The Production of activated carbon from local palm-date pits for pollution removal process

Omar Ghazi Omar Al-Attas

Civil Engineering

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Abstract

The Kingdom of Saudi Arabia is one of the leading countries engaged in planting several millions of palm-date trees. Huge quantities of date pits are generated as wastes once dates are eaten. The generated pits can be reused to produce activated carbon that can be used for treating polluted water. The importance of this lies on utilizing the generated waste, which is the palm-date pits, in the form of activated carbon as a medium for wastewater treatment purposes. Thus, it will have an advantage from environmental and economical aspects.

The production of activated carbon appears to be one of the most important phases of this study. Different permutation-combinations were investigated to achieve an activated carbon with optimum physical characteristics. This part of the study involved three steps: boiling, soaking and a combined step of carbonization and activation of pits.

The produced AC was tested against methylene blue (MB). This test has been conducted to check the ability of the produced activated carbon (24-hr and 12-hr acid soaked pits) in order to remove the pollutants. The experiment lasted for 12 days for both the 24-hr and 12-hr acid soaked pits compared to the commercial activated carbon, which lasted for 35 days.

To investigate the pollutant removal efficiencies of the produced activated carbon, an experiment was performed by allowing an unchlorinated secondary effluent to pass through three columns, each filled with different types of activated carbon (i.e. 24-hr acid soaked pits, 12-hr acid soaked pits and commercial activated carbon). The experimental run continued for a period of seventeen days. All three columns were run simultaneously. The run was terminated when the breakthrough was reached. The samples taken from all ports were analyzed for pH and TOC on a daily basis, whereas the Total Coli-forms and the BOD were monitored on alternate days only.

The BOD and TOC average removals in the 24-hr acid soaked pits, 12-hr acid soaked pits and the commercial activated carbon were 71%, 69% and 73% respectively. With regard to total coli-forms, very good removal rates were achieved in al columns packed with the three types of carbon in the first few days. However, the removal rates decreased signaling the breakthrough conditions.

In conducting the present study, one of the objectives was to statistically determine the significance of activated carbon types (24-hr acid soaked pits, 12-hr acid soaked pits and commercial activated carbon) and the depth of the ports within each column (bottom, 5-cm and 10-cm) in terms of the removal of various pollutants from wastewater. The statistical analysis of the data confirmed that both the activated carbon types and the ports depth had significant effect on organics removal, whereas only the activated carbon types were found to have significant effect on the removal of total coli-forms considering 8% level of significance.

KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS
DHAHRAN, Saudi Arabia

COLLEGE OF GRADUATE STUDIES

This Thesis, written by **Omar Al-Attas** under the direction of his Thesis Advisor, and approved by his Thesis Committee, has been presented to and accepted by the Dean of the College of Graduate Studies, in partial fulfillment of the requirements for the degree of

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Thesis Committee

_____
Dr. Muhammad A. Al-Zahrani   (Chairman)

_____
Dr. Mohammad S. Al-Suwaiyan   (Member)

_____
Dr. Walid S. Al-Sabah   (Member)

_____
Dr. Hamad I. Al-Abdul Wahhab
Chairman, Dept. of Civil Engineering

_____
Dr. Osama A. Jannadi
Dean, College of Graduate Studies

Date
_____

بسم الله الرحمن الرحيم

Dedicated to

My parents and my wife

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تشتهر المملكة العربيّة السّعوديّة بزراعة الملايين من أشجار النّخيل المثمره والتي تُنتج كميات هائلة من التمور ولدى استهلاك هذه التمور يُتخلص من كميّات كبيره من النوى (مخلفات) والتي يمكن أن يُعَاد إستخدَامها لإنتاج مادة الكربون المنشّط (Activated Carbon) الذي يتم استْخدَامه لمعالجة المياه الملوّثه. وتعتمد أهمّيّة هذا البحث على استخدام نوى التمر كمادة فعالة، بعد تحويله إلى كربون منشط، لغرض معالجة المياه الملوثه مما سينتج عنه عدد من الجوانب الإيجابية المتعلقة بالمحافظة على البيئة بالإضافة إلى إنتاج مادة الكربون المنشط محلياً والإستغناء عن استيرادها من الخارج مما يسهم في التنميه الإقتصاديه محلياً.

إن إنتاج الكربون المنشّط من نوى التمر هو أحد أهمّ مراحل هذه الدّراسة حيث تم القيام بالعديد من التجارب والمحاولات المعمليه المختلفه والتي نتج عنها بالنهاية كربون منشّط ذو فعالية جيدة. تضمّن هذا الجزء من الدّراسة ثلاثة خطوات اساسية وهي: الغليان, النقع و اخيراً خطوة مشتركة من الكربنة (الحرق) والتنشيط.

ومن ثم تم اختبار قدرة الكربون المنشط المنتج من النوى على إزالة الألوان الصناعية مثل مادة (Methylene Blue) التي استخدمت في هذه الدراسة ومقارنة أداءه بالكربون المنشط التجاري المنتج بالخارج. وقد أظهرت التجربة قدرة الكربون المنشط المنتج من النوى على إمتصاص مادة الـ(Methylene Blue) لمدة ١٢ يومّا بينما استمر الكربون المنشط التجاري في إزالة المادة الملونه لمدة ٣٥ يوم.

وللتّحقق من فاعليّة الكربون المنشّط المنتج لإزالة الملوّثات، تم تعريض كلاً من الكربون المنشط المنتج من النوى والتجاري (المستورد) لمياه ملوثة تم معالجتها ثانوياً حيث تم تعبئة ثلاثة أعمدة يحتوي كل واحد منها على (الكربون المنشط التجاري، الكربون المنشط المنتج لمدة ٢٤ ساعة والكربون المنشط لمدة ١٢ ساعة) وتعريضها للمياه الملوثة في آن واحد. ولقد استمرّت التجربة لمدة سبعة عشر يوم حيث تم ايقافها عندما تم ملاحظة أن نوعية كلاً من المياه الملوثه الداخله من أعلى الأعمدة تقارب نوعية المياه الخارجه من الأسفل. وخلال اجراء التجربه تم جمع عيّنات من المياه من ارتفاعات مختلفة (٠، ٥ و ١٠ سم) من الأعمدة حيث حُلّلت لإيجاد قيم كلٍ من: الرقم الهيدروجيني (pH)، BOD، TOC والكليفورم الكلي (Total Coliforms) بالإضافة إلى قياس نسبة التعكر والعوالق لمياه المصدر والمياه العابرة خلال الأعمدة.

وقد دلت النتائج المتحصله على كفاءة الكربون المنشط المنتج من النوى على إزالة الملوثات الموجودة بالمياه الملوثه بكفاءة وقدره تقارب، في أغلب الأحيان، قدرة وكفاءة الكربون المنشط التجاري.

وفي ختام هذه الدراسه، تم إجراء بعض التحليلات الإحصائية لإختبار تأثير كلاً من أنوع الكربون المنشط المستخدم والأعماق المختلفة (٠، ٥ و ١٠ سم) لكلّ الأعمدة المستخدمة على إزالة الملوثات من المياه المستخدمه. وقد أثبتت التّحاليل الإحصائية للبيانات أن كلاً من أنوع الكربون المنشط و الأعماق المختلفة (٠، ٥ و ١٠ سم) لكلّ الأعمدة المستخدمة أثر هامّ في إزالة المواد العضوية، بينما وُجِدَ أن أنواع الكربون المنشّط فقط أثرت على إزالة الكوليفورم الكلي (Total Coliforms).

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ABSTRACT

NAME: OMAR GHAZY AL-ATTAS
TITLE: THE PRODUCTION OF ACTIVATED CARBON FROM LOCAL PALM-DATE PITS FOR POLLUTION REMOVAL PROCESS
MAJOR FIELD: CIVIL ENGINEERING (ENVIROMNMENTAL)
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The Kingdom of Saudi Arabia is one of the leading countries engaged in planting several millions of palm-date trees. Huge quantities of date pits are generated as wastes once dates are eaten. The generated pits can be reused to produce activated carbon that can be used for treating polluted water. The importance of this lies on utilizing the generated waste, which is the palm-date pits, in the form of activated carbon as a medium for wastewater treatment purposes. Thus, it will have an advantage from environmental and economical aspects.

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In conducting the present study, one of the objectives was to statistically determine the significance of activated carbon types (24-hr acid soaked pits, 12-hr acid soaked pits and commercial activated carbon) and the depth of the ports within each column (bottom, 5-cm and 10-cm) in terms of the removal of various pollutants from wastewater. The statistical analysis of the data confirmed that both the activated carbon types and the ports depth had significant effect on organics removal, whereas only the activated carbon types were found to have significant effect on the removal of total coliforms considering 8% level of significance.

MASTER OF SCIENCE DEGREE
KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS
DHAHRAN, SAUDI ARABIA
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C H A P T E R   1

INTRODUCTION

It is well known that activated carbon is produced from a wide variety of carbon rich raw materials including wood, coal, peat, coconut shells, nutshells, bones and fruit stones. New materials are currently under investigation as sources for the production of activated carbon. For example, palm-date pit is a potential new candidate as a source of activated carbon.

In the process of packing dates, a number of by-products are becoming available for which use should be found in order to improve the economics of the date processing operation as a whole and to minimize the disposal problems and costs. In the past, people used the pits as an animal feed source because of its chemical composition. Although whole dates are eaten by camels, cattle, goats, and sheep, it is not uncommon to see the pit coming out from the other end, undigested, thus losing its effect as a feed source.

In the Kingdom of Saudi Arabia, the date farms contain about 14,000,000 palm trees. They grow primarily in the world's largest oasis, Al-Hasa, in the eastern province. There is an enormous variety of dates grown throughout the Kingdom. Table 1.1 summarizes the different kinds of dates and their regions in the Kingdom of Saudi Arabia (Saudi Embassy, 1997). The date pits become available in concentrated quantities when pitted dates are produced in packing plants or in

TABLE 1.1: Different Kinds of Dates and Their Regions (Saudi Embassy, 1997)

Region	Kind of Date
Eastern Province	Khalas, Ruzeiz, Kheneizy and Bukeira
Central region and Qasim	Nebut seif, Khudairi, Sefri, Barhi, Sukkari and Sullaj
Western Province	Anbara, Agwa, Berni, Hilwa, Hloya, Safawi, Shalabi and Sukkaret

industrial date processing plants based on juice extraction. In the latter case, they may still be mixed with the exhausted press cake or they may be screened out in the process (Barreveld, 1993).

1.1 IMPORTANCE OF THE STUDY

The Kingdom of Saudi Arabia is one of the leading countries engaged in growing palm-date trees. Dates, which are produced from palm trees, are considered a major source of food. Huge quantities of date pits are generated as wastes once dates are eaten. The generated pits can be reused to produce activated carbon that can be used for treating polluted water. Thus, the waste, which is the pits, can be utilized for producing activated carbon and "could" replace the imported activated carbon. The importance of this lies on using a treated local waste, which is the pits, as a medium for treating purposes. Thus, it will have an advantage from environmental and economical aspects.

As far as the economical aspect of the production of activated carbon from the local palm-date pits is concerned, it is evident that the production cost of the local pits is much less than the commercial activated carbon. This is due to the fact that the date pits in the kingdom are considered as useless waste generated during the consumption and processing phases. Furthermore, the cost of importing commercial activated carbon from outside the Kingdom is so high, which reflects on the overall

cost of production of activated carbon.

1.2 RESEARCH OBJECTIVES

The main objective of this study is to identify the adsorption capacity of the palm-date pits. The specific objectives are to:

- Produce activated carbon from palm-date pits.

- Compare the removal efficiencies of unchlorinated secondary effluent by using commercial activated carbon and the locally produced activated carbon.

- Compare the removal efficiencies of methylene blue by using commercial activated carbon and the locally produced activated carbon.

C H A P T E R 2

LITERATURE REVIEW

One of the most important environmental problems in the world is water pollution. Fecal pollution of natural water and drinking water has frequently caused waterborne diseases. In general, waterborne diseases have been well controlled, especially in developed countries. Today, toxic chemicals pose a great threat to the safety of water supplies in developed and developing countries alike. There are many sources of toxic chemicals in the environment, such as badly designed landfills, industrial pollution and pesticide runoff. However, industrial wastewater is an important point source of water pollution. Thus, there is an increasing global demand for the treatment of industrial wastewater to protect the limited water resources. Microbial degradation, chemical oxidation and photolysis are used in the treatment of industrial wastewater. However, many hazardous organics in water are either non-biodegradable or refractory by-products. Some of these organics can be removed by adsorption on an active solid surface. Activated carbons are the most common adsorbent used for this purpose.

Activated carbon is extensively used to remove pollutants from gaseous and liquid process streams. It is produced by chemical or physical activation of carbonaceous materials. The features of carbons such as porosity, surface area, density, and mechanical stability govern the use of activated carbons as adsorbents.

Very often the choice of material is made by industrial "users" of carbon, not by carbon researchers, and it happens that the decision is based on the so-called "common belief" (Salame and Bandosz, 2000).

Wood, coal, lignite, coconut shell, and peat are some of the raw materials currently used to produce activated carbons. Nutshells have also been used to produce activated carbons. Their advantages as carbon feed stocks include high density, availability as renewable resources, low cost, low ash content, and they are capable of producing activated carbons of high adsorption capacity (Johns et al., 1999).

The widespread use of a particular raw material as a source of activated carbon is limited by the supply of that material. As a result, wood is by far the most common source of activated carbon followed by coal, coconut shells and peat. The raw material from which a given activated carbon is produced often has large effect on its porosity distribution and surface area. As a result, activated carbons produced from different raw materials may have different adsorption capacities (Table 2.1). New materials are currently under investigation as sources for activated carbon. Almost any organic matter with a large percentage of carbon could theoretically be activated to enhance its sorptive capacity. In practice however, the best candidates for activated carbon should satisfy the following conditions (1) Contain a minimum amount of organic material, (2) Have a long storage life, (3) Consist of hard structures to maintain their properties under usage conditions, and (4) Can be

TABLE 2.1: Characteristics and Applications of Activated Carbon Produced from

Different Raw Materials (http://www.cee.vt.edu/...)

Raw Material	Density (kg/L)	Texture of AC	Applications
Soft wood	0.4 - 0.5	Soft, large pore volume	Aqueous phase adsorption
Nutshells	1.4	Hard, large micropore volume	Vapor phase adsorption
Hard coal	1.5 - 1.8	Hard, large pore volume	Gas vapor adsorption
Lignite	1.00 - 1.35	Hard, small pore volume	Wastewater treatment

obtained at a low cost. (http://www.cee.vt.edu/…)

Warhurst et al. (1996) worked on the production of activated carbon for water treatment in Malawi using the waste seeds of Moringa oleifera (multi-purpose tree). They showed that the seeds of this tree could be used as a coagulant in water treatment. The same seeds can be converted into activated carbon by carbonization at 485°C under N_2 for 30 minutes, followed by activation in steam at 850°C for 5 minutes.

Philip and Girgis (1996) studied the feasibility of apricot stone shells to be chemically activated. They used different concentrations of phosphoric acid (20-50 wt %) for the chemical activation, followed by carbonization at 573-773 K. A series of wide range microporous activated carbons were obtained, with surface areas of 640 up to 1600 m^2/g. It was found that increasing the acid concentration at 573 and 673 K increases the surface area and pore volume, whereas at 733 K (460ºC) a small decrease in both parameters appears at higher H_3PO_4 concentrations.

Sai et al. (1997) succeeded in producing an activated carbon from coconut shell char using steam or carbon dioxide as the reacting gas in a 100-mm diameter fluidized bed reactor. The effect of the process parameters such as reaction time, fluidizing velocity, particle size, static bed height, temperature of activation, fluidizing medium, and solid raw material on activation, was studied and it was found that the increase in these parameters resulted in better activation. It was observed that the maximum surface areas can be obtained for the following

conditions: 24 cm/s fluidization velocity, 1.55 mm particle size, 100 mm static bed height, temperature of 850ºC, and steam as fluidization medium. Finally, it was concluded from the experimental investigations that the fluidized bed reactor could be more effectively employed for the production of activated carbon from coconut shell char compared to the conventional processes.

Pitch-based activated carbons (PAC) with high specific surface area were produced by Qiao et al. (1997) through direct chemical activation route in which oxidative stabilized pitch derived from ethylene tar oil was reacted with potassium hydroxide (KOH) under various activation conditions. It was found that PACs with surface area of around 2600 to 3600 m^2/g could be obtained under suitable activation conditions. Compared with a commercially available activated carbon, it was concluded that the PAC has larger adsorptive capacity to benzene due to its higher surface area.

Johns et al. (1998) produced granular activated carbons (GACs) from low value agricultural by-products and used them for environmental remediation. They characterized and evaluated the GACs as effective removers of organics and metals from water. The by-products included rice straw, soybean hull, sugarcane bagasse, peanut shell, and harder materials such as pecan and walnut shells. These by-products were CO_2 or steam activated and then oxidized to enhance the metal adsorption. Table 2.2 summarizes the results of carbonization and activation additional to the surface area for the carbons activated. The results of this study

indicated that the GACs made from selected agricultural by-products can be more effective than commercial GACs in the adsorption of organic and metal contaminants from water.

Gharaibeh et al. (1998) compared the carbonized solid residue of olive mill products (called J-carbon) with Sigma activated carbon (powder) and Chemviron activated carbon (0.6 - 0.7 mm) in the treatment of the effluent of Flexsys' wastewater (industrial wastewater from a treatment plant that uses a pure oxygen activated sludge system). The removal of NH_3, TOC as non-specific organics, and six specific leading organic pollutants (benzothiazole, 1,2-dihydro-2,2,4-trimethylequinoline, N-dimorpholinyl ketone, methylsulphyl benzothiazole, methyl-2-benzothiazole sulphone and tetrachloroethene) from Flexsys' wastewater effluent was examined. All the three different carbon sources have almost similar behavior in removing the above pollutants. The removal efficiencies (percent removal) were as follows: (1) Sigma carbon: 100% benzothiazole, 1,2-dihydro-2,2,4-trimethylequinoline, N-dimorpholinyl ketone, methylsulphyl benzothiazole and methyl-2-benzothiazole sulphone; 50% tetrachloroethene; 94% TOC; 82% NH_3. (2) Chemviron carbon: 100% benzothiazole, 1,2-dihydro-2,2,4-trimethylequinoline, N-dimorpholinyl ketone, methylsulphyl benzothiazole and methyl-2-benzothiazole sulphone; 31% tetrachloroethene; 40% TOC; 87% NH_3. (3) J-carbon: 100% benzothiazole, methylsulphyl benzothiazole and methyl-2-benzothiazole sulphone; 70% 1,2-dihydro-2,2,4-trimethylequinoline; 58% N-dimorpholinyl ketone; 70%

TABLE 2.2: Produced Granular Activated Carbons from Agricultural By-products
(Johns et al., 1998)

Type of By-product	Char Yield (%)	Activation Temp. (ºC)	Duration (Hours)	Activant	Burn-off (%)	Surface Area (m^2/g)
Peanut Shell Pellets	30	850	10	CO_2	17.3	127
Peanut Shell Pellets	30	800	12	Steam	25.0	478
Rice Straw Pellets	35	850	10	CO_2	27.2	127
Rice Straw Pellets	35	800	12	Steam	11.7	400
Sugarcane Bagasse Pellets	35	850	10	CO_2	20.3	490
Sugarcane Bagasse Pellets	35	800	12	Steam	15.1	365
Soybean Hull Pellets	25	850	5	CO_2	27.2	38
Soybean Hull Pellets	25	800	12	Steam	57.0	380
Walnut Shell	26	850	15	CO_2	20.7	456
Walnut Shell	26	800	12	Steam	16.7	602
Pecan Shell	27	800	15	CO_2	34.0	547
Pecan Shell	26	800	12	Steam	32.0	721

tetrachloroethene. 37% TOC; 78% NH_3.

Teng and Yeh (1998) prepared activated carbons by chemical activation from two Australian bituminous coals. The preparation process consisted of zinc chloride impregnation followed by carbonization in nitrogen. The carbonization temperature ranged from 400 to 700ºC. The experimental results revealed that an acid-washing process following the carbonization with $ZnCl_2$ is necessary for preparing high-porosity carbons. Table 2.3 summarizes the effects of carbonization temperature on the surface properties of the carbons from $ZnCl_2$ activation. It was found that the surface area, pore volume, and average pore diameter of the resulting carbons increased with the carbonization temperature to a maximum at 500ºC and then began to decrease with the temperature. Teng and Hsu (1999) also, prepared activated carbons by potassium hydroxide (KOH) activation from the same Australian bituminous coals. The preparation process consisted of KOH impregnation followed by carbonization in nitrogen. The carbonization temperature ranged from 500 to 1000ºC for 0-3 hours. The surface area and pore volume of the resulting carbons were found to increase with the carbonization temperature to a maximum at 800ºC and then begin to decrease. The optimum values of the surface area and the pore volume were found to be 3000 m^2/g and 1.5 cm^3/g, respectively.

Ahmadpour et al. (1998) produced activated carbons by using chemical activation of coal and macadamia nutshell precursors with KOH and $ZnCl_2$. Table 2.4 shows the physical characteristics of the produced activated carbons. The

TABLE 2.3: Effects of Carbonization Temperature on the Surface Properties of Two Australian Bituminous Coals by $ZnCl_2$ Activation (Teng and Yeh, 1998)

Carbonization temperature (ºC)	Surface Area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter ($Å$)
(Type I)			
400	501	0.28	22
500	1300	0.83	25
600	895	0.55	24
700	858	0.49	23
(Type II)			
400	775	0.41	21
500	1080	0.65	24
600	994	0.58	23
700	874	0.50	23

TABLE 2.4: Physical Characteristics of the Activated Carbons Produced by Chemical Activation of Coal and Macadamia Nutshells (Ahmadpour et al., 1998)

Sample	Activant	Temperature (ºC)	Activation time (min)	Surface Area (m^2/g)
Coal	KOH	700	120	850
Coal	ZnCl$_2$	500	60	1062
Nutshell	KOH	700	60	1075
Nutshell	ZnCl$_2$	500	60	1718

equilibrium and dynamic characteristics of the produced activated carbons were then compared with the following micropore properties: surface area, volume, and half-width. Carbons activated by KOH resulted in a more microporous structure, while those activated by zinc chloride were more mesoporous. High surface area samples were further studied in terms of their methane adsorption uptake and it was found that macadamia nutshell-derived activated carbons have a higher adsorption capacity per unit mass than those derived from coal.

Cox et al. (1999) produced carbon adsorbent from flax shive by treatment with sulfuric acid. Several factors were considered in the preparation: reaction time, temperature, and the amount and concentration of sulfuric acid. Based on the temperature considered, two types of carbon were produced, C160 and C200. The first type (C160) with a mixture of flax shive and sulfuric acid was heated to 160ºC for 15-20 minutes, whereas the second type (C200) was heated to a temperature of 200ºC for the same duration. The two types of carbon were tested for the removal of cadmium (II) and mercury (II) from aqueous solution. It was concluded that the carbon prepared at 160ºC, which is C160, is suitable for the removal of mercury (II) from aqueous solution which has different mechanism from cadmium (II) and this material can be considered as an efficient alternative to activated carbon for removing heavy metals from aqueous solution.

Lua and Guo (1999) studied the chars carbonized from extracted oil palm fibers for the production of activated carbons. The effects of carbonization

temperature and duration on density, porosity, yield, micropore surface areas, total pore volume, and pore size distributions of chars were investigated. The optimum condition for the carbonization was found to be at a temperature of 850ºC for a duration of 3.5 hours. The experimental results showed that it was feasible to produce chars with high surface areas (520.6 m^2/g) from extracted oil palm fibers. Then, the produced chars were subjected to steam or carbon dioxide activation to prepare the activated carbon to be used as gas adsorbents for air pollution control.

Johns et al. (1999) applied the following activation techniques: (1) steam, (2) carbon dioxide (CO_2), and (3) phosphoric acid (H_3PO_4) to produce granular activated carbons (GACs) from pecan shell chars. All the three activation methods resulted in surface areas that were equal to or greater than commercial activated carbons as can be seen from Table 2.5. Carbon dioxide activation favored microporosity, while the other activations increased both mesoporosity and microporosity. All the three types were tested for the adsorption of metals (copper) and organic compounds. It was found that the GACs made from pecan shells by different activation methods can be more effective than commercial GACs in the adsorption of metal and organic contaminants from water.

Tam and Antal (1999) adopted a three-step process for the production of high quality activated carbons from macadamia nutshell and coconut shell charcoals. In this process, the charcoal is (i) heated to a high temperature of $900^{o}C$ for 15 minutes ("carbonized"), (ii) oxidized in air following a stepwise heating program from low

TABLE 2.5: Surface Areas of Commercial Carbons and Pecan Shell Carbons Activated by Steam, Carbon Dioxide and Phosphoric Acid (Johns et al., 1999)

Pecan Shell Carbons	
Activation Type	**Surface Area (m^2/g)**
Steam	1149
Carbon Dioxide (CO_2)	877
Phosphoric Acid (H_3PO_4)	1561
Commercial Activated Carbons	
Commercial Activated Carbon Type	**Surface Area (m^2/g)**
Filtrasorb 400	944
GRC-20	928
RO 3515	791
Hydrodarco GCW	874
Hydrodarco 4000	575

(177°C) to high (387°C) temperatures ("oxygenated"), and (iii) heated again in an inert environment to a high temperature of 827°C ("activated"). According to this procedure, activated carbons with surface areas greater than 1000 m^2/g could be produced.

Dai and Antal (1999) produced an activated carbon from macadamia nutshell charcoal by heating it in an inert environment to temperatures above 1000 K (> 900°C) for 25 minutes ("carbonized"), reacted with oxygen at temperatures between 525 and 586 K (252 - 313°C) for a period varying from 4.5 to 260 minutes ("oxygenated"), and heated again in an inert environment to temperatures above 1000 K (> 900 $^{\circ}$C) for 15 minutes ("activated"). According to this procedure, activated carbons with surface areas ranging between 101 and 138 m^2/g could be produced. The processing conditions employed (low oxidation temperatures, short processing times, and applying cheap activation agents) were found to be quite attractive compared to the conventional activation methods.

Salame and Bandosz (2000) compared the surface features of two carbons of wood origin. One sample was manufactured using phosphoric acid activation and the other using potassium hydroxide activation. The carbon obtained using KOH activation was found to be homogeneously microporous with high surface area of around 2300 m^2/g. On the other hand, the carbon produced using phosphoric acid was found to contain high volume of mesopores and its surface area was significantly lower.

Mameri et al. (2000) developed a process for producing high quality activated carbon from Algerian mill waste. The solid olive mill residue was carbonized at $800^{o}C$ and physically activated with CO_2, air or steam. An optimum activation temperature of about $850^{o}C$ was determined for all the activation agents used. Steam appeared to be the most efficient activator as compared to air and CO_2. An optimal activation time of about 2 hours was then determined with steam as the optimum activation agent and the specific surfaces produced were exceeding 1500 m^2/g. Then, experiments were conducted on the adsorption of phenol into the activated carbon prepared. It was found that the activated carbon produced was effectively adsorbing the phenol solution that was prepared and the adsorption capacity was about 11.24 mg of phenol per gram of the activated carbon produced.

An activated carbon prepared from oil-palm shells was produced by Guo and Lua (2000). This type of carbon was produced by impregnating the oil-palm shells with potassium hydroxide (KOH). The preparation of the carbon started by crushing and sieving the oil-palm shells to different sizes. After impregnating with 10% KOH at room temperature for 24-hr, the shells were filtered, washed with hot water and dried. Thereafter, the sample was carbonized in a vertical tube furnace under a nitrogen flow. The furnace temperature was increased from room temperature to $600^{o}C$ at the rate of 10 $^{o}C/min$ maintaining this temperature for 2 hours. The resulting chars were activated with carbon dioxide at $800^{o}C$ for 1 hour to produce the final products. The surface area of the activated carbon produced was found to

be 1408 m^2/g. The produced carbon was then used to study the adsorption of sulfur dioxide (SO_2). The experimental results showed that SO_2 could be adsorbed effectively by KOH-impregnated oil-palm shell activated carbons, whose adsorptive capacities were comparable to those of some commercial activated carbon.

Table 2.6 summarizes the raw materials, applications and the preparation methods used by different researchers to produce activated carbon, in addition to the surface areas of each type. The raw material used in this research (palm-date pits) has not been used before to produce activated carbon. This shows the importance of this research in utilizing the local waste (palm-date pits) in the production of activated carbon that can be used for wastewater treatment purposes.

As mentioned in Table 2.6, activated carbon is used in the adsorption process to remove dissolved organics. Adsorption, in general, is the process of collecting soluble substances present in a solution on a liquid-solid interface.

TABLE 2.6: Summary of the Applications, Preparations and Surface Areas of Different
Raw Materials Used in the Production of Activated Carbon

Raw material	Application	Preparation	Surface Area (m^2/g)	Reference
Macadamia Nut and Coconut Shell	Remove pollutants from gaseous and liquid streams.	Physical activation using steam or CO_2.	> 1000	(Tam and Antal, 1999)
Bituminous Coal		Chemical activation using potassium hydroxide (KOH).	> 3000	(Teng and Hsu, 1999)
Olive Mill Solid Residue	Treatment of wastewater from a treatment plant that uses pure oxygen activated sludge system.			(Gharaibeh et al., 1998)
Coal and Macadamia Nutsell	Methane adsorption.	Chemical activation using KOH and $ZnCl_2$.	850-1718	(Ahmadpour et al., 1998)
Flax shive	Removal of cadmium (II) and mercury (II) from aqueous solution.	Chemical activation using dehydration with sulfuric acid (H_2SO_4).	22	(Cox et al., 1999)
Oil-Palm Shells	Adsorption of sulfur dioxide (SO_2).	Chemical activation using potassium hydroxide (KOH).	520.6	(Guo and Lua, 2000)
Macadamia Nutshell Charcoal		Physical activation using air gasification.	138	(Dai and Antal, 1999)
Agricultural By-products	Adsorption of dissolved metals and organics.	Physical activation using steam and CO_2.	38-970	(Johns et al., 1998)
Bituminous Coals		Chemical activation using zinc chloride ($ZnCl_2$).	1300	(Teng and Yeh, 1998)
Pitch-based AC		Chemical activation using potassium hydroxide (KOH).	3600	(Qiao et al., 1997)
Agricultural Wastes	Gold mining and soft drinks industries.	Physical activation using steam, air or CO_2.	1400	(Lartey et al., 1999)
Oil-Palm Wastes	Gas adsorption for air pollution control.	Physical activation using steam or carbon dioxide.	970	(Lua and Guo, 1999)
Olive Mill Solid Residue	Phenol adsorption.	Physical activation using CO_2, air or steam.	> 1500	(Mameri et al., 2000)
Coconut Shell		Physical activation using CO_2 or steam.	4300	(Sai et al., 1997)
Pecan Shell	Metal (copper) and organic adsorption.	Physical activation using steam or CO_2 and chemical activation using phosphoric acid (H_3PO_4).	> 1500	(Johns et al., 1999)
Two Types of Wood		Chemical activation using phosphoric acid (H_3PO_4) and potassium hydroxide (KOH).	2300	(Salame and Bandosz, 2000)
Apricot Stones		Chemical activation using phosphoric acid (H_3PO_4).	2300	(Salame and Bandosz, 2000)

C H A P T E R 3

PRODUCTION OF ACTIVATED CARBON

This chapter highlights the procedure to be followed in the production of activated carbon from local palm-date pits.

3.1 PALM-DATE PITS

Almost any organic matter with a large percentage of carbon could theoretically be activated to enhance its sorptive characteristics. Table 3.1 shows that palm-date pits contain approximately 55-56% of carbohydrates. In view of this, high-grade activated carbon can be obtained from palm-date pits due to their high carbon content (Table 3.2). In practice, however, the best candidates for activated carbon should contain a minimum amount of organic material, have a long storage life, consist of hard structures to maintain their properties under usage condition and can be obtained at a low cost.

3.2 PRODUCTION OF ACTIVATED CARBON

The production of activated carbon is one of the most important phases of this study. Different permutation-combinations were investigated to achieve an activated carbon with optimum physical characteristics. This part of the study involved three steps: boiling, soaking and a combined step of carbonization and activation of pits.

TABLE 3.1: Basic Compositions of Palm-date Pits (Barreveld, 1993)

Component	%
Moisture	5-10
Protein (N x 6.25)	5-7
Oil	7-10
Crude fiber	10-20
Carbohydrates	55-65
Ash	1-2

TABLE 3.2: Summary of Major Components of Raw Palm-date Pits and Burned
Palm-date Pits

Compounds	Raw Palm-date Pits		Burned Palm-date Pits	
	Phase	Wt %	Phase	Wt %
Amorphous Phase [C, O, H (Organic)]	Major	92	Major	88
Potassium Barium Phosphate Hydride [$KbaP_3O_9.H_2O$]	Minor	5	Minor	7
Potassium Hydroxide Hydride [$KOH.H_2O$]	Minor	2.5	Minor	3
Potassium Carbon Sulfur [K_2CS_2]	Minor	0.5	Minor	1.5
Hydrogen Phosphate [$H_4P_2O_7$]	Minor	_	Minor	0.5

In the first step, the pits were initially boiled in a pressure cooker for 2 hours. An approximate amount of 2 kg of pits was placed in the pressure cooker to enhance the adsorption capacity of the pits during the soaking process. The use of the pressure cooker prior to soaking was necessary because earlier attempts without it could not lead to a satisfactory result.

In the second step, which is soaking, the cooked pits were placed in a Pyrex glass beaker of 3-L capacity. The two solutions commonly used in the chemical treatment process of producing activated carbon are Zinc Chloride (Cl_2Zn) and Phosphoric Acid (H_3PO_4). Phosphoric acid was selected over zinc chloride because it is relatively safer than zinc chloride. During this step, a concentrated phosphoric acid (85% H_3PO_4) was poured carefully into the beaker containing the pits. To identify the effect of phosphoric acid on the performance of the pits, two soaking times of 12 & 24 hours were selected from among many soaking durations. At the end of each soaking duration, a change in color of the solution was observed.

The final step adopted in this study with the aim of producing activated carbon from palm-date pits is the process of carbonization and activation. The soaked pits were placed on a metallic plate and subjected to an average temperature of 400°C for 3 hours. This heating period was selected based on the previous trials of different heating durations. From the various experimental trials performed, it was observed that brown color was persistently appearing during the washing process with water when the heating duration was less than 3 hours. When

the heating duration was raised to more than 3 hours, it was observed that the pits were completely carbonized into ash. The flow of hot air coming from the flames was passing through the pits, forcing the formation of mesopores. The pits were cooled and then washed with hot water for fourteen (14) hours without interruption, until the desired pH was achieved (5.5 - 8.5).

In order to make sure that the pores were created, Electron Microscopy was conducted on the prepared samples in the Research Institute at King Fahd University of Petroleum and Minerals (KFUPM). Figures 3.1 and 3.2 show the magnified photos (x 300) of the 24-hr and 12-hr acid soaked pits, respectively.
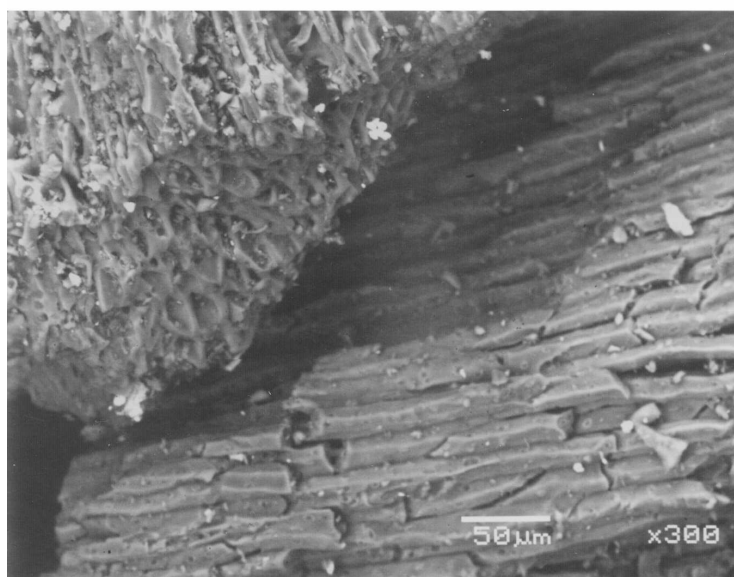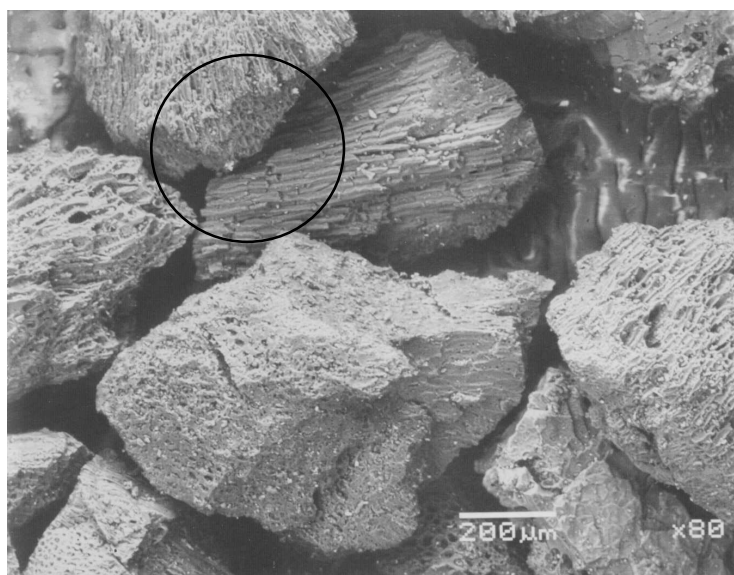
Figure 3.1: Electron Microscopy of the 24-hr Acid Soaked Pits
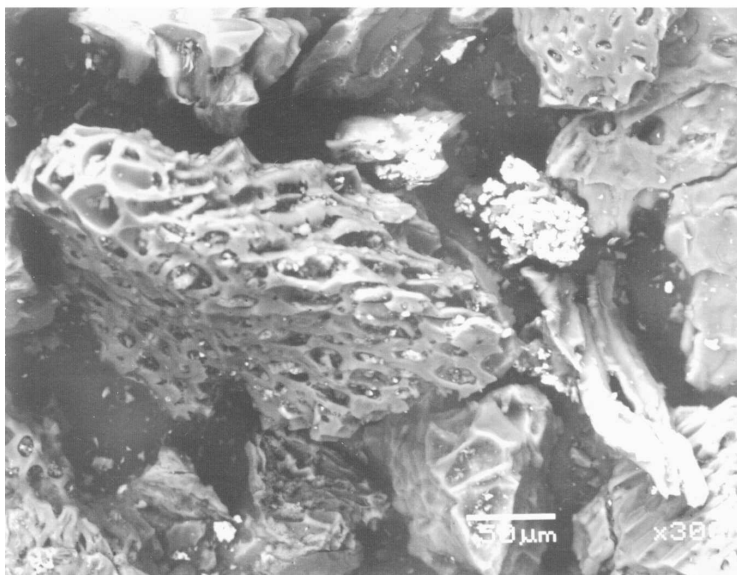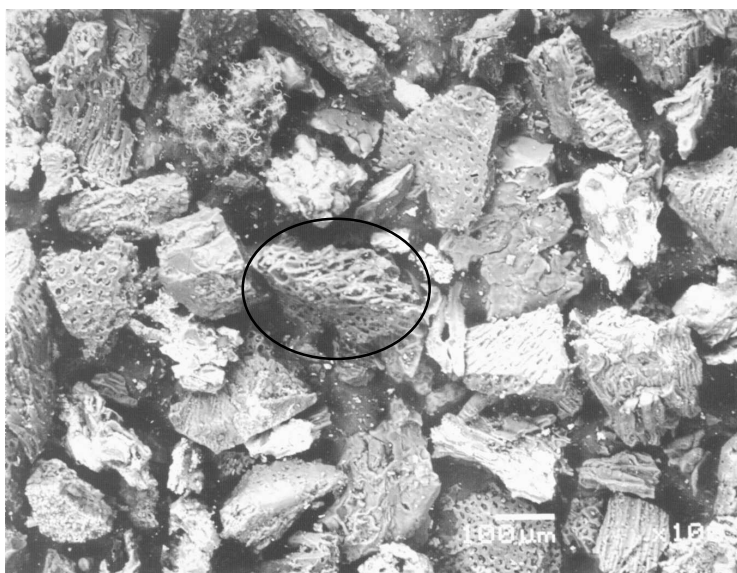
Figure 3.2: Electron Microscopy of the 12-hr Acid Soaked Pits

C H A P T E R 4

EXPERIMENTAL SETUP AND PROCEDURE

The experimental work consisted of a preliminary study with methylene blue followed by a column study using unchlorinated secondary effluent from the North Saudi ARAMCO Wastewater Treatment Plant.

4.1 MATERIALS

The materials used in the experiments for testing the performance of palm-date pits activated carbon in removing pollutants were unchlorinated secondary effluent and three fabricated PVC columns.

4.1.1 Fabrication of Columns

For the experimental run in this study, PVC columns of internal diameter of 10 cm and a length of 60 cm were used. Each column had 4 ports along its length and their distribution was as follows:

1. 1st sample port at the bottom of the column

2. 2nd sample port at 5 cm from the bottom

3. 3rd sample port at 10 cm from the bottom

4. Overflow port at 20 cm from the top (to keep the flowing head constant)

The columns were fitted with Plexiglas showers at the top to create a shower

effect so as to allow a uniform distribution throughout the top area of the columns. At the bottom, the outlets were connected to a common drain through a plastic pipe of 5 cm (internal diameter). All these features are shown in Figure 4.1.

The overhead tank filled with secondary effluent was placed on a movable stand located at a height of 1 meter above the top of the columns so that the effluent could flow by gravity.

The effluent was pumped from a storage sump through a 0.25-hp pump into the overhead tank and from there it flowed into the columns by gravity. A constant head was maintained in the columns by providing an overflow outlet of 1 cm diameter at 20 cm from the top of the columns. The experimental setup is shown in Figure 4.2 and Plate 4.1.

4.1.2 Source of Wastewater

In the present study, the wastewater used was unchlorinated secondary effluent taken from the North Saudi ARAMCO Wastewater Treatment Plant (NAWTP) every day over the period of the experimental run. The desired amount of effluent was to be taken daily and fed into the columns. Detailed analysis of raw effluent was conducted immediately to determine its physio-chemical and microbiological properties as listed in Table 4.1. The NAWTP has a design capacity of 30,000 m^3/day (8000,000 gallon/day) and is currently serving the Saudi ARAMCO community in addition to KFUPM. It is an extended aeration plant, yielding high quality secondary effluent.
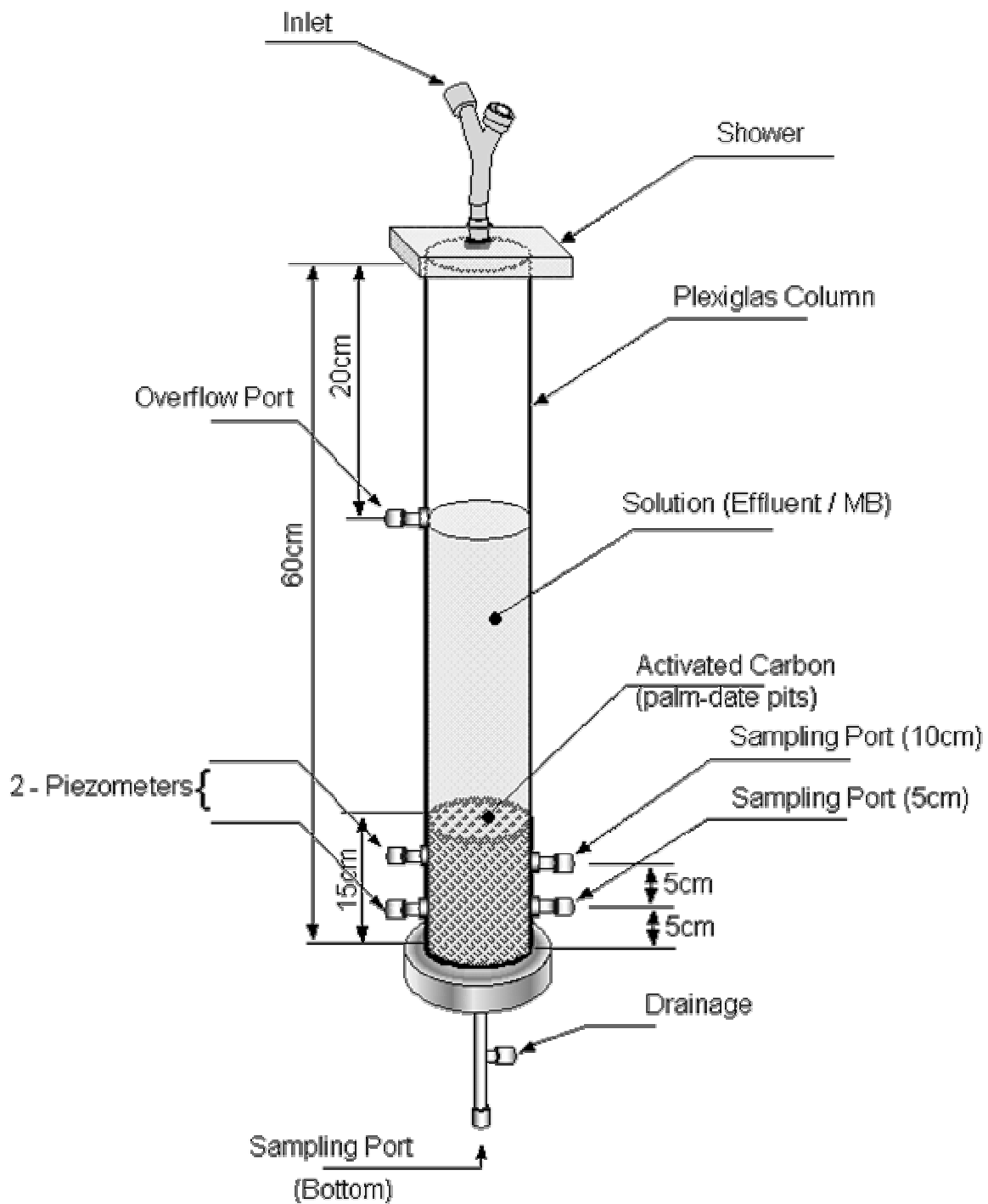
Figure 4.1: Sketch Showing a Representative Column
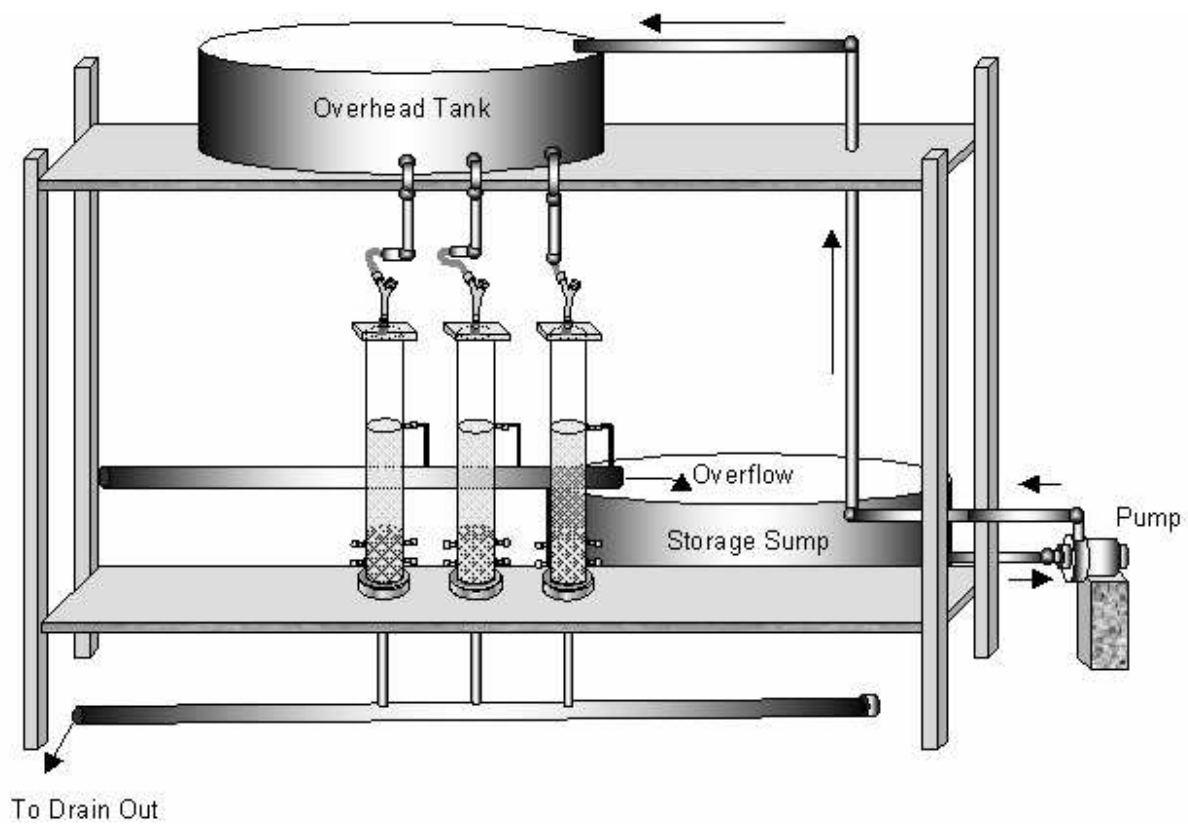
Figure 4.2: Details of the Experimental Setup

Plate 4.1: Photograph Showing the Columns During the Experimental Run

TABLE 4.1: Summary of the Daily Raw Unchlorinated Secondary Effluent
Quality Obtained from the North Saudi ARAMCO Wastewater Treatment Plant

Parameter	Range	Average value
pH	6.47 – 8.27	7.72
Turbidity (NTU)	0.60 – 5.10	2.85
Suspended Solids (mg/l)	11.00 – 26.00	18.50
TOC (mg/l)	11.00 – 18.50	14.75
BOD (mg/l)	16.98 – 27.51	22.24
DO (mg/l)	5.60 – 7.50	6.44
Total Coliform (MPN/100ml)	80000 – 110000	95000
Conductivity (μmhos/cm)	4250 – 4700	4437.50

4.2 SAMPLING & ANALYSIS

A sampling plan was thoroughly prepared to achieve data for the analysis. This plan consisted of taking samples from the ports at one-day intervals. Samples were divided into two main groups: one for physio-chemical analysis and the other group for performing microbiological analysis. The samples for Total Coliform analysis were immediately processed while the samples for TOC analysis were acidified with H_2SO_4 to a pH of less than 2.

4.2.1 Color Removal

Before starting the experiment, the columns were flushed with water to check for leaks. For the preliminary study, the produced AC was tested against methylene blue (MB). The solution was prepared by mixing 5 mg/l of MB with one liter of distilled water. The initial concentration of MB was determined using a UV-160 IPC Spectrophotometer. Absorbance at 660 nm was used for quantification of MB. The prepared solution of MB was pumped through a 0.25-hp centrifugal pump into an overhead tank, from where the solution was fed into the columns by gravity. The experimental run lasted for approximately two weeks. The rate limiting step was kept to be the appearance of faint blue color from the ports of the columns.

4.2.2 Unchlorinated Secondary Effluent

The unchlorinated secondary effluent used in this study was taken from the

North Saudi ARAMCO Wastewater Treatment Plant. A number of 200-L capacity drums were used to collect the samples. The samples were stored in a reservoir from where they were pumped up by a 0.25-hp pump to a storage tank at a height of 2 m. The effluent flowed from this tank to the columns by gravity and an overflow port was used to control the flow. The excess effluent was drained back to the drums by this overflow mechanism in the columns.

Depending on the nature of the parameters, samples were taken once or every other day as in the case of total coliforms. After the samples were withdrawn from the ports, some of them were tested immediately and the others were acidified and kept in the refrigerator. A group of the samples were to be used in the enumeration of total coliforms. Parameters such as pH, turbidity and suspended solids were examined immediately after sampling.

As has been mentioned in the fabrication of columns, two sampling ports were provided along the height of the columns. The distances from the bottom of the column to the ports were 5 cm and 10 cm, respectively. An additional port was provided at the bottom. The bottom port was fitted with T-joint, one end of which was connected to the draining facility and the other end was used for sampling purposes. This arrangement made it possible to study the removal efficiency at these ports.

In general, a seasonal variation in the effluent quality was observed in the daily samples. The combination of rainwater and scum cleaning contributed tremendously

in the change of quality of the effluent. This affected negatively the performance of activated carbons produced from palm-date pits in removing suspended solids and organic matters.

C H A P T E R   5

RESULTS AND DISCUSSION

5.1 PHYSICAL AND DESCRIPTIVE ANALYSIS

5.1.1 Color Removal

This test has been conducted to check the ability of the produced activated carbon (24-hr and 12-hr acid soaked pits) in removing pollutants. A stock solution of 100 mg/l of methylene blue (MB) was prepared for calibration purposes. From the stock, different concentrations of methylene blue were prepared by diluting with distilled water. A spectrophotometer UP-160 SHIMATZU was used for the determination of absorbance for the different concentrations of methylene blue. Subsequently, a calibration curve of methylene blue concentrations versus absorbance was constructed (Figure 5.1).

This run was thought to be useful in testing the ability of the produced activated carbon and the commercial activated carbon to remove colors. This was done by filling adsorption bottles with 200 ml of methylene blue of a 100-mg/l concentration. In each bottle, different masses of palm-date pits activated carbon (10, 20, 50, 80, 100, 150 and 200 mg) were placed. Along with these bottles, two
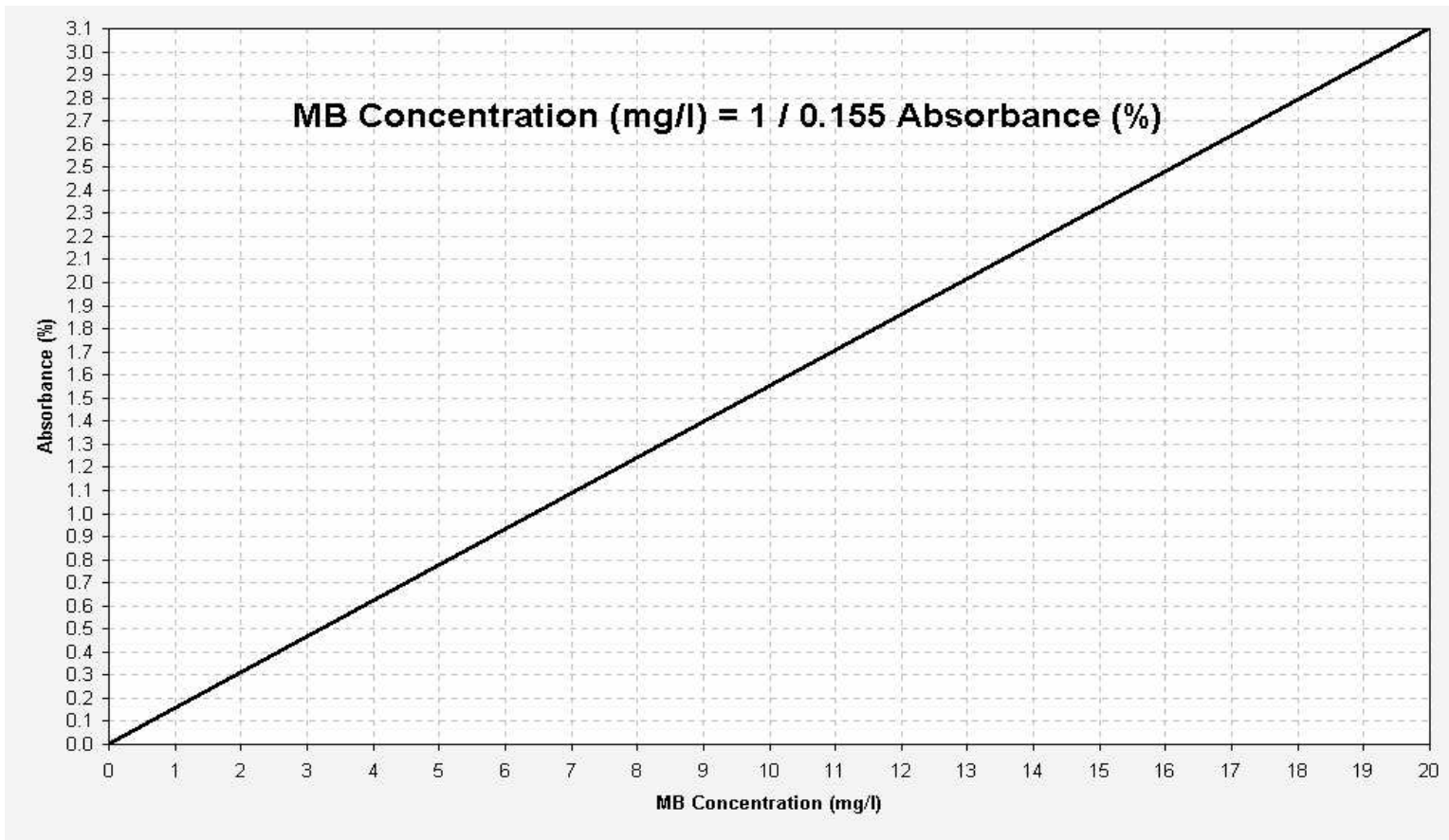
Figure 5.1: Calibration Curve for Methylene Blue at a Wavelength of 664 nm

blanks were also run. The whole set was placed in a gyratory shaker for 24 hours. After this specified time of shaking, residual concentrations of methylene blue were determined using spectrophotometer with a wavelength of 664 nm and the results are given in Table 5.1. From this table, it is evident that both carbons (palm-date pits and commercial activated carbons) did not behave well in the removal of methylene blue at a mass of 10 mg of carbon. The produced activated carbon at a mass of 100 mg achieved only 53% removal whereas the commercial activated carbon achieved 96% removal using the same mass of carbon. It can be concluded from the table that the produced activated carbon can be used to remove methylene blue at higher amounts of carbon compared to the commercial activated carbon.

Using the data in Table 5.2, two isotherm curves were plotted for both commercial activated carbon and activated carbon produced from palm-date pits as shown in Figure 5.2. This was done to investigate the performance of the two types of carbon and it was concluded that both types are following Langmuir isotherm, which indicates good performance in the adsorption of color (methylene blue).

A solution of 5 mg/l methylene blue was passed through the columns packed with both the produced and commercial activated carbons. The high density and rugged structure of the produced carbon made it an outstanding material for color removal. The relatively sufficient surface area created by the unique network of pores in the produced activated carbon resulted in an exceptionally high capacity and activity for removal of impurities.

TABLE 5.1: Adsorption Data for Palm-date Pits Activated Carbon and Commercial
Activated Carbon after 24-hr Shaking

Weight of Carbon (mg)	Palm-date Pits Activated Carbon			Commercial Activated Carbon		
	Absorbance (%)	MB Residual Concentrations (mg/l)	Percent Removal (%)	Absorbance (%)	MB Residual Concentrations (mg/l)	Percent Removal (%)
200	0.021	5.42	94.58	0.003	0.77	99.23
150	0.074	19.10	80.90	0.003	0.77	99.23
100	0.182	46.97	53.03	0.015	3.87	96.13
80	0.191	49.29	50.71	0.058	14.97	85.03
50	0.265	68.39	31.61	0.012	30.10	96.90
20	0.345	89.03	10.97	0.154	39.74	60.26
10	0.372	96.00	4.00	0.274	70.71	29.29

TABLE 5.2: Adsorption Data for Palm-date Pits Activated Carbon and Commercial
Activated Carbon after 24-hr Shaking Used to Generate the Isotherms

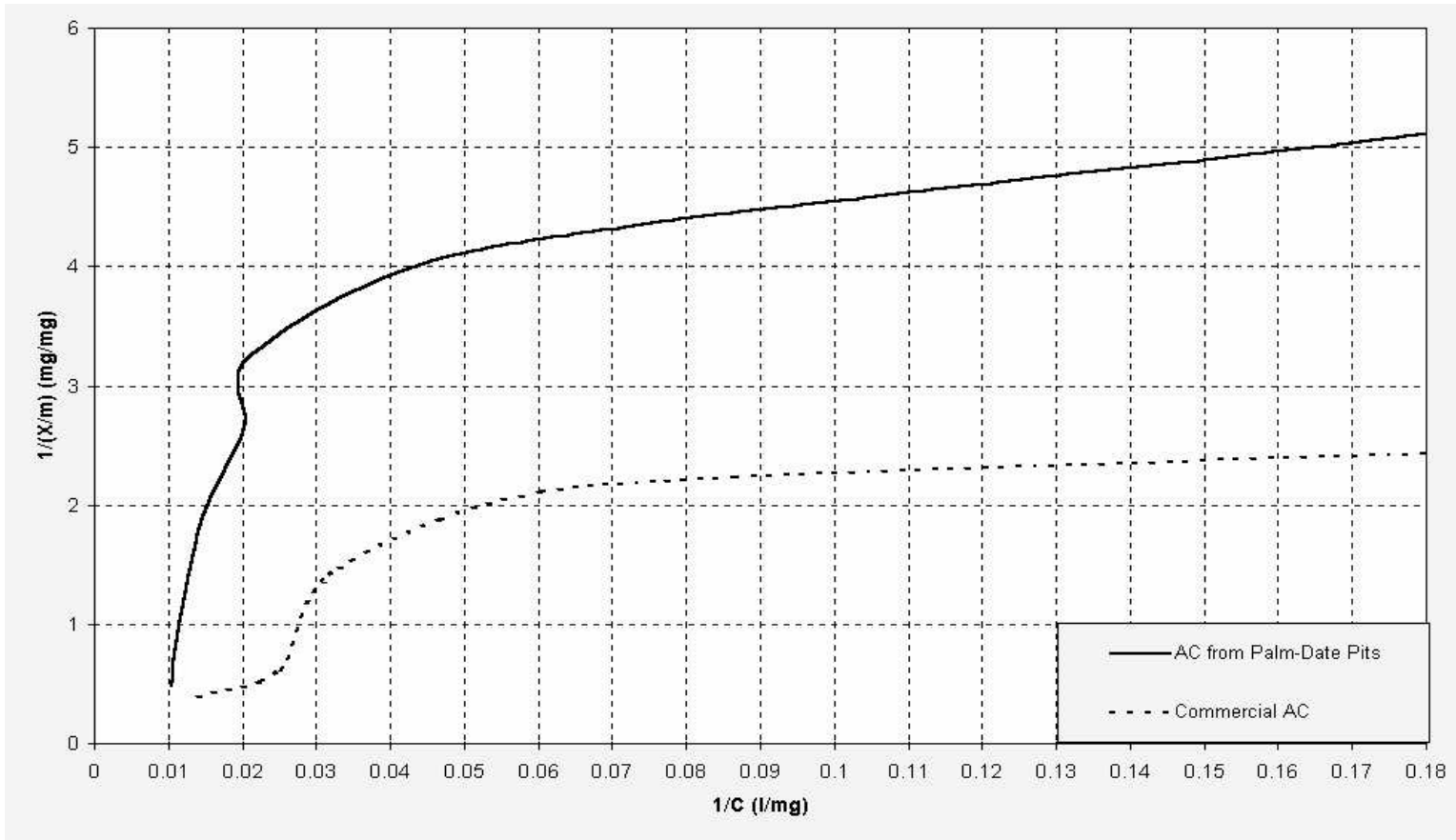| Weight of Carbon (m) (mg)	Palm-date Pits Activated Carbon		Commercial Activated Carbon	
	MB Residual Concentrations (C) (mg/l)	Amount of color adsorbed / carbon weight (X/m) (mg/mg)	MB Residual Concentrations (C) (mg/l)	Amount of color adsorbed / carbon weight (X/m) (mg/mg)
0	200	-	200	-
10	96	2.08	70.71	2.59
20	89.032	1.11	39.742	1.60
50	68.387	0.53	30.097	0.68
80	49.29	0.38	14.968	0.46
100	46.968	0.31	3.871	0.39
150	19.097	0.24	0.774	0.27
200	5.419	0.19	0.774	0.20

Figure 5.2: Isotherm Curves of the Adsorption of Methylene Blue on both Commercial AC and Palm-date Pits AC

The experiment lasted for 12 days for both the 24-hr and 12-hr acid soaked pits compared to the commercial activated carbon, which lasted for 35 days. As for the commercial activated carbon, the performance was exceedingly better than the palm-date pits activated carbon by obtaining absorbance of 0.046%, which corresponds to a concentration of 0.29 mg/l after 35 days of continuous operation. After these periods of time (12 and 35 days), the appearance of methylene blue from the bottom port was evident and this was the limiting factor of the run. From the color determination with the spectrophotometer, absorbance of 0.042% and 0.035% were obtained for 24-hr and 12-hr acid soaked pits corresponding to concentrations of 0.27 and 0.22 mg/l, respectively.

After this preliminary study, the results obtained have encouraged further exposure of the produced carbons in removing pollutants from the unchlorinated secondary treated effluent.

5.1.2 Unchlorinated Secondary Effluent Treatment

Once the experimental setup was constructed, the unchlorinated secondary effluent taken from Saudi ARAMCO was used to investigate the removal efficiencies of the produced activated carbon. The experimental run continued for a period of seventeen (17) days. All the three columns were run simultaneously. The run was terminated when the breakthrough of the total coliforms was reached. This was achieved when the quality of the effluent, which is coming out of the columns, was the same as the quality of the source. The samples taken from all ports were

analyzed for pH and TOC on a daily basis, whereas the Total Coliforms and BOD were monitored on alternate days only. In addition, the Turbidity and Suspended Solids of the effluent were also measured. All these analyses were performed as per the procedures outlined in the Standard Methods for the Examination of Water and Wastewater (APHA 2000, 20th Edition). The results and discussion of these analyses are presented in the following sections.

5.1.2.1 pH

The hydrogen ion concentration is an important quality parameter of both natural waters and wastewaters. The concentration range suitable for the existence of most biological life is quite narrow and critical. Wastewater with high concentration of hydrogen ion is difficult to treat by biological means, and if the concentration is not controlled before discharge, the wastewater effluent may alter the concentration in the natural waters. The pH adjustment is used to optimize many reactions and in wastewater treatment, pH must be maintained in a range favorable for biological activities.

The temporal variation of the pH through a column packed with 24-hr acid soaked pits is given in Figure 5.3. The figure reveals that in the early stages of the experiment, the observed pH of the solution from the three ports were showing slightly higher values than the pH of the source. This could be attributed to the chemical treatment of the pits, which involved the use of phosphoric acid. As the experiment progressed (starting from the 29th of October, 2002), further washing of
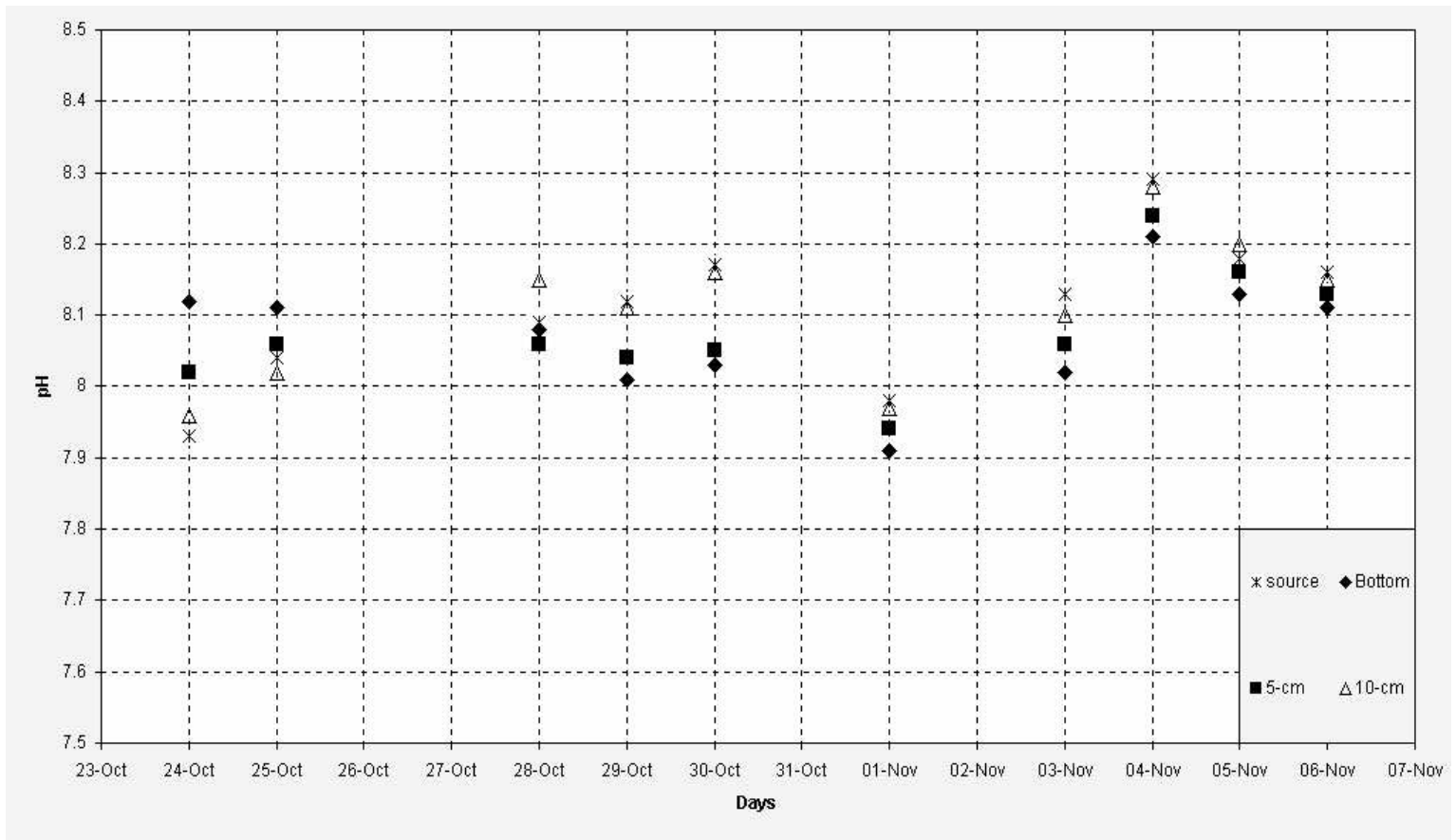
Figure 5.3: pH Variation over Time for the 24-hr Acid Soaked Pits

the pits has occurred and consequently lower values of pH compared to the pH of the source at the three ports were observed. Starting from the 29th of October 2002, the pH of the source controlled the behavior of the pH from all the three ports. The pH from the three ports reached its lowest value on the 1st of November, just three days before the start of the rain, which fell on the Saudi ARAMCO treatment plant on the 4th of November that caused a sudden raise in the value of pH.

The same interpretation could be given to the variation of pH in the 12-hr acid soaked pits (Figure 5.4) with the only difference that the pH of the three ports started to become lower than the pH of the source on the 28th of October, one day before the 24-hr acid soaked pits. This could be due to the shorter period of acid soaking (12 hours) where the acid content inside the pits is smaller than the 24-hr acid soaked pits.

The pH range favored the growth of varieties of microorganisms in the columns. This flora has contributed tremendously to the reduction of voids inside the pits. Another reason for the growth of microorganisms inside the columns with palm-date pits activated carbon could be attributed to the mineralogical composition of the pits as can be observed from Figures 5.5 and 5.6 that were obtained by the XRD analysis conducted in the Research Institute at KFUPM. The figures show that the mineralogical compositions needed for the growth of microorganisms are available, such as phosphorous, calcium, magnesium and potassium. The absence of such minerals in the case of commercial activated carbon explains the absence of
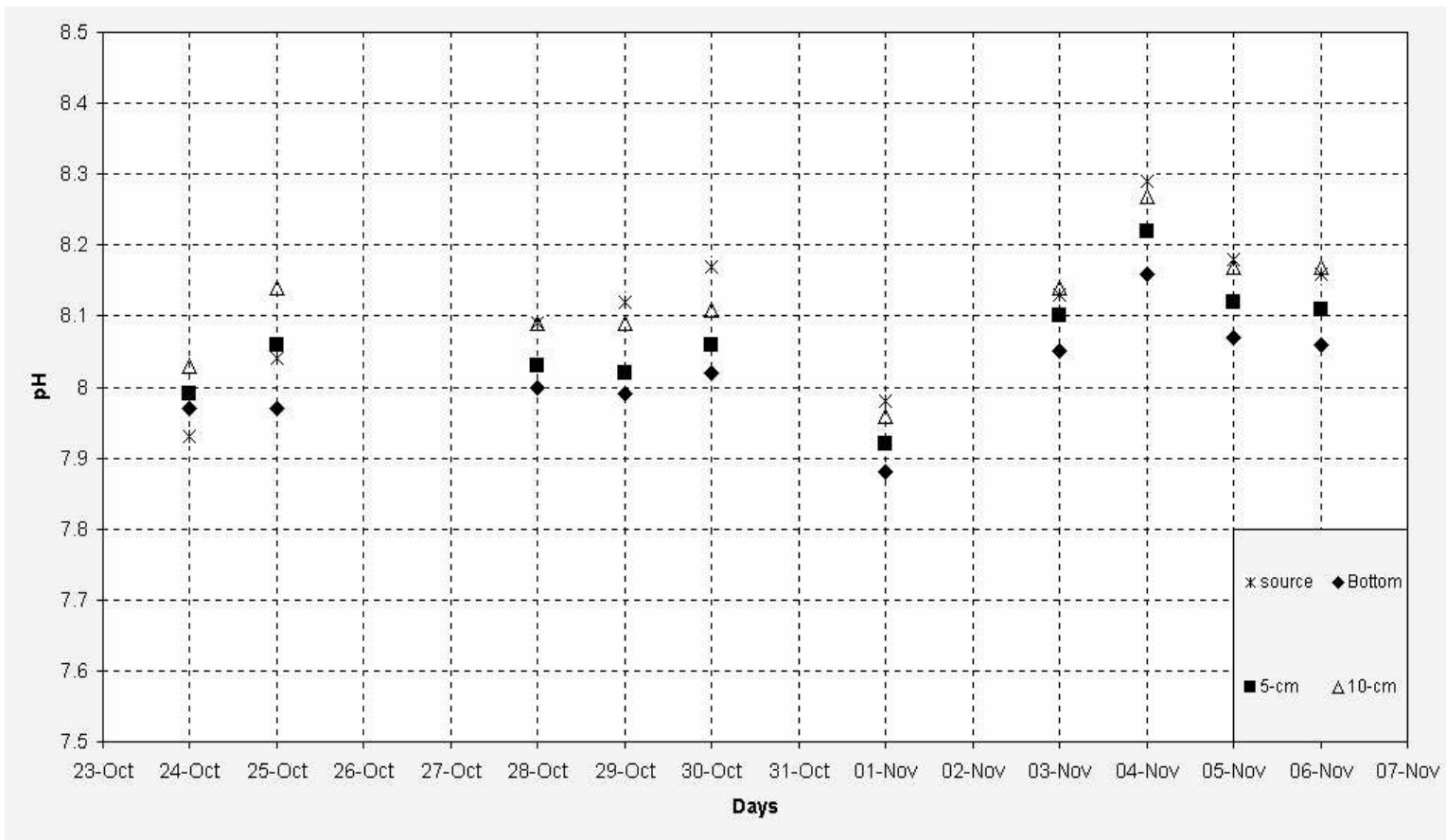
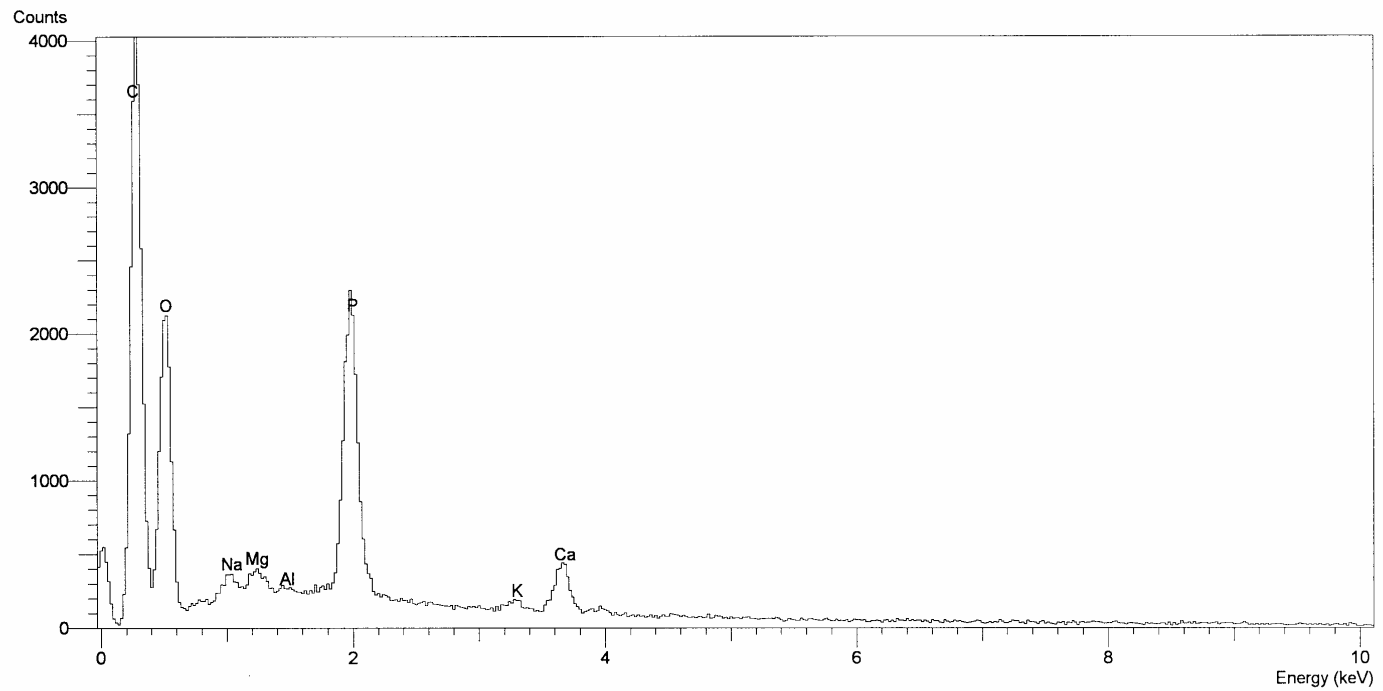Figure 5.4: pH Variation over Time for the 12-hr Acid Soaked Pits

Figure 5.5: The Mineralogical Composition of the 24-hr Acid Soaked Pits
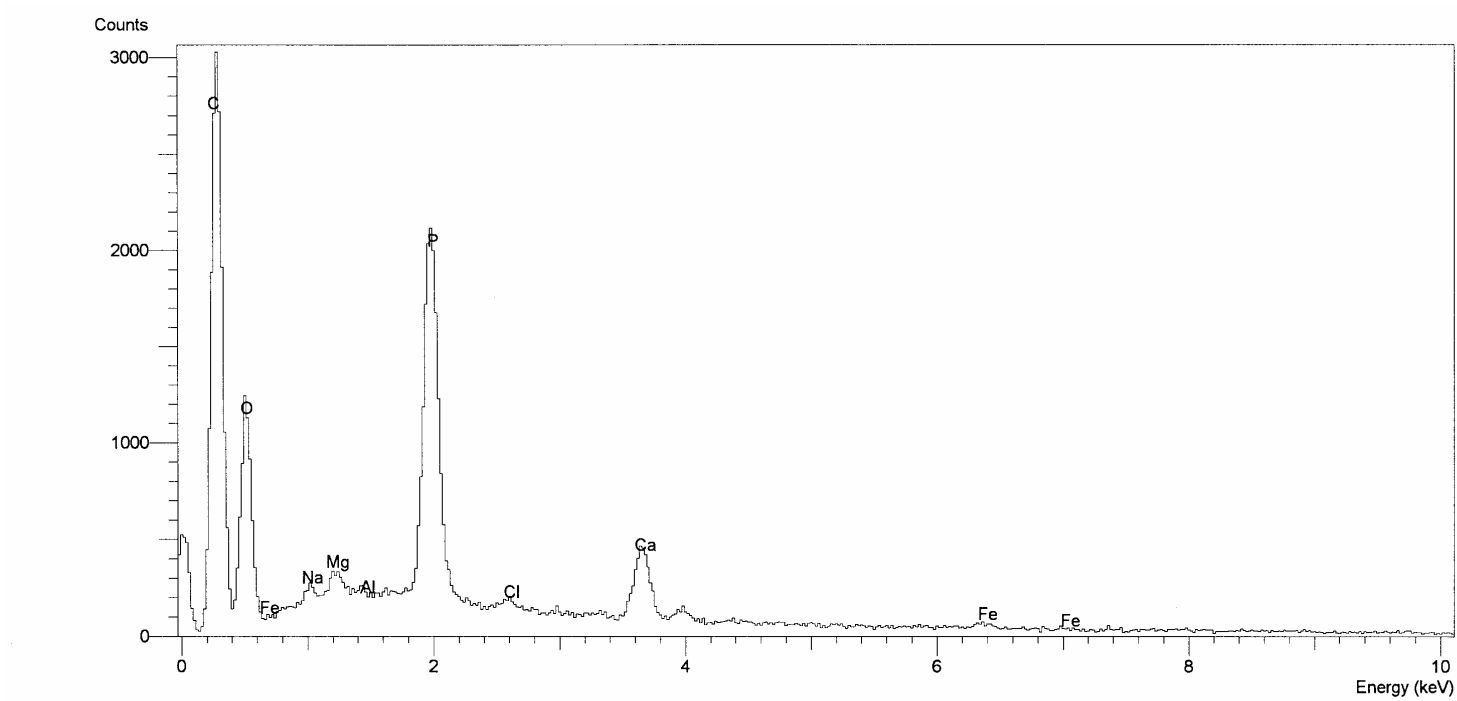
Figure 5.6: The Mineralogical Composition of the 12-hr Acid Soaked Pits

growth inside the media, as depicted in Figure 5.7.

In the case of commercial activated carbon, which was used as control, the trend is totally different as shown in Figure 5.8. In the 1st week of operation, the pH trend was higher than the pH of the source. This could be explained by the alkaline properties of the activated carbon prior to its use. From the figure, it is clearly seen that there was hardly any effect on pH during the entire experimental run. The intrinsic properties of the activated carbon made it possible to behave like a buffer against the pH variation of the source.

5.1.2.2 Turbidity

Turbidity is related to how clear the water is. The greater the amount of total suspended solids (TSS) in the water, the murkier it appears and the higher is the measured turbidity. The major source of turbidity is the organic detritus from stream and/or wastewater discharges. The major effect turbidity has on humans might be simply aesthetic (i.e. people do not like the look of dirty water). However, turbidity also adds real costs to the treatment of surface water supplies used for drinking water since turbidity must be virtually eliminated for effective disinfection (usually by chlorine in a variety of forms) to occur. Particulates also provide attachment sites for heavy metals such as cadmium, mercury and lead, for many toxic organic contaminants such as polychlorinated biphenyls (PCBs) and hexachlorobenzenes (PAHs), and for many pesticides.

Turbidity is measured in nephelometric units (NTUs), which refers to the type
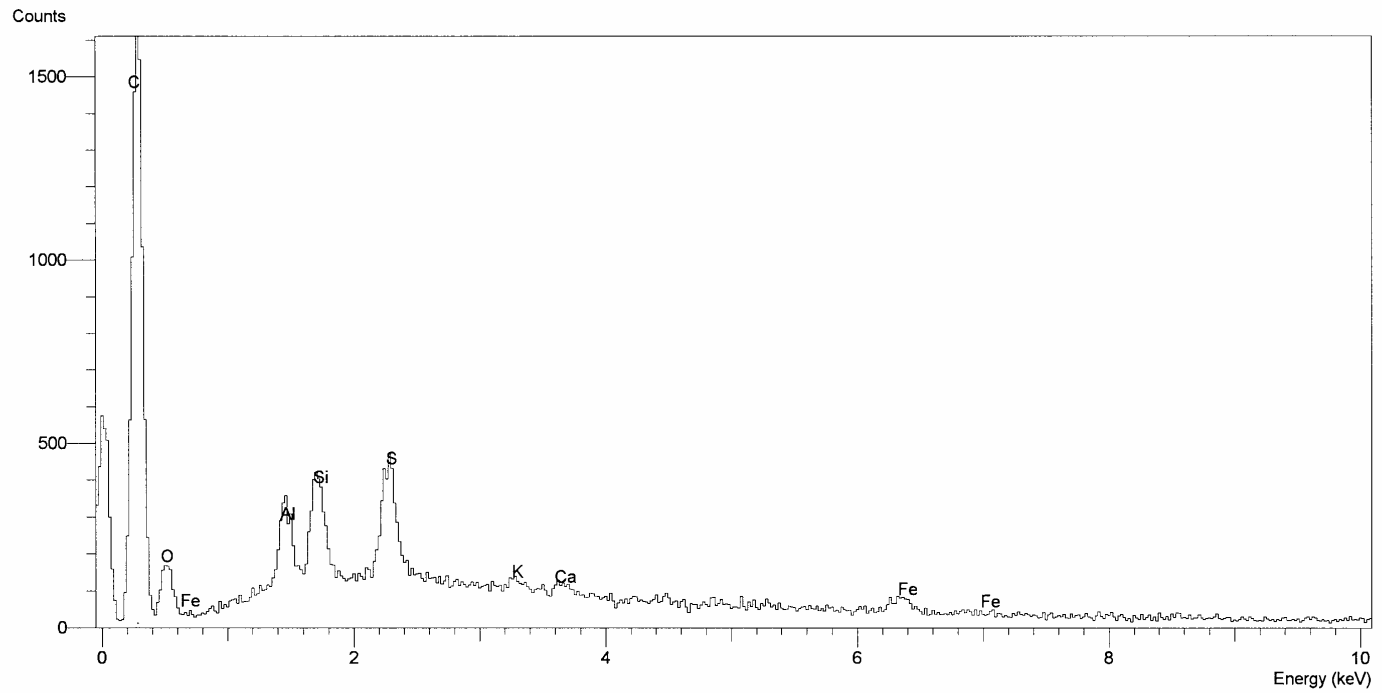
Figure 5.7: The Mineralogical Composition of the Commercial AC
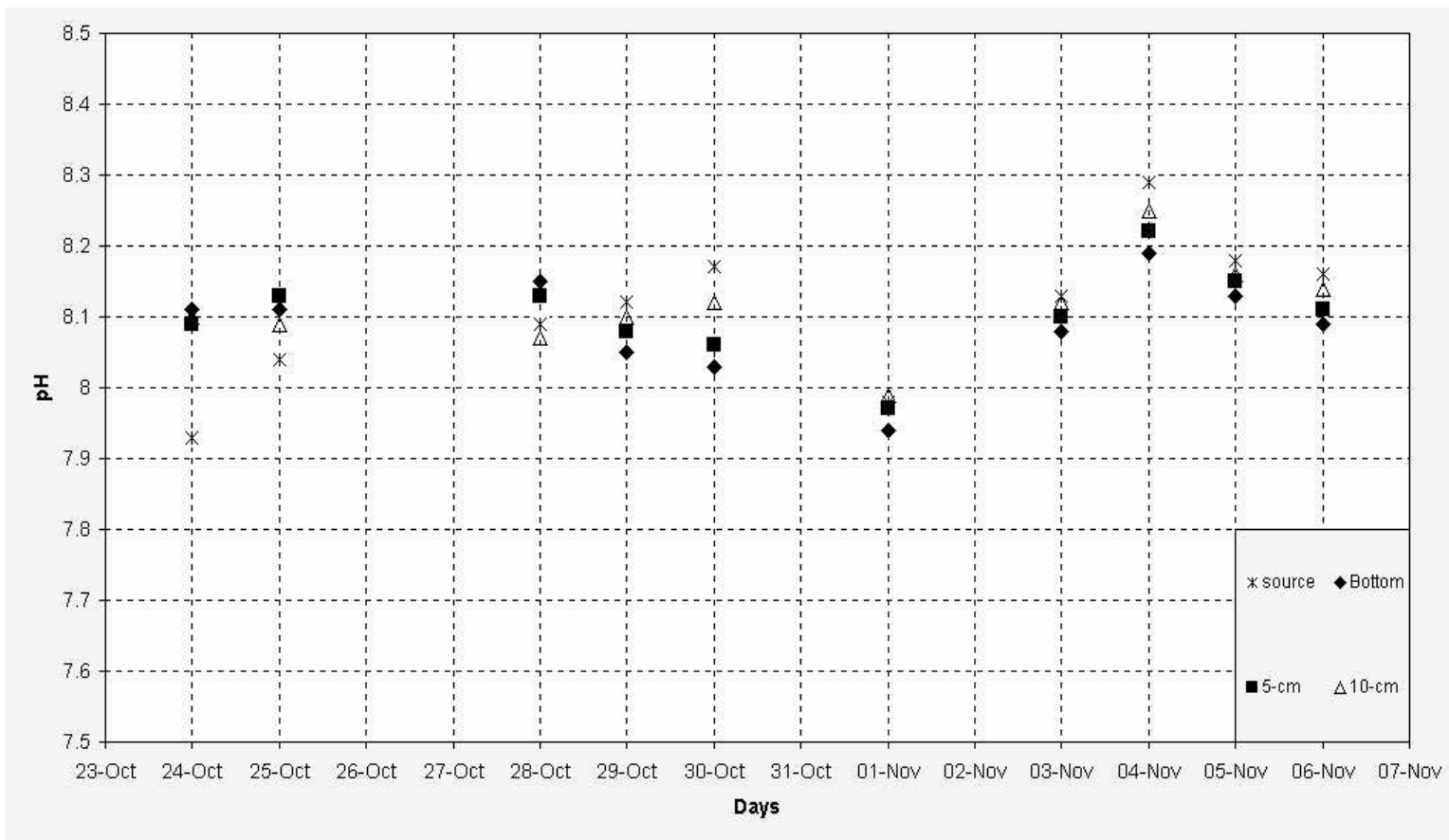
Figure 5.8: pH Variation over Time for the Commercial AC

of instrument (turbidimeter or nephelometer) used for estimating light scattering from suspended particulate material. In general, there is a relationship between TSS and turbidity for each system since turbidity is easily measured and TSS analyses are not very sensitive at the typically low concentrations found in many receiving bodies (http://wow.nrri.umn.edu/…).

The variation of source turbidity over time is shown in Figure 5.9 for the secondary effluent and all the three types of activated carbon used. At the beginning of the experimental run, the source turbidity was about 6.5 NTU but on the 4th of November, turbidity jumped to a value of 27 NTU. This was due to the rain which had fallen on the Saudi ARAMCO treatment plant the day before, and the runoff contributed to the loading of the plant. Despite the presence of high turbidity, the turbidity that was measured from the bottom of each column was constantly showing zero (0) value, until the three types of activated carbon were unable to further reduce the turbidity. This high turbidity has disturbed the removal performance of the palm-date pits (24-hr and 12-hr) as well as the commercial activated carbon and has shortened the duration of the experiment.

5.1.2.3 Total Suspended Solids

Total Suspended Solids (TSS) are solids in water that can be trapped by a filter. TSS can include a wide variety of materials, such as silt, decaying plant and animal matter, industrial wastes, and sewage. High concentrations of suspended solids can cause many problems for stream health and aquatic life where they cause
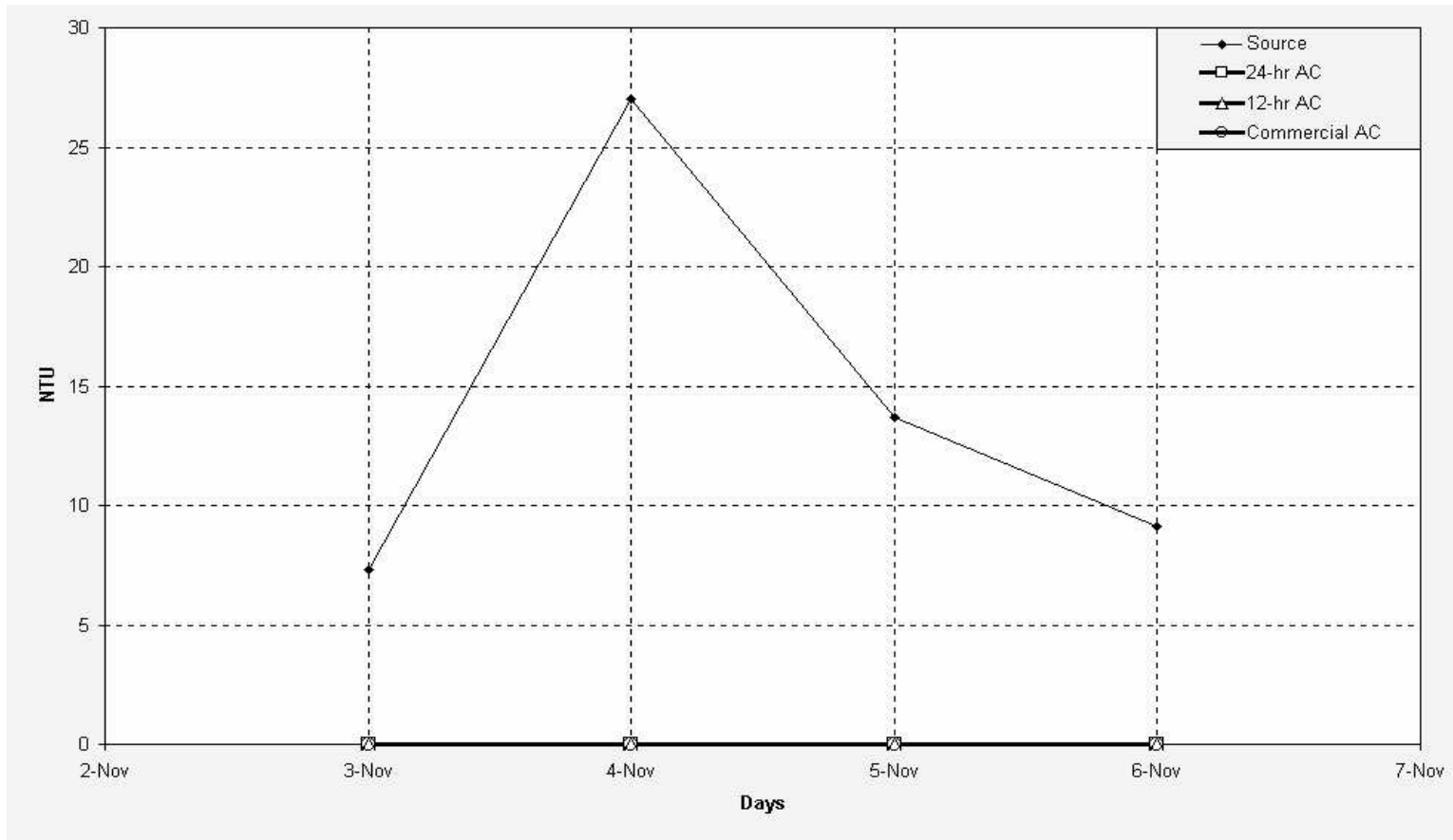
Figure 5.9: Turbidity Variation over Time of the Unchlorinated Secondary
Effluent and the Three Activated Carbon Types

an increase in surface water temperature, since the suspended particles absorb heat from sunlight. This can cause dissolved oxygen (DO) levels to fall because warmer waters can hold less dissolved oxygen, and can harm aquatic life in many other ways. Water bodies can be affected by high TSS as well, which often means higher concentrations of bacteria, nutrients, pesticides, and metals in the water. These pollutants may attach themselves to sediment particles on the land and can be carried into water bodies with the storm water. Also, high TSS can cause problems for industrial use because the solids may clog or scour pipes and machineries (Metcalf & Eddy, 1991).

Figure 5.10 shows the variation of source total suspended solids over time for the secondary effluent as well as for the three types of activated carbon used (24-hr pits, 12-hr pits and commercial AC). At the beginning of the experimental run, the source TSS was about 20 mg/l but on the 4th of November, the TSS jumped to a value of 164 mg/l. This was due to the rain which had fallen on the Saudi ARAMCO treatment plant the day before, whereas the TSS that was measured from the bottom of each column was constantly showing zero (0) value.

Although a similar trend is observed in both Figures 5.9 and 5.10, no direct relationship between the turbidity and TSS can be detected for the whole duration of four days. The daily basis correlation between the two parameters can be obtained with the exception on the 4th of November 2002 when the turbidity as well as the TSS jumped to a high value due to the unexpected rain.
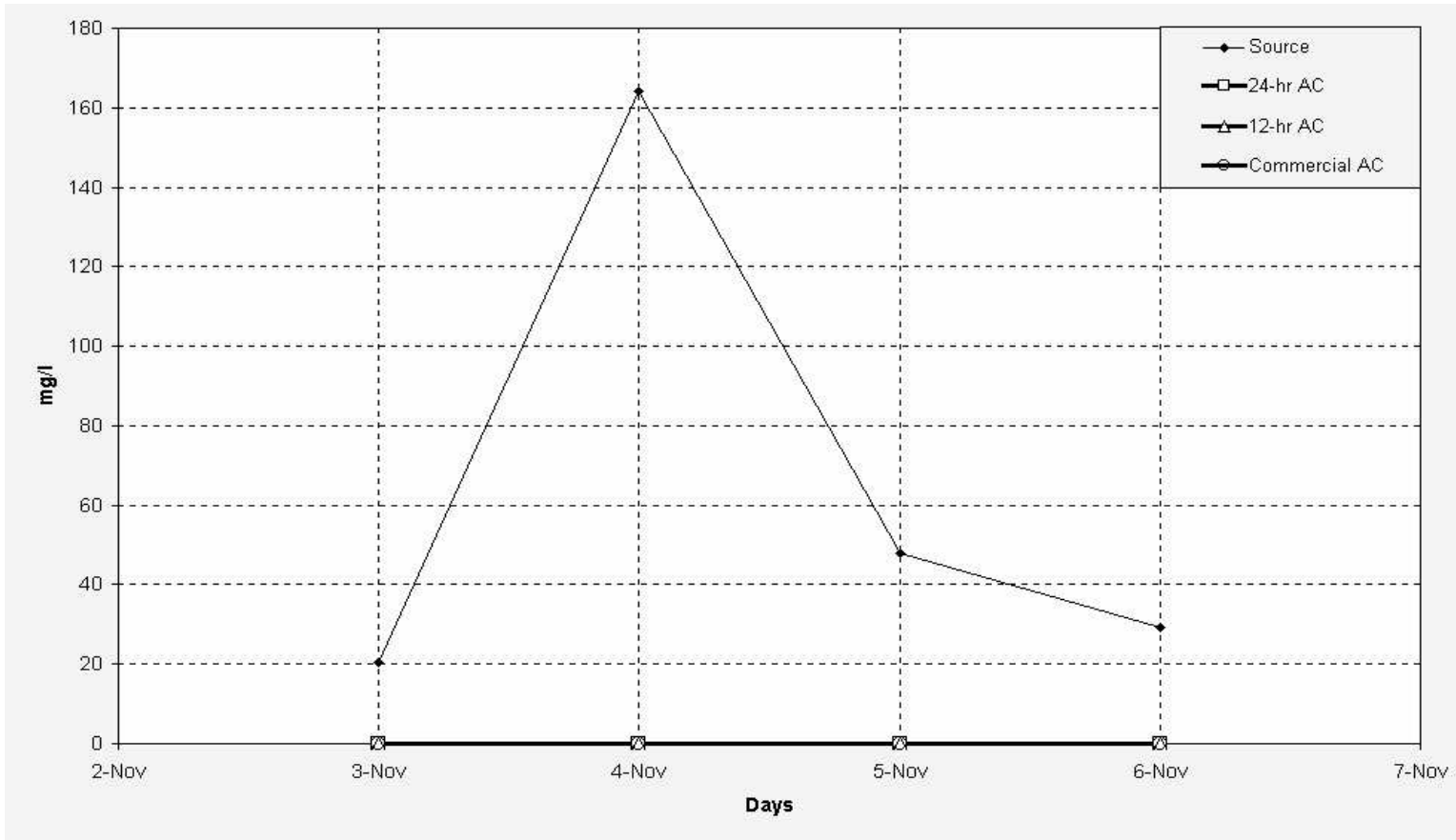
Figure 5.10: Total Suspended Solids (TSS) Variation over Time of the
Unchlorinated Secondary Effluent and the Three Activated Carbon Types

The produced activated carbons as well as the commercial activated carbon showed superior performance on the removal of both turbidity and total suspended solids over the whole period of the experimental run even on the rainy day (4th of November, 2002) when a sudden increase in the value of both parameters was observed.

The monitoring of turbidity and TSS was shown only on these four days (3rd, 4th, 5th and 6th of November, 2002) because the values of both the turbidity and TSS of the source were almost the same with average values of 7 and 20 mg/l, respectively, prior to the 4th of November, 2002 when rain fell on the Saudi ARAMCO treatment plant.

5.1.2.4 Organics Removal

For most of the medium strength wastewater, about 75 percent of the suspended solids and 40 percent of the filterable solids are usually organic in nature. The sources of these solids are from both the animal and plant kingdoms. These organic compounds are normally composed of carbon, hydrogen, and oxygen. Other important elements, such as sulfur, phosphorus, and iron, may also be present. Also a few small drinking water systems face contamination of raw water by natural or synthetic organic chemicals (SOCs). Natural organic materials might be present in water supplies, especially from surface water sources. Dissolved organics may cause taste, odor, or color problems in a community's drinking water, resulting in consumer complaints. Sources of SOCs include leaking underground

gasoline/storage tanks, agricultural runoff containing herbicides or pesticides, solid waste or hazardous waste landfills, and improperly disposed chemical waste (Metcalf & Eddy, 1991).

A number of different tests have been developed over the years to determine the organic content of wastewaters. The gross organic content loading of wastewater and surface water is usually characterized by three different laboratory tests, namely the Biochemical Oxygen Demand (BOD), the Chemical Oxygen Demand (COD), and the Total Organic Carbon (TOC). In this experimental program, both the BOD and the TOC were monitored for the secondary effluent as well as for all samples from the ports.

5.1.2.4.1 BOD Removal

Biochemical Oxygen Demand or BOD as it is commonly abbreviated, is one of the most important and useful parameters (measured characteristics) that indicates the organic strength of a wastewater. BOD measurement permits an estimate of the waste strength in terms of the amount of dissolved oxygen required to break down the wastewater. The BOD test is one of the most basic tests used in the wastewater field. It is essentially a measure of the biological and chemical component of the waste in terms of the dissolved oxygen needed by the natural aerobic biological systems in the wastewater to break down the waste under defined conditions.

The BOD test is a biochemical test involving the use of microorganisms. The BOD determination is an empirical test that is widely used for measuring waste

(loading to and from wastewater treatment plants) as well as for evaluating the organic removal efficiency of treatment processes. The BOD test measures (1) the molecular oxygen consumed during a specific incubation period for the biochemical degradation of organic matter (carbonaceous BOD); (2) oxygen used to oxidize inorganic material such as sulfide and ferrous ion; and (3) reduced forms of nitrogen (nitrogenous BOD) with an inhibitor.

The extent of oxidation of nitrogenous compound during the 5-day incubation period depends upon the type and concentration of microorganisms that carry out bio-oxidation.

The BOD test procedure is found in the Standard Methods for Examination of Water and Wastewater (APHA, AWWA, and WPCF, 2000). When the dilution water is seeded, oxygen uptake is assumed to be the same as the uptake in the seeded blank. The difference between the sample BOD and the blank BOD corrected for the amount of seed used in the sample, is the true BOD.

When dilution water is not seeded:

$$BOD_5, mg/l = \frac{D_1 - D_2}{P}$$
(5.1)

When dilution water is seeded:

$$BOD_5, mg/l = \frac{(D_1 - D_2) - (B_1 - B_2)f}{P}$$
(5.2)

where:

D_1 = Dissolved Oxygen (DO) of diluted sample immediately after

preparation, mg/l.

D_2 = Dissolved Oxygen (DO) of diluted sample after 5 days incubation at 20°C, mg/l.

P = decimal volumetric fraction of sample used, ml of sample / 300 ml.

B_1 = DO of seed control before incubation, mg/l.

B_2 = DO of seed control after incubation, mg/l.

f = ratio of seed in diluted sample to seed in seed control.

Figures 5.11, 5.12 and 5.13, which were plotted using the data in Table 5.3, show the variation of BOD with time along the ports of columns packed with 24-hr acid soaked pits, 12-hr acid soaked pits and commercial activated carbon, respectively. The BOD_5 for the unchlorinated secondary effluent ranged from 14 to 25 mg/l with an average value of 22 mg/l. These values are indicative of the low organic content of the secondary effluent of the North Saudi ARAMCO Wastewater Treatment Plant.

In the column packed with 24-hr acid soaked pits, almost 86% of the applied BOD was removed in the first day of operation. The average BOD removal in this column was 69% (over all the ports and the whole period of the run). Figure 5.12 represents the temporal variation of 12-hr acid soaked pits. The organic loading in this column was the same as in the 24-hr acid soaked pits. The average BOD value from the three ports of this column was 6 mg/l with a range from 3 to 8.6 mg/l. The removal efficiency with respect to the bottom of the column
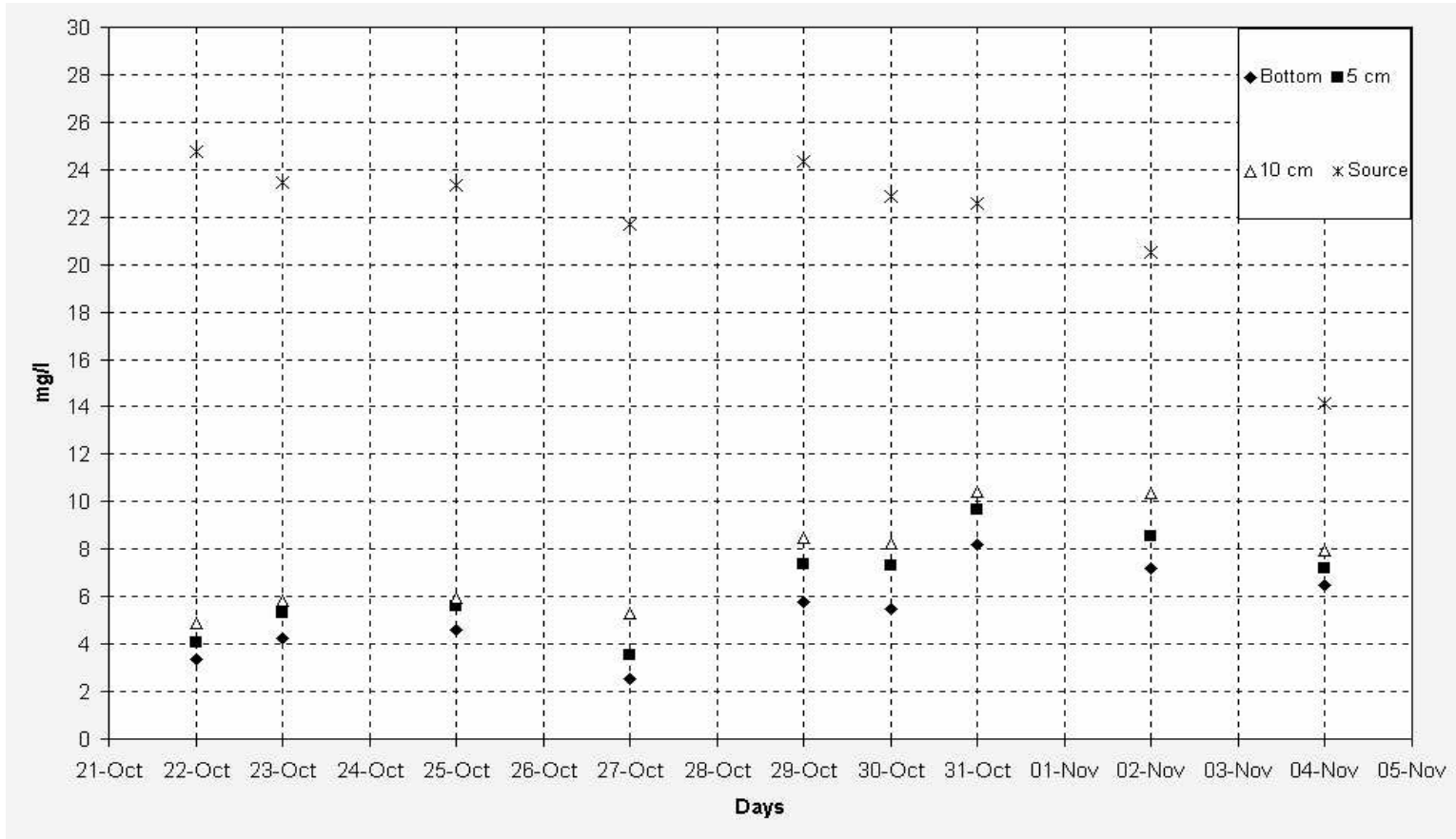
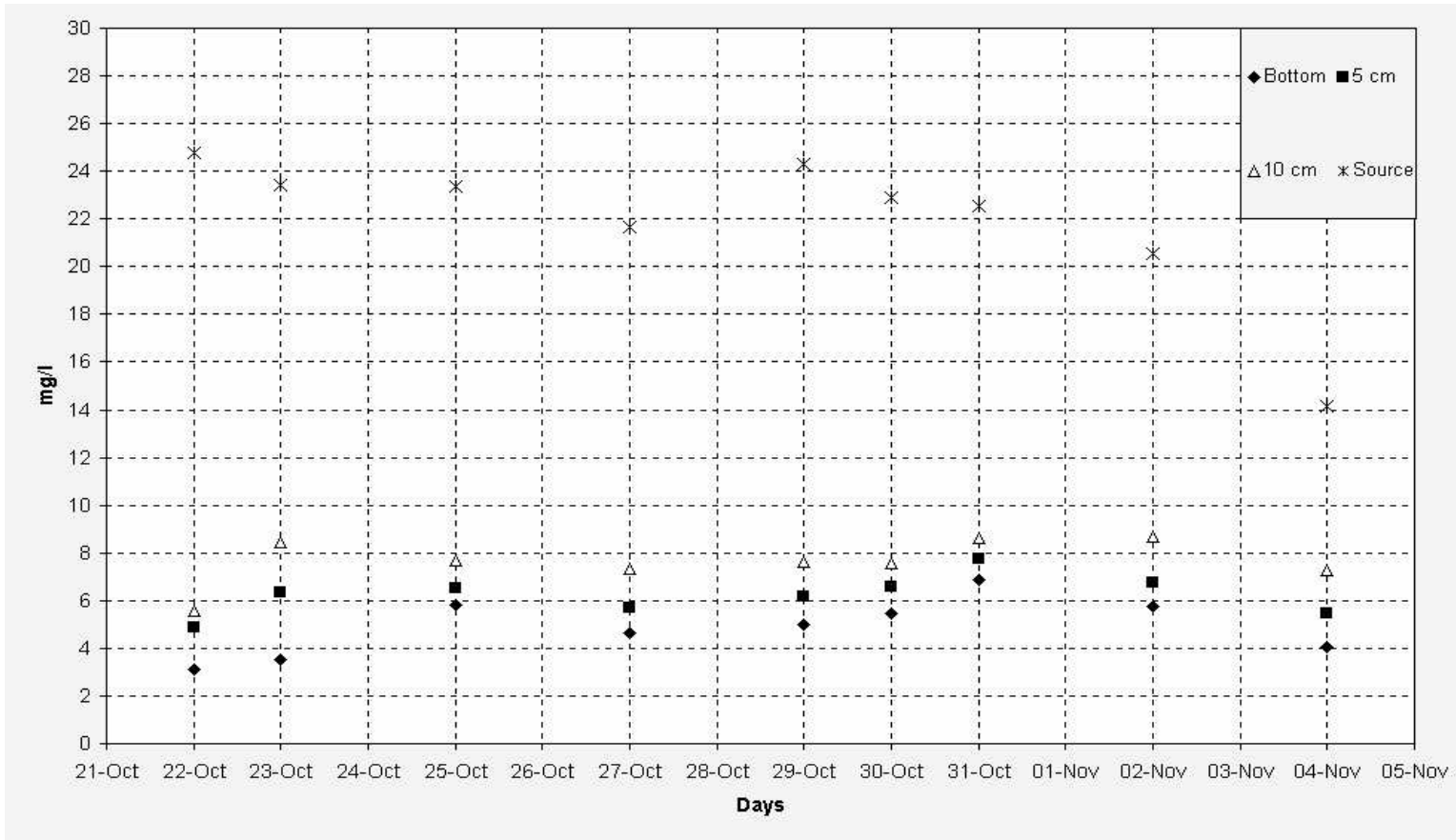Figure 5.11: BOD Variation over Time for the 24-hr Acid Soaked Pits

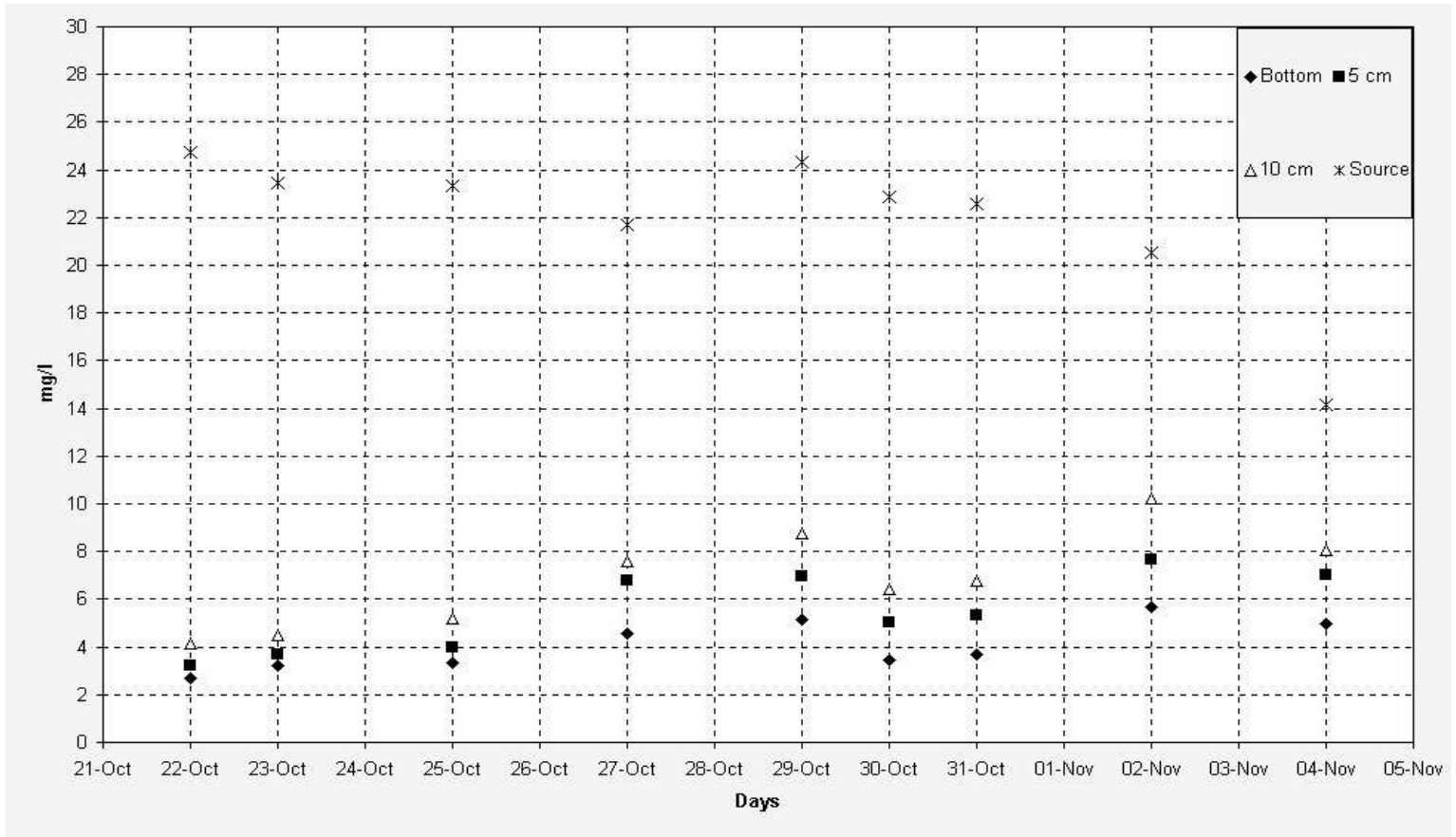Figure 5.12: BOD Variation over Time for the 12-hr Acid Soaked Pits

Figure 5.13: BOD Variation over Time for the Commercial Activated Carbon

TABLE 5.3: Summary of the BOD Results from the Columns Study

Date	Source (mg/l)	24-hr Acid Soaked Pits (mg/l)			12-hr Acid Soaked Pits (mg/l)			Commercial AC (mg/l)		
		Bottom	5 cm	10 cm	Bottom	5 cm	10 cm	Bottom	5 cm	10 cm
22 Oct.	24.759	3.389	4.093	4.888	3.102	4.891	5.570	2.718	3.208	4.178
23 Oct.	23.448	4.227	5.322	5.820	3.540	6.315	8.451	3.188	3.656	4.496
25 Oct.	23.338	4.592	5.583	5.946	5.832	6.507	7.692	3.322	4.005	5.231
27 Oct.	21.675	2.550	3.550	5.288	4.619	5.704	7.341	4.558	6.769	7.605
29 Oct.	24.335	5.801	7.380	8.487	5.004	6.191	7.647	5.139	6.980	8.795
30 Oct.	22.894	5.495	7.332	8.271	5.444	6.572	7.595	3.453	5.024	6.450
31 Oct.	22.549	8.209	9.656	10.436	6.875	7.735	8.602	3.677	5.343	6.768
02 Nov.	20.526	7.212	8.547	10.379	5.775	6.749	8.702	5.663	7.677	10.237
04 Nov.	14.158	6.488	7.205	7.929	4.036	5.454	7.265	4.971	7.046	8.056
Percent Removal with respect to the Source (Influent) (%)										
Date		Bottom	5 cm	10 cm	Bottom	5 cm	10 cm	Bottom	5 cm	10 cm
22 Oct.		86.31	83.47	80.26	87.47	80.25	77.50	89.02	87.04	83.12
23 Oct.		81.97	77.30	75.18	84.90	73.07	63.96	86.41	84.41	80.83
25 Oct.		80.32	76.08	74.52	75.01	72.12	67.04	85.77	82.84	77.59
27 Oct.		88.24	83.62	75.61	78.69	73.69	66.13	78.97	68.77	64.91
29 Oct.		76.16	69.67	65.12	79.44	74.56	68.58	78.88	71.32	63.86
30 Oct.		76.00	67.98	63.87	76.22	71.29	66.82	84.92	78.06	71.83
31 Oct.		63.59	57.18	53.72	69.51	65.70	61.85	83.69	76.30	69.99
02 Nov.		64.86	58.36	49.44	71.86	67.12	57.60	72.41	62.60	50.13
04 Nov.		54.18	49.11	44.00	71.49	61.48	48.68	64.89	50.23	43.10

was 71%.

For comparison purposes, Figure 5.13 shows the variation of BOD_5 of the commercial activated carbon with time. The average BOD values from the bottom port ranged from 2.7 to 5.6 mg/l. The removal efficiency with respect to the bottom of the columns was 81%, thus showing barely better performance compared to the 24-hr and 12-hr acid soaked pits.

5.1.2.4.2 TOC Removal

The TOC test measures all the carbon present in a water sample as CO_2 and, therefore, the inorganic carbon (HCO_3, CO_2, CO_3, etc.) must be removed prior to the test. Acidifying and aerating the sample is the method used to remove inorganic carbon. This test can be carried out by oxidizing the organic carbon to carbon dioxide at higher temperature in the presence of a catalyst. Carbon dioxide is then determined by non-destructive infrared absorption. TOC is now regularly specified in permits for industrial wastewater treated effluent. The theoretical relationship between COD and TOC is that the COD is 2.5 times greater than the TOC.

Figures 5.14, 5.15 and 5.16 were plotted using the TOC data shown in Table 5.4. These figures depict the variation of TOC with time along the ports of columns packed with 24-hr acid soaked pits, 12-hr acid soaked pits and commercial activated carbon, respectively. In Figure 5.14, the influent concentration ranged between 11 and 18 mg/l. As can be seen from the figure, up to the last day of October, the TOC value did not change substantially but as rain fell on the Saudi ARAMCO treatment
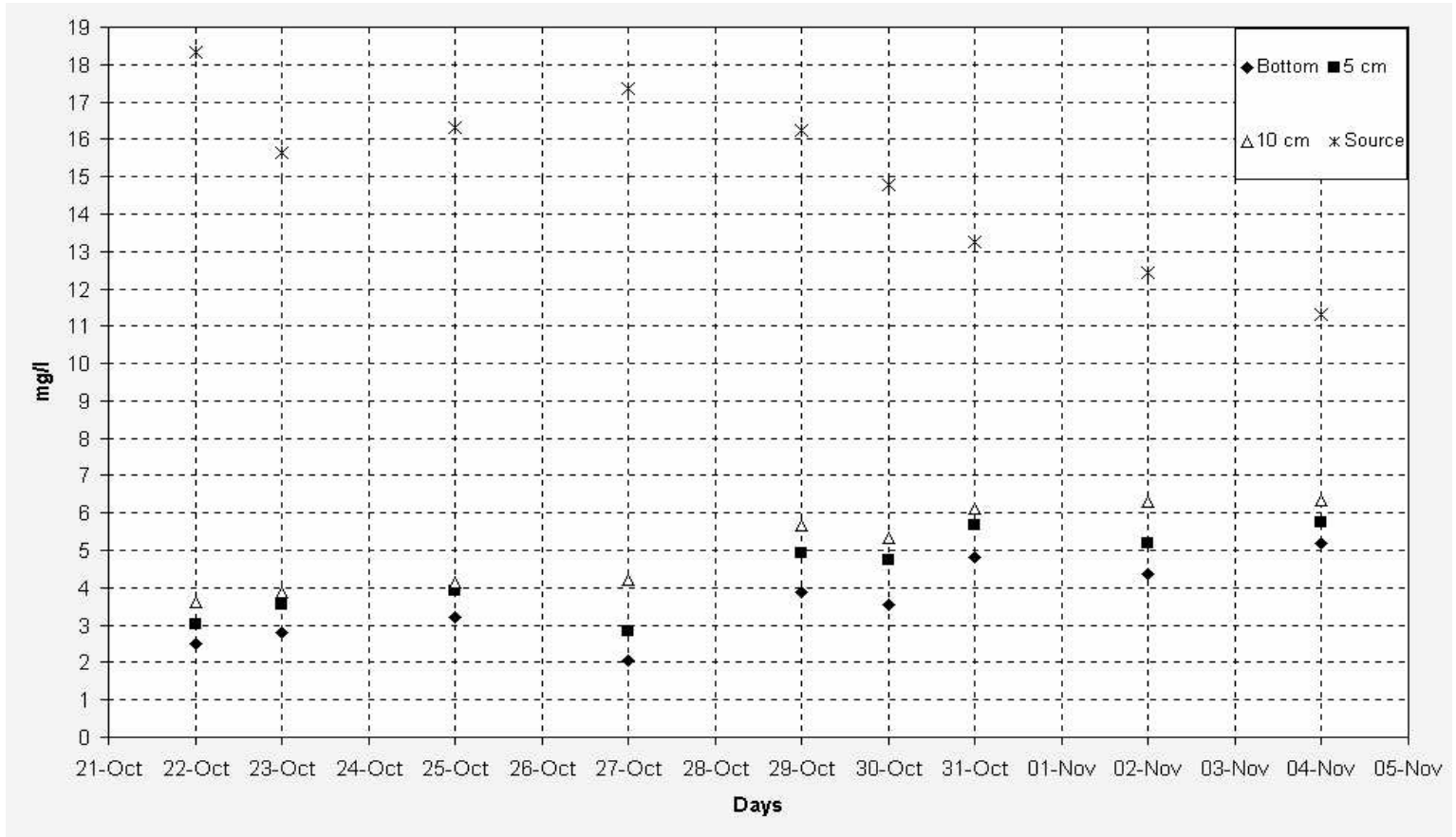
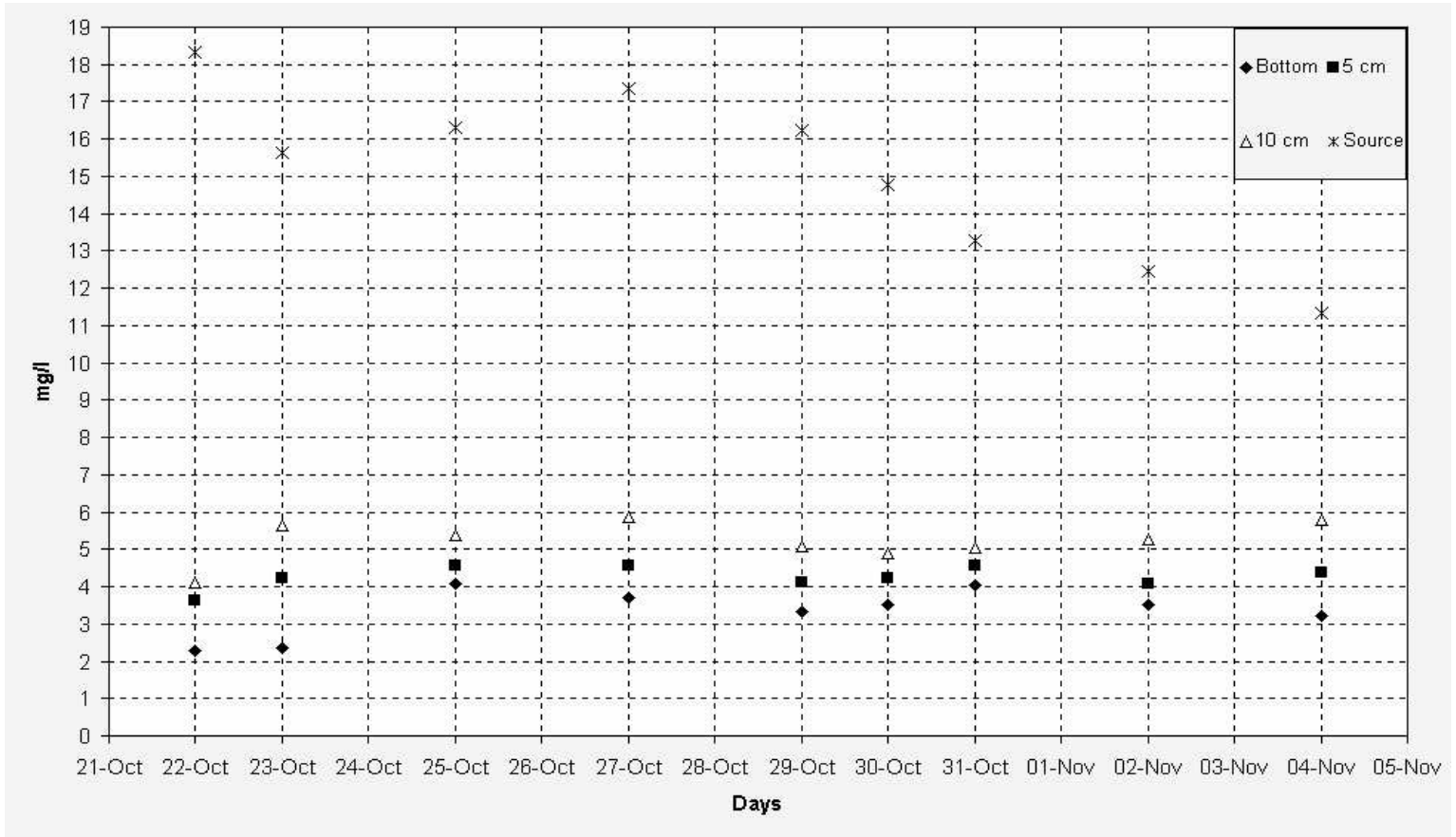Figure 5.14: TOC Variation over Time for the 24-hr Acid Soaked Pits

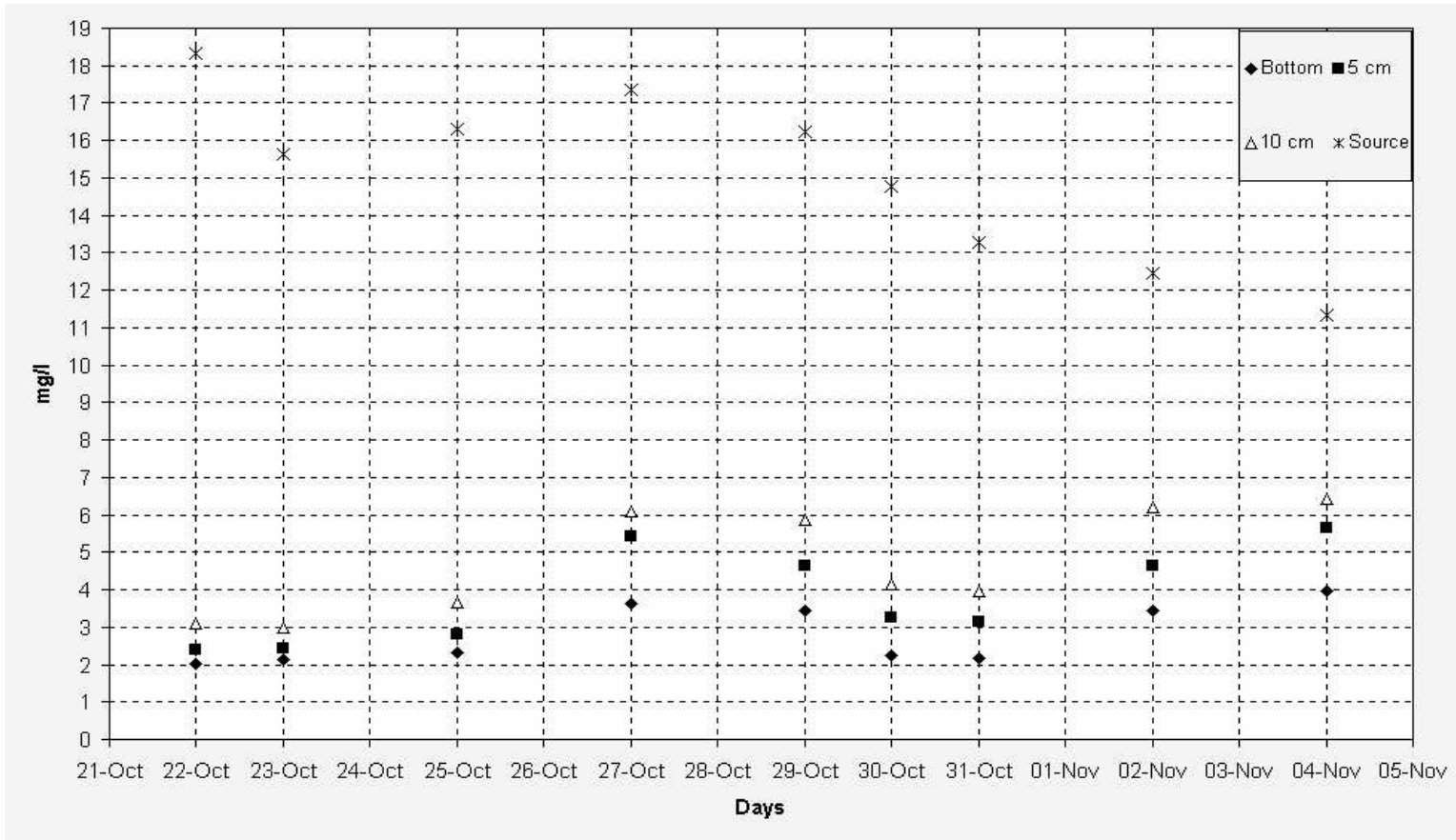Figure 5.15: TOC Variation over Time for the 12-hr Acid Soaked Pits

Figure 5.16: TOC Variation over Time for the Commercial Activated Carbon

TABLE 5.4: Summary of the TOC Results from the Columns Study

Date	Source (mg/l)	24-hr Acid Soaked Pits (mg/l)			12-hr Acid Soaked Pits (mg/l)			Commercial AC (mg/l)		
		Bottom	5 cm	10 cm	Bottom	5 cm	10 cm	Bottom	5 cm	10 cm
22 Oct.	18.340	2.510	3.032	3.621	2.298	3.623	4.126	2.013	2.376	3.095
23 Oct.	15.632	2.818	3.548	3.880	2.360	4.210	5.634	2.125	2.437	2.997
25 Oct.	16.320	3.211	3.904	4.158	4.078	4.550	5.379	2.323	2.801	3.658
27 Oct.	17.340	2.040	2.840	4.230	3.695	4.563	5.873	3.646	5.415	6.084
29 Oct.	16.223	3.867	4.920	5.658	3.336	4.127	5.098	3.426	4.653	5.863
30 Oct.	14.770	3.545	4.730	5.336	3.512	4.240	4.900	2.228	3.241	4.161
31 Oct.	13.264	4.829	5.680	6.139	4.044	4.550	5.060	2.163	3.143	3.981
02 Nov.	12.440	4.371	5.180	6.290	3.500	4.090	5.274	3.432	4.653	6.204
04 Nov.	11.326	5.190	5.764	6.343	3.229	4.363	5.812	3.977	5.637	6.445
Percent Removal with respect to the Source (Influent) (%)										
Date		Bottom	5 cm	10 cm	Bottom	5 cm	10 cm	Bottom	5 cm	10 cm
22 Oct.		86.31	83.47	80.26	87.47	80.25	77.50	89.02	87.04	83.12
23 Oct.		81.97	77.30	75.18	84.90	73.07	63.96	86.41	84.41	80.83
25 Oct.		80.32	76.08	74.52	75.01	72.12	67.04	85.77	82.84	77.59
27 Oct.		88.24	83.62	75.61	78.69	73.69	66.13	78.97	68.77	64.91
29 Oct.		76.16	69.67	65.12	79.44	74.56	68.58	78.88	71.32	63.86
30 Oct.		76.00	67.98	63.87	76.22	71.29	66.82	84.92	78.06	71.83
31 Oct.		63.59	57.18	53.72	69.51	65.70	61.85	83.69	76.30	69.99
02 Nov.		64.86	58.36	49.44	71.86	67.12	57.60	72.41	62.60	50.13
04 Nov.		54.18	49.11	44.00	71.49	61.48	48.68	64.89	50.23	43.10

plant, the organic matter became diluted, thus achieving a relatively low value of TOC. Similar trends were observed in the effluents from the three ports. TOC values from the effluents ranged from 2.5 to 6.2 mg/l. It is interesting to note that during the rainy period, the effluent concentrations of TOC were not low as per the influent and this could be attributed to the fact that the column was approaching the breakthrough conditions. The same observations could be reached in the case of Figure 5.15. There was hardly any significant difference observed in both figures (Figures 5.14 and 5.15).

Figure 5.16 illustrates the variation of TOC of commercial activated carbon with time. From the bottom of the column and 5-cm, the effluent concentration of TOC after the first day of operation was about 2 mg/l whereas the effluent concentration of the 10-cm port was about 3 mg/l. An increased concentration of TOC from the three ports was observed till the 29th of October, after which there was a sudden drop in the TOC concentration. Afterwards, the values suddenly jumped to unexpected higher values and that could be attributed to the organic matter contributed by the washout of rain, which had fallen. After the 4th of November, in terms of organic removal, the system was able to sustain the removal of TOC for all the three types of carbon.

5.1.2.5 Total Coliforms Removal

Pathogenic bacteria and viruses causing enteric diseases in human beings originate from fecal discharge of diseased persons. Consequently, water

contaminated by fecal pollution is identified as potentially dangerous due to the presence of bacteria. Bacterial contamination cannot be detected without a test.

In the present study, total coliform was used as a parameter to check the suitability of palm-date pits activated carbon and the commercial activated carbon in removing pathogenic microorganisms. Coliforms bacteria were chosen as an indicator since they do not cause diseases. The correlation between coliforms and human pathogens in water is not, however, absolute since these bacteria can originate from both the feces of humans and other warm-blooded animals. The number of coliforms in domestic wastewater far outnumber the number of pathogenic microorganisms since fecal coliforms are contributed by the entire population while pathogens are only from persons with enteric illnesses.

A total of ten (10) water samples were collected on alternate days from the ports of the three columns and the raw unchlorinated secondary effluent during the entire run of the experiment. All samples were collected in sterile glass bottles and processed immediately after the collection. For the total count analysis, a series of five fermentation tubes of lauryl sulphate broth (LSB) were inoculated with appropriate volumes of 10-fold dilutions of water samples and incubated at 37°C for 48 hours. All gas-positive LSB tubes were subcultured to the tubes of brilliant green lactose bile broth (BGLB) and incubated at 37°C for 48 hours. Gas-positive BGLB tubes were considered positive for the presence of total coliforms (APHA 2000, 20th Edition).

The microbiological tests were started two days after the start of the experiment. This was done to ensure that the system was stabilized. The results obtained from these tests are shown in Table 5.5 and they were used to plot Figures 5.17, 5.18, and 5.19. Figure 5.17 shows the temporal variation of total coliforms in the 24-hr acid soaked pits for the columns at 3 different depths. The figure also shows that in the first week of operation, 5-cm depth and the bottom were showing almost the same concentrations of total coliforms whereas the concentration of total coliforms from the 10-cm port was showing significantly higher values, indicating that the top port (10-cm) was reaching the breakthrough faster than the other two ports (5-cm and the bottom). This could be attributed to the fact that carbon grains are relatively held loosely in a bed, and open paths can result from the buildup of impurities in the filter and rapid water movement under pressure through the unit. In this situation, the contact time between carbon and water is reduced and the treatment is less effective. It is also evident from the figure that the concentration of total coliforms in the samples withdrawn from the ports of the columns was increasing slowly with time. This could be explained since the columns were approaching the breakthrough stage. The figure also clearly depicts a sudden drop in the concentration of total coliforms and that corresponds to the 4th of November when heavy rain fell on the Saudi ARAMCO treatment plant that caused the dilution of the effluent.

Figure 5.18 shows the variation of total coliforms in the 12-hr acid soaked pits

TABLE 5.5: Summary of the Total Coliforms Results from the Columns Study

| Date	Source (MPN/100ml)	24-hr Acid Soaked Pits (MPN/100ml)			12-hr Acid Soaked Pits (MPN/100ml)			Commercial AC (MPN/100ml)		
		Bottom	5 cm	10 cm	Bottom	5 cm	10 cm	Bottom	5 cm	10 cm
22 Oct.	1.1E+05	9.4E+03	1.7E+04	2.3E+04	2.0E+04	2.7E+04	4.0E+04	8.2E+03	1.3E+04	2.0E+04
23 Oct.	9.8E+04	3.2E+04	3.6E+04	5.0E+04	4.9E+04	5.2E+04	6.2E+04	3.1E+04	3.5E+04	5.1E+04
25 Oct.	1.0E+05	2.7E+04	3.3E+04	4.7E+04	4.3E+04	4.8E+04	5.8E+04	2.5E+04	3.0E+04	4.5E+04
27 Oct.	9.0E+04	3.0E+04	3.4E+04	4.8E+04	4.8E+04	4.9E+04	5.9E+04	3.0E+04	3.2E+04	4.6E+04
29 Oct.	9.8E+04	3.8E+04	3.9E+04	5.4E+04	5.3E+04	6.5E+04	6.7E+04	3.6E+04	3.8E+04	5.3E+04
31 Oct.	9.2E+04	5.5E+04	5.5E+04	5.8E+04	6.5E+04	7.3E+04	7.2E+04	3.0E+04	3.9E+04	5.4E+04
02 Nov.	9.8E+04	7.8E+04	8.0E+04	8.2E+04	8.9E+04	8.9E+04	9.1E+04	7.6E+04	8.1E+04	8.2E+04
04 Nov.	8.2E+04	7.3E+04	7.4E+04	7.4E+04	7.8E+04	7.9E+04	7.8E+04	7.2E+04	7.2E+04	7.3E+04
06 Nov.	9.0E+04	8.9E+04	8.9E+04	8.8E+04	9.0E+04	8.9E+04	9.0E+04	8.4E+04	8.5E+04	8.7E+04
Percent Removal with respect to the Source (Influent) (%)										
Date		Bottom	5 cm	10 cm	Bottom	5 cm	10 cm	Bottom	5 cm	10 cm
22 Oct.		91.45	84.55	79.09	81.82	75.45	63.64	92.55	88.18	81.82
23 Oct.		67.35	63.27	48.98	50.00	46.94	36.73	68.37	64.29	47.96
25 Oct.		73.00	67.00	53.00	57.00	52.00	42.00	75.00	70.00	55.00
27 Oct.		66.67	62.22	46.67	46.67	45.56	34.44	66.67	64.44	48.89
29 Oct.		61.22	60.20	44.90	45.92	33.67	31.63	63.27	61.22	45.92
31 Oct.		40.22	40.22	36.96	29.35	20.65	21.74	67.39	57.61	41.30
02 Nov.		20.41	18.37	16.33	9.18	9.18	7.14	22.45	17.35	16.33
04 Nov.		10.98	9.76	9.76	4.88	3.66	4.88	12.20	12.20	10.98
06 Nov.		1.11	1.11	2.22	0.00	1.11	0.00	6.67	5.56	3.33
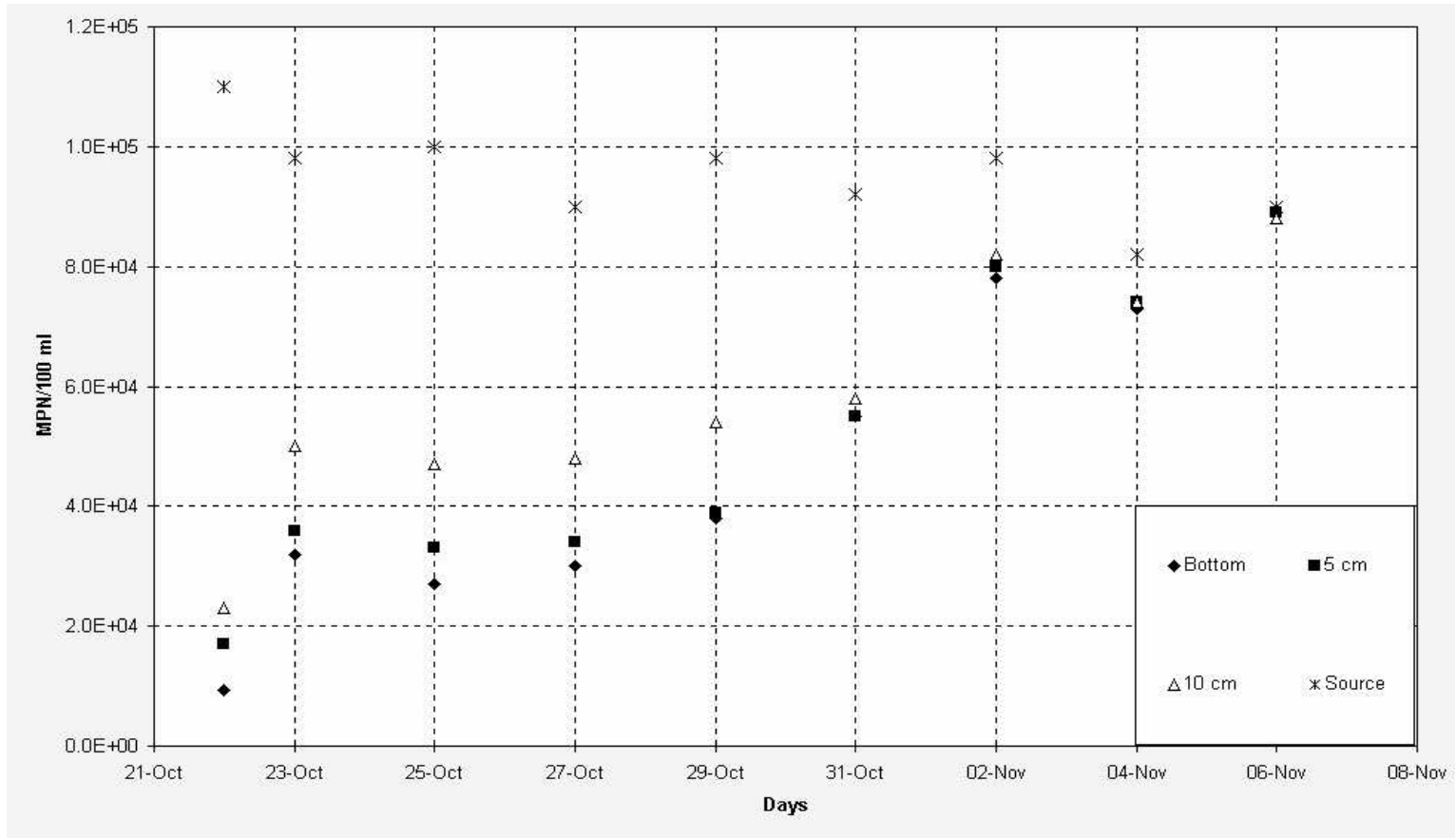
Figure 5.17: Total Coliforms Variation over Time for the 24-hr Acid Soaked Pits
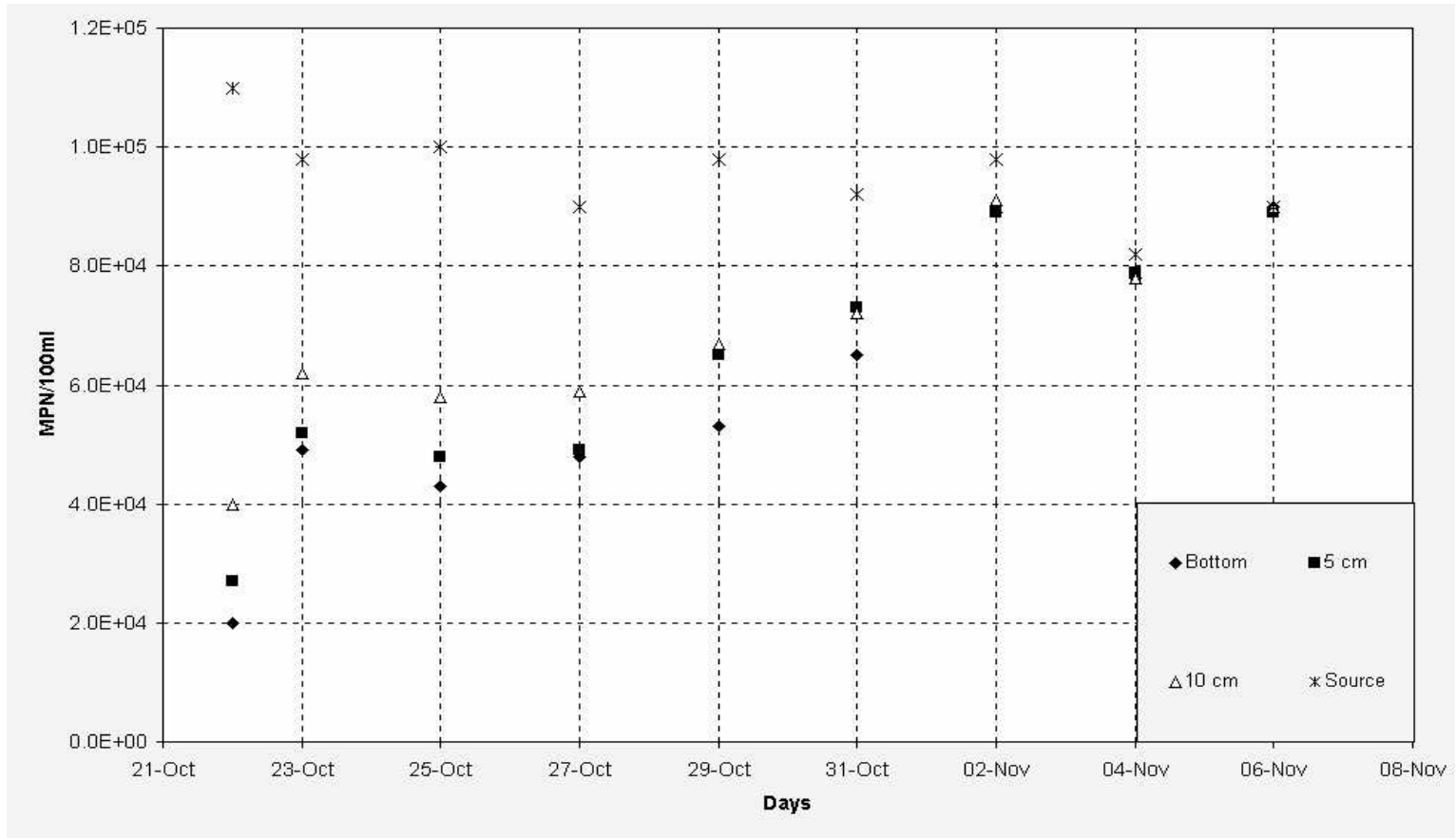
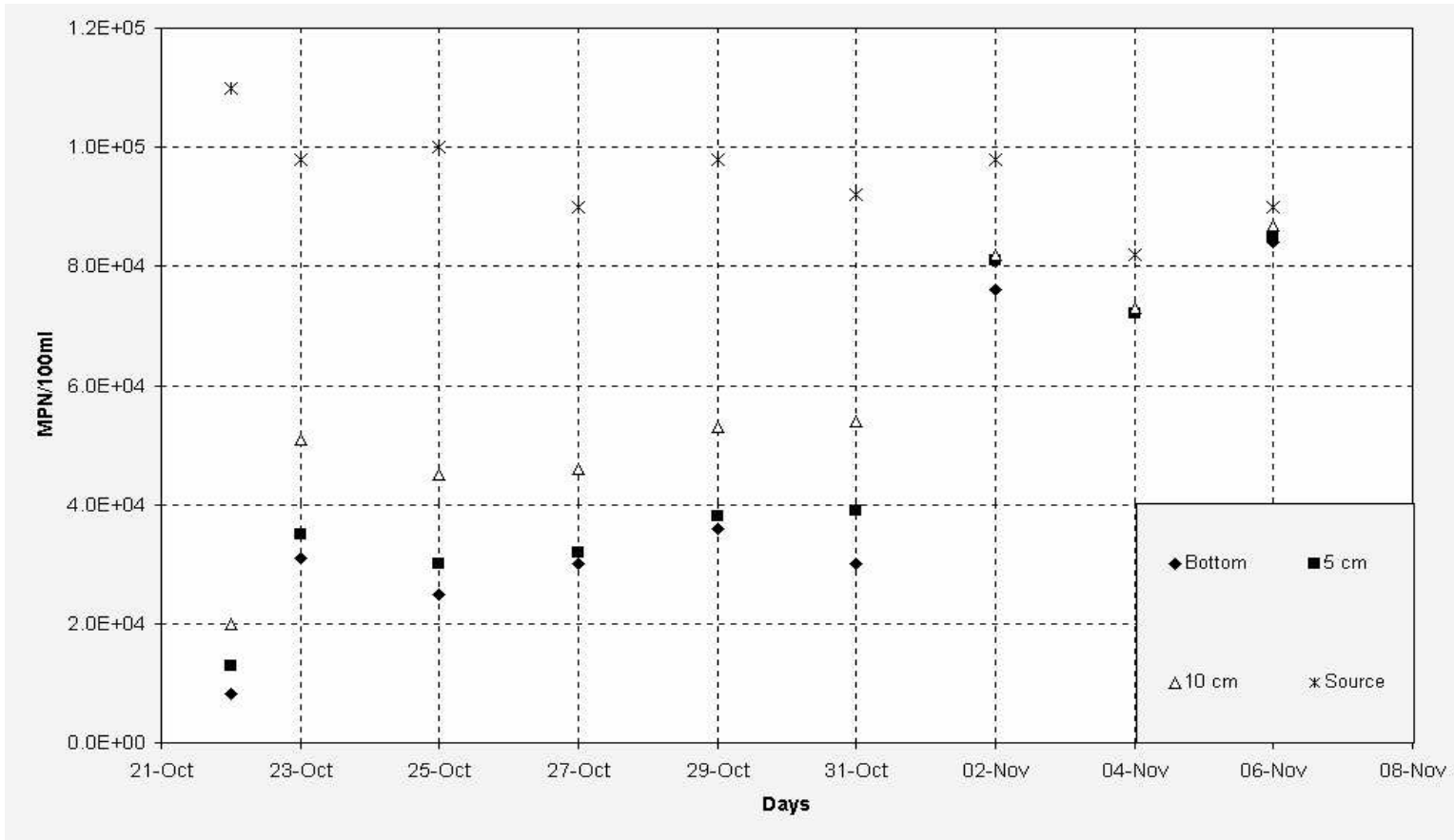Figure 5.18: Total Coliforms Variation over Time for the 12-hr Acid Soaked Pits

Figure 5.19: Total Coliforms Variation over Time for the Commercial AC

with time. As can be seen from the figure, the same trend of total coliforms concentration is observed as in Figure 5.17, and all the remarks made in Figure 5.17 are also justified in Figure 5.18.

Figure 5.19 shows the temporal variation of the removal of total coliforms using the commercial activated carbon with the exception of one outlier reading (on the 31st of October, from the bottom of the column), which could be due to human error resulting either from collecting the sample or in performing the total coliforms test. From the figure, it can be concluded that commercial activated carbon is not efficient in removing total coliforms for longer periods of operation and this was known earlier since it cannot remove effectively some conventional pollutants like hardness and heavy metals. This trial has been conducted to compare the performance of the commercial activated carbon with the locally produced pits.

The percent removal of the three carbon types was calculated based on the data collected. The results obtained are illustrated in Figures 5.20, 5.21, and 5.22. After one week of operation, the percent removal from the bottom (location of maximum removal) of the three columns (24-hr AC, 12-hr AC and commercial AC) were 61.22%, 45.92% and 63.27%, respectively. After 9 days of continuous operation, the removal dropped to 1.11% in the 24-hr pits and 0% in the case of 12-hr pits, while it was 6.67% in the case of commercial activated carbon. It can be concluded from the three figures that most of the removal is happening between the bottom and the 5-cm port. Also, it is clearly seen that the 24-hr acid soaked pits and the commercial
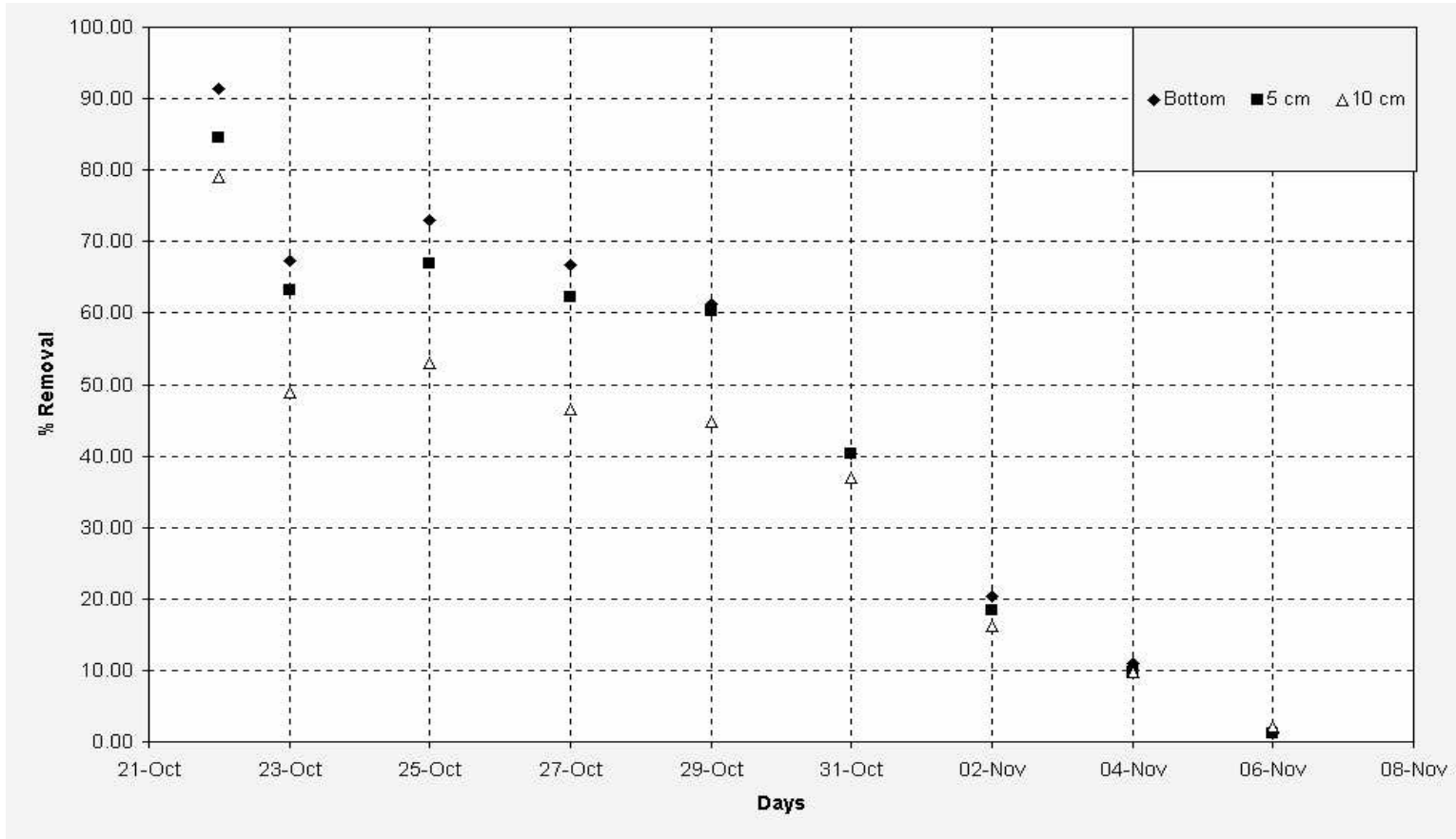
Figure 5.20: Percent Removal of Total Coliforms over Time for the 24-hr Acid
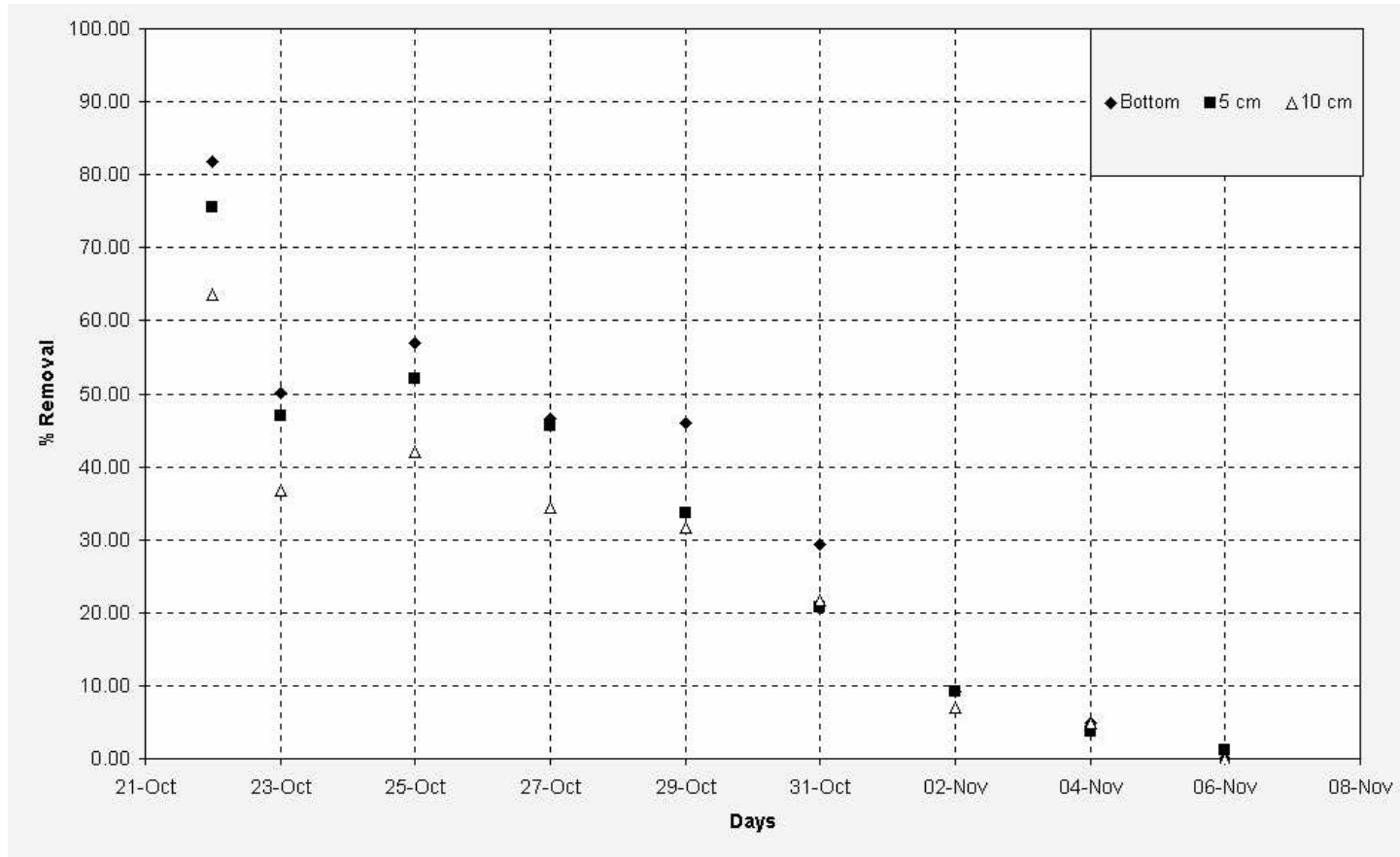Soaked Pits

Figure 5.21: Percent Removal of Total Coliforms over Time for the 12-hr Acid
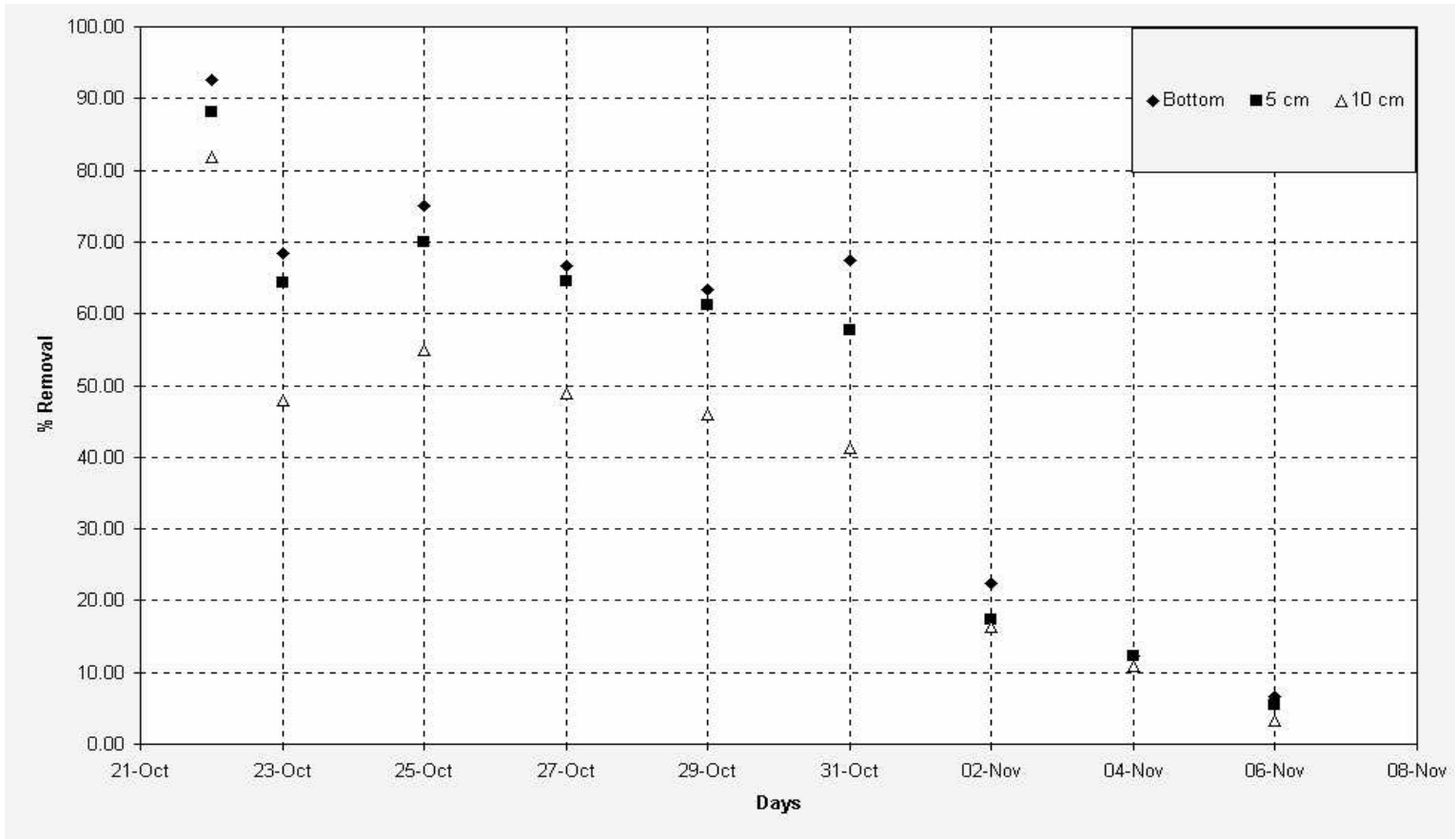Soaked Pits

Figure 5.22: Percent Removal of Total Coliforms over Time for the Commercial
AC

activated carbon were removing total coliforms with almost the same percentage as in the first 2 days of the experiment. Figure 5.22 shows that there is a clear distinction among the three ports of the commercial activated carbon until the 2nd of November when the 5-cm and the 10-cm ports started to removal with almost the same percentage, indicating that the media were reaching the breakthrough stage.

5.2 STATISTICAL ANALYSIS

An experiment can be defined as a test or series of tests in which objective changes are made on the input variables of a process or system so that the reasons for changes in the output response, we may be observed and identified.

Statistics can be defined as a tool or means of comparing and analyzing data so that meaningful results can be obtained. The idea of scientific investigation suggests objectivity in the examination of the information collected in the course of the investigation. The conclusions reached must be free of any bias on the part of the experimenter. Statistics has a very important role to play in helping to maintain objectivity. Statistical methods should be used to analyze the data so that the results and conclusions are objective rather than judgmental in nature (Montgomery, 1997).

While conducting this present study, one of the objectives was to statistically determine the significance of activated carbon types (24-hr acid soaked pits, 12-hr acid soaked pits and commercial activated carbon) and the depth of the ports within each column (bottom, 5-cm and 10-cm) with regard to the removal of various pollutants from wastewater. Therefore, an experimental design was formulated,

keeping this objective in mind.

5.2.1 Statistical Methods Applied

Statistical methods provide guidelines as to the reliability and validity of the results obtained from the experiments. Properly applied statistical methods do not allow anything to be proved experimentally but they do allow to measure the likely error in conclusion or to attach a level of confidence to a statement. The primary advantage of statistical methods is that they add objectivity to the decision-making process. Statistical techniques coupled with good engineering or process knowledge and common sense will lead to sound conclusions (Montgomery, 1997). The major statistical analysis consisted of testing the effect of activated carbon types (24-hr acid soaked pits, 12-hr acid soaked pits and commercial activated carbon) and the depth of the ports within each column (bottom, 5-cm and 10-cm) on the removal of various pollutants from wastewater.

5.2.1.1 Two-Stage Nested Design

It was decided to use a two-stage nested model since the levels of the activated carbon types are similar but not identical for different levels of the ports depth. Such an arrangement is called a nested design where the depths of the ports (bottom, 5-cm and 10-cm) are nested under the activated carbon types (24-hr acid soaked pits, 12-hr acid soaked pits and commercial activated carbon) considering the data of the entire period of the experimental run as shown in Figure 5.23.
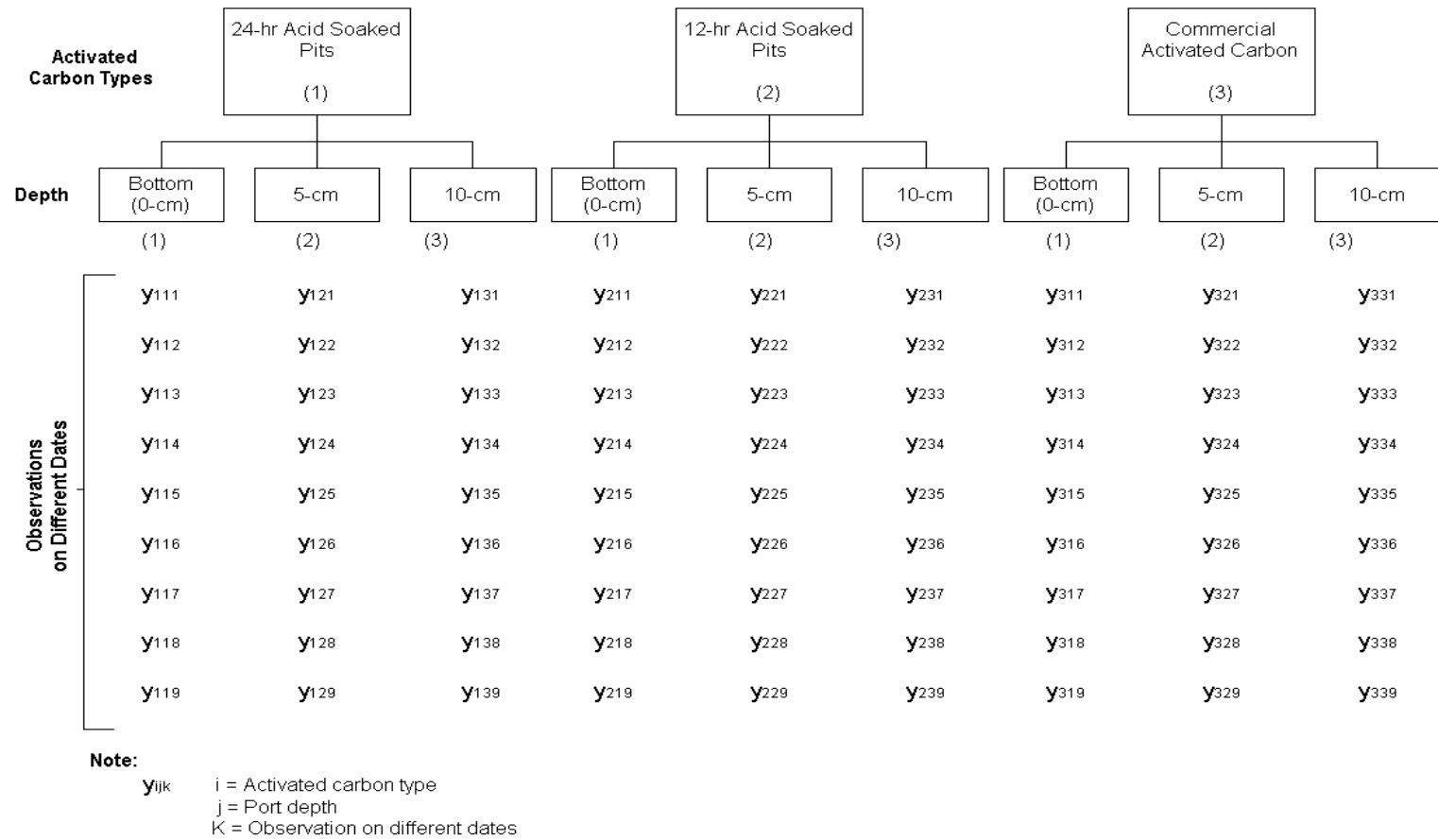
Figure 5.23: The Two-Stage Nested Design

The linear statistical model for the two-stage nested design is

$$y_{ijk} = \mu + \tau_i + \beta_{j(i)} + \varepsilon_{(ij)k} \qquad \begin{cases} i = 1,2,...,a \\ j = 1,2,...,b \\ k = 1,2,...,n \end{cases} \qquad (5.3)$$

Where μ is the overall mean effect, τ_i is the effect of the ith level of the activated carbon type, β_j is the effect of the jth level of the ports depth, and ε_{ijk} is a random error component. As can be seen from Figure 5.23, a = 3 levels of the activated carbon types (24-hr acid soaked pits, 12-hr acid soaked pits and commercial activated carbon), b = 3 levels of the ports depth (bottom, 5-cm and 10-cm) nested under each type of activated carbon, and n = 9 observations (replicates). The subscript $j(i)$ indicates that the jth level of the ports depth is nested under the ith level of the activated carbon types. It is convenient to think of the observations as being nested within the combination of levels of ports depth and types of activated carbon; thus, the subscript $(ij)k$ is used for error term. The used nested model can be considered as balanced nested design since there is an equal number of levels of ports depth (3 levels) within each level of the activated carbon types (3 levels). Since every level of ports depth does not appear with every level of the activated carbon types, there can be no interaction between them. In performing the statistical analysis, the two-stage nested model was used for the analysis of variance (ANOVA) as well as in generating the descriptive statistics (mean and box-whisker plots).

5.2.1.1.1 Analysis of Variance (ANOVA) Test

The appropriate procedure for testing the quality of several means is the analysis of variance. It is probably the most useful technique in the field of statistical inference.

The experiment here involves the study of the effects of two factors, activated carbon types and the ports depth of each type, which can be represented by factors A and B, respectively. Factorial designs are most efficient for this type of experiment. In a factorial design, all possible combinations of the levels of factors are investigated over the complete trial of the experiment.

Considering equation (5.3), the following hypotheses are tested using the nested model specified:

i) Hypothesis about the equality of factor A (activated carbon types):

H_0: $\tau_1 = \tau_2 = ... = \tau_a = 0$

H_1: At least one $\tau_i \neq 0$

H_0 means that there is no difference between the activated carbon types.

ii) Hypothesis about the equality of factor B (depth of the ports):

H_0: $\beta_1 = \beta_2 = ... = \beta_b = 0$

H_1: At least one $\beta_j \neq 0$

H_0 means that there is no difference between the port depths.

H_0 is called the null hypothesis and H_1 is the alternate hypothesis. These hypotheses are tested using the analysis of variance for a two-stage nested design,

where the total sum of squares (SS_T) is partitioned into sum of squares due to factor A (activated carbon types) (SS_A), sum of squares due to factor B (depth of the ports) within each carbon type ($SS_{B(A)}$), and a sum of squares due to error (SS_E). This can be represented in equation form as follows:

$$SS_T = SS_A + SS_{B(A)} + SS_E$$

The number of degrees of freedom associated with each sum of squares, mean squares and the F value (F-distribution) are presented in Table 5.6. The F value calculated from the ANOVA table is then compared with the $F_{critical}$ value from the percentage points of F distribution tables, and is interpreted as follows:

If $F = \dfrac{MS_{effect}}{MS_E} > F_{critical}$, then that effect is significant.

If $F = \dfrac{MS_{effect}}{MS_E} \leq F_{critical}$, then that effect is insignificant.

Where $F_{critical}$ is determined by the specified significance level α.

Another way to report the results of the hypothesis test is by using the p-value approach. The p-value of the test is then computed to a specified level of significance α and H_0 is rejected if the p-value is smaller than α.

5.2.1.1.2 Box and Whisker Plot

Box and whisker plot is a very useful way to display data. Through this plot, the data can be presented in a very compact and concise form. This plot has several graphic elements where the lower and upper lines of the "box" are the 25th and 75th

TABLE 5.6: Analysis of Variance Table for the Two-Stage Nested Design

Source of Variation	Sum of Squares	Degree of Freedom	Mean Square	F_0
A	SS_A	a-1	$MS_A = SS_A / (a-1)$	MS_A / MS_E
B within A	$SS_{B(A)}$	a (b-1)	$MS_{B(A)} = SS_{B(A)} / a (b-1)$	$MS_{B(A)} / MS_E$
Error	SS_E	ab (n-1)	$MS_E = SS_E / ab (n-1)$	
Total	SS_T	abn -1		

percentiles of the sample. The distance between the top and bottom of the box is the interquartile range. The small box in the middle of the box is the sample median. If the median is not centered in the box, that is an indication of skewness. Assuming no outliers, the maximum of the sample is the top of the upper whisker. The minimum of the sample is the bottom of the lower whisker.

5.2.2 Results of the Statistical Analysis

The statistical analysis was performed for BOD, TOC, and Total Coliforms data from the experimental run. The statistical analysis included ANOVA and descriptive statistics using the mean and box-whisker plots. All the analyses were performed using the statistical software package (STATISTICA, Version 5.1).

5.2.2.1 Organics Data Analysis

The BOD and TOC tests were performed for characterizing the organic content of the wastewater and for estimating its removals through the columns packed with 24-hr acid soaked pits, 12-hr acid soaked pits and commercial activated carbon.

5.2.2.1.1 BOD Data Analysis

The behavior of the 24-hr acid soaked pits and the 12-hr acid soaked pits in the removal of BOD was similar and it can be considered comparable to the commercial activated carbon as shown in Figure 5.24. The summary of the data in the form of box and whisker plots is presented in Figures 5.25 and 5.26. Figure 5.25 shows that the median value of the BOD of the commercial activated carbon is smaller than the

Plot of Means (unweighted)
AC_TYPE Main Effect
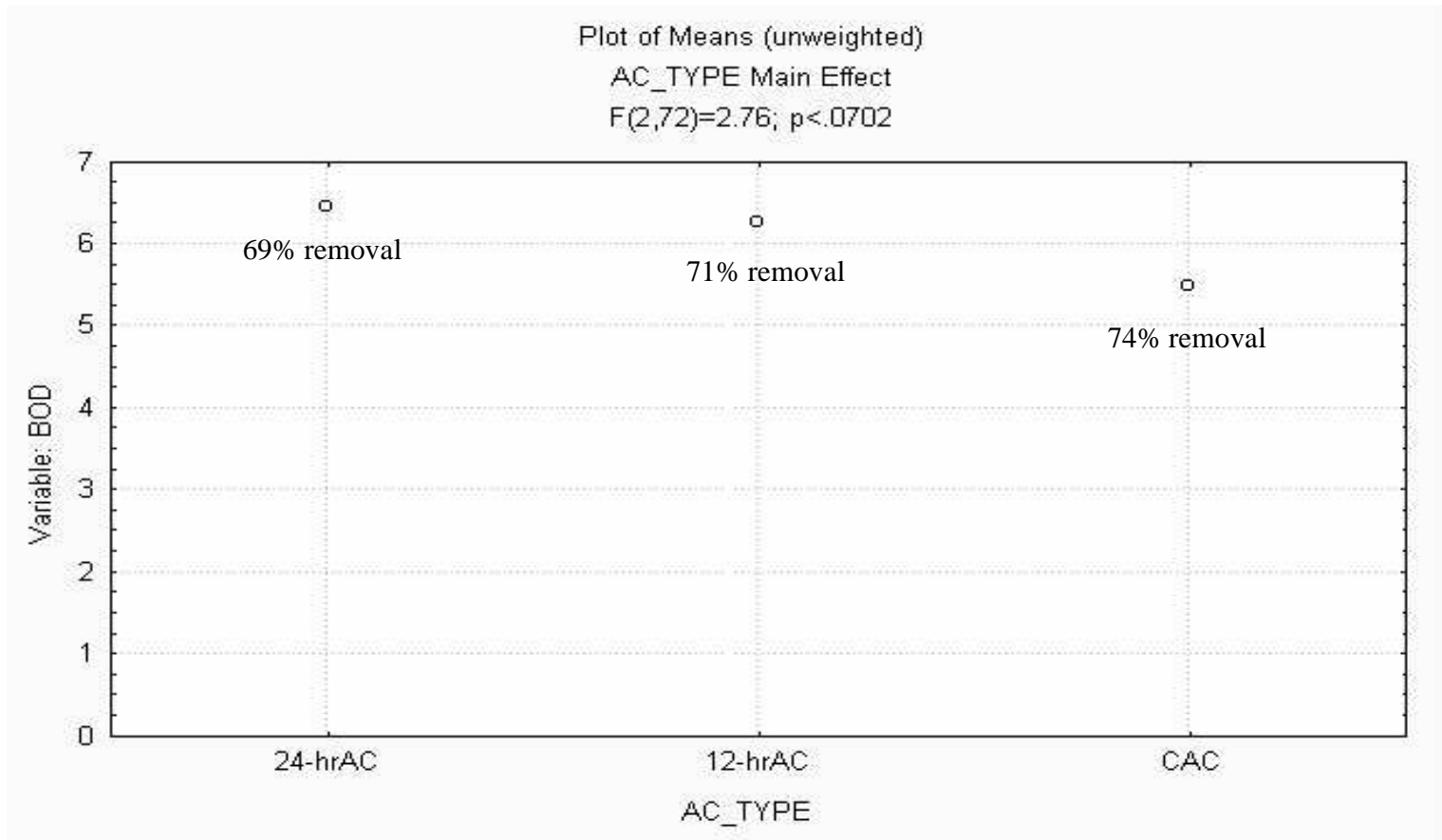$F_{(2,72)}=2.76$; $p<.0702$

69% removal

71% removal

74% removal

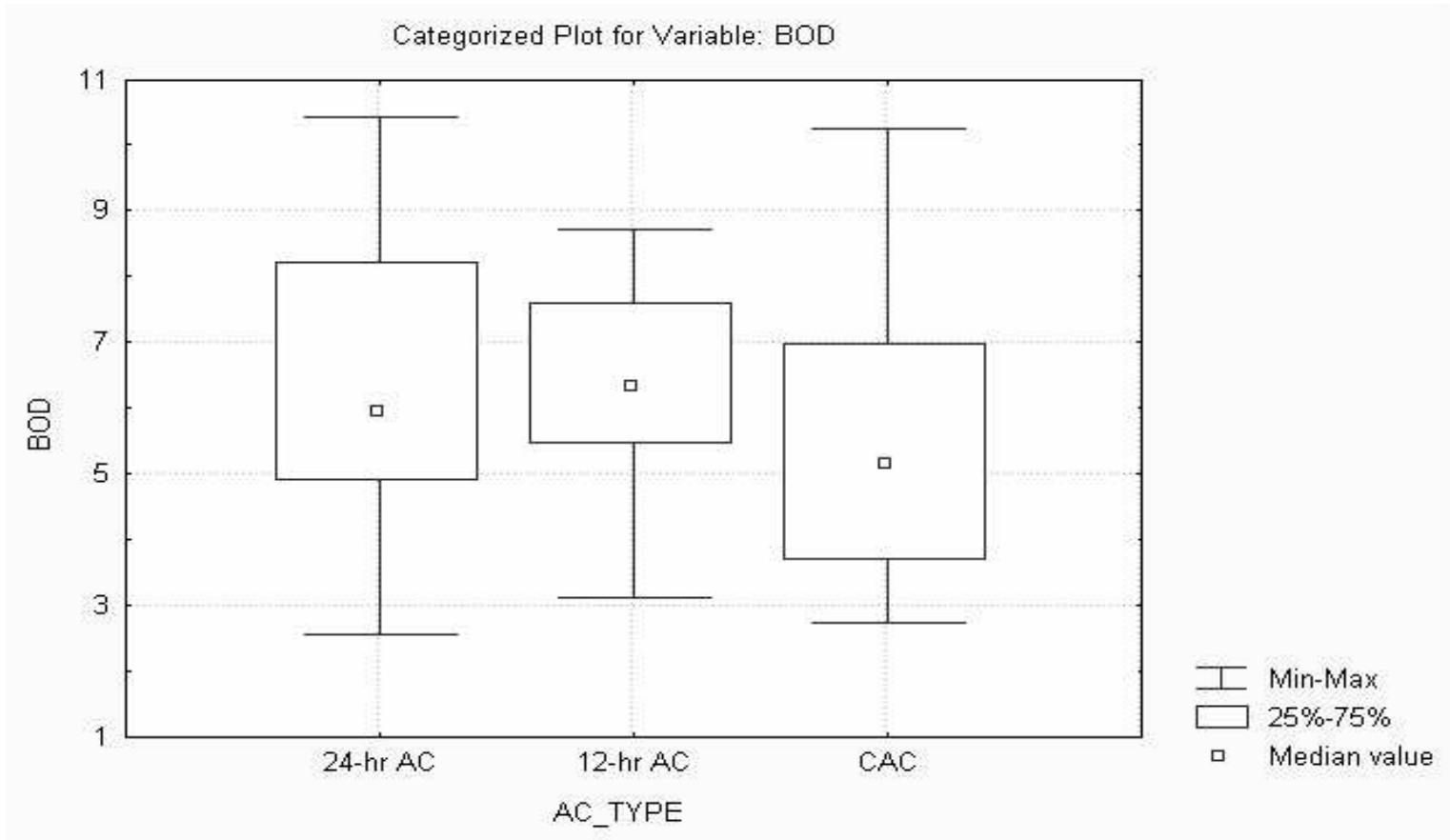Figure 5.24: Means Plot of the Three Types of Activated Carbon for BOD

Figure 5.25: Box and Whisker Plot of the Three Types of Activated Carbon for BOD
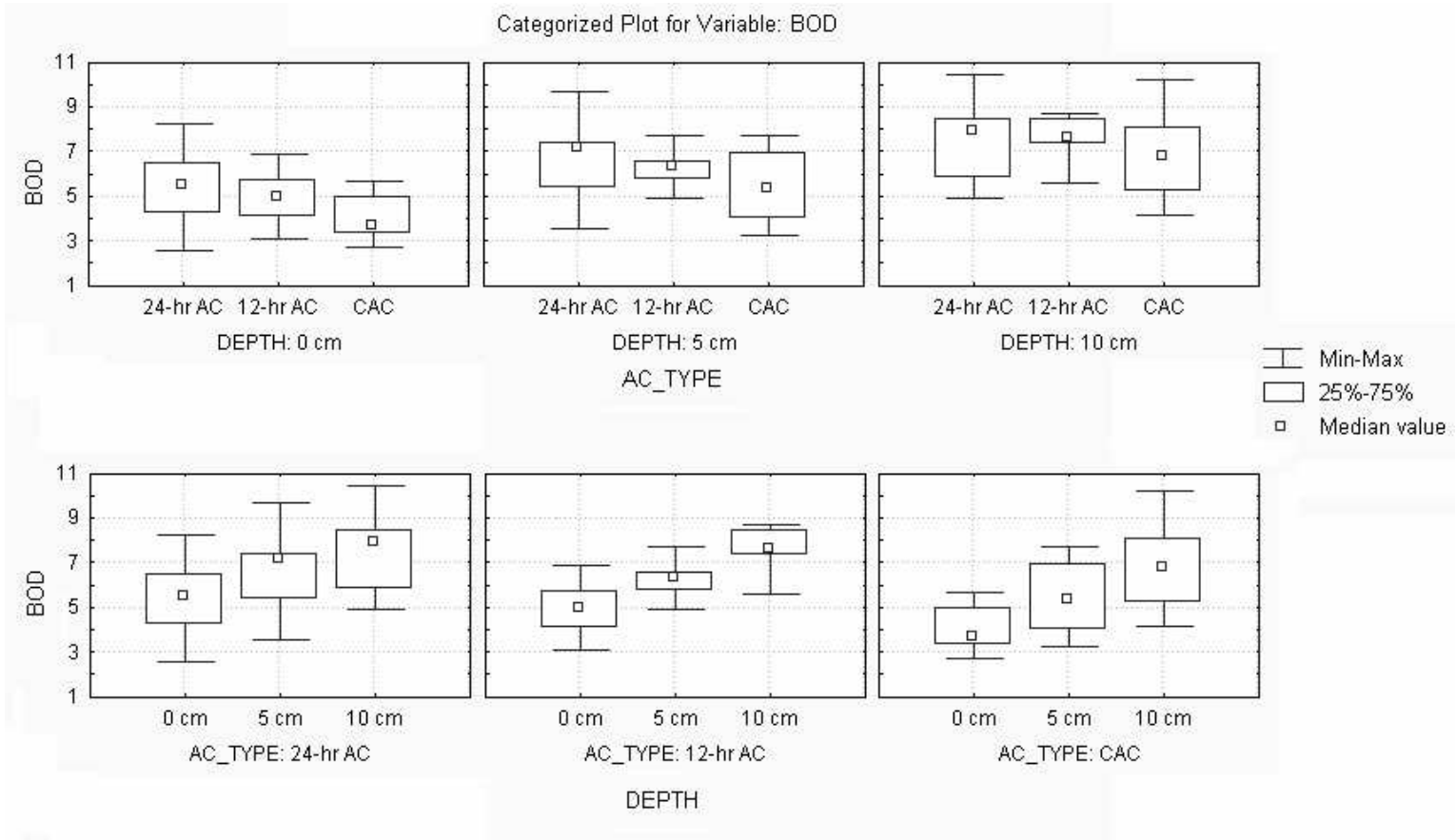
Figure 5.26: Categorized Box and Whisker Plot for BOD

other two carbons (24-hr and 12-hr acid soaked pits), which indicates that the removal efficiency of the commercial activated carbon was slightly higher over the entire period of the run. As can be seen from Figure 5.26, in all types of activated carbon, the percent removal of BOD increased with depth (achieving low values of BOD) as flow moves from the top port (10-cm) to the bottom (0-cm).

The ANOVA test was performed so as to check the significance of the activated carbon type and depth of ports with regard to BOD removals. The test results are summarized in Table 5.7. By considering 8% level of significance, the results show that both factors (activated carbon type and ports depth) have significant effect on the BOD removal. Although the ports depth chosen was small (0, 5 and 10 cm), the effect of depth appeared to be significant on the removal of BOD because there was a clear distinction between the ports depth of each carbon type and no overlap between the curves joining the points over the entire period of the run as shown in Figures 5.11, 5.12 and 5.13.

5.2.2.1.2 TOC Data Analysis

The removal efficiency of TOC was found similar to the removal efficiency of BOD for all types of activated carbon. Figure 5.27 shows that the removal efficiency of TOC for the commercial activated carbon was slightly higher than the other two carbons. The same conclusion can be observed from Figure 5.28 where 75% of the data as well as the median of the commercial activated carbon were close to the minimum value. The 24-hr and 12-hr acid soaked pits were behaving in a similar

TABLE 5.7: Analysis of Variance Table for BOD Data

STAT. GENERAL ANOVA	Summary of all Effects; design: (bod.sta) 1-AC_TYPE, 2-DEPTH					
Effect	df Effect	MS Effect	df Error	MS Error	F	p-level
1	2	6.99668	72	2.538225	2.756526	.070222
2	6	14.99743	72	2.538225	5.908629	.000047
12	--	--	--	--	--	--

Plot of Means (unweighted)
AC_TYPE Main Effect
F(2,72)=2.72; p<.0725
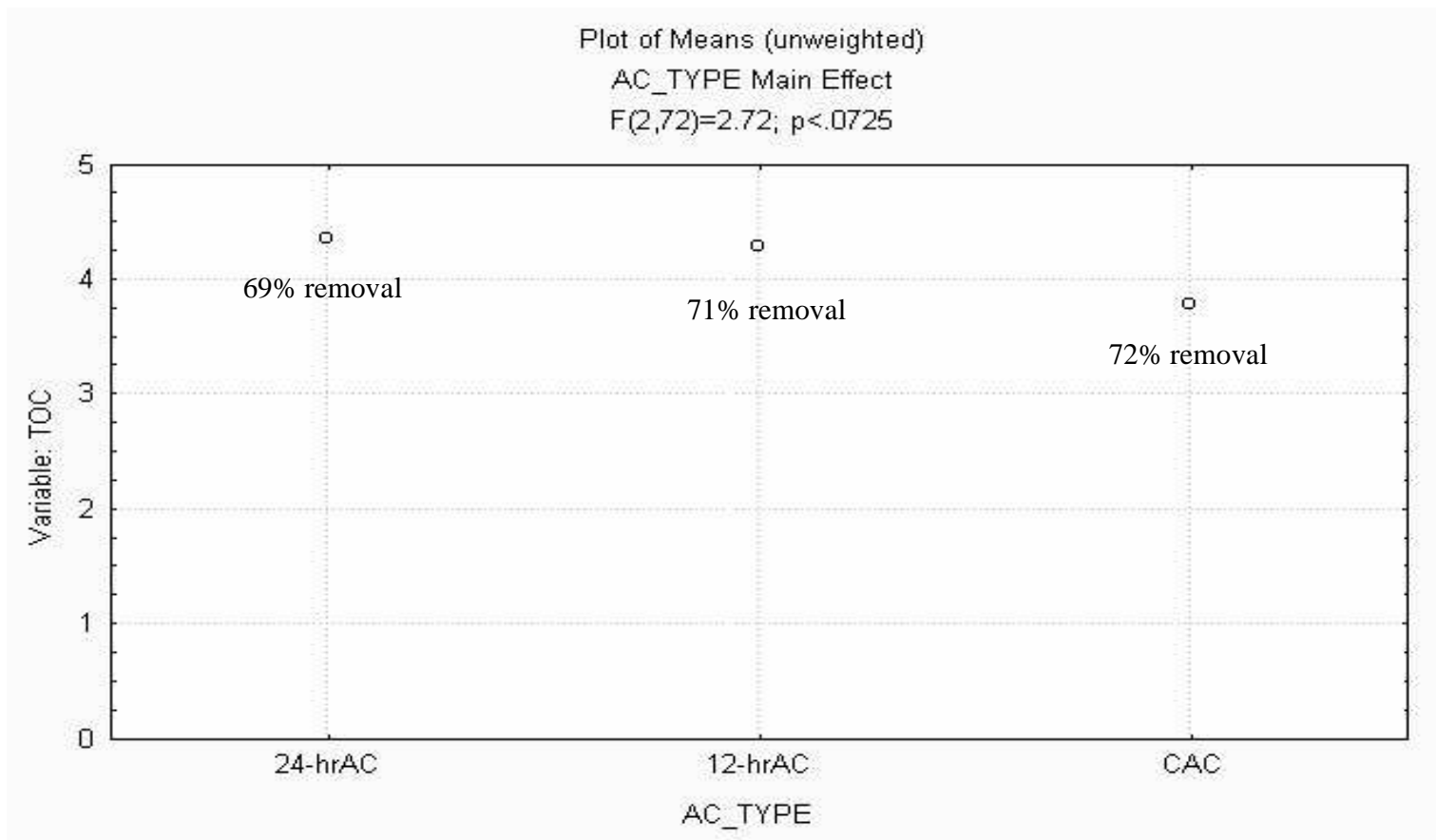
69% removal

71% removal

72% removal

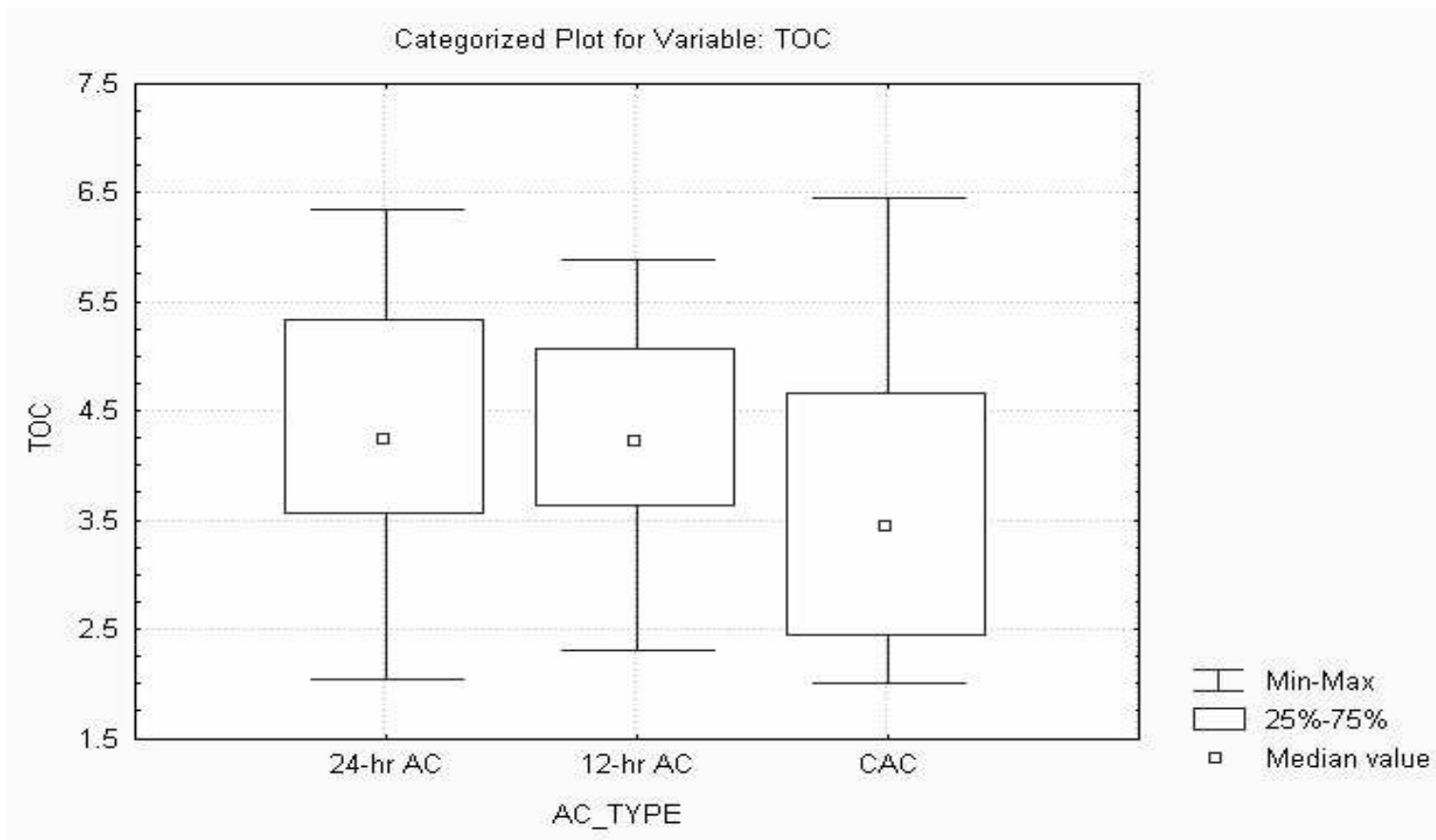Figure 5.27: Means Plot of the Three Types of Activated Carbon for TOC

Figure 5.28: Box and Whisker Plot of the Three Types of Activated Carbon for TOC

way in the removal of TOC and their performance can be considered comparable to the commercial activated carbon where the difference in percent removal of TOC was not high. As shown in Figure 5.29, in all the three types of activated carbon, the percent removal of TOC increased with depth (achieving low values of TOC) from the top port (10-cm) to the bottom (0-cm). The variation of the removal of TOC for the 12-hr acid soaked pits was very small compared to the 24-hr acid soaked pits and the commercial activated carbon indicating lower removal efficiency.

The ANOVA results for TOC analysis (Table 5.8) showed that there is a significant effect of both activated carbon types and ports depth on the removal efficiency of TOC considering 8% level of significance. Although the ports depth chosen was small (0, 5 and 10 cm), the effect of depth appeared to be significant on the removal of TOC because there was a clear distinction between the ports depth of each carbon type and no overlap between the curves joining the points over the entire period of the run as shown in Figures 5.14, 5.15 and 5.16.

5.2.2.2 Total Coliforms Data Analysis

The Total Coliforms (TC) density was monitored for assessing the microbial removal efficiency. The most probable number (MPN) technique was used for this purpose. Considering the data collected for the removal of total coliforms, it was found that the means of the 24-hr acid soaked pits and the commercial activated carbon were close to each other, indicating that the performance of both carbons in removing total coliforms can be considered the same as shown in Figure 5.30.
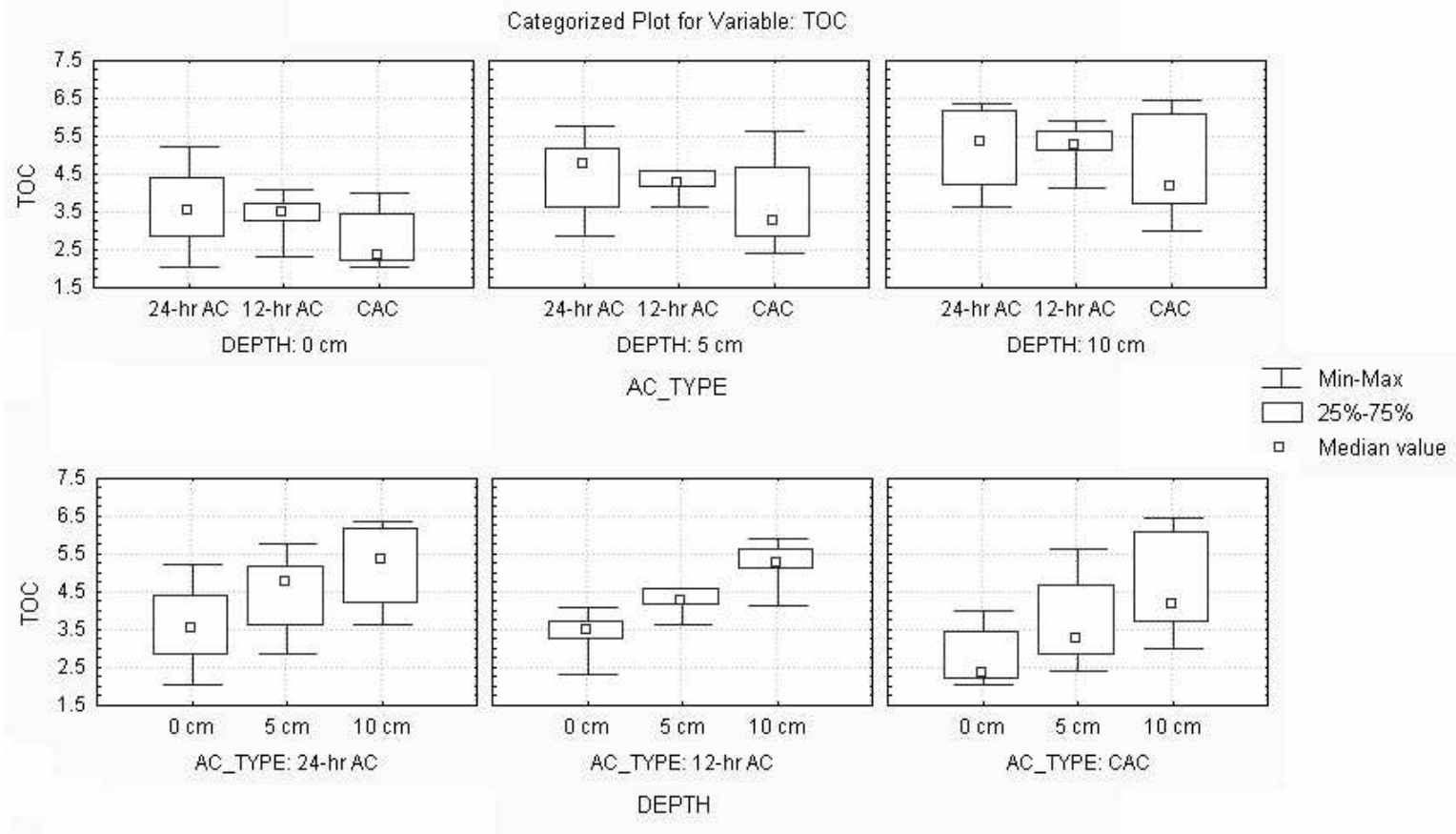
Figure 5.29: Categorized Box and Whisker Plot for TOC

TABLE 5.8: Analysis of Variance Table for TOC Data

STAT. GENERAL ANOVA	Summary of all Effects; design: (toc.sta) 1-AC_TYPE, 2-DEPTH					
Effect	df Effect	MS Effect	df Error	MS Error	F	p-level
1	2	2.601934	72	0.955896	2.721986	.072513
2	6	7.072812	72	0.955896	7.399147	.000047
12	--	--	--	--	--	--

Although the removal efficiency of both the 24-hr acid soaked pits and the commercial activated carbon was not satisfactory, they were better than the 12-hr acid soaked pits which shows low percent removal considering all the data for the entire period of the run. The box and whisker plot in Figure 5.31 shows that the data of the 12-hr acid soaked pits is clustered towards the higher value of total coliforms indicating less variability in the removal. More variability means slow deterioration of the performance of the carbon, thus suggesting that the 12-hr acid soaked pits deteriorated faster than the other two carbons (24-hr acid soaked pits and the commercial activated carbon). Also, it can be noticed from the figure that all the three types of carbon have the same high values and this could be attributed to the fact that all the three carbons reached a low percent removal of less than 3% at the end of the experimental run. Considering the depth of each carbon type presented by box and whisker plot in Figure 5.32, the median values of the total coliforms at 5-cm and 10-cm depth for the 12-hr acid soaked pits were almost the same while it is not true for the other two carbons (24-hr acid soaked pits and the commercial activated carbon).

The ANOVA analysis of the total coliforms data is shown in Table 5.9. It shows that the activated carbon type has a significant effect on the TC removal whereas the ports depth has no significant effect considering 8% level of significance, and this could be attributed to the small depth chosen between the ports (5-cm between each port). Although the ports depth of all the three types of carbon
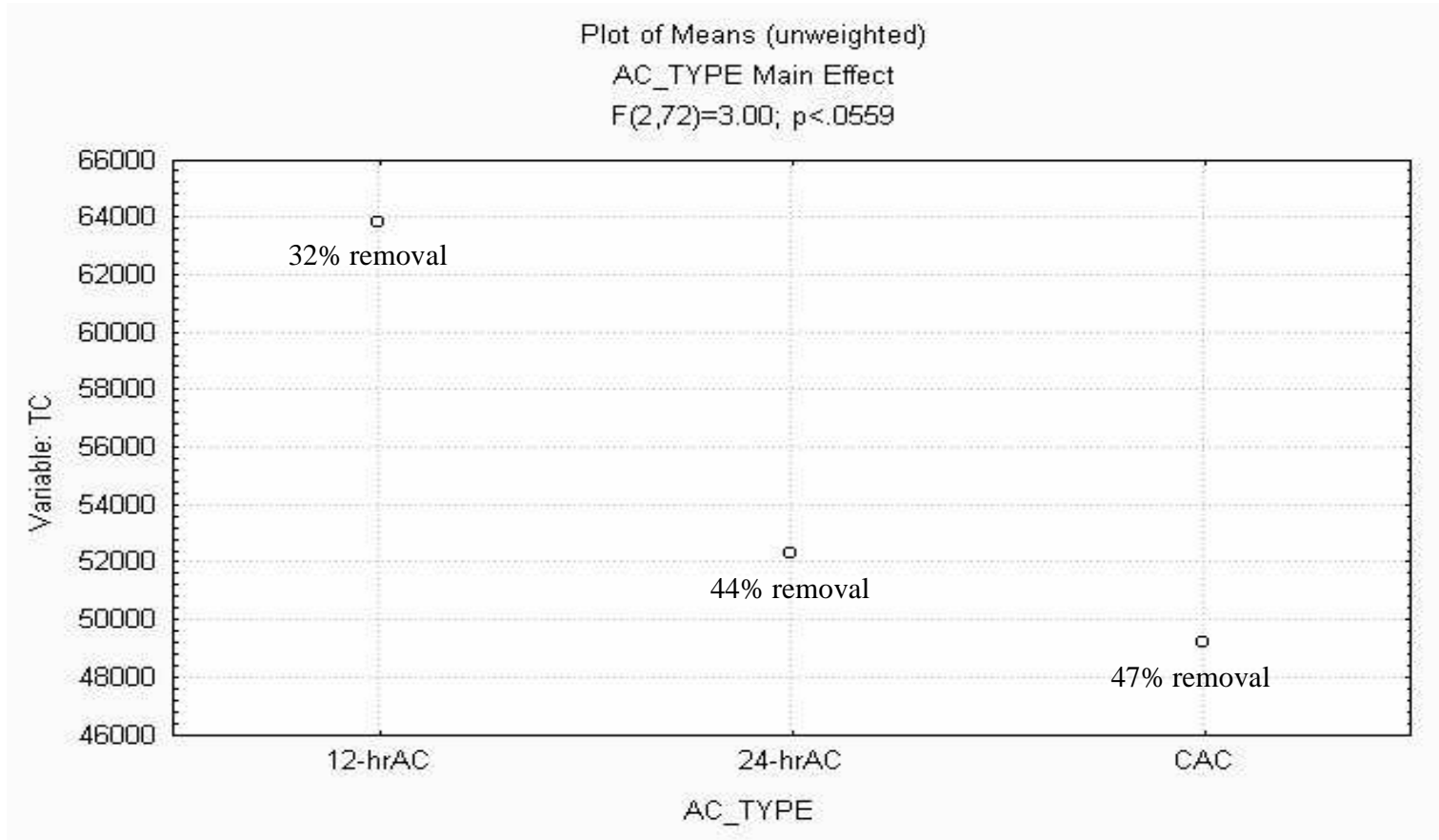
Figure 5.30: Means Plot of the Three Types of Activated Carbon for Total Coliforms
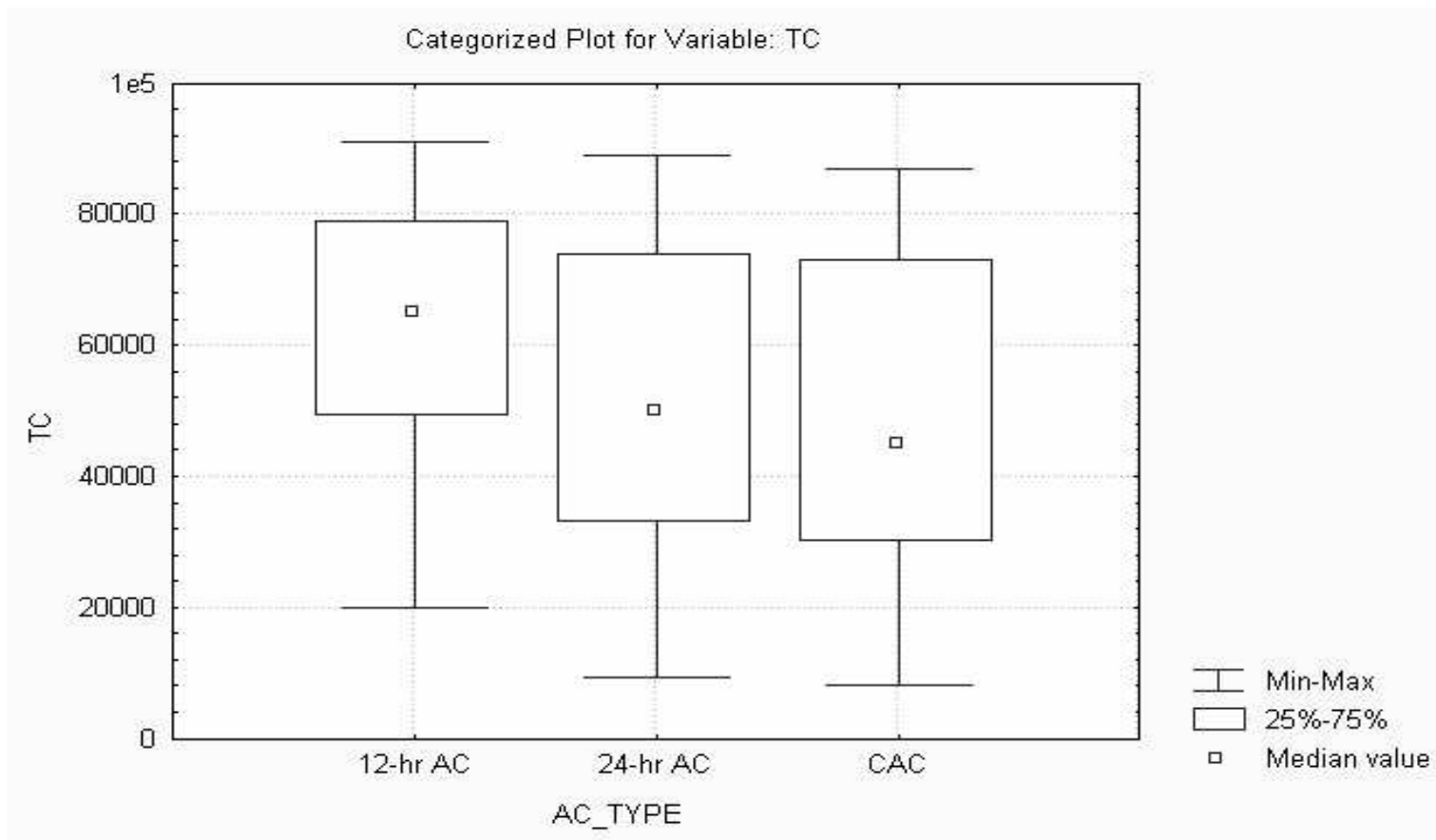
Figure 5.31: Box and Whisker Plot of the Three Types of Activated Carbon for Total Coliforms
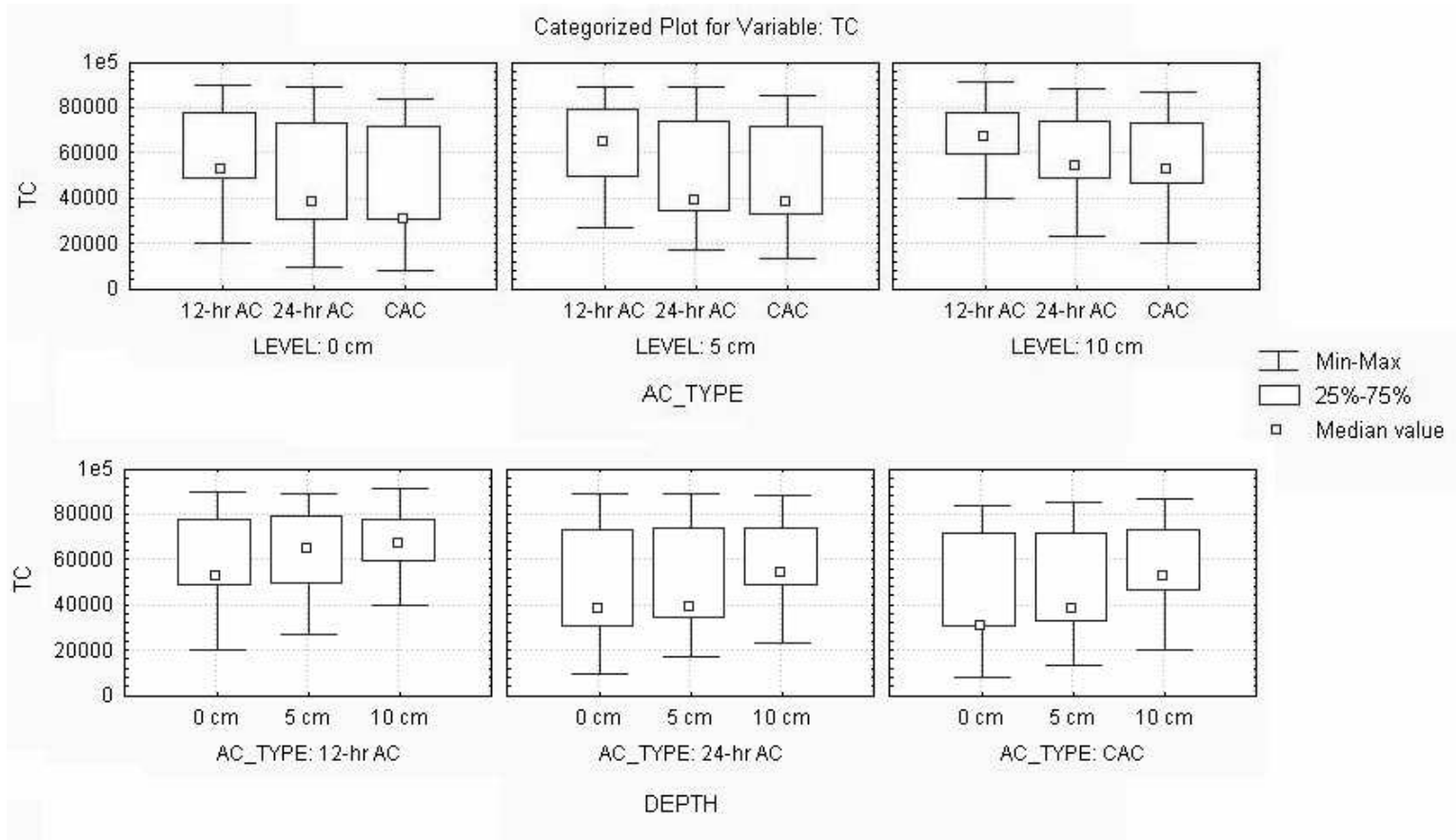
Figure 5.32: Categorized Box and Whisker Plot for Total Coliforms

TABLE 5.9: Analysis of Variance Table for Total Coliforms Data

STAT. GENERAL ANOVA	Summary of all Effects; design: (tc.sta) 1-AC_TYPE, 2-DEPTH					
Effect	df Effect	MS Effect	df Error	MS Error	F	p-level
1	2	160141E4	72	533206E3	3.003367	.055875
2	6	28669E3	72	533206E3	.537633	.777896
12	--	--	--	--	--	--

has no significant effect on the removal of total coliforms, the removal efficiency from the three ports (0, 5 and 10 cm) of the 24-hr acid soaked pits and the commercial activated carbon was found to be higher than the 12-hr acid soaked pits which shows almost similar removal efficiency in all the three ports as shown in Figure 5.32.

C H A P T E R   6

SUMMARY AND CONCLUSIONS

This research was conducted to study the performance of activated carbon produced from local palm-date pits compared to the commercial activated carbon on the removal of contaminants when unchlorinated secondary effluent was passed through both types of carbons. The infiltration rates in all columns resembled initially fast but it decreased with time. However, it was noted that during the course of time, the rate of decrease in the infiltration was slightly higher in the columns with activated carbon from the local palm-date pits (24-hr and 12-hr acid soaked pits).

The turbidity as well as the total suspended solids removals during the experimental run in all the three columns were very high as can be seen from the figures showing these removals. In this study, organics removal was also investigated. The BOD and TOC results show that organic carbon concentration is very low in the unchlorinated secondary effluent. This is believed to be the major cause of such a relatively moderate performance with regard to organics removal. The BOD and TOC average removals in the 24-hr acid soaked pits, 12-hr acid soaked pits and the commercial activated carbon were 71%, 69% and 73%, respectively. With regard to total coliforms, very good removal rates were achieved in all columns packed with the three types of carbon in the first few days. However,

the removal rates decreased signalling the breakthrough conditions. These unusual findings of coliforms removal could be explained with certainty; however, the main reason is thought to be the variable influent concentration with respect to time.

The statistical analysis of the data confirmed that both the activated carbon types and the ports depth had significant effect on organics removal, whereas only the activated carbon types were found to have significant effect on the removal of total coliforms considering 8% level of significance. The behavior of the 24-hr acid soaked pits and the 12-hr acid soaked pits in the removal of organics was similar and can be considered comparable to the commercial activated carbon. In all types of activated carbon, the percent removal of organics increased with depth (achieving low values of BOD and TOC) as flow moves from the top port (10-cm) to the bottom (0-cm). Although the ports depth chosen was small (0, 5 and 10 cm), the effect of depth appears to be significant on the removal of organics because there was a clear distinction between the ports depth of each carbon type and no intersection between these points over the entire period of the run.

C H A P T E R   7

RECOMMENDATIONS

Based on the results achieved in this study, the following recommendations can be forwarded:

- Cycles and trials of producing activated carbon from palm-date pits with high performance in adsorption must be conducted.

- It is worth investigating the production of palm-date pits activated carbon using steam activation.

- The most difficult and important part of the whole process is washing of the produced activated carbon from acids. A special technique has to be excogitated to facilitate this process.

- High surface area carbon can be achieved with a combination of different burning temperatures and concentrations of acid.

- The produced activated carbon should be tested against different contaminants from either domestic or industrial wastewater.

- Different depths of palm-date pits activated carbon used in the removal of contaminants should be investigated so that optimum depth could be achieved.

- Carbon amended sand should be investigated to determine the percentage of amendment of the produced activated carbon to be mixed with sand.

- A similar study should be conducted using chlorinated secondary effluent.

- The produced activated carbon should be tested for the possibility of regeneration.

- Further investigation on Freundlich and BET isotherms should be conducted in order to get the full picture on the performance of the produced activated carbon.

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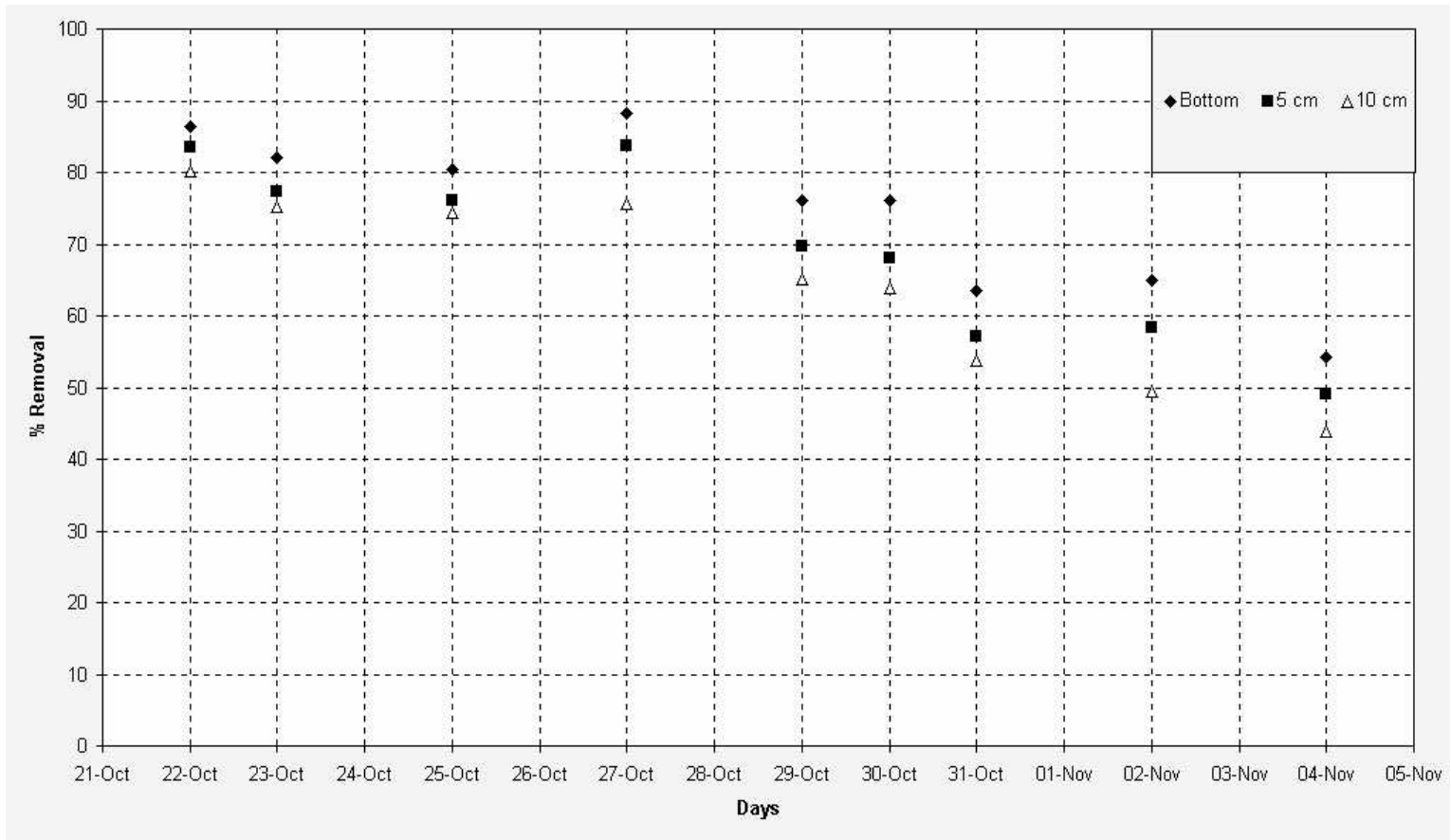
APPENDIX - A

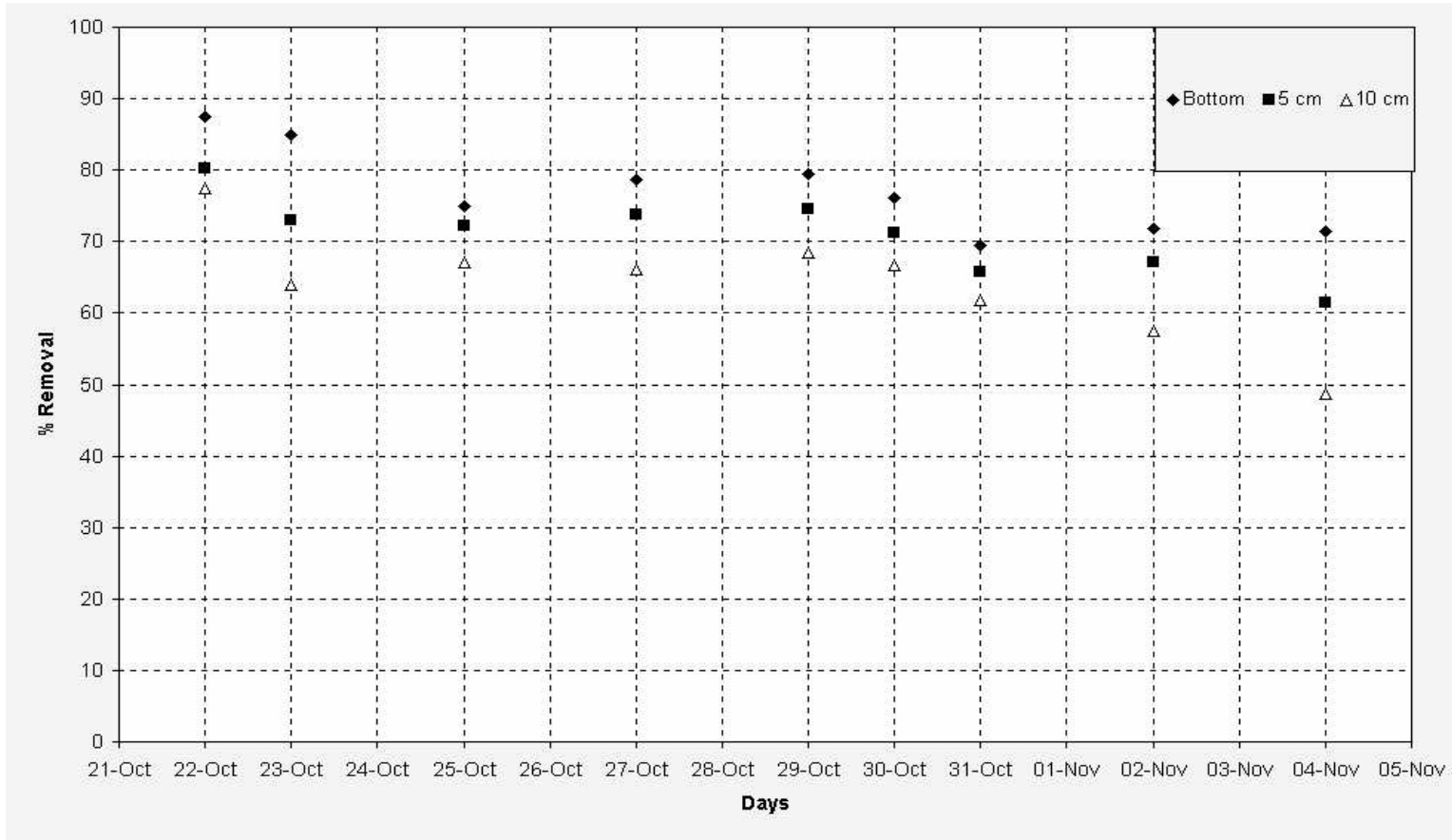Figure A.1: Percent Removal of BOD over Time for the 24-hr Acid Soaked Pits

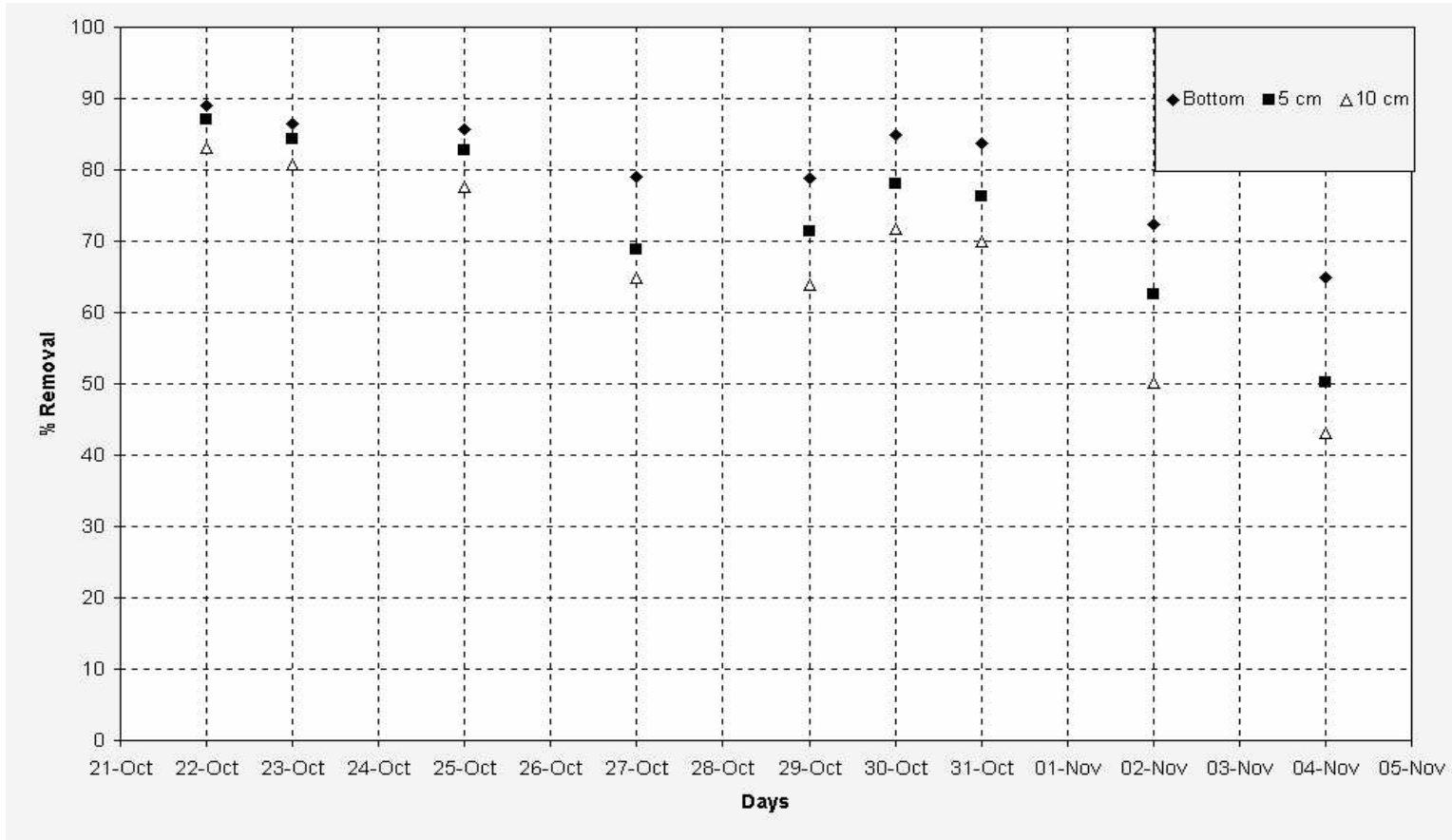Figure A.2: Percent Removal of BOD over Time for the 12-hr Acid Soaked Pits

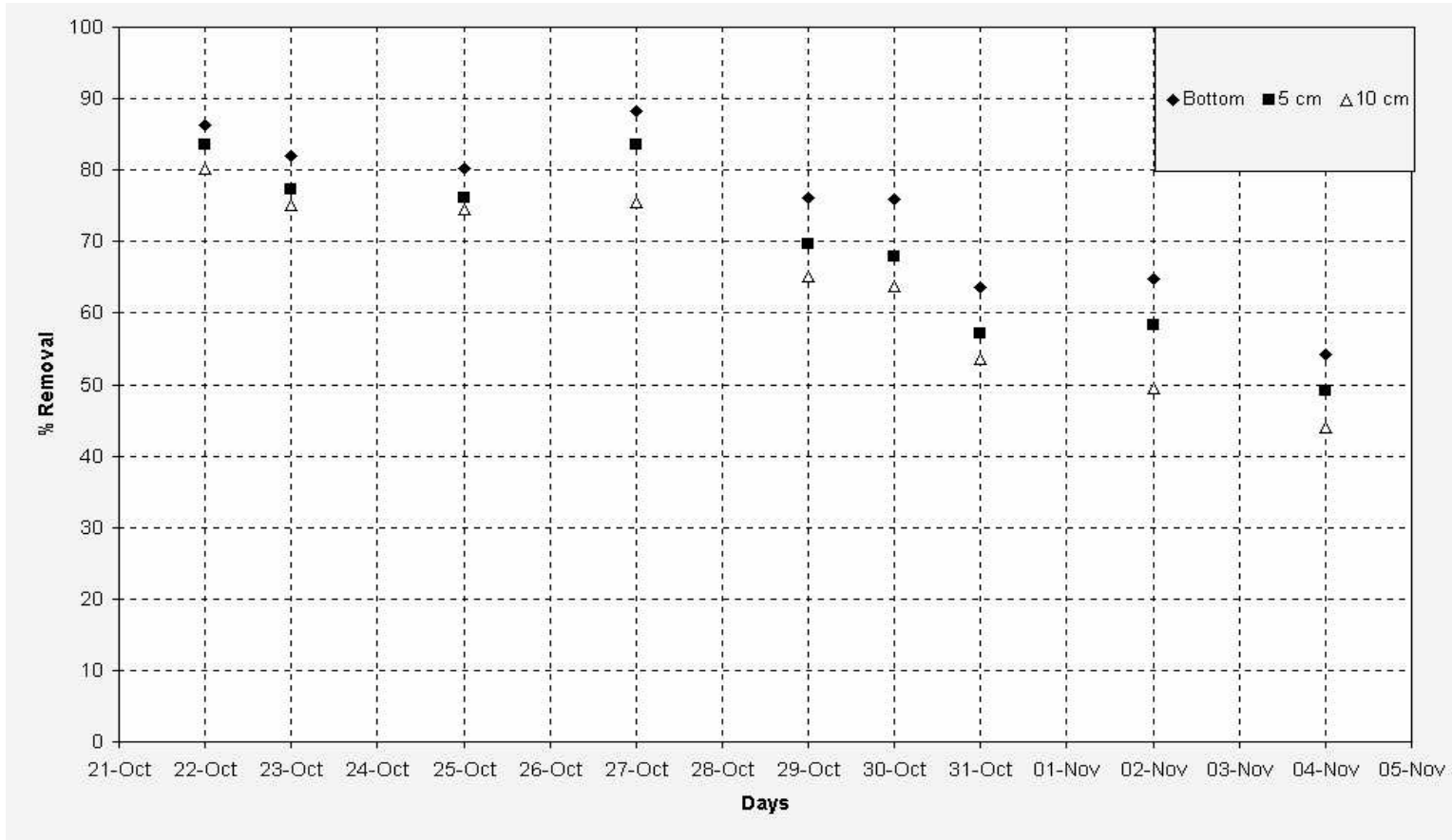Figure A.3: Percent Removal of BOD over Time for the Commercial Activated Carbon

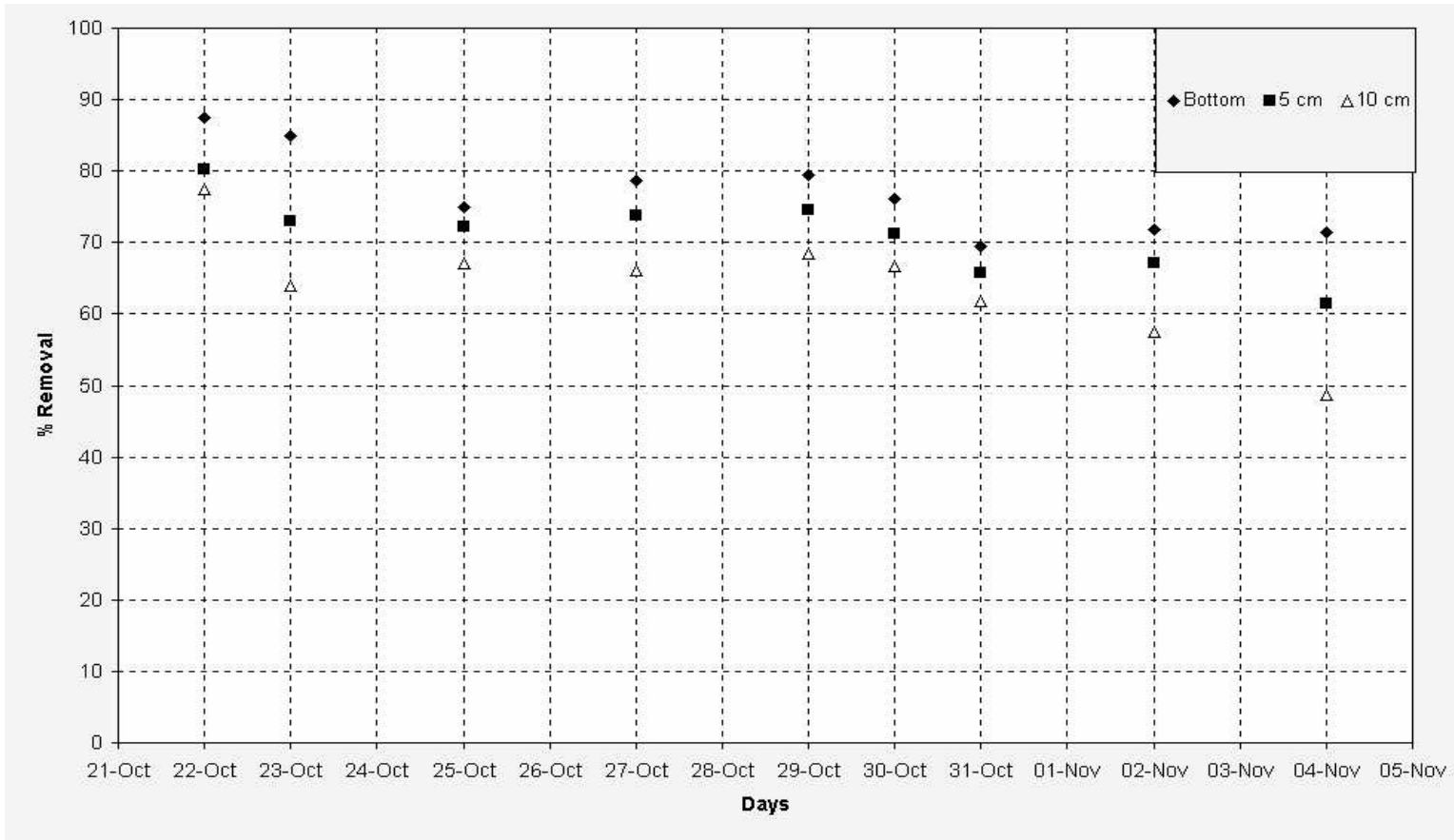Figure A.4: Percent Removal of TOC over Time for the 24-hr Acid Soaked Pits

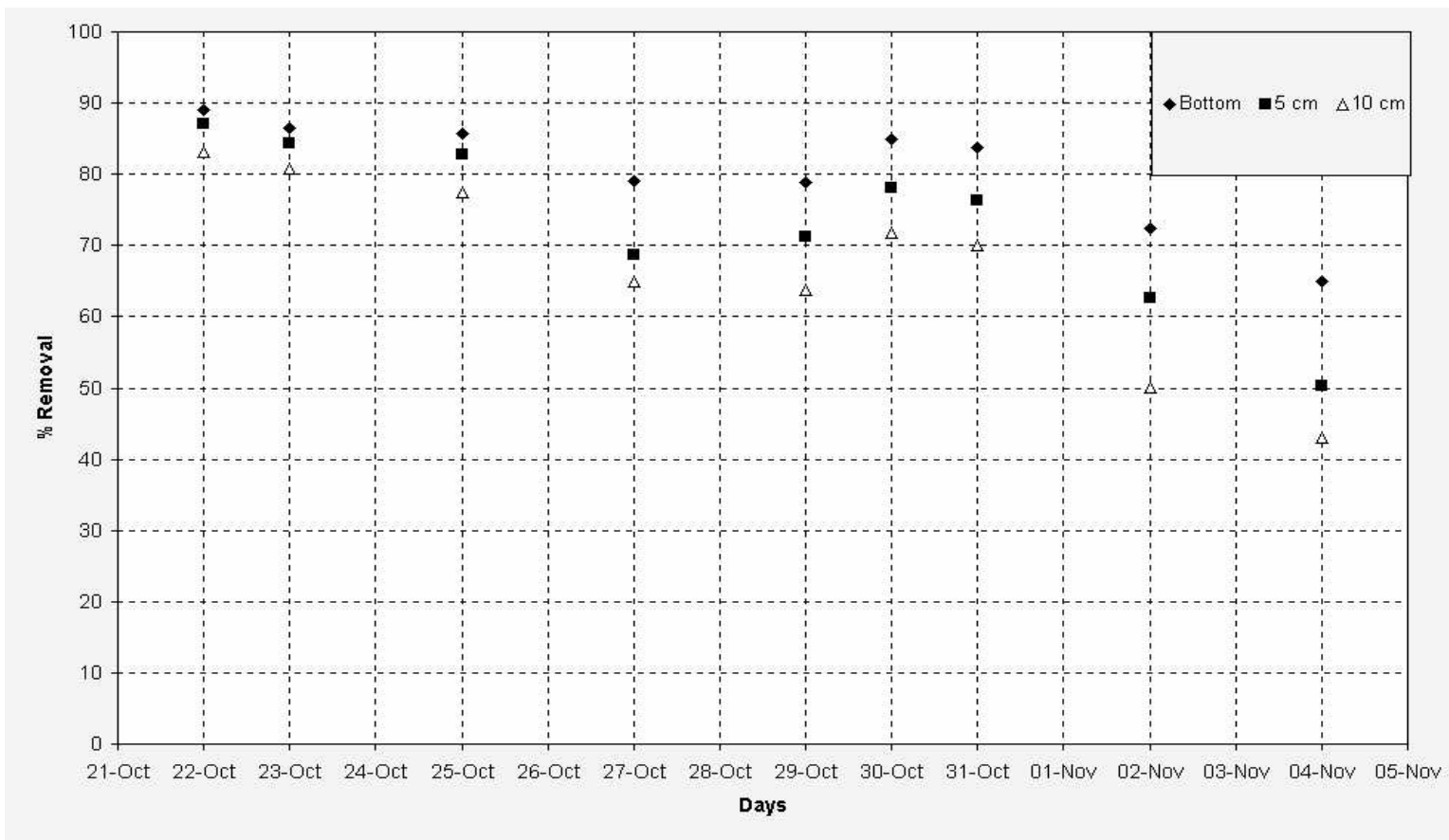Figure A.5: Percent Removal of TOC over Time for the 12-hr Acid Soaked Pits

Figure A.6: Percent Removal of TOC over Time for the Commercial Activated Carbon

VITA

- Omar Ghazy Omar Al-Attas.

- Born in Madinah, Saudi Arabia on April 21, 1978.

- Received Bachelor of Engineering degree with Highest Honors in Civil Engineering from King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia in May 2000.

- E-mail: alattas@kfupm.edu.sa