsed by the public in urban and agricultural areas, properly implemented nonpotable reuse projects can help communities meet water demand and supply challenges without any known significant health risks (EPA Guideline, 2004).

It is estimated that within the next 50 years, more than 40% of the worldés population will live in countries facing water stress or water scarcity. Growing competition between agriculture and urban areas for high quality freshwater supplies, particularly in arid, semi-arid and densely populated regions, will increase the pressure on this resource. More fresh water is abstracted and used in agriculture in arid and semi-arid countries than for any other purpose (i.e. for domestic uses and industrial uses combined). In many cases, it is better to use wastewater, excreta and greywater in agriculture than to use higher-quality fresh water, because crops benefit from the nutrients they contain. Thus, wastewater, excreta and greywater can help to meet water demand and allow the preservation of high-quality water resources for drinking water supplies (WHO Guideline, 2006).

Growing urbanization in water-scarce areas of the world exacerbates the situation of increasing water demands for domestic, industrial, commercial and agricultural purposes. Figure II.1 demonstrates the rapid growth rate of the urban population worldwide. In the year 2000, 2.85 billion people (out of a worldwide population of 6.06 billion) were living in urban regions. The increasing urban population results in a growing water demand to meet domestic, commercial, industrial and agricultural needs. Coupled with depleting freshwater sources, utility directors and managers are faced with the challenge to supply water to growing customer base (EPA Guideline, 2004).

Access to water supply and improved sanitation is one of key factors in improving health and economic productivity. In order to increase access to water supply the following three elements are especially important.

- Development of new water sources
- Prevention of water resource degradation
- Improvements in efficiency of water consumption

Wastewater reuse contributes to all of above three elements. Wastewater reuse can provide alternative source of water, reduce pollution load to water environment by less discharged wastewater. Moreover wastewater reuse in agriculture and industry enable more efficient water withdrawal for other purpose because freshwater withdrawal for agriculture and industry constitute a large share of global water usage and account for 67% and 20% of total use respectively. Therefore, wastewater reuse has a big potential to bring about environmental, economic and financial benefits (http://nett21.gec.jp/GESAP/themes/themes2.html).

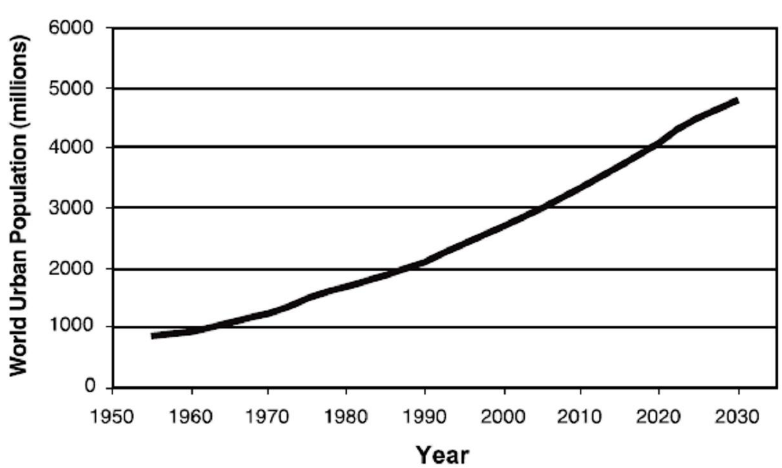


**Figure II.1** Estimated and Projected Urban Population in the World (EPA Guideline, 2004).

Wastewater resource is very worth of control and management. Management of wastewater through treatment has two major objectives. The first is to protect environment by reducing the pollution of fresh water resources and hence reducing health risks. The second is to mobilize this available water resource for mitigating water scarcity and improve food production (Bazza, 2003).

**II.1.1** Types of Wastewater Reuse Applications

In the planning and implementation of water reclamation and reuse, the reclaimed water application will usually govern the wastewater treatment needed to protect public health and the environment, and the degree of reliability required for the treatment processes and operations (Metcalf & Eddy, 2003). Wastewater reuse can be categorized by its sources, benefits, applications and required treatments. Major reuse application types are:

- Urban
- Agricultural
- Recreational
- Environmental
- Groundwater recharge
- Industrial
- Residential
- Augmentation of potable supplies (UNEP, 2004).

The examples of reuse according to major applications are given in Table II.1.

**Table II.1** Categories of Wastewater Reuse (UNEP, 2004)

| **Category of reuse** | **Examples of applications** |
|---|---|
| ÅUrban use | |
| Unrestricted | Landscape irrigation of parks, playgrounds, school yards, golf courses, cemeteries, residential, green belts, snow melting |
| Restricted | Irrigation of areas with infrequent and controlled access |
| Other | Fire protection, disaster preparedness, construction |
| ÅAgricultural | |
| Food crops | Irrigation for crops grown for human consumption |
| Non-food crops and crops consumed after processing | Irrigation for fodder, fiber, flowers, seed crops, pastures, commercial nurseries, sod farms |
| ÅRecreational use | |
| Unrestricted | No limitation on body contact: lakes and ponds used for swimming, snowmaking |
| Restricted | Fishing, boating, and other non-contact recreational activities |
| ÅEnvironmental enhancement | Artificial wetlands creation, natural wetland enhancement, stream flow |
| ÅGroundwater recharge | Groundwater replenishment for potable water, salt water intrusion control, subsidence control |
| ÅIndustrial reuse | Cooling system water, process water, boiler feed water, toilets, laundry, construction wash-down water, air conditioning |
| ÅResidential use | Cleaning, laundry, toilet, air conditioning |
| ÅPotable reuse | Blending with municipal water supply, pipe to pipe supply |

**Wastewater Reuse for Agriculture:** Agricultural irrigation is crucial for improving the quality and quantity of production. Worldwide, agriculture is the largest user of water. Agriculture receives 67% of total water withdrawal and accounts for 86% of consumption in 2000. In Africa and Asia, an estimated 85 to 90% of all the freshwater use is for agriculture. By 2025, agriculture is expected to increase its water requirements by 1.2 times. Large-scale irrigation projects have accelerated the disappearance of water bodies, such as the Aral Sea, the Iraqi Marshlands, and Lake Chad in West Africa. Thus, more efficient use of agricultural water through wastewater reuse is essential for sustainable water management (UNEP, 2004).

**Wastewater Reuse for Industry:** Industrial water use accounts for approximately 20% of global freshwater withdrawals. Power generation constitutes a large share of this water usage, with up to 70% of total industrial water used for hydropower, nuclear, and thermal power generation, and 30 to 40% used for other, non-power generation processes (Table II.2). Industrial water reuse has the potential for significant applications, as industrial water demand is expected to increase by 1.5 times by 2025 (UNEP, 2004).

**Table II.2** Types and Examples of Industrial Water Reuse (UNEP, 2004)

| **Types of water reuse** | **Examples** |
|---|---|
| Reuse of municipal wastewater | Cooling tower make-up water<br>Once-through cooling<br>Process applications |
| Internal recycling and cascading use of process water | Cooling tower make-up water<br>Once-through cooling and its reuse<br>Laundry reuse (water, heat, and detergent recovery)<br>Reuse of rinse water<br>Cleaning of premises |
| Non-industrial use of effluent | Heating water for pools and spas<br>Agricultural applications |

**Urban Applications:** In urban areas, the potential for introducing wastewater reuse is quite high, and reuse options may play a significant role in controlling water consumption and reducing its pollutant load on the environment. A large percentage of water used for urban activities does not need quality as high as that of drinking water. Dual distribution systems (one for drinking water and the other for reclaimed water) have been utilized widely in various countries, especially in highly concentrated cities of the developed countries. This system makes treated wastewater usable for various urban activities as an alternative water source in the area, and contributes to the conservation of limited water resources. In most cases, secondarily treated domestic wastewater followed by sand filtration and disinfection is used for non-potable purposes, such as toilet flushing in business or commercial premises, car washing, garden watering, park or other open space planting, and firefighting (UNEP, 2004).

**Wastewater Reuse for Environmental Water Enhancement:** Another area where wastewater reuse is being applied is in environmental enhancement, such as the augmentation of natural/artificial streams, fountains, and ponds. In metropolitan areas, urbanization, and the resulting increase in surface area coverage by buildings and pavements, has resulted in decreased water retention capacity. In addition, storm water is rapidly drained and discharged to a river and/or sea to prevent flooding, often leaving little water for environmental water usage.

**Groundwater Recharge:** A groundwater aquifer is important for freshwater storage and water transmission. It provides water resources that can be withdrawn for various purposes. Three common methods for aquifer recharge: recharge basin, vadose zone well, direct injection well.

### **II.1.2** Regulations for Wastewater Reuse

One of the most important factors in water and wastewater reclamation projects is complying with water quality standards to minimize health risks or establishing them if they do not exist. While the World Health Organization (WHO) guidelines for agricultural applications of wastewater are available, there are no international guidelines or criteria for other types of wastewater reuse. Therefore, guidelines and standards need to be developed by each country, with health risks as well as technical and economic feasibility being taken account. Technological options should be selected to meet such guidelines and standards and ensure the protection of human health and the environment (UNEP, 2004).

Table II.3 describes different health protection measure combinations to achieve the health-based targets. For specific settings, both the health-based targets and the combination of health protection measures need to be adapted. Planners and designers of wastewater use schemes may wish to explore and use other combinations of health protection control measures, and new treatment technologies will offer the opportunity of developing new options.

**Table II.3** Verification Monitoring[a] (E. coli numbers per 100 mL of treated wastewater) for the Various Levels of Wastewater Treatment in Options A ï G. (WHO Guidelines, 2006)

| Type of irrigation | Option | Required pathogen reduction by treatment (log units) | Verification monitoring level (E. coli per 100 mL) | Notes |
|---|---|---|---|---|
| Unrestricted | A | 4 | Ò $10^3$ | Root crops |
| | B | 3 | Ò $10^4$ | Leaf crops |
| | C | 2 | Ò $10^5$ | Drip irrigation of high-growing crops |
| | D | 4 | Ò$10^3$ | Drip irrigation of low-growing crops |
| Restricted | E | 6 or 7 | Ò$10^1$ or $10^0$ | Verification level depends on the requirements of the local regulatory agency[b] |
| | F | 3 | Ò$10^4$ | Labour-intensive agriculture (protective of adults and children under 15 years of age) |
| | G | 2 | Ò$10^5$ | Highly mechanized agriculture |
| | H | 0.5 | Ò$10^6$ | Pathogen removal in a septic tank |

[a] ñVerification monitoringò refers to what has previously been referred to as ñeffluent standardsò or ñeffluent guidelineò levels.
[b] For example, for secondary treatment, filtration and disinfection: five-day biochemical oxygen demand, <10 mg/l; turbidity, <2 nephelometric turbidity units (NTU); chlorine residual, 1 mg/L: pH, 6ï 9; and faecal coliforms, not detectable in 100 mL.

Option A, shows that the required pathogen reduction is achieved by the combination of (a) wastewater treatment, which provides a 4 log unit pathogen reduction (approximately equivalent to an *E. coli* level of 103/100 mL in unchlorinated effluents), (b) a 2 log unit reduction due to pathogen die-off between the last irrigation and consumption, and (c) a 1 log unit reduction due to normal household washing of the salad crops or vegetables with water prior to consumption.

This option, which provides a 7 log unit pathogen reduction, is suitable when root crops that may be eaten uncooked are irrigated with treated wastewater.

Option B has a lower degree of wastewater treatment than Option A (3 log units, rather than 4) combined with two post-treatment health protection control measures: a 2 log unit reduction due to die-off and a 1 log unit reduction due to washing the salad crops or vegetables with water prior to consumption. This option, which provides a 6 log unit pathogen reduction, is suitable for the irrigation of non-root salad crops (e.g. lettuce, cabbage) and vegetables eaten uncooked.

Option C combines an even lower degree of treatment (2 log units) with drip irrigation of high-growing crops (such as fruit trees, olives), which achieves the required remaining 4 log unit pathogen reduction.

Option D incorporates the drip irrigation of low-growing non-root crops (a 2 log unit reduction), so a greater degree of treatment (4 log units) is provided (a valid alternative would be, for example, a 2 log unit reduction by treatment followed by a 1 log unit reduction due to die-off and a 1-log unit reduction due to produce washing.

Option E relies solely on wastewater treatment to achieve the required 6ï 7 log unit reduction. A typical sequence of wastewater treatment processes to achieve this would comprise conventional wastewater treatment (e.g. primary sedimentation, activated sludge, including secondary sedimentation) followed by chemical coagulation, flocculation, sedimentation, filtration and disinfection (chlorination or UV irradiation). Such a sequence is used, for example, in California, to ensure compliance with the state water recycling criteria for unrestricted irrigation (Ò2.2 total coliforms per 100 mL and a turbidity of Ò2 NTU) (State of California, 2001). However, this option does not take into account pathogen reduction due to (a) natural die-off between final irrigation and consumption and (b) specific food preparation practices such as washing, disinfection, peeling and/or cooking. Moreover, the very high costs and operational complexity of the wastewater treatment processes required for this option will generally preclude its application in many developing countries.

Option F represents labour-intensive restricted irrigation; the healthbased target of an additional disease burden of Ò10-6 disability adjusted life years (DALY) loss per person per year is achieved by a 4 log unit pathogen reduction.

Option G represents restricted irrigation using highly mechanized agricultural practices (e.g. tractors, automatic sprinklers, etc.); wastewater treatment to 105ï 106 *E. coli* per 100 mL is required (i.e. a pathogen reduction of 3 log units).

Option H illustrates a typical single-household or institutional situation: minimal treatment in a septic tank (0.5 log unit pathogen reduction) followed by subsurface irrigation via the soil absorption system for the septic tank effluent. There is no contact between the crop and the pathogens in the septic tank effluent, so the subsurface irrigation system is credited with the remaining 6.5 log unit pathogen reduction required for root crops.

As stated previously, each country can and should establish national criteria and procedures that suit its epidemiological, social and economic needs. These should allow for the optimal combination of risk reduction elements to be designed and implemented at the system level. The WHO Committee of Experts that reviewed and endorsed these Guidelines felt that the in-depth risk analyses provided a sound epidemiological basis to conclude that options A, B, C and D provide a high degree of health risk reduction, which should meet the needs of most countries in a reasonably cost-effective manner. It concluded that these new risk assessment studies and the extensive review and evaluation carried out by the group generally validated the 1989 WHO recommended guidelines for unrestricted wastewater use in agriculture of 1000 *E. coli*/100 mL.(WHO Guidelines, 2006).

Considering the issue about the reuse of treated wastewater according to the legislation of the Republic of Turkey; It is indicated in **Turkish Water Pollution Control Regulation** (2004) that surface water in accordance with the quality has been divided into 4 classes. Class III (polluted water); can be used after a proper treatment in industrial water supply except food, such as textiles industries that require high quality water, and Class IV (very contaminated water); can be used improving the lower quality than the quality parameters of Class III data and to the high-quality class. The regulation in some cases allows even the use of polluted water, includes followings about the reuse of wastewater for irrigation;

**"Use of Treated Wastewater for Irrigation"**

**Article 28** - In the region that irrigation water is scarce and has economic worth, treated wastewater providing the irrigation water quality criteria of the Water Pollution Control Regulation Technical Principles is encouraged for use as irrigation water. For this purpose which must be applied to pre-treatment and investigations are done according to Technical Principles. ñCompliance with the use of such a mass of wastewater is determined by the commission that founded by the governor composed of the provincial directorate of environment and forests, the provincial directorate of agriculture and regional directorate of State Hydraulic Works (DSI)ò the provision was included.

Also, in item j) in the article 22 of the same regulation, it was determined the using qualities of wastewater treated with the following provision; "In case irrigation is performed by using wastewater, irrigation water amount and irrigation program is regulated as minimizing the water infiltrated into ground water as a permanent cause pollution hazard." (Turkish Water Pollution Control Regulation, 2004).

Reuse of wastewater is specified at the State Planning Organization Long-Term Strategy and Eighth 5-Year Development Plan, the Eighth Section Paragraph in 1660 "It will be provided the protection of groundwater and surface water resources before contamination and it will be encouraged to use wastewater in agriculture and industry after treatment" (http://www.dpt.gov.tr/DPT.portal).

Because of the increasing pressures of wastewater discharge on water supplies and the shortage of water resources, more and more attentions have been paid on the reuse of secondary effluent of municipal wastewater (Wang et al., 2008a). Although water reuse guidelines were developed for protection of health, it is evident that they were based on the control of conventional parameters such as pH, biochemical oxygen demand (BOD), total suspended solid (TSS), and pathogenic organisms (see Table II.4). Protozoan pathogens, helminths, or the trace organic compounds are not included in current water reuse regulations. High quality water can be produced using a combination of advanced wastewater treatment processes (Metcalf & Eddy, 2003).

Thus advanced wastewater treatment plays an increasingly critical role in the treatment of municipal and industrial wastewater to meet water quality objectives for water reuse and protect public health. Opportunities of adapting technological innovations are much greater in water reuse applications, because reclaimed water will have an economic value as an alternative water supply source. In evaluating water reclamation technologies, overriding considerations are the operational reliability of each unit process or operation, and the overall capability of the complete treatment system to provide reclaimed water that meets established wastewater reclamation criteria. After conventional biological treatment processes (e.g. activated sludge process, trickling filters, and oxidation ponds), tertiary or advanced treatment can be applied to remove additional dissolved and suspended contaminants, nutrients, specific metals, and other harmful constituents (Mujeriego and Asano, 1999).

**Table II.4** Summary of EPA Suggested Guidelines for Water Reuse[a] (Metcalf & Eddy, 2003)

| **Level of treatment** | **Types of reuse** | **Reclaimed water quality** | **Reclaimed water monitoring** | **Setback distances** |
|---|---|---|---|---|
| 1. Disinfected tertiary[b] | Urban reuse[c]<br>Food crop irrigation<br>Recreational impoundments | pH = 6 - 9<br>BOD Ò10 mg/L<br>Turb. Ò2 NTU<br>E.coli = none<br>Res. $C1_2$ Ó1 mg/L | pH = weekly<br>BOD = weekly<br>Turb. = cont.<br>E.coli = daily<br>Res. $C1_2$ = cont. | 15 m (50 ft) to potable water supply wells[d] |
| 2. Disinfected secondary | Restricted access area irrigation<br>Food crop irrigation (commercially processed)<br>Nonfood crop irrigation<br>Landscape impoundments<br>Construction<br>Wetlands habitat | pH = 6 - 9<br>BOD = 30 mg/L<br>TSS = 30 mg/L<br>E.coli = 200/100 mL<br>Res. $C1_2$ Ó1 mg/L | pH = weekly<br>BOD = weekly<br>TSS = daily<br>E.coli = daily<br>Res. $C1_2$ = cont. | 30 m (100 ft) to areas accessible to the public (if spray irrigation)<br>90 m (300 ft) to potable water supply well |

[a]From U.S. EPA (1992a).

[b]Filtration of secondary effluent.

[c]Uses include landscape irrigation, vehicle washing, toilet flushing, use in fire protection, and commercial air conditions.

[d]Setback increases to 150 m (500 ft) if impoundment bottom is not sealed

Acceptance of the concept of reuse has been accelerated by the development of new wastewater treatment processes that can economically yield clean, high quality water. One such process is the adsorption of wastewater contaminants by activated carbon treatment and disinfection by ozonation (see Table II.5) (Bansode, 2004).

**Table II.5** Summary of Unit Processes and Operations Used in Wastewater Reclamation and Potential for Contaminant Removal by Activated Carbon, Carbon Adsorption and Ozone (Metcalf & Eddy, 2003)

| | **Activated sludge** | **Carbon adsorption** | **Ozone** |
|---|---|---|---|
| **BOD** | >50% | >50% | 25% |
| **COD** | >50% | 25-50% | >50% |
| **TSS** | >50% | >50% | |
| **$NH_3$-N** | >50% | 25-50% | |
| **$NO_3$-N** | | 25% | |
| **Phosphorus** | 25-50% | >50% | |
| **Alkalinity** | 25-50% | | |
| **Oil and grease** | >50% | 25-50% | |
| **Total coliform** | >50% | >50% | >50% |
| **Arsenic** | 25-50% | 25% | |
| **Cadmium** | >50% | 25% | |
| **Chromium** | >50% | 25-50% | |
| **Copper** | >50% | 25-50% | |
| **Iron** | >50% | >50% | |
| **Lead** | >50% | 25-50% | |
| **Manganese** | 25-50% | 25-50% | |
| **Mercury** | 25% | 25% | |
| **Selenium** | 25% | 25% | |
| **Silver** | >50% | 25-50% | |
| **Zinc** | | >50% | |
| **Color** | 25-50% | >50% | >50% |
| **Foaming agents** | >50% | >50% | 25% |
| **Turbidity** | >50% | >50% | |
| **TOC** | >50% | >50% | >50% |

Activated carbon adsorption is effective in removing hydrophobic organic compounds from surface and groundwater sources. Compounds with low water solubilities, such as organic solvents and chlorinated organic solvents, are adsorbable because of their low water solubility. Water soluble compounds and larger compounds are better removed by oxidation or ultra filtration (Mujeriego and Asano, 1999)

Disinfection is essential component of many wastewater reclamation and reuse treatment systems. The objective of disinfection processes is to inactive/destroy pathogenic organisms. Chemical disinfection practices are based on addition of a strong oxidizing chemical such as chlorine, ozone, hydrogen peroxide, or bromine. Ultraviolet radiation is an alternate to oxidation process that can be achieve disinfection (Mujeriego and Asano, 1999).

Ozonation is generally considered to improve biodegradation of water pollutants and this improvement in biodegradation is believed to bring about increased organic removal during activated carbon conducting and it is also a strong oxidizer for organic matter.

## II.2. OZONATION

Ozonation is the most powerful oxidizing agent available for the drinking water treatment and also wastewater treatment especially treatment of industrial wastewaters. However, it is an unstable gas under conditions normal to water and wastewater treatment and because of this, it cannot be manufactured at some central facility, bottled, shipped, and stored. It must be generated and applied at its point of use. An additional complication for ozone is the fact that it is only partially soluble in water to a greater extent than oxygen, but still anything but totally water soluble. As a result, the introduction of ozone into water or wastewater involves gas/liquid contacting to maximize the mass transfer of ozone from the gas to the aqueous phase (Rice, 1997).

The main purpose for the application of ozone in water treatment is disinfection and oxidation (e.g. taste and odor control, decolorization, elimination of micro pollutants, etc.) or combination both. Ozone is an environmentally friendly oxidant since it finally decomposes into oxygen without producing self-derived byproducts in the oxidation reaction (Muruganandham et al., 2007).

Ozonation would be strongly recommended as a pretreatment in terms of removing organic matter. The permeate water quality by ozonationï microfiltration process was in good compliance with the guidelines for wastewater reuse proposed by South Korean Ministry of Environment (Park et al., 2010).

As one of the most powerful oxidants with an oxidation potential ($E^0$) of 2.07 V (Eq. (1)), ozone can act as a very strong oxidizing agent for the treatment of contaminated wastewater of high strength (Kurniawan et al., 2006):

$$O_3 + 2H^+ + 2e^- Ÿ\ O_2 + H_2O,\ E^0 = 2.07\ V \quad (II.1)$$

Ozone is not confined solely to treatment of natural waters for drinking water. Ozone has been used in wastewater treatment. Although the general objective of ozonation in wastewater treatment is disinfection after the secondary biological treatment, ozone also plays a variety of other roles, mainly to improve the efficiency of other unit operations such as coagulation-flocculation-sedimentation or carbon filtration; to remove biologically refractory or toxic compounds to improve biological oxidation units; or to reduce the amount of sludge generated in these latter systems. As a consequence, ozone is recommended in wastewater treatment as a complementary agent of other processes, manly to increase biodegradability, reduce toxicity of recalcitrant compound, etc. (Beltran, 1955).

An additional benefit associated with the use of ozone for disinfection is that the dissolved oxygen concentration of the effluent will be elevated to near saturation levels as ozone rapidly decomposes to oxygen after application. The increase in the oxygen concentration may eliminate the need for reaeration of the effluent to meet required dissolved oxygen water-quality standards. Further, because ozone decomposes rapidly, no chemical residual persists in the treated effluent that may require removal, as is the case with chlorine residuals (Metcalf &Eddy, 2003).

In recent years, ozonation has gained attention for its ability to oxidize endocrine disrupting chemicals (EDCs) and pharmaceuticals in both drinking water and wastewater (Wert et al., 2007).

### **II.2.1** Properties and Structure of Ozone

Ozone is a bluish, colored gas that has a boiling point of -119.9 and it has a distinct odor. Ozone can be detected at concentrations of $2 \times 10^{-5}$ to $1 \times 10^{-4}$ g/m$^3$

(0.01 to 0.05 ppm). Because it has an odor, ozone can usually be detected before health concerns develop. Ozone is fairly unstable in a watery solution; its half-life in water is about 20 minutes. In air, ozone has a half-life of 12 hours, which makes the stability of ozone in air superior. At atmospheric pressure, ozone can partially dissolve in water. Concentrated mixtures of ozone and oxygen that contain more than 20% ozone can become explosive in both fluids and gases. Gaseous ozone can be explosive when the concentration is reaches about 240 g/m$^3$ (20% weight in air). (Metcalf &Eddy, 2003; http://www.lenntech.com/ozone/ozone-properties.htm). The properties of ozone are summarized in Table II.6.

**Table II.6** Properties of Ozone (Metcalf & Eddy, 2003)

| **Property** | **Unit** | **Value** |
|---|---|---|
| Molecular weight | g | 48.0 |
| Boling point | $^o$C | -119.9 ± 0.3 |
| Melting point | $^o$C | -192.5 ± 0.4 |
| Latent heat of vaporization at 111.9$^o$C | kJ/kg | 14.90 |
| Liquid density at -183$^o$C | kg/m$^3$ | 1574 |
| Vapor density at 0$^o$C and 1 atm | g/mL | 2.154 |
| Solubility in water at 20.0$^o$C | mg/L | 12.07 |
| Vapor pressure at -183$^o$C | kPa | 11.0 |
| Vapor density compared to dry air at 0$^o$C and 1 atm | unitless | 1.666 |
| Specific volume of vapor at 0$^o$C and 1 atm | m$^3$/kg | 0.464 |
| Critical temperature | $^o$C | -12.1 |
| Critical pressure | kPa | 5532.3 |

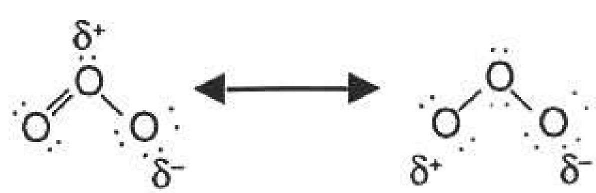

**Figure II.2** Structure of Ozone (http://www.lenntech.com/ozone/ozoneproperties.htm)

The symbols ŭ+ en ŭ- show that ozone molecules are short of electrons on the locations where these signs occur. This means that ozone is a dipolar molecule. This causes ozone to have characteristic properties. Ozone reacts very selectively and is electrophilic (http://www.lenntech.com/ozone/ozone-properties.htm).

The concentration of ozone in the gas phase can be reported in variaty of units such as: parts per mllion by volume (ppm), milligrams per standard liter of gas ($mg/L_{STD}$) or percent weight (w/w%). Ozone residual, transferred dose and utilized ozone are expressed in mg $O_3$/L of water (Alpak, 2009).

Ozone is an unstable gas produced when oxygen molecules dissociate into atomic oxygen. Ozone can be produced by electrolysis, photochemical reaction, or radiochemical reaction by electrical discharge. Ozone is often produced by ultraviolet light and lighting during thunderstorm. The electrical discharge method is used for the generation of ozone in water and wastewater disinfection applications (Metcalf &Eddy, 2003). As ozone is an unstable gas that must be generated on-site. A simplified representation of the chemistry involved in the formation of ozone ($O_3$) is as follows:

$$O_2 + \text{energy} \rightarrow O + O \qquad \text{(II.2)}$$

$$O + O_2 \rightarrow O_3 \qquad \text{(II.3)}$$

The energy required to produce nascent or elemental oxygen (O) from molecular oxygen ($O_2$) is usually supplied by an electric discharge with a peak voltage from 8 to 20 kV, depending on the apparatus used. Dry, refrigerated, particle-free air, oxygen, or oxygen-enriched air is passed through a narrow gap between two electrodes and a high-energy discharge is generated across the gap between the electrodes. This corona or cold plasma discharge is induced by an alternating current that creates a voltage cycle between the two electrodes. The yield of ozone will depend on the voltage, the frequency, the design of the ozone generator, and the type and quality of the feed gas used. Ozone streams containing up to 14 percent ozone by volume can be produced. Current ozone generators are available as low-frequency (50 to 60 Hz), medium-frequency (400 to 1000 Hz), and high-frequency (2000 to 3000 Hz) systems. Once generated, the ozone-enriched air or oxygen gas is passed through a gas absorption device to transfer ozone into solution. This can be achieved through a countercurrent multistage bubble contactor, an in-line gas injection system, or other such gas transfer devices (Singer and Reckhow, 1999).

**II.2.2** Ozone Chemistry in Aqueous Solution

When molecular ozone, $O_3$ dissolves in water, the molecule can remain as $O_3$ or it can decompose by variety of mechanisms, ultimately producing the hydroxyl free radical, ($OH^0$), which itself a stronger oxidizing agent than is molecular ozone (Rice, 1997). Ozone is very reactive with a number of common constituents in drinking water (e.g., natural organic matter (NOM)), and it also undergoes a spontaneous decomposition process (Singer and Reckhow, 1999). The decomposition reactions of ozone in water are as follows:

$$O_3 + H_2O \rightarrow HO_3^+ + OH^- \quad \text{(II.4)}$$

$$HO_3^+ + OH^- \rightarrow 2HO_2 \quad \text{(II.5)}$$

$$O_3 + HO_2 \rightarrow HO + 2O_2 \quad \text{(II.6)}$$

$$HO + HO_2 \rightarrow H_2O + O_2 \quad \text{(II.7)}$$

The free radicals, formed $HO_2$ and HO, have great oxidizing powers, and are probably the active form in the disinfection process. These free radicals also possess the oxidation power to react with other impurities in aqueous solutions (Metcalf &Eddy, 2003).

In natural waters the lifetime of ozone depends on several variables, including pH, temperature, total organic carbon (TOC) concentration, presence of ozone demanding constituents, ionic strength and bicarbonate and carbonate concentrations. Increases in pH, temperature, or concentrations of natural organic matter increase the rate of decomposition of molecular ozone into its daughters. For some wastewater treatment problems, ozone decomposition to ($OH^0$) is desired. Bicarbonate and carbonate increase the lifetime of ozone by reacting with the hydroxyl radical ($OH^0$) (Singer and Reckhow, 1999; Rice, 1997).

$$OH + HCO_3^- \rightarrow OH^- + HCO_3 \quad \text{(II.8)}$$

$$OH + CO_3^{-2} \rightarrow OH^- + CO_3^- \qquad (II.9)$$

The hydroxyl radical ($OH^0$), one of the intermediates produced by the decomposition of ozone, is one of the strongest chemical oxidants known and is capable of rapidly reacting with a myriad of organic and inorganic compounds (Figure II.3). Accordingly, the oxidative properties of ozone depend significantly on the oxidative characteristics of this free radical species (Singer and Reckhow, 1999).

Molecular ozone itself, being a weaker oxidizing agent than hydroxyl free radical, is a rather specific selective oxidant. It is because of this selectivity that most water and wastewater treatment processes can be performed with relatively low ozone dosages. A more reactive oxidant would be consumed in large amounts in extraneous oxidation reactions. Because of this high selectivity, most industrial wastewater treatment oxidations can be performed with molecular ozone, only a relatively few applications require the hydroxyl free radical (Rice, 1997).

Ozone reacts by two distinct types of pathways:

- Direct pathway involving molecular ozone ($O_3$) and
- Indirect pathway originating with the decomposition of ozone to produce the hydroxyl free radical ($OH^0$).

Direct reactions involving molecular ozone are very selective; ozone reacts very rapidly with some species ï for example, phenol and mercaptans ï but very slowly with other speciesð for example, benzene and tetrachloroethylene (PCE). Conversely, the OH radical is nonselective in its behavior, reacting rapidly with a large number of species. Additionally, the OH radical reacts rapidly with molecular ozone (see Figure II.3), thereby contributing to the autocatalytic rate of ozone decomposition. Hydroxyl radical scavengers, such as the bicarbonate and carbonate ion, react with the hydroxyl radical (see also Eqs. 8 and 9), removing it from the cycle and, in so doing, decelerating the kinetics of ozone decomposition, which promotes the stability of molecular ozone in solution, as already noted (Singer and Reckhow, 1999).

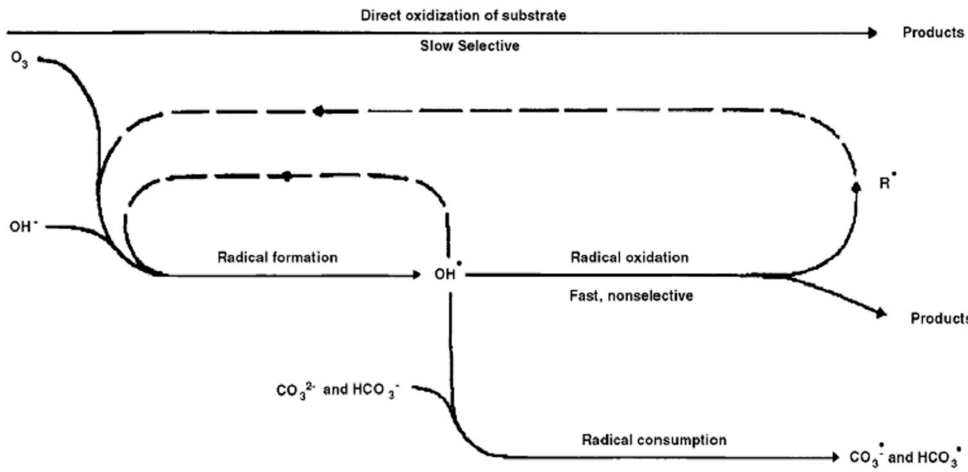


**Figure II.3** Reaction Pathways for Ozone (Singer and Reckhow, 1999)

When ozone is applied to a real wastewater there will likely be numerous series- parallel ozone reactions, depending on the wastewater complexity. The chemical composition of the wastewater determines its potential reactivity with ozone. Knowledge of the composition of the wastewater results is fundamental to predicting ozone reactivity and potential application. In addition, pH and concentration of the compounds present in the wastewater are other key factors for future kinetics (Beltran, 2004).

**II.2.3** Effect of Ozone on Disinfection

Disinfection is considered to be the primary mechanism for the inactivation/destruction of pathogenic organisms to prevent the spread of waterborne diseases to downstream users and the environment. It is important that wastewater be adequately treated prior to disinfection in order for any disinfectant to be effective (EPA, 1999).

More and more countries are taking measures to reuse wastewater. This has been prompted by the ever decreasing availability of good quality raw water and the increasing cost of producing potable water. Disinfection is a major treatment step in the direct reuse of reclaimed wastewater to ensure environmental and public health protection. ñDisinfection is the destruction, inactivation or removal of those micro-organisms likely to cause subsequent infection of people. Wastewater disinfection refers to the use of a process designed specifically to reduce the numbers of viable, infectious microbial organisms in an effluent, ...ò (Wright, 1997). Because of its high oxidation potential and specific lethality, ozone is the most effective disinfectant (killing bacteria, inactivating viruses and protozoa).

$O_3$ : 2.07 volt (pH = 7)

$Cl_2$ : 1.36 volt (pH = 2 - 6)

$ClO_2$ : 0.95 volt (pH = 7)

In addition to disinfection, wastewater treatment must address other factors such as lowering the chemical oxygen demand (COD), and to a lesser extent sometimes the BOD, as well as making improvements in color and odor. With ozone, oxidation of organic matter and precipitation of metals further improve the water quality and allow its reuse (Koltunski and Plumridge, 2007).

Ozonation has been shown to be highly effective for water disinfection. In drinking water treatment, ozonation is used to meet U.S. Environmental Protection Agency (USEPA) regulations for the inactivation of viruses, Cryptosporidium, and Giardia (Wert et al, 2007). The use of ozone for the disinfection of sewage effluent has been escalating since the early 1970s, primarily in United States (Rice et. al, 1981). Ozone's use in the treatment of municipal and industrial wastewater was thoroughly reviewed by Rice in 1997. He mentions that in the United States, the cities of Denver, CO, El Paso, TX, Tampa, FL and San Diego, CA have started wastewater reuse programmes, in which ozone plays an important role as a polishing and disinfecting agent. The city of Windhoek, Namibia, which has been treating its sewage for potable reuse for many years, is planning to substitute ozonation for chlorination prior to granular activated carbon (GAC) adsorption (Koltunski and Plumridge, 2007).

Ozone is an extremely reactive oxidant, and it is generally believed that bacterial kill through ozonation occurs directly because of cell wall disintegration (cell lysis). The impact of the wastewater characteristics on ozone disinfection is reported in Table II.7. The presence of oxidable compounds will cause the ozone inactivation curve to have a shoulder effect (Metcalf & Eddy, 2003).

**Table II.7** Impact of Wastewater Constituents on the Use of Ozone for Wastewater Disinfection (Metcalf & Eddy, 2003)

| Constituent | Effect |
|---|---|
| BOD, COD, TOC, etc. | Organic compounds that comprise the BOD and COD can exert an ozone demand. The degree of interference depends on their functional groups and their chemical structure |
| Humic materials | Affects the rate of ozone decomposition and the ozone demand |
| Oil and grease | Can exert an ozone demand |
| TSS | Increase ozone demand and shielding of embedded bacteria |
| Alkalinity | No or minor effect |
| Hardness | No or minor effect |
| Ammonia | No or minor effect, can react at high pH |
| Nitrite | Oxidized by ozone |
| Nitrate | Can reduce effectiveness of ozone |
| Iron | Oxidized by ozone |
| Manganese | Oxidized by ozone |
| pH | Affects the rate of ozone decomposition |
| Industrial discharges | Depending on the constituents, may lead to diurnal and seasonal variations in the ozone demand |

Ozone is very effective viricide and is generally believed to be more effective than chlorine. Ozonation does not produce dissolved solids and is not affected by the ammonium ion or pH influent to the process. For these reasons, ozonation is considered as an alternative to either chlorination or hypochlorination, especially where dechlorination may be required and high-purity oxygen facilities are available at the treatment plant (Metcalf & Eddy, 2003).

$O_3$ provided superior disinfection compared to $O_3/H_2O_2$ while minimizing DBP (disinfection byproduct) concentrations. These are important considerations for water reuse, aquifer storage and recovery; and advanced wastewater treatment applications (Wert et al., 2007). Ozone is produced when oxygen molecules are dissociated by an energy source into oxygen atoms and subsequently collide with an oxygen molecule to form an unstable gas, ozone, which is used to disinfect wastewater.

Ozone is a very strong oxidant and virucide. The mechanisms of disinfection using ozone include:

- Direct oxidation/destruction of the cell wall with leakage of cellular constituents outside of the cell.
- Reactions with radical by-products of ozone decomposition.
- Damage to the constituents of the nucleic acids (purines and pyrimidines).
- Breakage of carbon-nitrogen bonds leading to depolymerization (EPA, 1999).

**II.2.4** Effect of Ozone on Adsorption

Ozone oxidation combined with activated carbon has been used for many purposes in advanced wastewater treatment. Removal of soluble refractory organics, recalcitrant compounds, toxic chemicals, color and control of DBP formation are some of the benefits of the method.

The application of ozone before carbon adsorption was considered to be a promising method because of its reported success in European water treatment applications and in several pilot-plant studies for advanced wastewater treatment in the U.S. where pre-ozonation greatly increased the adsorptive capacity of granular activated carbon (Culp and Hansen, 1980).

During the ozonation of secondary effluent, ozone partially oxidizes organic materials from large molecules and refractory materials into smaller biologically degradable molecules that can be removed by filtration over sand or activated carbon or filtration with another biological system (Koltunski and Plumridge, 2007).

Ozone oxidation combined with activated carbon adsorption also has been identified as a suitable treatment option especially for removing toxic chemicals. Moreover, dissolved ozone may react with both dissolved organic contaminants and adsorbed species, increasing the extent of oxidation, and eventually, reducing genotoxic activity (Mondaca et al., 2000).

Control of DBP formation due to the addition of ozone as disinfectant can be removed by passage through a biologically active filter or carbon column or other biologically active process (Metcalf & Eddy, 2003).

Industrial grade phosphoric acid can be treated with ozone followed by GAC adsorption to remove dark colors and many organic impurities cost-effectively. Although GAC adsorption alone can provide these benefits, the pre-ozonation step greatly extends the useful lifetime of the GAC (Rice, 1997).

In recent years, a combination of ozonation and activated carbon (especially GAC) adsorption has emerged as one of the most promising options for the treatment of contaminated wastewater especially for the contaminated landfill leachate. Upon decomposition, ozone was reported capable of oxidizing organic substances to their highest stable oxidation states, producing water and carbon dioxide, while activated carbon could remarkably accelerate the kinetic rate of ozone decomposition through the formation of $OH^0$ radicals in the solution (Foo and Hameed, 2009; Kurniawan et al., 2006). Although GAC adsorption was more effective than ozonation alone in terms of COD removal, the combination of these two methods into an integrated process was found to be a more attractive option for the treatment of stabilized leachate, since it offered synergistic effects on the removal of many recalcitrant compounds such as xenobiotic and Adsorbable Organic Halogens (AOX) compounds. Ozone oxidation could rapidly react with most of the recalcitrant organic compounds in the leachate, breaking them down into smaller and more biodegradable ones, thus enabling the subsequently easier adsorption of the more oxidized by-products by GAC (Kurniawan et al., 2006).

Both ozonation and adsorption on activated carbon have proved to be efficient in removing color and some of the organic matter from highly colored effluents. Although effective, both processes present some disadvantages. Ozonation causes the decomposition of highly structured dye molecules into smaller molecules by attacking the cromophores. It is quite efficient in decolorizing solutions, but considerablyless efficient in terms of TOC removal. On the other hand, adsorption on activated carbon can lead to better results than ozonation in terms of TOC removal. The problem is that, when treating wastewaters with high organic content, this adsorbent can become saturated very easily, requiring regeneration or further replacement (Faria et al., 2005).

Takeuchi et al. (1997) studied the changes in equilibrium adsorption and in the biodegradability of organic substances dissolved in water before and after oxidation with ozone. The ratios of the concentrations of the effluents to the initial concentration in terms of TOC in the case of two experimental runs, e.g., biological activated carbon (BAC) treatment with and without ozone pre-oxidation. The removal ratio in the treatment without ozonation seemed to be higher than that with ozonation. The total amounts of TOC removed during this period with and without ozonation were found to be about $1.4 \times 10^{-3}$ kg and $1.6 \times 10^{-3}$ kg, respectively. Therefore, it can be concluded that reaction with ozone gives negative effects on adsorption behavior of organics. Ozonation of raw water before feeding it or the activated carbon bed made biological process better, while ozonation gave a littler bad effect to carbon adsorption in lowering of adsorbability.

It is also important to know the change of adsorbability in NOM by ozonation preceding GAC adsorption. Ozonation may have negative effect on GAC adsorption of NOM due to the increases in polarity and hydrophilicity and positive effect due to the decrease in molecular weight. Kim et al. (1997) showed ozonated NOM has lower adsorbability to GAC than NOM without ozonation. Benedek et al. (1979) showed the same result, however, they also showed that ozonated NOM after biostabilization has almost the same adsorbability as NOM without ozonation. Harrington and DiGiano (1989) showed different result from Benedek et al. (1979), that is, ozonated NOM after biostabilization has lower adsorbability to GAC than NOM without ozonation. The adsorption and desorption characteristics of biodegradable dissolved organic carbon (BDOC) produced by ozonation were also studied. It was found that biodegradable BDOC produced by ozonation showed the same or lower adsorption capacity then non-BDOC after biodegradation. The adsorption rate of BDOC on GAC was lower than that of non-BDOC. BDOC produced by ozonation had low desorbability and majority of BDOC produced was not replaced by non-BDOC (Nishijima and Speitel, 2004).

It is well established that ozonation increases the biodegradable portion of DOC. Studies up to now showed that the increase in biodegradable DOC enhanced biological DOC removal. The percent increase in BDOC upon ozonation on the average was 166%. Despite this huge increase, the biological DOC removal efficiency was not so much affected in the filters fed with ozonated water. The biological DOC removal was only 8% higher than in the CAgran column fed with raw water. In case of Norit 1240, no enhancement of DOC removal could be observed. Therefore, it was concluded that ozonation did not have a pronounced effect on DOC removal (Yapsaklēand Çeçen, 2009).

**II.2.5** Effect of Ozone on Biodegradability

Chemical oxidation can degrade organic compounds without any additional waste produced. The most common oxidants are ozone and $H_2O_2$ etc. Ozone is a very powerful oxidant (Redox potential 2.07V for ozone *versus* 2.8V for hydroxyl radical) for water and wastewater treatment. Once dissolved in water, ozone reacts with a large number of organic compounds in two possible ways: direct oxidation, as molecular ozone, or indirect reaction through the formation of secondary oxidants such as free radicals, particularly hydroxyl radical. Ozone treatment of several types of wastewaters, resulting in considerable organics elimination, had been reported by some researchers (Wang et al., 2008a).

The organic composition of wastewater is also different from natural organic matter found in surface water supplies and is commonly known as effluent organic matter (EfOM). EfOM is composed of recalcitrant NOM from drinking waters, synthetic organic chemicals added during anthropogenic use (including disinfection by-products), and soluble microbial products (Wert, 2007).

Ozonation of refractory organic compounds in water with high ozone dosages usually produces oxygenated organic products, which are more biodegradable. This effect is used in water works where ozone is applied to wastewater and especially effluents from municipal biological treatment plants in order to improve the removal of organic material. The biochemical oxygen demand is the parameter that measures the biodegradability of wastewater but the literature also reports the ratio BOD/COD as a more realistic parameter because it also considers the magnitude of pollution (that is, the magnitude of COD). The improved biodegradability is associated with the partial oxidation of organic matter to give low molecular weight oxygenated compound rather than complete oxidation to carbon dioxide. Although COD and TOC were not completely removed from the wastewater due to an ozone-resistant fraction, which remained after the treatment, the ability of ozone to cause alteration in the molecular structures of dissolved compounds may result in an increase in the wastewater biodegradability (Shiyun et al., 2002; Beltran, 2009).

As ozonation improve the biodegradability of wastewater, ozone alone is not recommended technology for the treatment of wastewater. Due to high levels of organic matter, in many cases, high consumption of ozone is observed with small percentage reductions of COD, although this always depends on the nature of the wastewater treated as mentioned ozone chemistry section. The beneficial effect of preozonation is clear, but oxidation did not provide any additional benefit when used as a stand-alone technology (Bijan and Mohseni, 2005; Beltran, 2009).

Ozone, particularly in combination with biological treatment, can be used to treat wastewaters which contain pollutants which can be oxidized by ozone to produce biodegradable derivatives. The combination of ozone oxidation followed by biological treatment has been installed full-scale at a large German industrial chemical complex (Rice, 1997).

Experimental results showed that ozonation could be successfully used as a pretreatment step to improve the biodegradability of wastewater containing antibiotics (Balcēoĵ lu and Ötker, 2002).

Furthermore, ozonation is expected to cause an increase of the biodegradable organic carbon for subsequent biological stages. The combined removal is partly attributed to the direct oxidation by ozone. More important is that ozonation increased the biodegradability of the influent, which increased effectively the removal efficiency of the sequent biofiltration unit (Wang et al., 2008a).

Yeom et al. (2002) was studied the effects of ozone pretreatment on the biodegradability and ozonated municipal wastewater sludge showed about 2-3 times greater biodegradation compared to the raw sludge in both aerobic and anaerobic conditions.

Marguerite et al. (1986) studied removal of mutagenic compounds in water by increasing the biodegradability of the organic matter with ozone. The ratio of biodegradable organics to nonbiodegradable organics showed an increase.

Ramirez and Velasquez (2004) also studied removal and transformation of recalcitrant organic matter from stabilized saline landfill leachates by coagulationï ozonation coupling processes and they found that indicators of biodegradability were found to increase significantly as a result of ozonation.

Previous applications of ozone-based processes for the treatment of pulp and paper mill effluents showed the merit of these technologies in enhancing the biodegradability, decreasing the toxicity, and increasing the removal of the organics from the effluents. Ozonation under basic condition could enhance the biodegradability of the alkaline effluent more than that under acidic pH. Ozonation under acidic condition only involved the selective reaction of ozone with unsaturated organics of the wastewater. The oxidation ability of ozone is by far lower than the oxidizing radicals (e.g. hydroxyl radical) formed under basic pH, as seen for several compounds found in the pulp mill bleach plant effluent. Treatment of alkaline bleach plant effluent using combination of ozonation with biological treatment provided significantly higher organics mineralization (measured as TOC) than the individual treatment stages. Ozonation alone performed similar to the biological treatment in mineralization of high content of biorefractory constituents in the effluent. Therefore, ozone oxidation did not provide any additional benefit when used as a stand-alone technology (Bijan and Mohseni, 2005).

UV absorbance at 254 ($UV_{254}$) represents the existence of unsaturated carbon bonds including aromatic compounds, which are generally recalcitrant for biodegradation, and decrease of UV absorbance results in the increase of biodegradability (Nishijima and Speitel, 2004).

### II.3 ADSORPTION

Adsorption of a substance involves its accumulation at the interface between two phases, such as a liquid and a solid or a gas and a solid. The molecule that accumulates, or adsorbs, at the interface is called an *adsorbate,* and the solid on which adsorption occurs is the *adsorbent.* Adsorbents of interest in water treatment include activated carbon; ion exchange resins; adsorbent resins; metal oxides, hydroxides, and carbonates; activated alumina; clays; and other solids that are suspended in or in contact with water (Snoeyink and Summers, 1999).

Although adsorption is used at the air-liquid interface in the flotation process, only the case of adsorption at the liquid-solid interface will be considered in this study. The adsorption process has not been used extensively in wastewater treatment, but demands for a better quality of treated wastewater effluent, including toxicity reduction, have led to an intensive examination and use of the process of adsorption on activated carbon. Activated carbon treatment of wastewater is usually thought of as a polishing process for water that has already received normal biological treatment. The carbon in this case is used to remove a portion of the remaining dissolved organic matter. The purpose of this section is to introduce the basic concepts of adsorption and to consider carbon adsorption (Metcalf & Eddy, 2003).

### **II.3.1** Adsorption Equilibrium

Adsorption of molecules can be represented as a chemical reaction:

A + B ź AĀB (II.10)

where A is the adsorbate, B is the adsorbent, and AĀB is the adsorbed compound. Adsorbates are held on the surface by various types of chemical forces such as hydrogen bonds, dipole-dipole interactions, and van der Waals forces. If the reaction is reversible, as it is for many compounds adsorbed to activated carbon, molecules continue to accumulate on the surface until the rate of the forward reaction (adsorption) equals the rate of the reverse reaction (desorption).When this condition exists, equilibrium has been reached and no further accumulation will occur (Snoeyink and Summers, 1999).

#### **II.3.1.1** Isotherm Equations

The quantity of adsorbate that can be taken by an adsorbent is a function of both the characteristics and concentration of adsorbate and temperature. The characteristics of the adsorbate that are of importance include: solubility, molecular structure, molecular weight, polarity, and hydrocarbon saturation (Metcalf & Eddy, 2003). Adsorption isotherms are a graphical representation showing the quantity of adsorbate adsorbed by a unit weight of adsorbent. Adsorption isotherms describe the thermodynamics of adsorption and are used to describe adsorption equilibria that may require long contact times for compounds that adsorb only slowly. It also provides a panorama of the course taken by the system under study in a concise form, indicating how efficiently a carbon will adsorb and allows an estimate of the economic feasibility of the carbons commercial application for the specified solute. Adsorption isotherms can be generated based on numerous theoretical models where the Langmuir and Freundlich models are the most commonly used. The Langmuir model is the simplest model that can be used to describe monolayer adsorption based on a kinetic approach and assumes a uniform surface, a single layer of adsorbed material and constant temperature. Adsorption isotherms expressed as the Freundlich model have been found to be a better measure of the adsorptive properties of activated carbons and are based on the distribution of solute between the activated carbon (solid phase) and aqueous phase at equilibrium. The Freundlich model is suitable for use with the heterogeneous surfaces for a single solute system, an assumption made in our experiment with respect to the organic matter in municipal wastewater system (Bansode et al., 2004).

One of the most important characteristics of an adsorbent is the quantity of adsorbate it can accumulate. The constant-temperature equilibrium relationship between the quantity of adsorbate per unit of adsorbent $q_e$ and its equilibrium solution concentration $C_e$ is called the adsorption isotherm. Several equations or models are available that describe this function, but only the more common equations for single-solute adsorption, the Freundlich and the Langmuir equations, are presented here (Snoeyink and Summers, 1999).

The Freundlich equation is an empirical equation that is very useful because it accurately describes much adsorption data. This equation has the form

$$q_e = KC_e^{1/n} \qquad \text{(II.11)}$$

and can be linearized as follows:

$$\log q_e = \log K + \frac{1}{n} \log C_e \qquad \text{(II.12)}$$

The parameters $q_e$ (with units of mass adsorbate/mass adsorbent, or mole adsorbate/mass adsorbent) and $C_e$ (with units of mass/volume, or moles/volume) are the equilibrium surface and solution concentrations, respectively. The terms K and 1/n are constants for a given system; 1/n is unitless, and the units of K are determined by the units of $q_e$ and $C_e$. Although the Freundlich equation was developed to empirically fit adsorption data, a theory of adsorption that leads to the Freundlich equation was later developed by Halsey, G and H. S. Taylor in 1947 (Snoeyink and Summers, 1999).

The parameter K in the Freundlich equation is related primarily to the capacity of the adsorbent for the adsorbate, and 1/n is a function of the strength of adsorption. For fixed values of $C_e$ and 1/n, the larger the value of K, the larger the capacity $q_e$. For fixed values of K and $C_e$, the smaller the value of 1/n, the stronger is the adsorption bond. As 1/n becomes very small, the capacity tends to be independent of $C_e$ and the isotherm plot approaches the horizontal level; the value of $q_e$ then is essentially constant, and the isotherm is termed irreversible. If the value of 1/n is large, the adsorption bond is weak, and the value of $q_e$ changes markedly with small changes in $C_e$ (Snoeyink and Summers, 1999).

The Freundlich equation cannot apply to all values of $C_e$, however. As $C_e$ increases, for example, $q_e$ increases (in accordance with Equation II.11) only until the adsorbent approaches saturation. At saturation, $q_e$ is a constant, independent of further increases in $C_e$, and the Freundlich equation no longer applies. Also, no assurance exists that adsorption data will conform to the Freundlich equation over all concentrations less than saturation, so care must be exercised in extending the equation to concentration ranges that have not been tested (Snoeyink and Summers, 1999).

The Langmuir equation,

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \tag{II.13}$$

where b and $q_{max}$ are constants and $q_e$ and $C_e$ are as defined earlier, has a firm theoretical basis (Langmuir, 1918). The constant $q_{max}$ corresponds to the surface concentration at monolayer coverage and represents the maximum value of $q_e$ that can be achieved as $C_e$ is increased. The constant b is related to the energy of adsorption and increases as the strength of the adsorption bond increases. The Langmuir equation often does not describe adsorption data as accurately as the Freundlich equation. The experimentally determined values of $q_{max}$ and b often are not constant over the concentration range of interest, possibly because of the heterogeneous nature of the adsorbent surface (a homogeneous surface was assumed in the model development), lateral interactions between adsorbed molecules (all interaction was neglected in the model development), and other factors (Snoeyink and Summers, 1999).

#### **II.3.1.2** Factors Affecting Adsorption Equilibria

Important adsorbent characteristics that affect isotherms include surface area, pore size distribution, and surface chemistry. The maximum amount of adsorption is proportional to the amount of surface area within pores that is accessible to the adsorbate. Surface areas range from a few hundred to more than 1500 $m^2/g$, but not all of the area is accessible to aqueous adsorbates. A relatively large volume of micropores (pores less than 2 nm diameter d) generally corresponds to a large surface area and a large adsorption capacity for small molecules, whereas a large volume of mesopores ($2 < d < 50$ nm) and macropores ($d > 50$ nm) is usually directly correlated to capacity for large molecules (Snoeyink and Summers, 1999).

The surface chemistry of activated carbon and adsorbate properties also can affect adsorption. Several researchers demonstrated that extensive oxidation of carbon surfaces led to large decreases in the amounts of phenol, nitrobenzene, benzene, and benzenesulfonate that could be adsorbed. Oxygenating a carbon surface decreases its affinity for simple aromatic compounds (Snoeyink and Summers, 1999).

Adsorption isotherms may be determined for heterogeneous mixtures of compounds using group parameters such as total organic carbon, dissolved organic carbon, chemical oxygen demand, dissolved organic halogen (DOX), UV absorbance, and fluorescence as a measure of the total concentration of substances present (Snoeyink and Summers, 1999).

The affinity of weak organic acids or bases for activated carbon is an important function of pH. When pH is in a range at which the molecule is in the neutral form, adsorption capacity is relatively high. When pH is in a range at which the species is ionized, however, the affinity for water increases and activated carbon capacity accordingly decreases (Snoeyink and Summers, 1999).

#### **II.3.1.3** Adsorption Kinetics

Removal of organic compounds by physical adsorption on porous adsorbents involves a number of steps, each of which can affect the rate of removal. Adsorption process, as illustrated on Figure II.4, takes place in four or more definable steps: (1) bulk solution transport, (2) External (film) diffusion (resistance to) transport, (3) Internal (pore) transport, and (4) adsorption (or sorption) (Snoeyink and Summers, 1999; Metcalf & Eddy, 2003).

1. *Bulk solution transport* Adsorbates must be transported from bulk solution to the boundary layer of water surrounding the adsorbent particle by advection or dispersion in carbon contactors (Snoeyink and Summers, 1999; Metcalf & Eddy,

2003). The transport occurs through diffusion if the adsorbent is suspended in quiescent water such as a sedimentation basin, or through turbulent mixing such as during turbulent flow through a packed bed of GAC, or when PAC is being mixed in a rapid mix unit or flocculator (Snoeyink and Summers, 1999).

2. *External (film) resistance to transport* Adsorbates must be transported by molecular diffusion through the stationary layer of water (hydrodynamic boundary layer) that surrounds adsorbent particles when water is flowing past them. The distance of transport, and thus the time for this step, is determined by the flow rate past the particle. The higher the flow rate, the shorter the distance (Snoeyink and Summers, 1999).

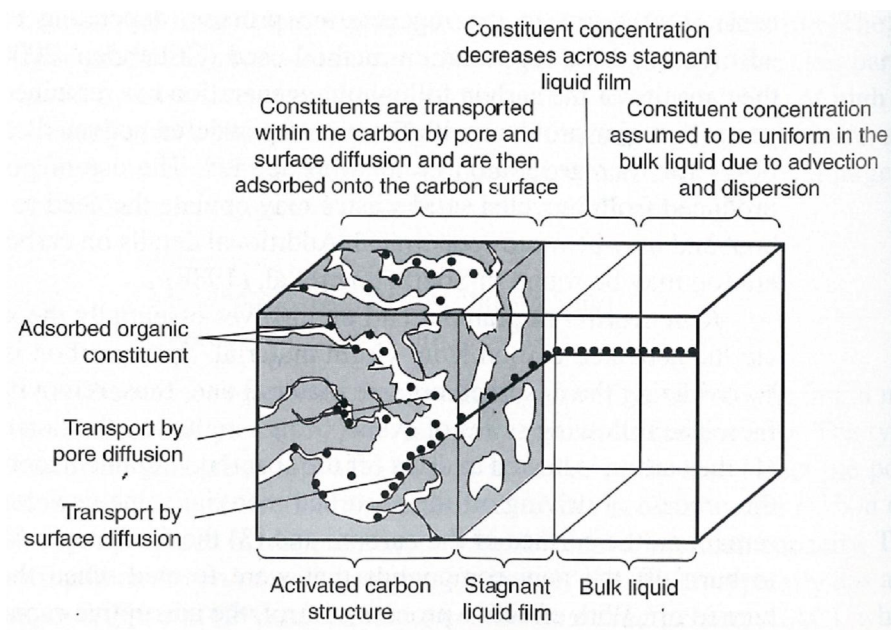


**Figure II.4** Definition Sketch for the Adsorption of an Organic Constituent with Activated Carbon

3. *Internal (pore) transport* After passing through the hydrodynamic boundary layer, adsorbates must be transported through the adsorbentӧs pores to available adsorption sites. Intraparticle transport may occur by molecular diffusion through the solution in the pores (pore diffusion), or by diffusion along the adsorbent surface (surface diffusion) after adsorption takes place (Snoeyink and Summers, 1999).

4. *Adsorption* After transport to an available site, an adsorption bond is formed between the adsorbate and adsorbent (Snoeyink and Summers, 1999). Adsorption can occur on the outher surface of the adsorbent and in the macropores, mesopores, and submicropores, but the surface areas of the macro-and mesopores is small compared with the surface area of the micropores and submicropores and the amount of material adsorbed there is usually considered negligible (Metcalf & Eddy, 2003). This step is very rapid for physical adsorption and as a result one of the preceding diffusion steps will control the rate at which molecules are removed from solution. If adsorption is accompanied by a chemical reaction that changes the nature of the molecule, the chemical reaction may be slower than the diffusion step and thereby control the rate of compound removal (Snoeyink and Summers, 1999).

Because the adsorption process occurs in a series of steps, the slowest step in the series is identified as the *rate limiting step*. In general, if physical adsorption is the principal method of adsorption, one of the diffusion transport steps will be the rate limiting, because the rate of physical adsorption is rapid. Where chemical adsorption is the principal method of adsorption, the adsorption step has often been observed to be rate limiting (Metcalf & Eddy, 2003).

Adsorption capacity depends on

1. Physical and chemical characteristics of the adsorbent (carbon);
2. Physical and chemical characteristics of the adsorbate (the food or beverage);
3. Concentration of the adsorbate in liquid solution;
4. Characteristics of the liquid phase (e.g. pH, temperature)
5. Amount of time the adsorbate is in contact with the adsorbent (residence time) (NOSB TAP, 2002).

Both molecular size and adsorbent particle size have important effects on the rate of adsorption. Diffusion coefficients, in particular, decrease as molecular size increases, and thus longer times are required to remove the large-molecular-weight humic substances than are needed for the low-molecular-weight phenols, for example. Adsorbent particle size is also important because it determines the time required for transport within the pore to available adsorption sites. If the rate of adsorbate uptake is controlled by intraparticle diffusion, and the effective diffusion coefficient is constant, the time to reach equilibrium is directly proportional to the diameter of the particle squared. The smaller the particle, the faster equilibrium is achieved in both column and complete-mix adsorption systems (Snoeyink and Summers, 1999).

**II.3.1.4** Type of Adsorbents

A notable trend in the development of activated carbon, an adsorbent with its large porous surface area, controllable pore structure, thermostability and low acid/base reactivity has been promulgated, owing to its superior ability for removal of a wide variety of organic and inorganic pollutants dissolved in aqueous media, even from gaseous environment (Foo and Hameed, 2009).

The principal types of adsorbents include activated carbon, synthetic polymeric, and silica-based adsorbents, although synthetic polymeric and silica-based adsorbents are seldom used for wastewater adsorption because of their high cost. Because activated carbon is used most commonly in advanced wastewater ï treatment applications, the focus of the following discussion is on activated carbon. The nature of activated carbon, the use of granular carbon and powdered carbon for wastewater treatment, and carbon regeneration and reactivation are discussed below (Metcalf & Eddy, 2003).

**II.3.2** Activated Carbon

Carbon has been used as an adsorbent for centuries. Early uses of carbon were reported for water filtration and for sugar solution purification. Ability of activated carbon to remove a large variety of compounds from contaminated waters has led to its increased use in the last thirty years. Recent changes in water discharge standards regarding toxic pollutants have placed additional emphasis on this technology (CARBTROL® Corporation, 1992).

Carbon is arranged in a quasi-graphitic form in a small particle size. It is solid, porous, black carbonaceous material and tasteless. Activated carbon is distinguished from elemental carbon by the removal of all non-carbon impurities and the oxidation of the carbon surface (NOSP TAB, 2002).

Activated carbon is used on an enormous scale in gas and water purification, metal extraction, medicine and many other applications. It is prepared from a variety of carbonaceous precursors, including coal, peat, coal and nutshells which are carbonized and then ‚activatedö, either by oxidization with $CO_2$ or steam, or by treatment with acids, bases or other chemicals (Harris et al., 2008). Another method is carbonization. In this process, carbon content is heated up to 600-900$^0$C, in an atmosphere of inert gases such as argon or nitrogen. Another method, called Oxidation, exposes the carbonized materials to oxidizing atmospheres such as oxygen, carbon dioxide, or steam, at temperatures between 600-1,200$^0$C. Both techniques physically alter the structure of the molecules, which increase the surface area available for chemical reactions or adsorption (http://www.theactivatedcarbon.com). The resulting carbon can have a surface area of 1,500 $m^2$/g or more, explaining its huge adsorptive capacity. Its precise atomic structure, however, is unknown (Harris et. al., 2008). Experimental activated carbons have been made with over 3,000 $m^2$/g surface areas which are capable of adsorbing more than their own weight of organic substances (Conney, 1999).

Through physical adsorption, activated carbon removes taste and odor causing organic compounds, volatile organic compounds, and many organic compounds that do not undergo biological degradation from the atmosphere and from water, including potable supplies, process streams, and waste streams. The action can be compared to precipitation. Activated carbon is generally nonpolar, and because of this it adsorbs other nonpolar, mainly organic, substances. Extensive porosity (pore volume) and large available internal surface area of the pores are responsible for adsorption (http://scienceray.com/technology/industry/an-introduction-to-activated-carbon).

**II.3.2.1** General Characteristics of Activated Carbon

A number of parameters are used to describe the adsorption capacity of activated carbon.

The *molasses number* or *decolorizing index* is related to the ability of activated carbon to adsorb large-molecular-weight color bodies from molasses solution, and generally correlates well with the ability of the activated carbon to adsorb other large adsorbates (Snoeyink and Summers, 1999).

The *iodine number* measures the amount of iodine that will adsorb under a specified set of conditions, and generally correlates well with the surface area available for small molecules (Snoeyink and Summers, 1999).

The *methylene blue number* is the milligrams of methylene blue adsorbed by 1 g of carbon in equilibrium with a solution of 1 mg/L methylene blue. It has a molecular weight of 320 and an effective molecular diameter of about 15 Â, and thus its adsorption indicates something about the adsorption capacity of carbon for molecules of this size (Cooney, 1999).

*Apparent or Bulk density* is used to determine the weight of a fixed volume of activated carbon. It usually measured in g/mL or pounds per cubic foot (http://www.norit-americas.com).

*Total ash content* is the measure of the amount of mineral matter (Ca, Mg, Si, Fe) in activated carbon (http://www.norit-americas.com).

*Abrasion/Hardness number* is relative measure of the ability of granular or pelleted activated carbon to resist attrition during handling and use (http://www.norit-americas.com).

*Particle size* affects the rate of contaminant adsorption or catalytic activity (http://www.norit-americas.com).

Other numbers have been developed for specific applications, such as the *carbon tetrachloride activity* and the *phenol adsorption value*. The values of these numbers give useful information about the abilities of various activated carbons to adsorb different types of organics. However, isotherm data for the specific compounds to be removed in a given application, if available, are much better indicators of performance.

Two of the more important characteristics of an activated carbon are its pore size distribution and surface area. The manufacturer provides typical data that usually include the *Brunauer-Emmett-Teller (BET) surface area*. This parameter is determined by measuring the adsorption isotherm for nitrogen gas molecules and then analyzing the data using the Brunauer-Emmett-Teller isotherm equation to determine the amount of nitrogen required to form a complete monolayer of nitrogen molecules on the carbon surface.

Multiplying Tabulations of single-solute isotherm constants are very useful when only rough estimates of adsorption capacity are needed to determine whether a more intensive analysis of the adsorption process is warranted (Snoeyink and Summers, 1999).

**II.3.2.2** Activation of Activated Carbon

There are basically two methods for manufacturing activated carbons, i.e. physical and chemical activation. Physical activation consists of two steps, the carbonization of a carbonaceous precursor below $799.85^0$C under an inert atmosphere and thereafter the activation of the resulting product at upper temperature with activating agent such as $CO_2$, steam or air. The most widely used activating gas is steam because for a given temperature, the activated carbon produced with steam has larger adsorptive capacity and wider pore size distribution than that produced with $CO_2$. In the chemical activation process, however, these two steps proceed simultaneously by carrying out thermal decomposition of the raw material impregnated with certain chemical agent such as phosphoric acid, sulfuric acid, potassium hydroxide or zinc chloride in an inert atmosphere. These impregnants are used as dehydrating agents and oxidants that influence pyrolytic decomposition and inhibit formation of tar, thus enhancing the yield of carbon. Some authors have studied the combination of these two methods to obtain activated carbon with specific surface properties (Wang et al., 2008b).

**II.3.2.3** Types of Activated Carbon

Activated carbon is prepared by first making a char from organic materials such as almond, coconut, and walnut hulls; other materials including woods, bone and coal have also been used. The char is produced by heating the base material to a red heat (less than $700^0$C) in a retort to drive off the hydrocarbons, but with an insufficient supply of oxygen to sustain combustion. The carbonization of char-producing process is essentially a pyrolysis process. The char particle is then activated by exposure to oxidizing gases such as steam and $CO_2$ at high temperatures, in the range from 800 to $900^0$C. These gases develop a porous structure in the char and thus creates a large internal surface area. The resulting pore sizes are defined as follows:

| | |
|---|---|
| Macropores | $> 25$ nm |
| Mesopores | $> 1$ nm and $< 25$ nm |
| Micropores | $< 1$ nm |

The surface properties that result are a function of both the initial material used and the preparation procedure, so that many variations are possible. The type of base material from which the activated carbon is derived may also affect the pore-size distribution and the regeneration characteristics. After activation, the carbon can be separated into, or prepared in, different sizes with different adsorption capacity. The two size classifications are PAC, which typically has a diameter of less than 0.074 mm (200 sieve), and granular activated carbon, which has a diameter greater than 0.1 mm (~ 140 sieve) (Metcalf & Eddy, 2003).

As seen in Table II.8 powdered activated carbon blog has a large surface area to volume ratio and granular activated carbon is larger than the powdered version consequently, has a smaller surface area to volume ratio. Granular activated material is usually employed for adsorption of gases and vapors and powdered activated material is used for purification of liquids such as raw water intakes, rapid mix basins, clarifiers, and gravity filters (Bansode, 2004; http://www.theactivatedcarbon.com).

Granulated activated carbon is used as a filter medium for contaminated water or air, while the powdered form is mixed into wastewater where it adsorbs the contaminants and is later filtered or settled from the mixture. Activated carbon has also been used in chemical analysis for prior removal and concentration of contaminants in water (http://scienceray.com/technology/industry/an-introduction-to-activated-carbon).

Raw material for the production of powdered carbon can be non-renewable material such as coal or lignite but also can be agricultural by-products with a soft structure, such as rice straw, sugarcane bagasse, soybean hulls, sawdust, wood or peanut shells (Bansode, 2004). They are so finely powdered that most of them can easily pass through a designated mesh sieve or sieve. Due to their small size they form large internal surface having small diffusion distance. PAC is normally used in processing units like, clarifiers, gravity filters, mix basins, etc (http://www.thewatertreatmentplant.com).

**Table II.8** Comparison of Granular and Powdered Activated Carbon (Metcalf & Eddy, 2003)

| | | Type of Activated Carbon[a] | |
|---|---|---|---|
| **Parameter** | **Unit** | **GAC** | **PAC** |
| Total Surface Area | $m^2$ / g | 700 ï 1300 | 800 ï 1800 |
| Bulk Density | kg / $m^3$ | 400 ï 500 | 360 ï 740 |
| Particle density, wetted in water | kg / L | 1.0 ï 1.5 | 1.3 ï 1.4 |
| Particle size range | mm (µm) | 0.1 ï 2.36 | 5 ï 50 |
| Effective size | mm | 0.6 ï 0.9 | na |
| Uniformity coefficient | UC | Ò1.9 | na |
| Mean pore radius | Â | 16 ï 30 | 20 ï 40 |
| Iodine number | | 600 ï 1100 | 800 ï 1200 |
| Abrasion number | minimum | 75 ï 85 | 70 ï 80 |
| Ash | % | Ò8 | Ò6 |
| Moisture as packed | % | 2 ï 8 | 3 ï 10 |

[a]Specific values will depend on the source material used for the production of the activated carbon.

A wide variety of raw materials can be used to make granular activated carbon, but wood, peat, lignite, subbituminous coal, and bituminous coal are the substances predominately used in the United States (Snoeyink and Summers, 1999). Granulated activated carbon forms smaller external surface because of their larger size as compared to PAC. GACs are used in the form of a carbon bed, usually within a column, for water treatment. The water flows through the bed, where organic molecules present as contaminants are adsorbed on to the carbon surface. Their main function includes deodorization and separation of components of flow system. When the carbon is saturated with the adsorbed molecules, the carbon loses its adsorptive ability, and is removed from the system and regenerated (Bansode, 2004; http://www.thewatertreatmentplant.com).

Powdered activated carbon has some advantages over granular activated carbon. Its initial cost is lower, it reacts faster and more completely, and its dosage can be adjusted to meet the changes in the composition of influent to the system. On the other hand, even the cost of powdered carbon is not sufficiently low to permit its discard after a single use. Some experimental work is now in progress on powdered carbon regeneration (Rose, 1979). Other disadvantages of powdered activated carbon are the inability to regenerate, the low TOC removal, the increased difficulty of sludge disposal, and the difficulty of completely removing the PAC particles from the water (Snoeyink and Summers, 1999).

**II.3.3** Application of Activated Carbon in Wastewater Treatment

Historically, the use of activated carbon has been limited to treatment applications for drinking water. In the last few decades, as in many areas water is becoming scarce source, it may be necessary to use water more than once, then more attention has been given to the potential use of activated carbons for wastewater treatment. Activated carbon adsorption has gained importance as an alternative tertiary wastewater treatment because it is one of the most effective media for removing a wide range of contaminants from industrial and municipal waste waters, landfill leachate and contaminated ground. It is recognized as the most efficient and promising fundamental approach in the wastewater treatment processes to produce effluents meeting current regulations for effluent quality and receiving water preservation (Hung, 2006; Foo and Hameed, 2009; Chaudhary, 2003; Rose, 1979, http://www.chemvironcarbon.com/en/applications/effluent-water-treatment /wastewater).

Many wastewaters contain significant levels of organic contaminants which are toxic or otherwise undesirable because they create odor, bad taste, unsightly color, foaming, etc. these substances are often resistant to degradation by biological methods, and are not removed effectively by conventional physicochemical treatment methods, such as coagulation / flocculation, sedimentation, filtration, and ozonation. Because activated carbon has a strong affinity for binding organic substances, even at low concentrations, it has become the premier method for treating organic-laden wastewaters, especially in reuse applications (Cooney, 1999).

Activated carbon or carbon adsorption process is used for removing various organic substances like Oils, Radioactive Compounds, Petroleum Hydrocarbons, Poly Aromatic Hydrocarbons and various halogenated compounds like Chlorine, Fluorine, Bromine and Iodine. Apart from organic compounds it also removes inorganic compounds like Arsenic, Cadmium, Chromium, Zinc, Lead, Mercury, Copper, etc. As carbon adsorption method is effective in removing pollutants, it is used in following industrial process for water treatment (http://www.thewatertreatmentplant.com):

- Ground Water Purification
- The De-Chlorination of Process Water
- Water Purification
- Wastewater Treatment

The design of carbon adsorption system for the treatment of wastewaters involves consideration of the following parameters:

- Type of carbon ï granular or powdered
- Physical configuration ï upflow or downflow, or mixed number of stages, parallel or series, packed bed or expanded bed, external regeneration or continuous flow.
- Carbon capacity ï detention time, dosage rate
- Method of operation ï pure adsorption, filtration, biochemical (Rose, 1979).

The typical range of environmental water contaminants that activated carbon is used to treat includes:

- Non-biodegradable organic compounds (COD)
- Adsorbable Organic Halogens
- Toxicity
- Colour compounds and dyestuffs
- Inhibitory compounds for biological treatment systems
- Aromatic compound including phenol and bis-phenol A (BPA)
- Chlorinated/halogenated organic compounds
- Pesticides

Over 80% of European Union List I and II toxic substances under the Dangerous Substance Discharges Directive of 1976 (76/464/EEC) and 1986 (86/280/EEC) are well adsorbed by activated carbon (http://www.chemvironcarbon.com/en/applications/effluent-water-treatment/wastewater).

**II.3.3.1** Treatment with Granular Activated Carbon

Treatment with GAC involves passing a liquid to be treated through a bed of activated carbon held in a reactor (sometimes called a contactor). Several types of activated carbon contactors are used for advanced wastewater treatment. Typical systems may be either pressure or granular type, and may be downflow or upflow fixed-bed units having two or three columns in series, or expanded bed upflow-countercurrent type (Metcalf & Eddy, 2003).

GAC filtration is a robust treatment process for removing dissolved, non-biodegradable organics, reducing them to very low levels. For optimal efficiency, 2-3 filters are used in series, the pseudo-moving bed (or merry-go-round) principle being applied. Exhausted GAC is often regenerated off-site by thermal reactivation. In wastewater treatment, GAC is used in fixed filter beds in most cases. Depending on the scale of operation, several options are available: Permanent filter vessels or mobile filters. Mobile filters reduce the need for on-site GAC handling and are attractive for temporary jobs, for example. In many cases, the total GAC treatment costs are dominated by GAC replacement or reactivation, rather than the capital costs. This means that process optimization is focussed on achieving the highest bed life (for example, through pre-treatment), still respecting the effluent standards. Dedicated small, transportable filters are available. Here, the total treatment chain should typically be as simple as possible, avoiding too many different unit operations for a small wastewater flow (http://www.norit-ac.com).

**II.3.3.2** Treatment with Powdered Activated Carbon

An alternative means of achieving adsorption is through the application of powdered activated carbon. Powdered activated carbon can be applied to the effluent from biological treatment process, directly to the various biological treatment processes, and in physical treatment process flow diagrams. In the case of biological treatment plant effluent PAC is added to the effluent in a contacting basin. After a certain time for contact, the carbon is allowed to settle to the bottom of the tank, and the treated water is then removed from tank. The addition of PAC directly to the aeration basin of an activated ï sludge treatment process has proved to be effective in the removal of number of soluble refractory organics. In physical ï chemical treatment processes, PAC is used in conjunction with chemicals used for the precipitation of specific constituents (Metcalf & Eddy, 2003).

In most wastewater cases where PAC is used, the PAC is mixed with the bio-sludge of an active sludge system (biophysical process or PACTTM process).

Benefits of this PAC addition as compared to conventional active sludge treatment include:

- enhanced removal efficiency for specific organics
- better process stability
- reduced foam build-up
- improved settling characteristics of the sludge.

Key advantage of the biophysical process is the low investment cost involved in converting an existing active sludge plant. Alternatively, PAC is applied in combination with a coagulation/ flocculation stage (http://www.norit-ac.com).

## II.4 POWDERED ACTIVATED CARBON/ACTIVATED SLUDGE SYSTEM

Activated sludge has been employed to treat a wide variety of wastewaters, and over 90% of the municipal wastewater treatment plants use it as the core part of the treatment process. Due to the rapid urbanization and implementation of higher standards for effluent in many countries in recent decades, the activated sludge, unavoidable by-product generated in typical secondary municipal sewage treatment, is being produced in an ever increasing amount. The sludge production is too high to be disregarded, and handling, treatment and disposal of this solid waste account for 25–65% of the total operating cost of a secondary treatment plant (Wang et al., 2008b).

In many ecological ecosystems a combination of biological and adsorption processes is a common phenomenon. Organic pollutants and refractory halogenated compounds, discharged from industries, are removed from the environment due to simultaneous adsorption and biodegradation. Wastewater purification, by powdered activated carbon treatment (PACT), which was introduced by DuPont has been based on these two processes. The mechanisms involved in the complicated simultaneous adsorption and biodegradation process still needs to be studied (Bornhardt et al., 1997; Orshansky and Narkis, 1997). Further work suggested that the improved organic removals may not be explained by adsorption alone and that interaction between the PAC and biomass may play an important role in the removal of organisms by PACT systems. These interactions can be grouped into three different phenomena: enhanced bioactivity, bioregeneration of the PAC, and metabolic end product (MEP) adsorption (Schultz and Keinath, 1984).

In this process, when the activated carbon is added directly to the aeration thank, biological oxidation and physical adsorption occur simultaneously. A feature of this process is that it can be integrated into existing activated sludge systems at nominal capital cost. The addition of powered activated carbon has several process advantages, including (1) system stability during shock loads, especially for toxic substances, (2) reduction of refractory priority pollutants, (3) color and ammonia removal, (4) improved sludge settleability, (5) lower effluent suspended solid concentration, and (6) little foaming. In some industrial waste applications, where nitrification is inhibited by toxic organics, the application of powdered activated carbon may reduce or limit this inhibition (Metcalf & Eddy, 2003; Widjaja et al., 2004).

The study of Orshansky and Narkis (1997) proved that final water of higher quality can be obtained in simultaneous adsorption and biodegradation of phenol or aniline solutions, than in biological treatment alone.

One of the possibilities of using activated carbon in wastewater treatment is the direct addition of powdered activated carbon to an activated sludge system, thus combining adsorption and biodegradation. The technical superiority of PAC-enhanced activated sludge system over a conventional AS system has been demonstrated in many pilot and full scale test treatments (Martin et al., 2004).

Activated carbon addition in the form of PAC is known for its ability to enhance biological treatment efficiency, remove refractory organic compounds and to enhance nitrification. Therefore, PAC addition to activated sludge could also be tested in leachate treatment systems. Organic matter removal in PACT system is a combination for adsorption and biodegradation. Activated carbon in conjunction with activated sludge increases the removal efficiency by adsorbing non-biodegradable, toxic and/or inhibitory organics and also some metals. Thus, the PACT system could remove an organic compound more efficiently than would be expected from either biodegradation or adsorption alone (Çeçen and Aktaк, 2001a and 2001b).

Çeçen and Aktaк (2001b) investigated the combined biological treatability of landfill leachate and domestic wastewater in both semi-continuously fed batch (SCFB) and continues-flow (CF) activated sludge with recycle with the addition of

PAC. They observed the positive effect of PAC on COD reduction and nitrification was more striking in CF operation than in SCFB operation.

The treatment of such wastewaters presents several difficulties since many synthetic chemicals are considered non-biodegradable while others may exhibit toxic and inhibitory effects. In spite of this fact, the basic treatment scheme for chemical synthesis wastewaters consists of aerobic biological treatment systems such as activated sludge. In this group of industries, the organic solvents used in the production step may appear in the wastewater if not recovered by in-plant control. Some of the more toxic solvents include chloroform, isopropyl alcohol, methanol and methylene chloride. Inhibition of activated sludge can be decreased by addition of powdered activated carbon. Removal of organic matter in a PACT system is a combination of adsorption and biodegradation. Activated carbon in conjunction with activated sludge increases the removal efficiency by adsorbing non-biodegradable, toxic and/or inhibitory organics also some metals. Thus PACT system could remove an organic compound more efficiently than would be expected by either biodegradation or adsorption alone as a consequence of the stimulation of biological activity. Others have suggested that the improvement in wastewater purification was due to a simple combination of adsorption and biodegradation. The effect of direct PAC addition to activated sludge has been extensively evaluated for other wastewaters (Çeçen and Aktaк, 2001b). PAC addition to biological system proved to be effective in the treatment of chemical synthesis wastewaters. Also the non-biodegradable matter could be decreased. Since pretreatment with PAC did not bring an additional advantage, direct PAC addition to activated sludge was considered a better alternative (Çeçen and Aktaк, 2001b).

Çeçen (1994) was studied the effect of PAC addition to activated sludge in the treatment of pulp bleaching effluents which contain a large amount of nonbiodegradable matter. Carbon addition to activated sludge resulted in a high decrease in substrate concentration, particularly for color. However, the results indicated that there was no noticeable biological enhancement with PAC addition. Then the combined PAC and activated sludge process seemed to be a combination of adsorption and biodegradation.

DeWalle et al. (1977) stated that when the carbon is added to the aeration basin, using glucose or secondary effluent as a substrate, did not observe any increase in magnitude of the final oxygen uptake by bacteria in the presence of PAC, indicating that physical adsorption was the main removal mechanism.

# CHAPTER III

## THE STUDY

The main goal of this study is to develop a cost effective technology for further treatment of Paкaköy Advanced Biological Treatment Plant effluent for reuse purposes. To serve this purpose carbon adsorption was tested on PABTP effluent as well as on preozonated PABTP effluent. Applying powdered activated carbon adsorption and activated sludge process simultaneously onto the preozonated effluent was another treatment alternative that was considered in this study. In the first stage of the study, batch adsorption tests were run on PABTP effluent and on preozonated PABTP effluent. During batch adsorption experiments, adsorption efficiencies of 3 different PAC types were compared with respect to their adsorption isotherms. In the second stage, ozone was applied to the effluent to convert nonbiodegradable organics to biodegradable organic matter. Then, the preozonated PABTP effluent was subjected to activated carbon adsorption and activated sludge processes in the same reactor. The activated carbon used during the powdered activated carbon+activated sludge system (PAC+AS) was selected based on the results of the batch adsorption tests. The selected PAC had very high dissolved organic matter removal capacity. Finally, to investigate the effect of preozonation to PAC+AS system, the same experiments were repeated with the PABTP effluent that was not subjected to preozonation.

### III.1 EXPERIMENTAL SET-UP

**III.1.1** Batch Adsorption Experiments

To determine the adsorption isotherm of each activated carbon tested, batch adsorption tests were carried out using 12 of 300 mL erlenmeyer-flasks containing 200 mL of sample (either raw or preozonated PABTP effluent) and precisely weighed powdered activated carbon doses ranging between 23 and 532 mg/L. The samples were shaken in a shaker (KS 4000 ic control) set to 200 rpm for 64 h at 25°C (see Figure III.1) until equilibrium is reached. After a sedimentation time of 30 min, the supernatant was separated for further relevant analysis. The supernatant was filtered through a 0.45 µm syringe driven PVDF filter (Millipore) and the DOC and $UV_{254}$ absorbance of the samples were determined. To determine the amount of contact time necessary to reach adsorption equilibrium, the same system was used, but this time the weight of powdered activated carbon (250 mg/L) was kept the same in each flask and contact time was varied between 2 minutes to 40 minutes.


**Figure III.1** KS 4000 ic Control Model Shaker

**III.1.2** Ozone Generator and Contact Unit

$O_3$ feed gas was produced from oxygen gas using a laboratory-scale generator (PCI Model GL-1 type oxygen-feed corona discharge ozone generator) for the ozonation of PABTP effluent samples. Teflon tubing was used for all the connections from the ozone generator to the contact unit. A 25 L made of HDPE cylindrical reactor with a tap for sampling was used as a contact unit. The ozone gas was sparked into reactor using fine pore glass ï bonded silica diffuser. 787.5 mg $O_3$/min ozone for 32 SCFH (cubic feet per hour at specific standard conditions) oxygen flowrate and 100% ozone output are produced by the ozone generator. 4 SCFH oxygen flowrate and 10-40 % ozone output were applied in the experiments. The ozone generator and contact unit are shown in Figure III.2.

**Figure III.2** Ozone Generator and Contact Unit

**III.1.3** Powdered Activated Carbon + Activated Sludge Reactors

4 different reactor configurations (only aeration, only PAC, PAC + AS, only AS) were conducted using 2 L glass reactors (Figure III.3). Champion CX-0089 air pump aerated the reactors with using a diffuser. 2 L of PABTP effluent, either raw or preozonated were added into each reactor. 250 mg/L PAC was added into PAC and PAC +AS system reactors. The PAC + AS and only activated sludge systems were seeded with 10 mL activated sludge obtained from Paкaköy Advanced Biological Treatment Plant. The experiments were carried out in a temperature controlled room at 25± $2^0$C. The reactors were aerated for 7 days. After 7 days, the supernatant from each reactor was filtered through a 0.45 µm syringe driven PVDF filter (Millipore) to analyze DOC, $BOD_5$ and $UV_{254}$ which were the main parameters monitored throughout the PAC + AS system.


**Figure III.3** Powdered Activated Carbon + Activated Sludge Reactors

### III.2 MATERIALS and REAGENTS

Sewage effluent water from Paкaköy Advanced Biological Treatment Plant was used as the test sample in this study. The plant has an average flow of 100,000 $m^3$/day and provides carbon, nitrogen and phosphorus removal by using A2/O process (anaerobic zone followed by anoxic zone then oxic zones aeration units). The plant discharges its effluent to the Riva River that finally flows into the Black Sea.

#### **III.2.1** PAC Properties

3 types of commercial powdered activated carbon (Norit Hydrodarco C, Norit W 35, and Norit SAE Super) were used during the experiments. They were obtained from Norit Netherlands BV. According to the supplier specifications, Hydrodarco C and SAE Super are especially developed for wastewater treatment. Due to the presence of both micro-and mesopores, they are multi-purpose grade, being able to adsorb low and high molecular weight organics (color bodies, COD, organic micro pollutants). Norit W 35 is especially suitable for the removal of dissolved organic

material of both low and high molecular weight in potable water treatment such as taste and odor, detergents and phenolics. The activated carbons were used without pretreatment. The properties of activated carbons are shown in Table III.1.

**Table III.1** Physical and Chemical Properties of Powdered Activated Carbons

| **Property** | **Unit** | **Carbon** | | |
|---|---|---|---|---|
| | | **Hydrodarco C** | **W 35** | **SAE Super** |
| **Origin** | | Lignite coal | Vegetable raw material | Peat/wood |
| **Activation method** | | Steam activation | Steam activation | Steam activation |
| **Molasses number (EUR)** | - | NA | NA | max. 250 |
| **Moisture (as packed)** | mass-% | max. 4 | max. 6 | max. 6 |
| **Iodine number** | - | 550 | 850 | 1050 |
| **Methylene blue adsorption** | g/100 g | 10 | 15 | 24 |
| **Phenol adsorption** | g/100 g | 2.5 | 4 | |
| **Total surface area (B.E.T)** | $m^2/g$ | 600 | 875 | 1150 |
| **Apparent density (tamped)** | $kg/m^3$ | 510 | 425 | 425 |
| **Particle size > 150 µm** | mass-% | 1 | 5 | 3 |
| **Particle size $D_{50}$** | µm | 25 | 15 | 15 |
| **pH** | - | Alkaline | Alkaline | alkaline |

**III.2.2** Reagents

$K_2Cr_2O_7$ and $HgSO_4$ were used to prepare digestion solution and $Ag_2SO_4$, and $H_2SO_4$ were used as sulfuric acid reagent for COD measurements. Potassium Hydrogen Phthalate (KHP) was used to prepare KHP standard for COD analysis.

WTW NTH 600 model nitrification inhibitor ($C_4H_8N_2S$) and WTW NTH 600 model NaOH pellets were used for BOD analysis.

$Na_2O_3S_2$ solution, which was purchased from Sigma- Aldrich, was used for quenching the remaining oxidants in the samples for COD and $BOD_5$ analysis.

### III.3 ANALYTICAL METHODS

**III.3.1** Total Organic Carbon Measurement

TOC and DOC were the main parameter monitored to effectively evaluate the outcomes of this study. Tekmar Dohrmann Series Apollo 9000 TOC analyzer was used for the measurement of TOC and DOC (Figure III.4). The combustion method (Standard Methods 5310 B) was used for the analysis. TOC is measured by oxidizing the organic carbon to $CO_2$ and $H_2O$ and measuring the $CO_2$ gas using the infrared carbon analyzer. The oxidation is done by direct injection of the sample into a high temperature (680 ï 950°C) combustion chamber or by injection of sample. The only difference between the TOC and DOC measurements is that, in case of DOC determination, the sample was passed through a 0.45εm syringe driven filter (Millipore).

After the analyzer was started, injector was placed inside distilled water vial for cleaning the system before performing measurements. Each sample was analyzed two times. Results were monitored by Apollo 9000 computer software which was connected to system.

**Figure III.4** Tekmar Dohrmann Series Apollo 9000 TOC analyzer

**III.3.2** Biochemical Oxygen Demand Measurement

The aerobic biodegradability of the effluent and preozonated effluent was tested using $BOD_5$ method according to Standard Methods (5120) by respirometric single measuring system WTW OxiTop® procedure. 420 mL effluent was used.

Bottles were seeded with 2 mL activated sludge obtained from Paкaköy Wastewater Treatment Plant. 4 drops nitrification inhibitor and 2 NaOH pellets were used. Results were monitored by OxiTop®-measuring head.

**III.3.3** Chemical Oxygen Demand Measurement

According to the Standard Methods (Closed Reflux Colorimetric Method, 5220 D), effluent was placed into the COD tubes, then KHP solution, digestion solution and sulfuric acid reagent were added. COD tubes were heated at $150^0$C for two hours in Hach Company COD reactor (Figure III.5). After 2 hours, samples were cooled to room temperature slowly to avoid precipitate formation, then results were monitored by Hach Company DR 2500 spectrophotometer (Figure III.6).

**Figure III.5** Hach Heater

**Figure III.6** Hach Company DR 2500 spectrophotometer

**III.3.4** UV Absorbance Measurement

$UV_{254}$ measurements were made to determine the aromatic content of wastewater. Absorbances were measured at 254 nm by Shimadzu UV-2450 model UV-Visible double beam spectrophotometer (UV-Vis). Measurements were performed using 1 cm quartz cell. To prevent accumulation of residues on the cell walls and their interference with the measurements, sample cells were washed and cleaned after each analysis. The measurement results were recorded by the system software as absorbance units. The spectrophotometer is shown in Figure III.7.


**Figure III.7** Shimadzu UV-2450 model UV-Visible Double Beam Spectrophotometer

## III.4. EXPERIMENTAL PROCEDURES

### III.4.1 Determination of Optimum Ozone Dosage

To determine the optimum ozone dosage that produces the maximum amount of biodegradable organic compounds, wastewater samples were ozonated at 30 mg $O_3$/min gas phase ozone application rate. Ozone contact unit was filled with 15 L sample before each experiment. Once the ozone was introduced into the wastewater, 1 L samples were taken at 5, 10, 15, 20 and 25 minute intervals to provide detailed data about biodegradability by $BOD_5$, TOC, $UV_{254}$ and COD analysis. Applied ozone dosage corresponding to maximum biodegradability was calculated from the reaction time at which the highest $BOD_5$/COD ratio was observed using Equation III.1. Table III.2 shows the amount of applied ozone concentration at any reaction time.

$$Ozone\ \mathrm{concentration}(mg / L\ of\ sample) = \frac{Ozone\ Aplication\ Rate\,(mg\ O_3\ /\ \mathrm{min}) \times Time\,(\mathrm{min})}{\mathrm{Sample}\ Volume\,(L)} \quad \text{(III.1)}$$

**Table III.2** Applied Ozone Concentration for Different Time Intervals

| | Sampling Time (min) | | | | |
|---|---|---|---|---|---|
| | *5* | *10* | *15* | *20* | *25* |
| **Gas phase ozone application rate ($mgO_3$/min)** | **Applied ozone concentration (mg/L)** | | | | |
| 30 | 10.0 | 21.4 | 34.6 | 50.0 | 68.2 |

**III.4.2** Batch Adsorption Experiments

Isotherm experiments were carried out to determine the effect of ozonation on adsorbility of powdered activated carbon and chose the best PAC type for the powdered activated carbon + activated sludge system.

Adsorption isotherms were conducted using PAC within the range of 23 and 532 mg/L. 12 different PAC concentrations were used to perform adsorption test for each carbon type in effluent or preozonated PABTP effluent. The ozone demand determined for maximum biodegradability was 50 mg/L. The ozone demand for each experiment was kept constant. One flask was used as blank (without PAC) for isotherm equations calculations.

**III.4.3** Powdered Activated Carbon + Activated Sludge Reactors

Experiments were conducted in batch activated sludge reactors with and without added PAC to investigate the merit of combined treatments and to study the biodegradability of individual fractions before and after ozonation. The experiments were performed on the effluent and preozonated effluent (50 mg/L). The working volume of 2 L effluent was placed in the reactors and seed for activated sludge was obtained from Paкaköy Advanced Biological Wastewater Treatment Plant. In experiments where activated carbon was used, 250 mg/L of activated carbon was fed to reactors. The reactors were aerated for 7 days.

Four different reactor configurations were used for effluent and preozonated effluent:

Aeration only: In this reactor the effluent was aerated without any addition of PAC or activated sludge. The reactor was run to understand the performance of other reactors in terms of organic matter removal.

Powdered activated carbon (PAC): Only 250 mg/L of activated carbon was fed to this reactor. The reactor was run to understand the adsorption onto PAC.

Powdered activated Carbon + Activated Sludge (PAC + AS): This reactor was fed with both 10 mL activated sludge and 250 mg/L activated carbon. The reactor was run to understand the combined effect of biological treatment and adsorption onto PAC.

Activated Sludge (AS): This reactor was fed with 10 mL activated sludge. The reactor was run to understand the organic matter removal in activated sludge system.

# CHAPTER IV

## RESULTS AND DISCUSSION

### IV.1 CHARACTERIZATION of PAĶAKÖY ADVANCED BIOLOGICAL WASTEWATER TREATMENT PLANT EFFLUENT

**IV.1.1** Wastewater Quality Parameters

Treated wastewater samples were brought from the Paкaköy Advanced Wastewater Treatment Plant, which treats 100,000 $m^3$ wastewater per day. The plant was got into operation to protect the catchment basin of Ömerli Dam in 2000. The plant treats the wastewater of nearly 10,732 hectare area and is connected to the Riva River via a tunnel (3 m diameter and 6 km length) by Istanbul Water and Sewerage Administration (ISKI) in order to prevent domestic and industrial wastewater inputs into the reservoir of Ömerli Dam. The study was done between May and November 2009 and the round measurements for this period are shown in Table IV.1.

**Table IV.1** Typical Water Quality Characteristics of Paкaköy Advanced Biological Wastewater Treatment Plant Effluent

| Parameter | Unit | Value |
|---|---|---|
| $BOD_5$ | mg/L | 3-8 |
| COD | mg/L | 12-22 |
| TOC | mg/L | 7-11 |
| $UV_{254}$ | $cm^{-1}$ | 0.140-0.225 |
| pH | - | 7.2-7.6 |

**IV.1.2** Ozone Demand for Maximum Biodegradation

The nature of the reactions that ozone undergoes in wastewater can be established by characterization of wastewater. Ozone reactivity depends on the concentration (and also the nature) of pollutants present in wastewater. However, in real wastewater, the actual pollution concentration is unknown and surrogate parameters (COD, TOC, etc.) are used to express the pollution concentration. The magnitude of these parameters, especially COD, gives an estimate of the potential ozone reactivity. In addition to TOC and COD, other parameters are employed to measure the degree of pollution. These parameters include BOD and the measurement of wastewater absorptivity in the UV-C region, especially at 254 nm wavelength (Beltran, 2004).

In this study, ozone was applied to the effluent to improve biodegradability of the effluent via changing the biological and chemical properties of its constituent during oxidation process. To determine the optimum ozone concentration that produces the maximum amount of biodegradable organic compounds, wastewater samples were ozonated at 30 mg $O_3$/min gas phase ozone application rate. $BOD_5$/COD ratio increased from 0.18 to 0.50, 0.60, 0.80 and 0.67 for 5 min, 15 min, 20 min and 25 min, respectively. The optimal ozonation time was found to be 20 min as this contact time ensures the highest efficiency of biodegradation in terms of $BOD_5$/COD ratio. Effluent biodegradability was found to be significantly enhanced through ozonation: $BOD_5$ values reached 400% (Figure IV.1), and the $BOD_5$/COD ratio increased from 0.18 to 0.80. As shown in Figure IV.2, further increase in the dosage did not enhance the $BOD_5$/COD ratio in the ozonation process. Therefore, the 50 mg/L of applied ozone concentration was found to be optimum for efficient biodegradability increment.

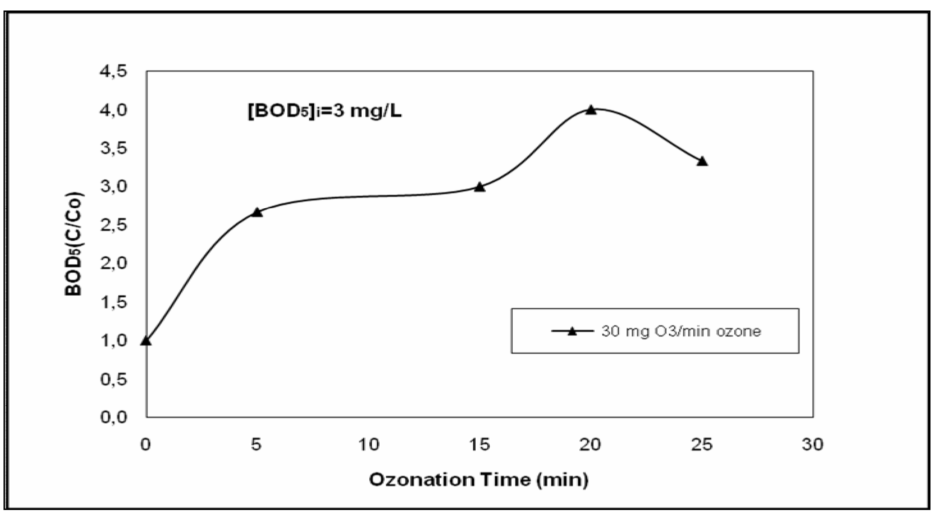


**Figure IV.1** Effect of Ozonation on Biodegradability in Means of $BOD_5$

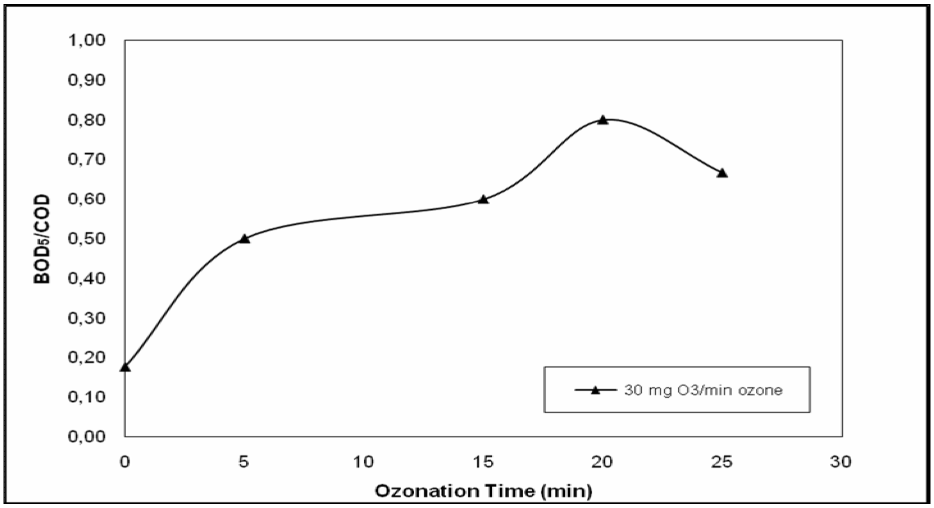


**Figure IV.2** Effect of Ozonation on Biodegradability in Means of $BOD_5$/COD Ratio

Regarding ozonation as a pretreatment process for conventional treatment methods, it is important to examine its influence to properties of organic substances like biodegradability. It is known that mostly biodegradable fraction of wastewater can be increased by ozonation, which leads to the formation of low molecular weight oxygenated byproducts that are more amenable to biodegradation. Hence, $BOD_5$/COD ratios can be increased from 0 to 0.15 and 0.5 under optimum ozone conditions (Balcœĵ lu and Ötker, 2003). According to Ramirez and Velasquez (2004) ozone contributes greatly to changing the recalcitrant characteristics of organic matter. They found that $BOD_5$ values reached 265%, and the $BOD_5$/COD ratio increased from 0.003 to 0.015. Contreras (2003) observed that $BOD_x$/COD ratio increased substantially in the range between 90 and 120 mg /L absorbed ozone dose, being 0.25 for $BOD_5$/COD after an ozone dose of 120 mg/L, respectively (0.48 the same ratio at 21 days). As a reference, a $BOD_5$/COD ratio of 0.4 is generally considered to be the cut-off point between biodegradable and difficult to biodegrade waste. Domestic wastewater typically has a $BOD_5$/COD ratio of between 0.4 and 0.8.

Balcœĵ lu and Ötker (2003) used the aromaticity removal as a parameter for the evaluation of ozonation performance of wastewater and higher removal rates in aromaticity resulted in higher $BOD_5$/COD ratio. In their study in order to assess the effect of ozonation on the biodegradability of the wastewater, $BOD_5$ measurements were conducted and biodegradability of wastewater was represented as $BOD_5$/COD ratio. $BOD_5$ value of untreated veterinary antibiotic wastewater ($COD_i$ = 900 mg/l) was 70 mg/l whereas untreated human I and human II antibiotic wastewaters were determined as nonbiodegradable. Initially, the $BOD_5$/COD ratio for all synthetic wastewater was noticeably low. It has been previously suggested that increasing the ozone contact time first produces more biodegradable intermediates and that upon extension of the ozonation period biodegradability levels off, decreases or in some cases even further increases depending upon the specific pollutant type in question. In this study, while the biodegradability of human antibiotic I leveled off, that of human antibiotic II and veterinary antibiotic indicated further increase with an increasing contact time. Correspondingly, only for this wastewater, $BOD_5$ was comparably low.

In order to determine the effect of ozone on biodegradability, several tests on the $BOD_5$ of the oxidation effluent were carried out by several researchers. Ramirez and Velasquez (2004) studied removal and transformation of recalcitrant organic matter from stabilized saline landfill leachates by coagulationï ozonation coupling processes and they found that indicators of biodegradability increased significantly as a result of ozonation with $BOD_5$ rising to 265%. Bijan and Mohseni (2005) reported that ozonation enhanced the total amount of biodegradable compounds, measured as $BOD_5$, by 13% (72%) for the overall ozone dosage of 800 mg/L wastewater. Increasing $BOD_5$, accompanied by decreasing COD, indicates that the biodegradability of the wastewater improved.

In this study, as seen in Figure IV.3, maximum rate of COD removal (12 %) was obtained in the first 15 minutes of ozone application with an applied ozone concentration of 34,6 mg/L of wastewater. After 15 minutes, there was no change in COD removal. Rice (1997) reported that a specific ozone demand of 69 mg $O_3$/L of wastewater and a reaction time of 12 minutes provided 45% reduction of COD value.

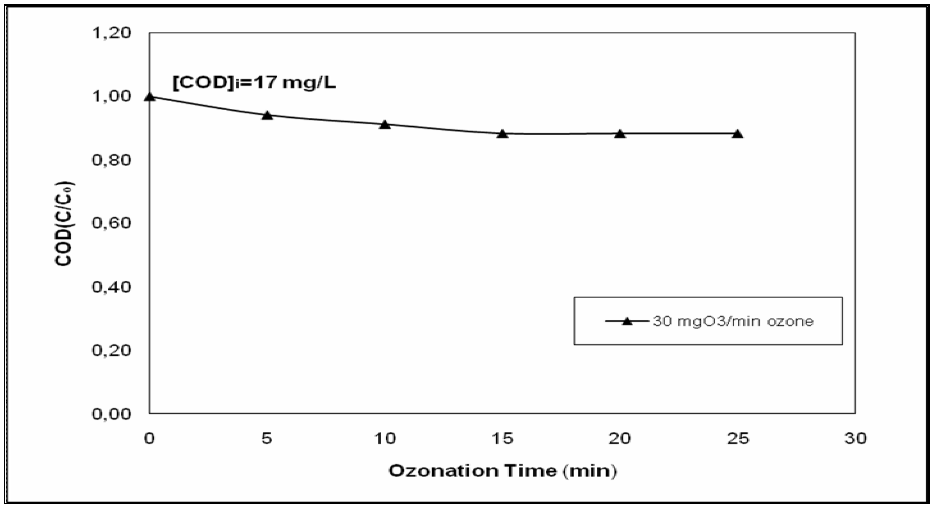


**Figure IV.3** Effect of Ozonation on COD Removal

As the TOC removal represents the complete destruction of compounds, TOCï ozonation time profiles are given in Figure IV.4. TOC removal was 19% in 10 min contact time of ozone with an applied ozone concentration of 21,4 mg/L, and there was no significant change after 10 min contact time. The higher ozone dosage did not make any significant change on TOC removal.

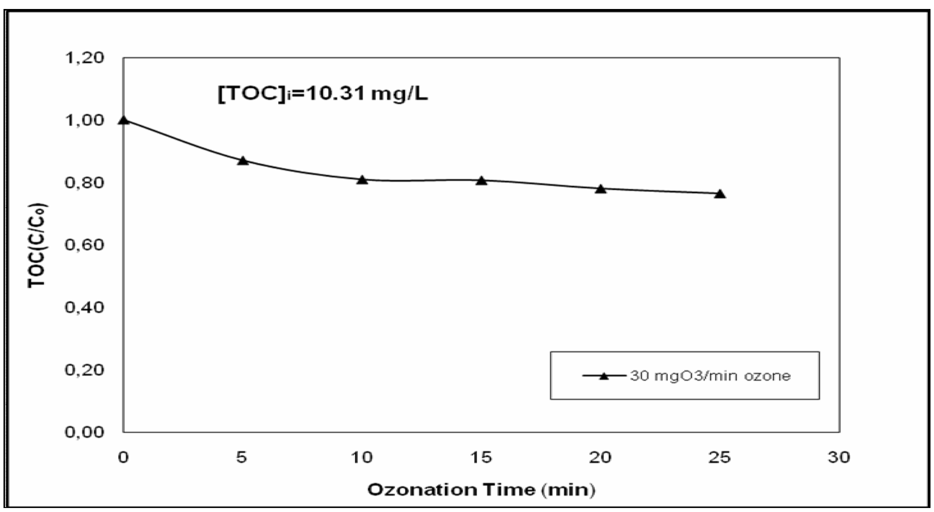


**Figure IV.4** Effect of Ozonation on TOC Removal

Shiyun (2002) studied ozonation of 11 naphthalene sulfonic acids (NSA) in the aqueous solution by bubbling at 31$^{o}$C at an ozone dose rate of 5.56 mg min$^{-1}$/ L. COD, TOC and $BOD_5$ of these compounds were tested. From this study, it can be seen that TOC reduction during the 2 h of ozonation is significant, yet not as great as COD reduction. That is because the ozone applied to the aqueous system was to produce not only volatile oxidation compounds, which contribute to TOC elimination but also non-volatile ones. Substituent(s) effect also contributes to the difference in TOC removal of these compounds. TOC of the aqueous solutions of compounds 10 and 4, 1,5-naphthalene disulfonic acid and 6-amino-1,3,6-naphthalene trisulfonic acid, decreased less than 5% during 2 h of ozonation in the study of Shiyun. It is also shown that TOC removal did not follow the same order as that of COD. Compounds 1 (2-amino-1-NSA), 2 (2,3-Dihydroxy-6-NSA) and 8 (6-amino-1,4-naphthalene disulfonic acid) resulted in TOC reductions of more than 27% while compounds 5 (1-hydroxy-7-amino-5-NSA), 6 (6-hydroxy-1-NSA) and 11 (1-hydroxy-6-amino-3-NSA) all decreased around 20%. TOC removal of compound 3 was similar to compound 9, much lower than that of compound 7, to which its COD-time profile was more similar (Shiyun, 2002).

In the study of Wang et al. (2008a) the original TOC of the domestic secondary effluent ranged from 9 to 13 mg/L. It was observed that the removal efficiency reached 15% or so by ozonation alone. Wang et al. (2008a) also reported that ozonation can increase the biodegradability of the water, which enhanced the efficiency of the biological treatment, even though the organic matters cannot be mineralized thoroughly by ozonation alone.

Ozonation causes substantial structural changes to the humic substances which include; a strong and rapid decrease in color and UV-absorbance (254 nm) due to a loss of aromaticity and depolymerization; a small reduction in TOC (e.g., 10 % at 1 mg $O_3$/mg C); a slight decrease in the high apparent molecular weight fraction, and a slight increase in the smaller fractions; a significant increase of the carboxylic functions; formation of ozonation byproducts; conversion of humic into nonhumic material and increase in polarity. These byproducts have been reported to be mainly aldehydes (formaldehyde, acetaldehyde, glyoxal, methylglyoxal) and carboxylic acids (formic, acetic, glyoxylic, pyruvic and ketomalonic acids). The shift of molecular distribution to lower values is important in enhancing the biodegradability of NOM because low molecular compounds are more easily transported across the cell membrane and are attacked by metabolic enzymes (Nishijima and Speitel, 2004).

The 254 nm UV absorption values may also be considered as a rough indication of organic compounds contained in the reclaimed wastewater, mostly in the form of humic-like substances (Park et al., 2010). Also, UV absorbance at 254 nm represents the existence of unsaturated carbon bonds including aromatic compounds, which are generally recalcitrant for biodegradation, and decrease of UV absorbance results in the increase of biodegradability (Nishijima and Speitel, 2004).

The effect of ozonation on UV absorbance at 254 nm was monitored and it was observed that the UV absorbance decreased from original 0.198 nm to 0.057 by ozonation within 15 min contacting time at an applied ozone concentration of 34,6 mg/L, that is, 71% removal was realized (Figure IV.5). This result also indicated that ozonation can significantly decrease the absorbance.

In the study of Park, the reduction of UV absorbance after coagulation-flocculation did not exceed 9.5%, whereas the highest UV absorbance reduction, slightly exceeded 58.5%, was observed at the outlet of ozonation unit. The $UV_{254}$ absorbance values were significantly decreased by ozonation, at an ozone dosage of 15 mg/L, and the highest $UV_{254}$ absorbance removal efficiency slightly exceeded 58.5% (Park et al., 2010).

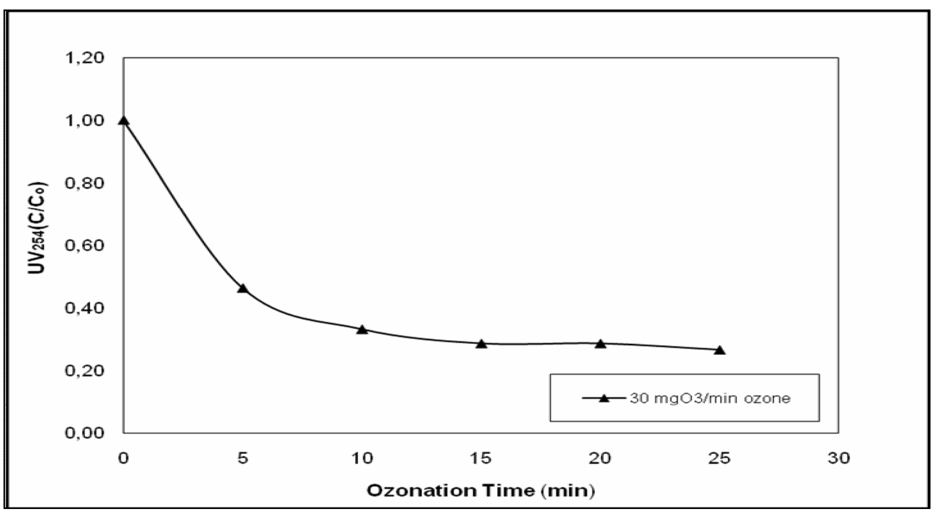


**Figure IV.5** Effect of Ozonation on UV Absorbance Removal

$UV_{254}$/TOC was also chosen as an indicator of biodegradability in this study. As shown in Figure IV.6, $UV_{254}$/TOC ratio was decreased from 0.019 to 0.09 in 10 min contact time of ozone with an applied ozone concentration of 21,4 mg/L, and there was no significant change after 10 min contact time. According to the study of Balcıoğlu and Ötker (2003) although significant aromaticity removal was achieved at initial period of ozonation for all wastewaters, the $UV_{254}$/COD ratio of human antibiotic I wastewater was still high at the end of ozonation period.

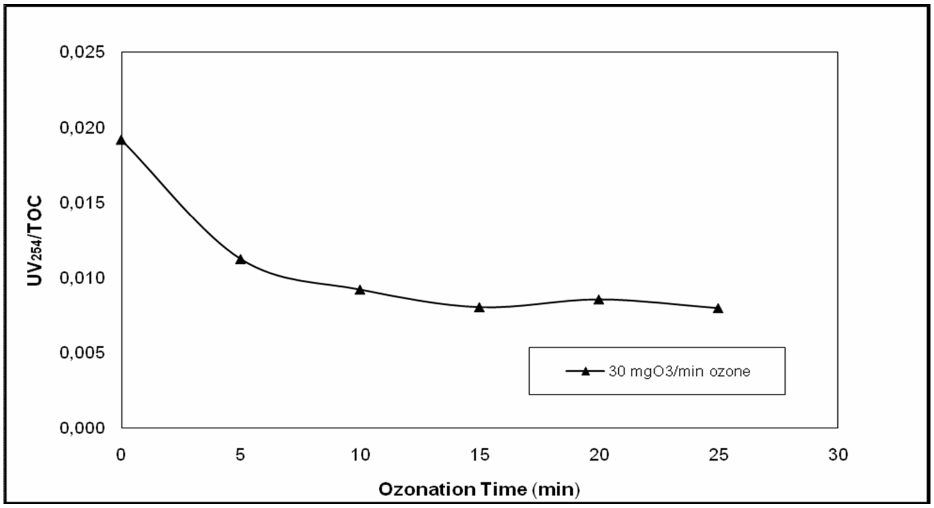


**Figure IV.6** Effect of Ozonation on Biodegradability in Means of $UV_{254}$/TOC Ratio

## IV.2 BATCH ADSORPTION EXPERIMENTS

### IV.2.1 Application of Freundlich Model to Organic Matter Adsorption Measured as DOC

In this study batch adsorption tests were run on PABTP effluent and on preozonated PABTP effluent (explained in Section III.4.1) with three powdered activated carbon (explained in details in Section III.4.2) to choose the most appropriate PAC type for PAC/AS system. Both the Freundlich and Langmuir adsorption models were applied in data analysis.

For wastewaters comprising many compounds, the empirical Freundlich isotherm usually provides a satisfactory correlation (Bansode, 2004; Snoeyink and Summers, 1999).

Adsorption of DOC onto PAC was described by the Freundlich equation of the following form:

$$q_e = K\,C_e^{1/n} \qquad \text{(IV.1)}$$

and can be linearized as follows:

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad \text{(IV.2)}$$

The parameters $q_e$ (with units of mass adsorbate/mass adsorbent, or mole adsorbate/mass adsorbent or mg DOC/mg PAC) and $C_e$ (with units of mass/volume, or moles/volume or mg/L DOC) are the equilibrium surface and solution concentrations, respectively. The terms K and 1/n are constants for a given system; 1/n is unitless, and the units of K are determined by the units of $q_e$ and $C_e$ (Snoeyink and Summers, 1999).

The respective constants K and 1/n are presented in Table IV.2. The representation of the experimental data by the Freundlich equation resulted in a linear curve with $R^2$ values of a least 0.74. The Freundlich model, therefore, appears to be a good fit of the adsorption data. In Figure IV.7, Figure IV.8 and Figure IV.9 for the three types of PAC, the log $q_e$ values represent the relative adsorption efficiency of the activated carbons and log $C_e$, the residual concentration of the organic solutes in the treated test solution. From these figures, it appears that steam-activated peat/wood-based carbon (SAE Super) had the highest $q_e$ at a given log $C_e$ value, while the steam activated lignite coal-based carbon (Hydrodarco C) had the lowest values.

Bansode (2004) made an investigation to compare the adsorption efficiency of pecan shell-based granular activated carbon with the adsorption efficiency of the commercial carbon Filtrasorb 200 with respect to uptake of the organic components responsible for the COD of municipal wastewater. The results showed that granular activated carbons made from agricultural waste (pecan shells) can be used with greater effectiveness for organic matter removal from municipal wastewater than a coal-based commercial carbon like the result of this study. The results seemed to indicate why acid and steam activation are preferred activation methods as commercial processes compared to carbon dioxide activation. Carbon dioxide is more expensive than steam, in addition to yielding a lower surface area under the same activation conditions of time and temperature.

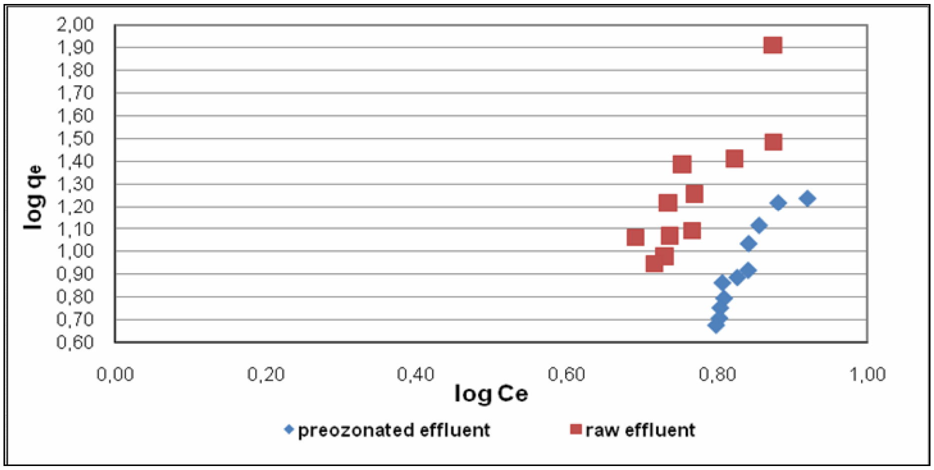


**Figure IV.7** Freundlich Adsorption Isotherms for Hydrodarco C

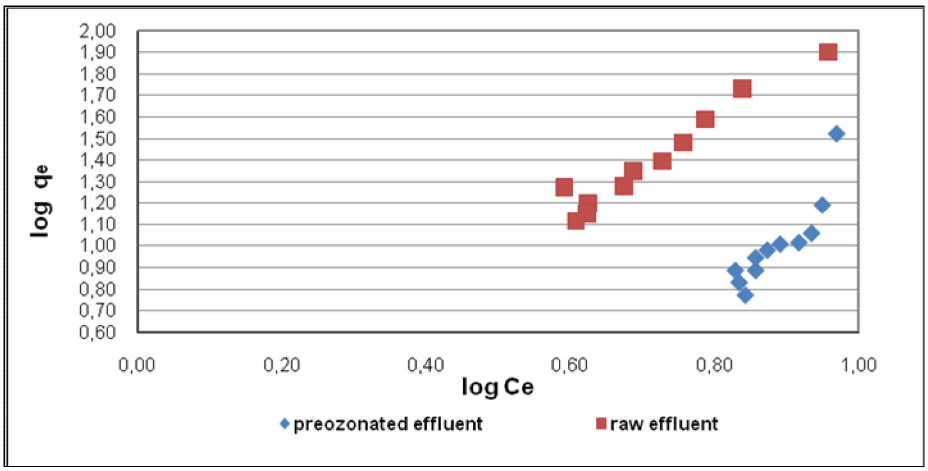


**Figure IV.8** Freundlich Adsorption Isotherms for W 35

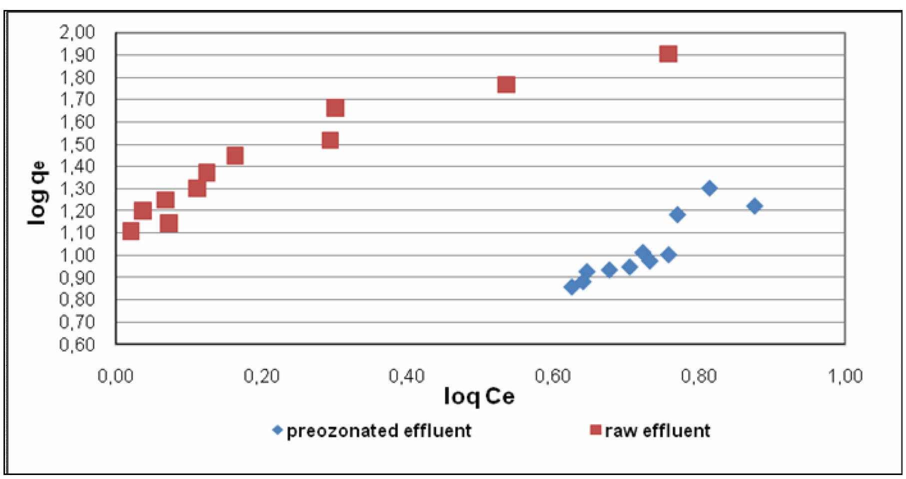


**Figure IV.9** Freundlich Adsorption Isotherms for SAE Super

The empirical constants K and 1/n for 3 types of carbons are given in Table IV.2. They are dimensionless constants that generally have meaning when compared to other values within a particular study. The values K and 1/n represent the intercept and slope of the adsorption isotherms in Figures IV.7, IV.8 and IV.9. Large K values indicate good adsorption efficiency for the particular activated carbon. A larger value for 1/n indicates a larger change in effectiveness over different equilibrium concentrations. As shown in Table IV.2, the K values were quite high, indicating a high adsorption capacity. The adsorption intensity, 1/n, is a function of the strength of adsorption and the smaller the value of 1/n, the stronger is the adsorption bond. Both for K and 1/n values showed that the organic matter in raw effluent was more adsorbable onto activated carbon. Among all three activated carbon types tested in this study, SAE Super had shown the best adsorption intensity and strongest adsorption bond.

**Table IV.2** Freundlich Isotherm Constants for DOC Adsorption

| **PAC Type** | **K** | **1/n** | **$R^2$** |
|---|---|---|---|
| **Raw Effluent** | | | |
| Hydrodarco C | 0,017 | 3,931 | 0,74 |
| W 35 | 0,933 | 2,016 | 0,95 |
| SAE Super | 15,230 | 1,072 | 0,90 |
| **Preozonated Effluent** | | | |
| Hydrodarco C | 0,001 | 4,812 | 0,88 |
| W 35 | 0,005 | 3,743 | 0,79 |
| SAE Super | 0,610 | 1,708 | 0,82 |

The theoretical Langmuir equation was also tested for SAE Super which had higher K values for raw and preozonated effluent. Langmuir equation, as implied by very low $R^2$ values both for raw and preozonated effluents (0.002 and 0.36, respectively) is not capable of describing this adsorption process. The Langmuir fits of the experimental data are presented in Figure IV.10. Hence, for the purposes of this study, the Freundlich equation was satisfactory in describing the collected data. Bansode (2004) and Yapsaklē (2008) also found that Freundlich equation was satisfactory for their data.

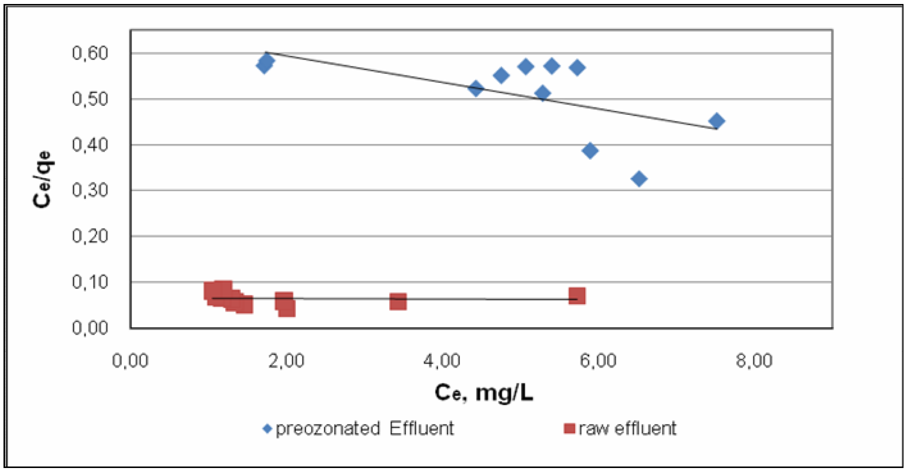


**Figure IV.10** Langmuir Adsorption Isotherms for SAE Super

The steam activated lignite coal-based Hydrodarco C showed the lowest adsorption of organic matter. This may be due to weaker electrostatic interactions of the surface with organic matter or more oxygen-containing surface groups with respect to other steam activated carbon types (Yapsaklē, 2008). Hydrodarco C had the lowest total surface area, 600 $m^2/g$, among all the carbons studied. Peat/wood based SAE Super had the highest total surface area of 1,150 $m^2/g$, which made it suitable for higher organic matter loadings. These results indicate that total surface area is a good indicator of the performance of the adsorbent within the scope of this study.

In the present study, SAE Super was the most efficient adsorbent for both raw and preozonated effluent. As a result, only activated carbons with appropriate adsorption characteristics and pore structure are useful for wastewater treatment.

**IV.2.2** DOC Removal by Activated Carbon

The effect of carbon dosage ranging from 26.0 to 525.5 g Carbon/L of solution on organic matter adsorption is presented in Figure IV.11. The initial DOC concentration of the raw effluent and preozonated effluent were 7.82 and 8.02 mg/L, respectively. Maximum removal of DOC with SAE Super for raw effluent and preozonated effluent were 87% and 47%, respectively. As can be seen in Figure IV.11, the removal of DOC did not increase considerably after a PAC dosage of nearly 200 mg/L. This means that even if the GAC concentration is increased, the equilibrium DOC concentration is not so much affected as observed by

Yapsaklı (2008). However, Seo and Ohgaki (2001) found that the TOC removal at a PAC concentration of 20 g/L was significantly higher than at 0.5-2 g PAC/L (83% and 66-68%, respectively).

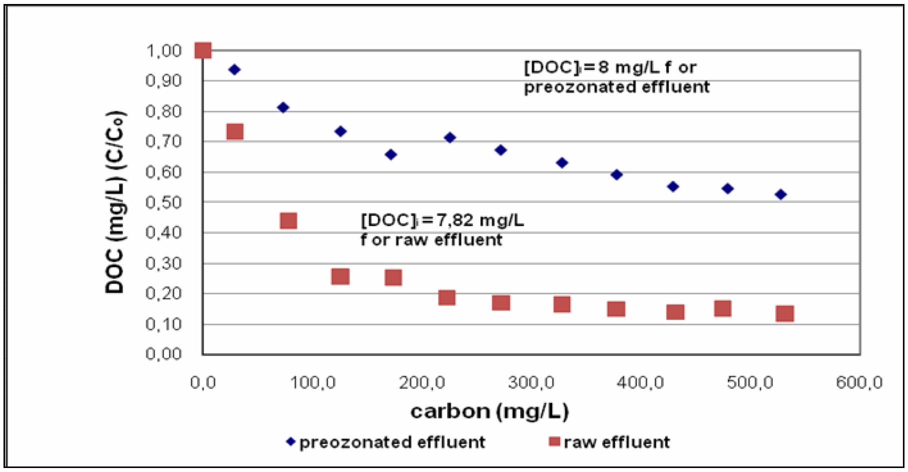


**Figure IV.11** Effect of SAE Super on DOC Removal

**IV.2.3** Effect of Ozone on Removal Efficiency of DOC

For all carbon types, adsorption became unfavorable, compared to raw effluent when the effluent was preozonated. The results indicated that preozonation did not enhance DOC removal by adsorption (Figure IV.12, Figure IV.13 and Figure IV.14). After treated with PAC, the DOC of raw effluent ranges from 1,05 to 5,2 mg/L indicating 87% and 47% removals and the DOC of preozonated effluent ranges from 4,22 to 6,96 mg/L which indicates 47% and 29% removals, respectively.

Yapsaklı (2008) studied the impact of ozonation on biodegradation efficiencies in biological activated carbon (BAC) columns for drinking water treatment. The results indicated that preozonation did not affect TOC removal at any time and the average TOC removal efficiency in both columns was approximately 26%.

Takeuchi et al. (1997), studied the combination of ozonation and biological activated carbon treatment to purify raw water for municipal use in some cases. The removal ratio of TOC without ozonation seemed to be higher than that with ozonation. The total amounts of TOC removed during this period with and without ozonation were found to be about 1.4 x $10^{-3}$ kg and 1.6 x $10^{-3}$ kg, respectively. Therefore, it can be concluded that reaction with ozone gives negative effects on adsorption behavior of organics.

Faria et al. (2005) investigated the degradation of organic matter in colored solutions of different classes of dyes by ozonation in the presence of activated carbon. The kinetics of the decolorization and mineralization of three different dye solutions were studied in a laboratory scale reactor by three different processes: adsorption on activated carbon, oxidation with ozone and ozonation in the presence of activated carbon. The mineralization of the solutions was followed by measuring the total organic carbon. Adsorption on activated carbon can lead to better results than ozonation in terms of TOC removal. The problem is that, when treating wastewaters with high organic content, this adsorbent can become saturated very easily, requiring regeneration or further replacement. Thus, in this case, better results are obtained when activated carbon is used alone.

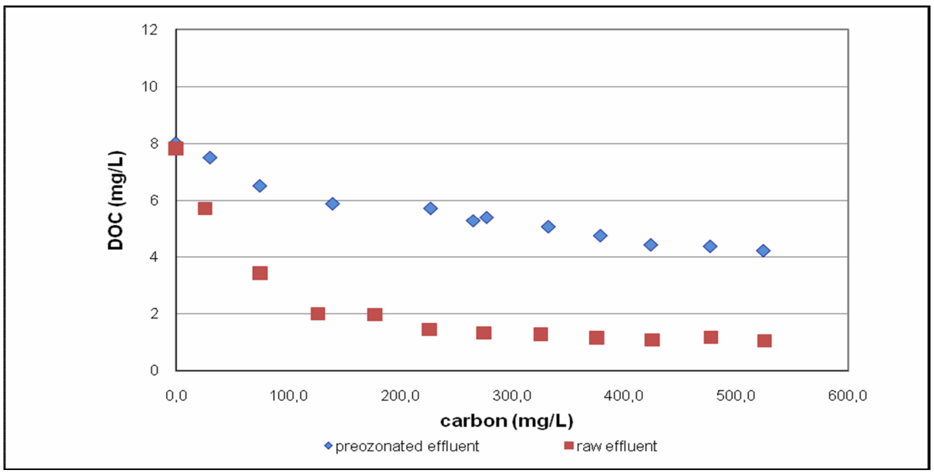


**Figure IV.12** Effect of Ozone on Removal Efficiency of DOC for SAE Super

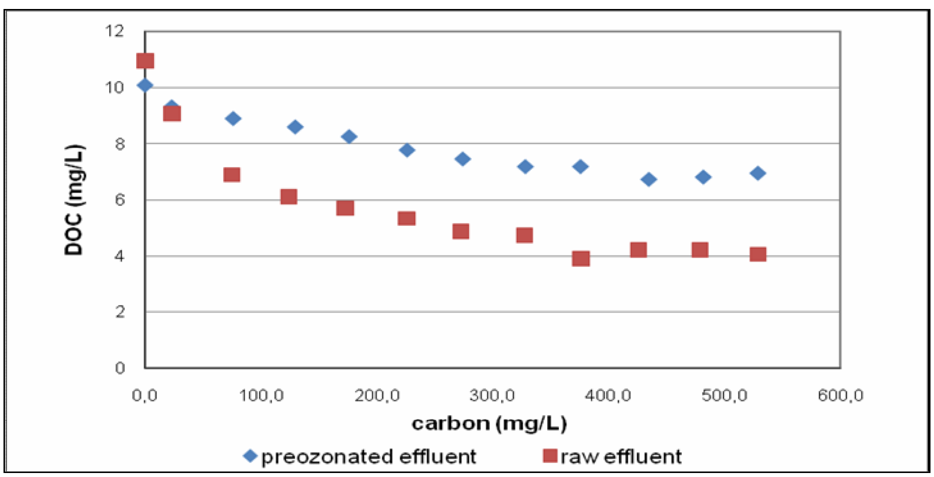


**Figure IV.13** Effect of Ozone on Removal Efficiency of DOC for W 35

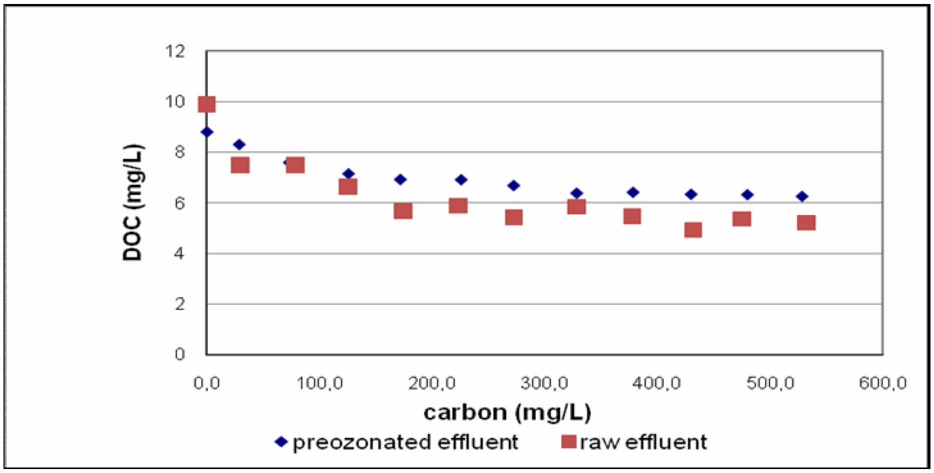


**Figure IV.14** Effect of Ozone on Removal Efficiency of DOC for Hydrodarco C

There may be several reasons why preozonation did not affect TOC/DOC removal efficiency positively. According to Takeuchi et al. (1997), it was supposed that ozonation caused the increase of the amount adsorbed of the substances of higher molecular weight. On the other hand, it was suggested that hydrophilication by ozonation caused a decrease of adsorbability of organic substances. Therefore it was thought that the influence of hydrophilication to adsorbability was much larger than that of decomposition by ozone treatment for organic substances with a molecular weight of less than several thousands.

Yapsaklē, 2008, mentioned in her study that in the case of CAgran, ozonation increased the amount of the nonadsorbable fraction. There may be several reasons for this result. The negative charge of NOM further increased in ozonated water and the net surface charge of CAgran varies from positive at pH <4.2 to negative values at higher pHs. Therefore, a bigger repulsive force between the NOM and carbon surface might have decreased the NOM adsorption at neutral pH values. Molecular size reduction upon ozonation may also play a role in decreasing the adsorption capacity. CAgran might have failed to adsorb lower molecular weight organics to a greater extent, due to its more macroporous structure. Therefore, the adsorption efficiency might have been further decreased by the size incompatibility between the carbon and NOM.

Faria et al. (2005) mentioned that oxidation of dyes with ozone leads to the formation of by-products that may stay in solution contributing to the TOC content. When activated carbon is used alone, there is no formation of secondary products, and the removal of color is accompanied by the decrease in organic content. Apparently, the basic dye molecules are more easily adsorbed on activated carbon than the secondary products resulting from dye oxidation, which are simultaneously resistant to oxidation.

It is also important to know the change of adsorbability in NOM by ozonation preceding GAC adsorption. Ozonation may have negative effect on GAC adsorption of NOM due to the increases in polarity and hydrophilicity and positive effect due to the decrease in molecular weight. Kim et al. (1997) showed that ozonated NOM has lower adsorbability to GAC than NOM without ozonation. Benedek et al. (1979) showed the same result, however, they also showed that ozonated NOM after biostabilization has almost the same adsorbability as NOM without ozonation (Nishijima and Spetial, 2004).

As known, $UV_{254}$ represents the organic matters with C=C, C=O structures, which have strong absorbance at 254 nm. Examples are phenolic, poly-aromatic hydrocarbons (PAHs), aromatic ketones, and aromatic aldehydes etc. In general, these compounds have phenyl structures (Wang et al., 2008a). The removal of $UV_{254}$ from raw and preozonated effluent is shown in Figure IV.15. In Figure IV.15, it can be seen that the removal efficiency of the $UV_{254}$ is 97% by adsorption alone. Furthermore, it is 98% by the combined process of ozonation and adsorption. It, therefore, proved that ozonation did not enhance the $UV_{254}$ removal of the effluent.

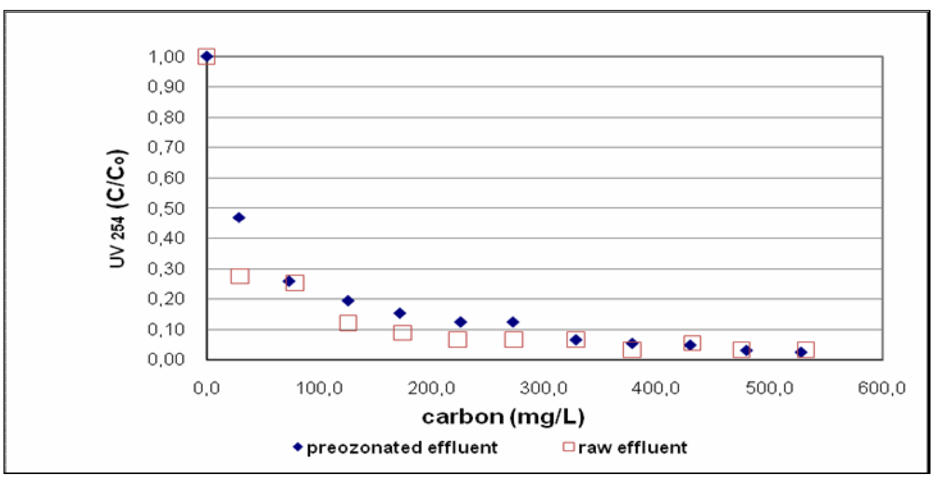


**Figure IV.15** Effect of Adsorption on UV Absorbance Removal

## IV.3 POWDERED ACTIVATED CARBON + ACTIVATED SLUDGE SYSTEM

**IV.3.1** Equilibrium Time for Adsorption of Powdered Activated Carbon

Two sets of adsorption equilibrium tests were carried out to study the system. As 250 mg/L PAC was added into PAC and PAC + AS reactors, the equilibrium tests with 250 mg/L PAC were conducted in a shaker (KS 4000 ic control) set to 200 rpm for 20 min at 25$^{o}$C. The tests showed that the adsorption equilibrium was reached after 4 min contact time for preozonated effluent and 15 min for raw effluent.

**IV.3.2** Comparison of Organic Removal in Reactors

Batch adsorption isotherm experiments (reported in Section IV.2) served as a basis for choosing the right PAC type to be employed in Powdered Activated Carbon + Activated Sludge system reactors.

Steam activated peat/wood based Norit SAE Super was the most efficient PAC type in terms of adsorption characteristics. It was concluded in Section IV.2 that, SAE Super could be used in PAC + AS experiments if the aim is to adsorb organics from effluent.

The time required for the PAC+AS system reactors to remove the organics was chosen 7 days to ensure biological activity to come to a full equilibrium condition.

The results of the PAC + AS systems in means of DOC, $UV_{254}$ and $BOD_5$ are given in Table IV.3.

**Table IV.3** DOC, $UV_{254}$ and $BOD_5$ Results of Reactor Configurations

| Reactor configuration | **DOC, mg/L** | | **$UV_{254}$, cm$^{-1}$** | | **$BOD_5$, mg/L** | |
|---|---|---|---|---|---|---|
| | Raw Effluent | Preozonated Effluent | Raw Effluent | Preozonated Effluent | Raw Effluent | Preozonated Effluent |
| Aeration | 8,97 | 7,00 | 0,162 | 0,069 | 1 | 4 |
| PAC | 3,47 | 2,98 | 0,006 | 0,021 | 1 | 1 |
| PAC + AS | 2,58 | 2,95 | 0,005 | 0,015 | 0 | 0 |
| AS | 8,01 | 7,39 | 0,134 | 0,071 | 0 | 0 |

The maximum reduction of DOC in the reactors was investigated in PAC+AS system for raw effluent. However, the DOC reductions of preozonated effluent were nearly the same for PAC and PAC+AS reactors (the difference was only 0.03 mg/L).

Çeçen and Aktaк (2001a) investigated the combined biological treatability of landfill leachate and domestic wastewater in both semi-continuously fed batch (SCFB) and continuous-flow (CF) activated sludge with recycle. The positive effect of PAC on COD reduction and nitrification was more striking in CF operation than in SCFB operation. For the SCFB run, AS and AS + PAC reactors diminished and finally the same levels were reached with respect to COD.

Nishijima and Speitel (2004) reported that majority of BDOC produced by ozonation are possible to be removed by both biodegradation and adsorption in BAC because BDOC has both biodegradability and adsorbability. However, BDOC in ozonated NOM may be removed by adsorption in the initial period of operation because BAC has a strong adsorption activity and the bacterial population is less. Kim et al. (1997) reported that more than 78% of BDOC produced by ozonation was removed by biodegradation in BAC throughout 56 days of operation in ozone-BAC treatment.

Addition of 0.50 and 300 mg/L PAC to activated sludge units having 5 and 10 day cell residence times resulted in decreased organic matter concentrations in the effluent (DeWalle, 1977).

The results of $UV_{254}$ absorbances were parallel to DOC reductions within the reactors. The maximum reductions of $UV_{254}$ absorbance for raw effluent were nearly the same for PAC and PAC+AS system reactors (97%) (the difference was only 0.001 $cm^{-1}$). The $UV_{254}$ absorbance reduction was observed in PAC+AS system reactors for preozonated effluent was less than raw effluent (78%).

$BOD_5$ reduction was the same for both raw and preozonated effluents. It was 1 mg/L for the PAC reactor and 0 for the PAC+AS system reactor.

These results indicate that nearly the same reductions for both PAC and PAC+AS reactors could be attained, which emphasizes the effectiveness of PAC in the system.

Çeçen and Aktaк (2001b) reported the same result for their system which investigated the effect of PAC on the biotreatment of an industrial wastewater taken from a chemical plant. In general, with PAC addition, the additional removal of compounds having absorption in the UV-Vis range was higher than the collective parameter SCOD. Therefore, these parameters should also be taken into consideration in testing the effectiveness of PAC. Evaluation of all results showed that if PAC and AS operations were combined, the maximum decrease in the $UV_{254}$ value was about 58%. By adsorption onto PAC, a reduction of about 45% in the $UV_{254}$ value could be attained. Only a small fraction (nearly 10%) of the compounds contributing to the initial $UV_{254}$ was removed by biodegradation. Direct PAC addition to activated sludge was considered to be a better alternative.

However, it also possible to find studies like Çeçen and Aktaк (2001a) and Bornhardt (1997) in the literature, which do not report parallel results.

Aktaк and Çeçen (2001a) investigated the effectiveness and applicability of the addition of PAC to activated sludge reactors for treatment of leachate from municipal landfill. Isotherms studies with leachate and leachate-domestic wastewater mixture indicated low adsorptivity of organic matter onto powdered activated carbon. On the other hand, in aerated and well mixed reactors containing PAC, COD removal exceeded that predicted by Freundlich isotherms. Thus, in an activated sludge system removal of organics by addition of PAC could not be explained by the PAC isotherms alone. PAC doses ranging from 100 to 3500 $mg/dm^3$ were applied. The main effect was observed in later periods where PAC adsorbed non-biodegradable matter and considerably lowered the final residual COD.

Bornhardt (1997) studied the effectiveness of different treatments with PAC to reduce organic halogen levels in municipal wastewater in a bench-scale AS treatment plant. He reported that the improvement caused by the addition of PAC is due only to an adsorptive effect, so that a subsequent treatment of the clarified wastewater would be more effective than a simultaneous PAC+AS treatment. In a subsequent treatment with 100 mg/L NORIT W-35 dosage, an additional AOX removal of up to 35% could be achieved. An effective combination of the benefits of a subsequent and simultaneous treatment is the here reported subsequent partial-flow treatment, but no evidence of synergistic effect of the PAC addition to activated sludge, nor bioregeneration of the activated carbon, could be observed.

The results of reactor systems show that only PAC addition to effluent was satisfactory for treatment of Paкaköy effluent for reuse purposes. This means that adsorption is the main removal mechanism for the system. As mentioned in Section

IV.3.1, equilibrium time for adsorption of powdered activated carbon was 4 min and 15 min for preozonated and raw effluent, respectively which means with the addition of PAC, all organics could effectively be removed from the effluent.

Çeçen (1994) studied the effect of PAC addition to activated sludge in the treatment of pulp bleaching effluents which contain a large amount of nonbiodegradable matter. Carbon addition to activated sludge resulted in a high decrease in substrate concentration, particularly for color. However, the results indicated that there was no noticeable biological enhancement with PAC addition. Then the combined PAC and activated sludge process seemed to be a combination of adsorption and biodegradation.

DeWalle et al. (1977) stated that when the carbon was added to the aeration basin, using glucose or secondary effluent as a substrate, there were not any increments in magnitude of the final oxygen uptake by bacteria in the presence of PAC and so he indicated that physical adsorption was the main removal mechanism.

Improvement of biodegradability of DOC by ozonation does not always induce improvement of DOC removal and extension of activated carbon service time, because most of the biodegradable DOC increased by ozonation is adsorbable on activated carbon (Kim et al., 1997).

## CHAPTER V

### CONCLUDING REMARKS AND RECOMMENDATIONS

The main goal of this study is to develop a cost effective technology for further treatment of Paкaköy Advanced Biological Treatment Plant effluent for reuse purposes. To serve this purpose carbon adsorption was tested on PABTP effluent as well as on preozonated PABTP effluent. Then, the preozonated PABTP effluent was subjected to activated carbon adsorption and activated sludge processes in the same reactor.

The specific conclusions derived from this study are as follows:

1. The optimal ozonation time was found 20 min as this contacting time ensures the highest efficiency of biodegradation in terms of $BOD_5$/COD ratio. Effluent biodegradability was found to be significantly enhanced through ozonation: $BOD_5$ values reached 400%, and the $BOD_5$/COD ratio increased from 0.18 to 080. Further increase in the dosage did not enhance the $BOD_5$/COD ratio in the ozonation process. Therefore, the 50 mg/L of applied ozone concentration was found to be optimum for efficient biodegradability increment. In the view of these experimental results, it can be concluded that ozonation could be successfully used as a pretreatment step to improve the biodegradability of municipal wastewater effluent.
2. The representation of the experimental data for batch adsorption experiments by the Freundlich equation resulted in a linear curve with $R^2$ values of a least 0.74. The Freundlich model, therefore, appears to be a good fit of the adsorption data.
3. Both for K and 1/n values showed that the organic matter in raw effluent was more adsorbable onto activated carbon. Among all three activated carbon types tested in this study, peat/wood based SAE Super had shown the best adsorption intensity and strongest adsorption bond.
4. The steam activated lignite coal-based Hydrodarco C showed the lowest adsorption of organic matter. This is probably due to the fact that, Hydrodarco C had the lowest total surface area, 600 $m^2$/g among all the carbons studied. Peat/wood based SAE Super had the highest total surface

area of 1,150 $m^2/g$ which made it suitable for higher organic matter loadings. These results indicate that total surface area is a good indicator of the performance of the adsorbent within the scope of this study and only activated carbons with appropriate adsorption characteristics and pore structure are useful for wastewater treatment.

5. For all carbon types, adsorption became unfavorable, compared to raw effluent when the effluent was preozonated. The results indicated that preozonation did not enhance DOC removal by adsorption.
6. The removal efficiency of the $UV_{254}$ is 97% by adsorption alone. Furthermore, it is 98% by the combined process of ozonation and adsorption. It, therefore, proved that ozonation did not enhance the removal of $UV_{254}$ of the effluent.
7. DOC, $BOD_5$ and $UV_{254}$ absorbance reductions were nearly the same for both raw and preozonated effluents in the PAC and PAC+AS systems.
8. Finally, the results of the reactor system show that only PAC addition to effluent is satisfactory for further treatment of Paкaköy effluent for reuse purposes. This means that adsorption is the main removal mechanism for the system.

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# CURRICULUM VITAE

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