

**EGE UNIVERSITY GRADUATE SCHOOL OF APPLIED AND
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(MASTER OF SCIENCE THESIS)**

**2,4-DICHLOROPHENOXYACETIC ACID AND
BIOLOGICAL CONTAMINATION IN THE ADSORPTION
PHENOMENA**

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ÖZET**2,4-DİKLOROFENOKSİASETİK ASİT VE BİYOLOJİK
KİRLİLİK ORTAMINDA ADSORPSİYON**

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2,4- Diklorofenoksiasetik asit (2,4-D) fenoksi grubu kimyasalları arasında en çok kullanılan pestisitlerdir. Su içerisindeki pestisitlerin varlığı hem çevre hem de insan sağlığında ciddi sorunlara sebep olduğu için, bu maddelerin sulu çözeltilerden uzaklaştırılması gerekmektedir.

Avrupa Komisyonu'nun içme suyu kalitesi hakkında aldığı kararda (1998) maksimum izin verilebilir pestisit konsantrasyonu tek bir pestisit için 0,1 µg/L, toplam pestisit miktarı için 0,5 µg/L olarak belirlenmiştir.

Bu çalışmada, 2,4-D'nin sulu çözeltilerden uzaklaştırılmasıyla ilgili bilgi elde edebilmek için adsorpsiyon çalışmaları kesikli, sürekli olmak üzere iki farklı yöntemle gerçekleştirilmiştir. Adsorbent olarak tane aktif karbon kullanılmıştır.

Kesikli deneylerde, kinetik, izoterm/konsantrasyon ve biyolojik kirliliğin adsorpsiyona etkisi çalışmaları yapılmıştır. Biyolojik kirliliği olarak Gent Üniversitesi (Gent/Belçika) BCCMTM/LMG bakterisi koleksiyonundan "Acidovorax avenae subsp. Avenae LMG 17238" kullanılmıştır. Deneylerden elde edilen verilerle adsorpsiyon difüzyon basamakları, adsorpsiyon kinetik basamakları, adsorpsiyon modelleri

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(Freundlich ve Langmuir), biyolojik kirliliğin denge izotermine etkisi incelenmiştir. Bu çalışmaların ışığında kolon denemeleri yapılmıştır.

Sürekli deneylerde, 2,4-D'nin aktif karbon ile giderimi sabit yataklı adsorpsiyon kolonunda incelenmiş, 2,4-D adsorpsiyonuna başlangıç 2,4-D konsantrasyonunun, akış hızının, kolon yüksekliğinin ve biyolojik kirlilik yüklemesinin etkileri çalışılmıştır.

Sürekli çalışmalardan elde edilen verilerle deneysel verilerin sürekli modellere uygunluğu araştırılmıştır.

Aqualine aktif karbon ile etkin bir giderim sağlandığı kesikli ve sürekli deneylerle görülmüş ve biyolojik kirliliğin adsorpsiyon verimini düşürdüğü gözlenmiştir.

Anahtar Sözcükler: 2,4- Diklorofenoksiasetik asit (2,4-D), aktif karbon, adsorpsiyon ,biyolojik kirlilik

ABSTRACT

**2,4-DICHLOROPHENOXYACETIC ACID AND
BIOLOGICAL CONTAMINATION IN THE ADSORPTION
PHENOMENA**

ŞİRİN, Sema

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2,4-Dichlorophenoxyacetic acid (2,4-D) is one of the widely used pesticide in the phenoxy class of chemicals. Environmental pollution with 2,4-D may occur as a result of the production and disposal of 2,4-D, or of its by-products, and of industrial effluent. Since the presence of pesticides in water can cause serious problems in both the environment and human being, their removal from aqueous solutions is often required.

The European Commission directive on the Quality of Water Intended for Human consumption (1998) defines a Maximum Admissible Concentration of 0,1 µg/L for individual pesticides and of 0,5 µg/L for total of all pesticides present.

In this study, experiments were performed with two different methods for the removal of 2,4-D in batch and continuous mode. The granular activated carbon was used as adsorbent.

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In batch experiments, kinetics, isotherms and effect of biological contamination on adsorption were studied. The “*Acidovorax avenae* subsp. *Avenae* LMG 17238” bacteria was used as biological contaminant where it was purchased from BCCMTM/LMG bacteria collection at the Gent university (Gent/Belgium). According to the data obtained from the experiments; diffusion steps, kinetic orders of adsorption and the effect of biological contamination on equilibrium isotherm were investigated.

In continuous experiments, adsorption of 2,4-D on activated carbon is investigated by using fixed bed adsorption column. The experiments were carried out as a function of initial concentration of 2,4-D, flowrate, bed height and the effect of biological contamination load .

The experimental data were analyzed and the continuous mathematical models have been developed to predict the dynamic behaviour of the column.

In this study, it is obtained that aqualine activated carbon is a very effective adsorbent in the removal of 2,4-D and the efficiency of the adsorption decreases with the biological contamination.

Key words: 2,4-Dichlorophenoxyacetic acid (2,4-D), activated carbon, adsorption, biological contamination.

TEŞEKKÜR

Hayatım boyunca yanımda olan anneme ve kardeşime, tez çalışmam boyunca ümitsizliğe düştüğüm anlar başta olmak üzere bana katlandıkları ve yine de yanımda olan yegane insanlar oldukları için minnettarım. Onlar olmasa başaramazdım.

Değerli bilgi ve tecrübeleriyle çalışmalarına ışık tutan, yeni bir dünyaya adım atmamı ve deneylerim süresince bütün imkanları ile çalışmamı sağlayan, tez danışmanım sayın Prof. Dr. Bikem Övez'e; tüm sorularımı büyük bir sabırla cevaplayan, yardımlarını esirgemeyen, saygı duyduğum sayın Prof. Dr. Mesut Yenigül'e ve Prof. Dr. Mustafa Demircioğlu'na saygı ve şükranlarımı sunarım.

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NOMENCLATURE

b	: Langmuir adsorption constant (L mg^{-1})
C_b	: bulk concentration in the solution in the column (mg L^{-1})
C_o	: inlet (feed) or initial concentration (mg L^{-1})
C	: effluent concentration (mg L^{-1})
C_{ad}	: ($= C_o - C$) adsorbed concentration in the column (mg L^{-1})
C	: break outlet concentration at breakthrough (or limit effluent concentration) (mg L^{-1})
C_{eq}	: nonadsorbed concentration at equilibrium in the column (mg L^{-1})
C_s	: concentration at the solid/liquid interface in the column (mg L^{-1})
D, E	: axial diffusion or dispersion coefficient ($\text{cm}^2 \text{ min}^{-1}$)
k_{AB}	: kinetic constant in the Adams–Bohart model ($\text{L mg}^{-1} \text{ min}^{-1}$)
k_{Th}	: kinetic constant in the Thomas model ($\text{mL mg}^{-1} \text{ min}^{-1}$)
k_{YN}	: kinetic constant in the Yoon and Nelson model (L min^{-1})
K_F	: Freundlich adsorption constant [$(\text{mg g}^{-1})(\text{mg L}^{-1})^n$]
n	: Freundlich adsorption constant
N_o	: saturation concentration in the Adams–Bohart model (mg L^{-1})
m_{total}	: total amount of adsorbate sent to column (mg)
q	: concentration in the solid phase in the column at any time (mg L^{-1})
q_{eq}	: equilibrium uptake per g of adsorbent in the column or in the batch system (mg g^{-1})
q_{total}	: total adsorbed quantity of adsorbate in the column (mg)
q_o	: ($= q_{eq}$) constant in the Thomas model (mg g^{-1})
Q	: flow rate (ml min^{-1})
Q_o	: Langmuir constant (mg g^{-1})

r	: adsorption rate ($\text{mg L}^{-1} \text{ min}^{-1}$)
t	: flow time (min)
t_{break}	: time at breakthrough (min)
t_{total}	: total flow time (min)
U_o	: superficial velocity (cm min^{-1})
V_{eff}	: effluent volume (mL)
X	: amount of sorbent in the column (g) or sorbent concentration in the batch system (g L^{-1})
Z	: height of the column (cm)
β_a	: kinetic coefficient of the external mass transfer in the Wolborska model (min^{-1})
β_o	: axial dispersion coefficient in the Wolborska model (min^{-1})
ε	: void fraction in the bed
γ	: migration rate (cm min^{-1})
τ	: time required for 50% adsorbate breakthrough (min)

1. INTRODUCTION

Water is a basic need of life and is used in many ways to cater the needs of daily life. Supplied by a combination of surface water and underground water (groundwater) sources, drinking water can become contaminated at the original water source, during treatment, or during distribution to the home.

Indiscriminate use of pesticides in the modern agricultural practices leads to the contamination of soils, surface and ground waters. These contaminants arise predominantly from agricultural and industrial sources (Vroumsia et al., 1999).

Pesticides are among the major organic compounds encountered in wastewater effluents of pesticide industry and domestic activities. These compounds are commonly used in agriculture to protect crops from pest organisms. Since most pesticides are used in open environment such as ploughed fields, their residues have become one of the major diffuse pollution risks to the world drinking water supplies. Numerous cases of pesticide residue have been reported in the literature (Moore and Ramamoorthy, 1984). Their residual concentrations in the food products are alarming especially in the developing countries. Leafy vegetables, cereals, fruits, rice, meat, milk, fish intestine and edible portions and even human milk have been reported to be contaminated by various pesticides in a range of concentrations 0.1 mgL^{-1} - 25.7 mg L^{-1} .

The contamination of water of ponds, rivers and ground water sources with various pesticides and herbicides is posing a direct threat to human health. They are considered dangerous and harmful to living

systems because of their toxicity and carcinogenicity even at low concentrations (IARC, 1987).

Environmental regulations in developed countries have become very strict for drinking water treatment over the last few years, especially regarding pesticide compounds.

To protect consumers from the adverse effects associated with high contamination intake, the United States, Canada, the European Union (EU), and the World Health Organization (WHO) have set standards to regulate contamination in water. (Sayre, 1988; Deininger et al., 1998; Nalcaci et al., 2006).

The subject of pesticide contamination in water has reached a particularly problematic level as a consequence of the European Commission directive on the Quality of Water Intended for Human consumption (1980), which defines a maximum admissible concentration of 0,1 µg/L for individual pesticides and of 0,5 µg/L for total of all pesticides present. (Nalcaci et al., 2006).

The removal of pesticides from water is an extremely complex problem due to the wide range of pesticides chemical structures and properties, so various treatment techniques have been employed to treat the water including pesticides like ion exchange, reverse osmosis and adsorption etc. Nevertheless, adsorption processes using suitable adsorbent have shown high removal efficiency and many economical, ecological and technological advantages.

In water treatment, activated carbon is a powerful adsorbent because it has a large surface area and pore volume, which remove

liquid-phase contaminants, including organic compounds (like pesticides), heavy metal ions and colors. In order to design effective activated carbon adsorption units and to develop mathematical models that can accurately describe their operation, sufficient information on both the adsorption and the desorption of individual pollutants under different operating conditions is required (Khan et al., 1997)

For example Granular activated-carbon (GAC) filters have been used for 35 years to remove dissolved organic matter by adsorption. More recently, it has been shown that, in addition to adsorption of organic matter, GAC is also a good material for the development of attached bacteria. The colonization of GAC filters by bacteria has been observed in some industrial treatment plants by various techniques: scanning electron microscopy (Weber et al. 1978). Studies have shown that GAC columns continue to yield effective organic matter removal far beyond the point where adsorption capacity would normally be exhausted (Rittmann and Snoeyink 1984; McFeeters et al. 1987). Also addition to advantage of the microbiological removal of organic matter, biological GAC filters need no regeneration of the GAC.

1.1 Drinking Water

Drinking water is usually supplied by a combination of surface water and underground water (groundwater) sources. Surface water includes rivers, lakes, and reservoirs. Groundwater lies under the surface of the land, where it travels through and fills openings in rocks.

Drinking water can become contaminated at the original water source, during treatment, or during distribution to the home. If water

comes from surface water (river or lake), it can be exposed to acid rain, storm water runoff, pesticide runoff, and industrial waste. This water is cleansed somewhat by exposure to sunlight, aeration, and micro-organisms in the water. If water comes from groundwater (private wells and some public water supplies), it generally takes longer to become contaminated but the natural treatment process also may take much longer. Groundwater moves slowly and is not exposed to sunlight, aeration, or aerobic (requiring oxygen) micro-organisms. Groundwater can be contaminated by disease-producing pathogens, leachate from landfills and septic systems, careless disposal of hazardous household products, agricultural chemicals, and leaking underground storage tanks.

1.1.1 Drinking Water Standards

The WHO, set up the latest guidelines for drinking-water quality on 1993 which are the international reference point for standards setting and drinking-water safety.

The EU drew up the Council Directive 98/83/EC on the quality of water intended for human consumption by reviewing the parametric values of the old Drinking Water Directive of 1980. The EU standards are more recent (1998), complete and strict than the WHO standards (1993).

The United States (U.S.) Environmental Protection Agency (EPA) is required by Safe Drinking Water Act (1974) to determine safe levels of chemicals in drinking water which do or may cause health problems.

A comparison of standards of some contaminants in drinking water respect to WHO and EU are tabulated in Table 1.1.

Table 1.1 Comparison of standards of some contaminants in drinking water respect to WHO(1993) and EU (1998)

Contaminants	WHO standards(1993)	EU standards(1998)
Aluminium (Al)	0.2 mg/L	0.2 mg/L
Ammonia (NH₄)	No guideline	0.50 mg/L
Antimony (Sb)	0.005 mg/L	0.005 mg/L
Arsenic (As)	0.01 mg/L	0.01 mg/L
Barium (Ba)	0.3 mg/L	Not mentioned
Boron (B)	0.3 mg/L	1.00 mg/L
Bromate (Br)	Not mentioned	0.01 mg/L
Cadmium (Cd)	0.003 mg/L	0.005 mg/L
Chromium (Cr)	0.05 mg/L	0.05 mg/L
Copper (Cu)	2 mg/L	2.0 mg/L
Iron (Fe)	No guideline	0.2 mg/L
Lead (Pb)	0.01 mg/L	0.01 mg/L
Manganese (Mn)	0.5 mg/L	0.05 mg/L
Mercury (Hg)	0.001 mg/L	0.001 mg/L
Molibdenum (Mo)	0.07 mg/L	Not mentioned
Nickel (Ni)	0.02 mg/L	0.02 mg/L
Nitrogen (total N)	50 mg/L	Not mentioned
Selenium (Se)	0.01 mg/L	0.01 mg/L
Silver (Ag)	No guideline	Not mentioned
Sodium (Na)	200 mg/L	200 mg/L
Uranium (U)	1.4 mg/L	Not mentioned
Zinc (Zn)	3 mg/L	Not mentioned
Chloride (Cl)	250 mg/L	250 mg/L
Cyanide (CN)	0.07 mg/L	0.05 mg/L
Fluoride (F)	1.5 mg/L	1.5 mg/L
Sulfate (SO₄)	500 mg/L	250 mg/L
Nitrate (NO₃)	(See Nitrogen)	50 mg/L
Nitrite (NO₂)	(See Nitrogen)	0.50 mg/L
2,4-D	30 µg/L	0,1 µg/L for individual pesticides and of 0,5 µg/L for total of all pesticides present
MCPA	2 µg/L	
Simazine	2 µg/L	
2,4-DB	90 µg/L	
Dichlorprop	100 µg/L	
Fenoprop	9 µg/L	
Mecoprop	10 µg/L	
2,4,5-T	9 µg/L	

1.1.2 Pesticide Consumption

The agricultural area in the current 15 member states of the EU comprises over 130 million hectare. Almost 7 million farmholdings exist. By the sales data taken from Eurostat (the statistical agency of the European Union) and Oskam et al. (1997), the highest consumption of pesticides was in Italy, followed by the United Kingdom and the lowest consumption of pesticides was in Finland between 1993-2000 as seen in Table 1.2.

Table 1.2 Pesticide consumption In EU (Eurostat; Oskam et al., (1997))

Country	1993-1995 (kg/ha)	1996 (tons)	1997 (tons)	1998 (tons)	1999 (tons)	2000 (tons)
Belgium	1.2	4787	4715	4718	4724	4124
Denmark	1.7	2632	2685	3283	2915	-
Germany	2.6	15941	17790	15394	12696	14834
Greece	13.5	-	2252	2442	2579	-
France	5.6	-	-	27419	36052	-
Italy	9.3	24468	25848	25921	24913	24943
Austria	4.0	1873	1549	1607	1536	
UK	6.4	20885	22733	22753	24131	24118
Sweden	4.4	1097	1507	975	1235	
Finland	1.2	841	915	815	674	734

By the means of values, the pesticide consumption in Turkey is less than the EU countries. However, as known, pesticide consumption in Turkey is quite heterogeneous (Delen et al.,1995). Table 1.3 is an evidence for heterogeneity of the pesticide consumption in Turkey.

Between years 1979 and 2002, 45,29 % increase was observed in consumption of pesticide, although increase of world pesticide consumption seemed to be stand still trend.(Delen et al., 2004).

Table 1.3 Pesticide consumption in Turkey according to years (kg or L)
(Delen et al., 2004)

Pesticide Groups	1979	1987	1994	1996	2002
Insecticides	2.287.658	3.303.446	2.064.991	3.027.380	2.250.898
Acaricide	203.107	240.360	192.279	223.857	296.809
Lipids	1.594.526	2.147.106	2.147.106	2.871.160	2.428.238
Fumigant& Nematicides	315.665	322.227	530.738	1.076.661	1.559.489
Rodenticides &Molluscicides	5.600	2.124	2.509	3.268	1.794
Fungicides	1.537.315	2.611.960	2.201.406	2.951.191	1.964.292
Herbicides	2.451.977	3.495.044	3.902.588	3.643.971	3.697.397
TOTAL	8.395.848	12.112.267	10.871.792	13.797.488	12.198.917

Not only the pesticide consumption is quite heterogeneous in Turkey, and also consumption of regions is heterogeneous too. While consumption in Aegean and Mediterranean regions had more than 33,3%, consumption in Eastern Anatolia and South Eastern Anatolia regions was 10% of country consumption according to Delen et al.(2004).

Amount of widely used pesticides in Izmir between 2000-2004, is given in Table 1.4. It is seen that 2,4-dichlorophenoxyacetic acid (2,4-D) which involved approximately 20% of total consumption between 2000-2004 is the second more common used pesticide after Trifluralin, an anilin group herbicide.

Table 1.4 Most used herbicides in Izmir during 2000-2004 (kg) (Izmir Agriculture Management, Plant Protection Department 2004)

Herbicide	Herbicide Group	2000	2001	2002	2003	2004	%
2,4-D	Phenoxy Herbicide	25.340	17.801	13.281	14.752	24.632	17.41
Trifluralin	Anilin	26.280	32.875	30.382	113.073	122.740	59.12
Glyhposate isopropylam in	Aminophosphonates	12.852	15.814	28.942	27.656	34.163	21.70
Metalochlor	Amides and Anilides	3.100	1.543	515	500	4.090	1.77
TOTAL		67.572	68.033	73.120	155.981	185.625	100

1.1.3 Pesticide Regulations

The WHO guidelines for drinking-water quality on 1993 set standart for pesticides from 0.03 µg/L to 100 µg/L. This levels are detected by cause any of the potential health problems. For example, the level for 2,4-D is set to be 30 µg/L.

In the EU Drinking Water Directive (1998), the values for individual pesticides and for total pesticides were retained 0.1µg/L and 0.5µg/L respectively, and more stringent values were introduced for certain pesticides 0.03µg/L.

EPA National Primary Drinking Water Regulations set some non-enforceable levels, based solely on possible health risks and exposure, are called Maximum Contaminant Level Goals (MCLG). The directory of MCLG values of contaminants are tabulated in EPA Drinking Water

Regulation sheets on web pages. For example , the MCLG for 2,4-D has been set at 70 parts per billion (ppb) because this level of protection would not cause any of the potential health problems. Based on MCLG, EPA has set an enforceable standard called a Maximum Contaminant Level (MCL). MCLs are set as close to the MCLGs as possible, considering the ability of public water systems to detect and remove contaminants using suitable treatment technologies. The MCL has been set at 70 ppb for 2,4-D because given present technology and resources, this is the lowest level to which water systems can reasonably be required to remove this contaminant should it occur in drinking water.

1.2 Pesticide

A pesticide may be a chemical substance or biological agent (such as a virus or bacteria) used against pests including insects, plant pathogens, weeds, mollusks, birds, mammals, fish, nematodes and microbes that compete with humans for food, destroy property, spread disease or are a nuisance. Pesticides are usually, but not always, poisonous to humans (WHO, 1985).

By the way, pesticides are chemicals used to control unwanted organisms such as weeds and pesticides can be derived from plants (e.g., pyrethrin, neem) or minerals, or they can be chemically manufactured (e.g., DDT, 2,4-D).

There are basically two ways properly applied pesticides may reach surface and ground waters through runoff and leaching (Figure 1.1). Runoff is the physical transport of pollutants over the ground surface by rainwater that does not penetrate the soil. Leaching is a process whereby

pollutants are flushed through the soil by rain or irrigation water as it moves downward (Ka et al., 1994).

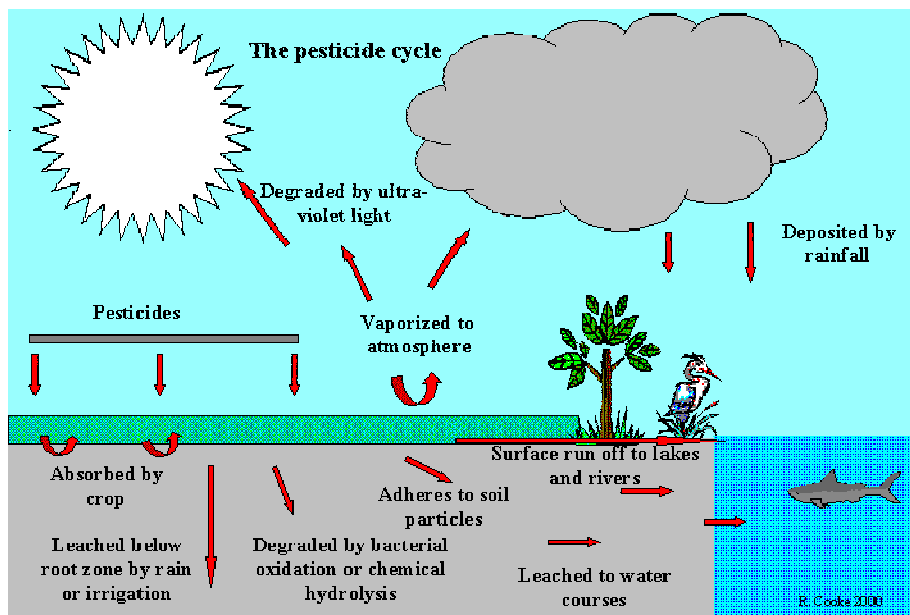


Figure 1.1 Figure of the pesticide cycle

Pesticides are referred to according to the type of pest they control. Types of pesticides and the target affect of those pesticide types are in Table 1.5.

Table 1.5 Types of pesticides

Bactericides	For the control of bacteria
Herbicides	For the control of weeds
Fungicides	For the control of fungi
Insecticides	For the control of insects
Miticides	For the control of mites
Nematicides	For the control of worms
Rodenticides	For the control of rodents
Virucides	For the control of viruses

1.2.1 Herbicide

Herbicide is a chemical compound that kills plants or inhibits their normal growth. A herbicide in a particular formulation and application can be described as selective or nonselective.

In agriculture, selective herbicides are often used instead of tillage, or in combination with tillage and other agronomic practices, to control weeds without damaging crops. For these no-till or low-till systems, scientists are using biotechnology to develop crop varieties with increased tolerance for herbicides. Nonselective herbicides (e.g., paraquat) toxic to all plants are used where complete control of plant growth is required.

Contact herbicides kill only the parts of the plant they touch; systemic herbicides are absorbed by foliage or roots and translocated to other parts of the plant. Premergence herbicides, mixed into the soil, will

kill germinating seeds and small seedlings. Postemergence herbicides either hinder photosynthesis or inhibit growth.

For a translocated herbicide to have a potentially lethal effect on a plant: (1) the herbicide must penetrate or be absorbed into the plant, (2) it must move through the plant, generally in the phloem, and (3) it must have a toxic reaction with the cells and tissues of the plant (Leonard and Crafts, 1956; Butts and Fang, 1956).

Herbicides vary widely. Some are water soluble enough to enter lakes or streams with rainfall or runoff irrigation water, but the hazard they represent depends on their persistence and interaction with the soil. They can also leach into ground water or move with eroding soil.

Many herbicides designed to be applied to emerge plants are inactivated once they reach the soil surface. Soil-applied herbicides, however, must be soluble in soil water in order to move into the root zones of target weeds. Some move deeply into the ground to kill deep-rooted perennials. Others don't move as deeply in order to kill shallow-rooted weeds and spare a deeper rooted crop.

Early chemical herbicides were inorganic compounds. Organic herbicides began to be produced in earnest with dinitrophenol compounds in 1932. A breakthrough occurred in the 1940s with 2,4-D (2,4-dichlorophenoxyacetic acid), a compound similar to plant hormones, which is a highly selective systemic herbicide when used in very small quantities. The phenoxyaliphatic acids and their derivatives, another major group of organic herbicides, succeeded because of their selectivity and ease of translocation.

1.2.2 Phenoxyalkanoic Acid Herbicides

Phenoxyalkanoic acid herbicides are widely used in agriculture to control the growth of broad-leaf weeds in crops (Figure 1.2). They are also used in lakes, ponds, and ditches for aquatic weed control (Smith, 1989; Smith et al. 1994). These compounds are considered potential pollutants owing to their high soil mobility, long halflives and large scale of application. Due to their persistence, polar nature and water solubility, they are present in several environmental compartments including water, soil, cereals and vegetables. Hence, there is increasing interest in methods for the determination of phenoxyalkanoic acid herbicide residues as well as their phenolic metabolites in natural samples (Biesaga et al. , 2005).

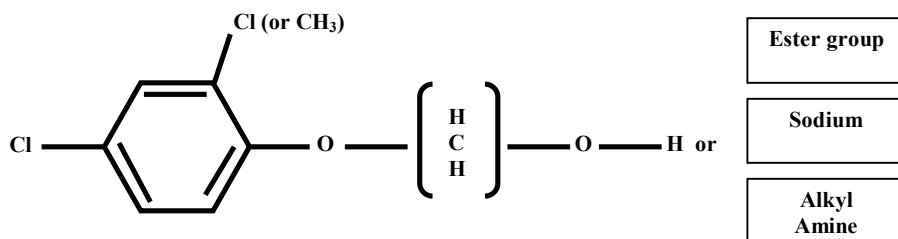


Figure 1.2 The general chemical structure of phenoxyalkanoic acid herbicides

One of the class of phenoxy herbicides includes; (1) the phenoxyacetic acids 2-methyl-4-chlorophenoxyacetic acid (**MCPA**), 2,4-dichlorophenoxyacetic acid (**2,4-D**), 2,4,5 trichlorophenoxyacetic acid (**2,4,5-T**); (2) the phenoxypropionic acids 2-(4-chloro-2 methylphenoxy)-propionic acid (**MCP**), 2-(2,4-dichlorophenoxy)propionic acid (**2,4-DP**), 2-(2,4,5-trichlorophenoxy) propionic acid (**2,4,5-TP**); (3) the

phenoxybutyric acids 4-(4-chloro-2-methylphenoxy)butanoic acid (MCPB) and 4-(2,4-dichlorophenoxy)butyric acid (**2,4-DB**) (Figure 1.3).

These herbicides are known as synthetic auxins and bring to cellular proliferation of components of the plants, which is rapid and out of control and causes their death. The phenoxy herbicides have low to moderate toxicity toward humans and animals. Some of them, such as 2,4-D and 2,4,5-T, have been extensively studied; however, their mechanism of action towards non-target organisms is not fully elucidated yet. (Zychlinski and Zolnierowicz, 1990; Suwalsky et al., 1996; Palmeira et al., 1994).

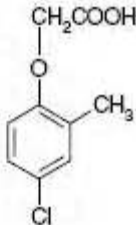
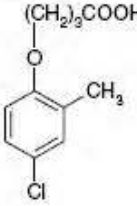
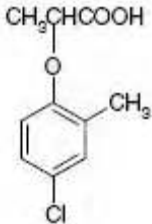
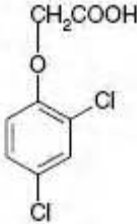
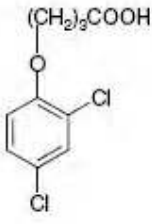
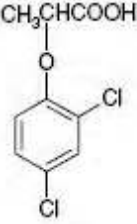
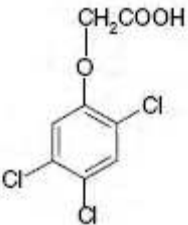
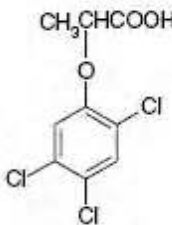
MCPA 	MCPB 
MCPP 	2,4-D 
2,4-DB 	2,4-DP 
2,4,5-T 	2,4,5-TP 

Fig 1.3 Names and structural formulas of the some phenoxyalkonic acid herbicides (Argese et al, 2005)

1.2.3 Chemical Characteristics of 2,4-dichlorophenoxyacetic Acid

The basic form of 2, 4-D is 2,4-dichlorophenoxyacetic acid (CAS 94-75-7) but is often formulated as an inorganic salt, amine or ester. (WHO, 1984).

The Chemical characteristics of 2, 4-D are given in Table 1.6.

Table 1.6 Chemical characteristics of 2, 4-D

Molecular weight	221.04
Melting point	135-142°C
Boiling point (at 4 mmHg)	160°C
Water solubility (average of 2 values near 25°C at pH=7)	3.39×10^4 ppm
Vapor pressure(at 25°C)	1.4×10^{-7} mmHg
Hydrolysis half-life (average of two values at 25°C, pH=7)	39 days
Aqueous photolysis half-life(at 25°C)	13.0 days
Anaerobic aquatic half-life	312 days
Aqueous aerobic half –life	15.0 days
Aerobic half-life	66.0 days
Soil photolysis half-life	393 days
Field dissipation half-life	59.3 days
Henry's constant	1.76×10^{-12}
Octanol-water coefficient (Kow)	$(9.15- 6.74) \times 10^2$
Soil adsorption coefficient (Koc) (data for four soil types)	$(0.067-1.1) \text{cm}^3/\text{g}$

1.2.4 Synthesis of 2, 4-dichlorophenoxyacetic Acid

2,4-D is commonly prepared by the condensation of 2,4-dichlorophenol with monochloroacetic acid in a strongly alkaline medium at moderate temperatures. The synthesis of Dow 2,4-dichlorophenoxyacetic acid is shown in Figure 1.4.

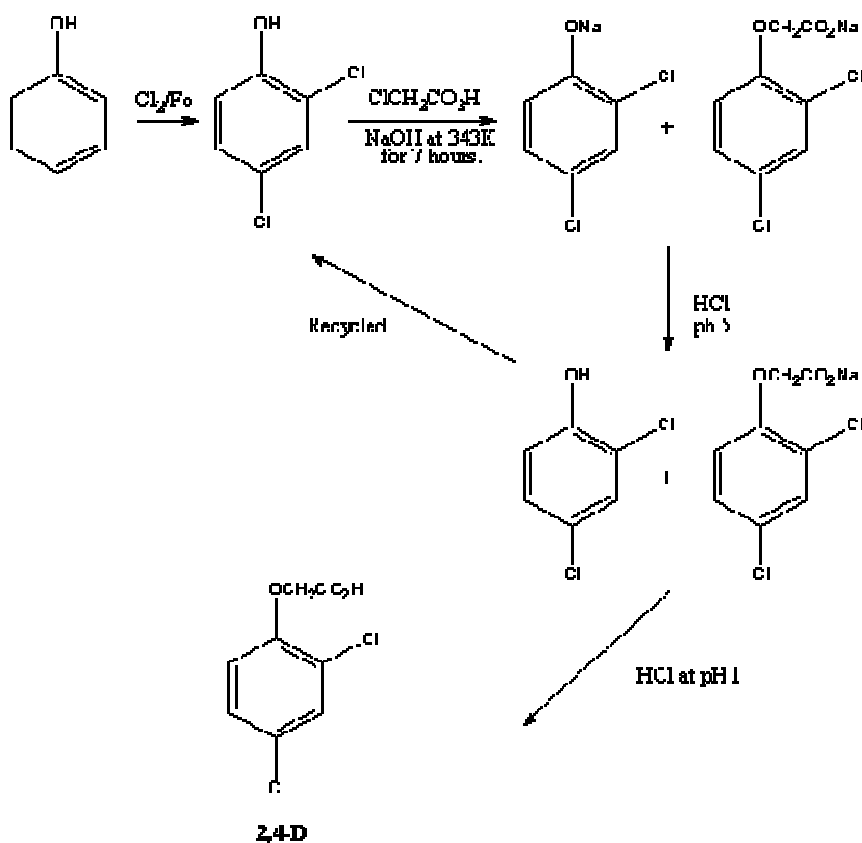


Figure 1.4 Synthesis of Dow 2,4-dichlorophenoxyacetic acid

1.2.5 Formulations of 2,4-dichlorophenoxyacetic Acid and Related Compounds

2,4-D and many of the related compounds are available in a number of formulations, which differ in cost, effectiveness and application requirements. The various formulations include the acid, simple salts, amine salts and esters, all of which are created by the substitution or addition of other atoms or molecules for the hydrogen of the carboxyl group. Organic structures of representative salts, amines, and esters are shown in Figure 1.5 with formulations and molecular weights. Table 1.7 shows available data concerning identification of the salts, amines, esters.

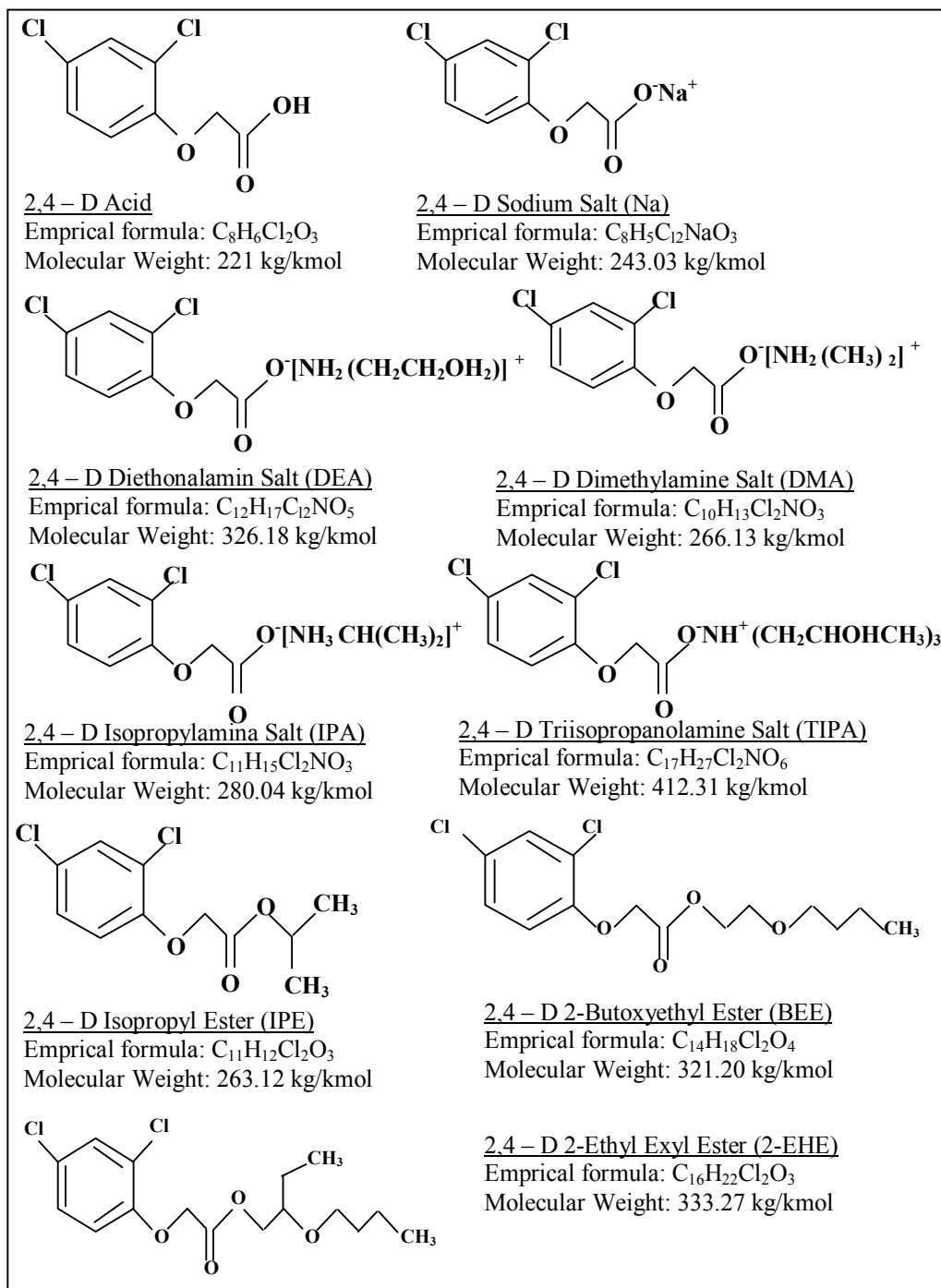


Fig 1.5. Chemical structures for supported forms of 2,4-D

Table 1.7 Available data concerning identification of the active ingredient

Active Ingredient	Color	Physical State	Melting/Boiling Point	Density Speci. Gravity	Vapor, Pressure	Solubility
2,4 – D acid	White	Crystalline solid	m.p. 138-141°C	sg = 1.416 at 25 °C	$1.4 \cdot 10^{-7}$ mmHg at 25°C	Water = 569 mg/l at 20°C
2,4 – D Na salt	White	Powder	m.p. 200 °C	bulk: 42.2 lb/ft ³ at 25°C	-	Water = 4.5 g/100ml at 20°C
2,4 – D DEA salt	Cream	Powder	m.p. 83 °C	bulk: 0.762 g/cm ³ at 25°C	$< 1.33 \cdot 10^{-5}$ Pa at 25°C	Water = 806 mg/g at 20°C
2,4 – D DMA salt	Amber	Aqueous liquid	m.p. 118-120 °C	sg = 1.29 at 20 °C	$< 1 \cdot 10^{-7}$ mmHg at 26°C	Water = 72.9g/100ml at 20°C (pH:5.3)
2,4 – D IPA salt	Amber	Aqueous liquid	m.p. 121°C	sg = 1.15 at 20 °C	-	Water = 17.4 g/100ml at 20°C (pH:5.3)
2,4 – D TIPA salt	Amber	Aqueous liquid	m.p. 87-110 °C	sg = 1.21 at 20 °C	-	Water = 46.1 g/100ml at 20°C (pH:7)
2,4 – D BEE	Dark amber	Liquid	m.p. 89 °C	sg = 1.225 at 20 °C	$2.4 \cdot 10^{-6}$ mmHg at 25°C	Water = insoluble g/100ml at 20°C
2,4 – D IPE	Pale amber	Liquid	m.p. 240°C	sg = 1.252 at 25 °C	$5.3 \cdot 10^{-6}$ mber	Water = 0.023 g/100ml

1.2.6 Mode of Action of 2,4-dichlorophenoxyacetic Acid

2,4-D is auxin or growth regulator which in some ways act like plant hormones but they disrupt the normal cell and plant life processes . This type of herbicide kills the target weed by mimicking the plant growth hormone auxin (indole acetic acid), and when administered at effective doses, causes uncontrolled and disorganized plant growth that leads to plant death. The exact mode of action of 2,4-D is not fully understood and it is possible that it causes a variety of effects which are fatal when combined. It is believed to acidify the cell walls which allows the cells to elongate in an uncontrolled manner.

There are many obstacles or variables affecting the performance of a translocated herbicide. Freed (1961), has estimated that less than 40 percent of the applied chemical finds its way into the plant to become effective.

Shaw and Centner (1957) graphically illustrated some of these obstacles in the following diagram (Figure 1.6).

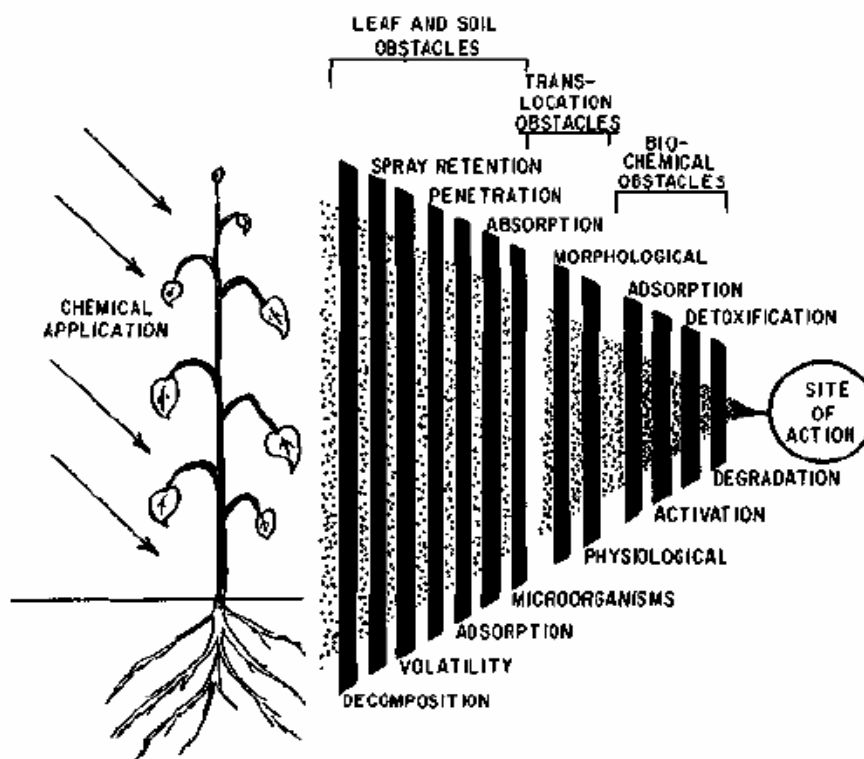


Figure 1.6 Obstacles which determine the concentration of toxic material at the site of action (Shaw and Centner, 1957)

1.2.7 Behavior of 2,4-dichlorophenoxyacetic Acid in the Environment

The WHO (1984) concluded that 2,4-D does not accumulate or persist in the environment. The fate of 2,4-D in the environment is largely dependent on the ambient pH (Aly & Faust, 1964). At pH levels above 7, 2,4-D is converted rapidly to the anion (negatively charged) form, which is more susceptible to photodegradation and microbial

metabolism, and less likely to adsorb to soil particles. At pH levels < 4 , microbial degradation is inhibited and 2,4-D retains its molecular form and resists degradation (Johnson et al., 1995a). The primary degradation mechanism is microbial metabolism, but mineralization and possibly photolysis may also play a role. 2,4-D degrades rapidly in sunlight under laboratory conditions, but photodegradation has not been demonstrated in the field. The average half-life (the time it takes for the herbicide concentration to decline by 50%) is 10 days, but rates of degradation can vary from several hours to several months or longer. Degradation rates are determined by the microbial population, environmental pH, soil moisture and temperature (Sandmann et al., 1988). The type of 2,4-D formulation applied does not significantly affect the rate of degradation (Wilson et al., 1997). 2,4-D does not readily undergo chemical degradation, relative to other herbicides (Que Hee and Sutherland, 1981).

1.2.7.1 Behavior in Soil

2,4-D may be applied in acid, salt, or ester formulations, but in most cases, each of these formulations are apparently converted rapidly to the acid form once it contacts soil. Consequently, the rate of dissipation from soils is often the same regardless of the formulation of 2,4-D that is applied.

Half-lives are short, ranging from a few days to several months but detectable residues can persist for up to a year.

Degradation is almost entirely through microbial metabolism. Soil conditions that maximize microbial populations (i.e. warm and moist with a high organic content) maximize degradation rates. Wilson et al. (1997) found that adequate soil moisture was the most influential

parameter affecting degradation rates. Johnson et al. (1995b) found that plants do not play a significant role in eliminating 2,4-D from soils.

Most formulations of 2,4-D do not bind tightly with soils and therefore, have the potential to leach down into the soil column and to move off-site in surface or subsurface water flows. In many cases, extensive leaching does not occur, most likely because of the rapid degradation of the herbicide (Que Hee and Sutherland, 1981). Where 2,4-D does leach, however, it will be more persistent because populations of microbes responsible for the degradation of 2,4-D tends to decrease with soil depth (Wilson et al., 1997).

2,4-D can also be lost from soils through volatilization. Volatilization rates are determined by the temperature and molecular form of the herbicide at the surface of the soil, which, in turn, is determined primarily by the soil's pH.

Johnson et al. (1995a) found that soil organic content and soil pH are the main determinants of 2,4-D adsorption in soils. As the herbicide concentration increases, the percentage of herbicide adsorbed decreases, possibly because the number of binding sites on soil particles are finite and become filled. Inorganic clays can also bind 2,4-D particles. A relatively high concentration of clay particles however, is required to bind small concentrations of 2,4-D (Aly and Faust, 1964).

1.2.7.2 Behavior in Water

2,4-D will change form and function with changes in water pH (Que Hee & Sutherland, 1981). In alkaline (high pH; $\text{pH} > 7$) waters, 2,4-D takes an ionized (negatively charged) form that is water-soluble and remains in the water column. Theoretically, in water of a lower pH, 2,4-D will remain in a neutral molecular form, increasing its potential for adsorption to organic particles in water and increasing its persistence (Wang et al., 1994a). 2,4-D is most likely to adsorb to suspended particles in muddy waters with a fine silt load, but little adsorption has been observed in the field

Degradation mechanisms are difficult to isolate in the field. Aly & Faust (1964) concluded that, in sediments with sufficient microbial populations, 2,4-D can be degraded in a matter of hours and it was unlikely that sufficient amount of ultraviolet radiation would reach the surface of natural waters to degrade 2,4-D.

Que Hee and Sutherland (1981) reported that concentrations of most 2,4-D residues found in lakes and streams are < 1 ppm, although concentrations of up to 61 ppm have been reported immediately following direct application to water bodies. These concentrations are well above the 0.1 ppm established as “permissible” levels for potable water by the E.P.A. (EPA, 1998).

1.2.8 Environmental Toxicity of 2,4-dichlorophenoxyacetic Acid

The lethal potential of a chemical is usually measured as the dose (mg/kg body weight), or as the concentration in the air, diet or water

(mg/kg, mg/m³, mg/litre, respectively). These amounts are referred to as the LD₅₀ or LC₅₀.

The LD₅₀ value indicates the lethal dose of an active ingredient which is expected to cause death to 50% of the test animals treated. The higher the LD₅₀ the lower the acute toxicity of the compound. The LD₅₀ is one way to measure the short-term poisoning potential (acute toxicity) of a material.

The LC₅₀ value indicates the lethal concentration of an active ingredient which is expected to cause death to 50% of the test animals treated. The higher the LC₅₀ the lower the acute toxicity of the compound.

Toxicity on Birds and Mammals

2,4-D is considered of moderate toxicity to animals, although LD₅₀ levels vary significantly between formulations and animal species. The majority of LD₅₀ values range between 300-1,000 mg/kg. For example, the LD₅₀ for 2,4-D acid in rats and bobwhite quail is 764 mg/kg and 500 mg/kg, respectively. Some animals such as dogs, however, are significantly more sensitive to 2,4-D organic acids than are rats and humans (Ibrahim et al., 1991).

2,4-D can bio-accumulate in animals. In Russia, residues of more than ten times the allowable level were found in eggs, milk, and meat products served by public caterers and one study reported residues in 46% of tested cattle (Que Hee & Sutherland, 1981). Risk to browsing wildlife, however, is low, it is analyzed 2,4-D residues in forest browse

following aerial application to forests in Oregon and found them to be below the concentrations known to cause effects in mammals.

Toxicity on Aquatic Species

LC₅₀ levels for bluegill sunfish and rainbow trout are 263 and 377 mg/L, respectively. Wang et al. (1994b) studied bioaccumulation of 2,4-D in carp and tilapia and found that accumulation of up to 18 times the ambient concentration occurred within two days of exposure. 2,4-D was found in oysters and clams in concentrations up to 3.8 ppm, and it persisted for up to two months (Thomas & Duffy, 1968). The highest concentrations of 2,4-D were generally reached shortly after application, and dissipated within three weeks following exposure.

2,4-D can accumulate in fish exposed to concentrations as low as 0.05 ppm (Wang et al 1994b) and concentrations of 1.5 ppm can kill the eggs of fathead minnows in 48 hours (Thomas & Duffy, 1968). After animals are removed from contaminated waters, they tend to excrete residues.

Toxicity on Other Non-Target Organisms

It is found that honey-bees directly sprayed with 2,4-D showed no injury and no residues were found in the bees or their honey (cited in Que Hee & Sutherland, 1981). These results, however, are questionable as the LD₅₀ for honey-bees is only 1 µg/bee (WSSA, 1994).

1.2.9 Human Toxicology of 2,4-dichlorophenoxyacetic Acid

2,4-D can be absorbed through the skin or through the lungs if inhaled. It is reported airborne residues of 1-35 micrograms/cubic meter of air when 2,4-D was applied using hand-held spray guns along power line right-of-ways. These workers later excreted <0.01-30 mg/kg of body weight in their urine. Absorption through the skin accounts for 90% of the 2,4-D absorbed by applicators.

Once in the body, 2,4-D is distributed rapidly with the greatest concentrations appearing in the kidneys and liver. The majority of the compound is excreted unmetabolized. Due to its solubility in water, 2,4-D is not believed to accumulate in tissues, but is excreted in the urine in less than a week (Ibrahim et al., 1991). Nevertheless, some agricultural workers and other applicators have experienced long term complications including pain, paresthesias (tingling or numbness), and paralysis following exposure to 2,4-D.

Accidental inhalation resulted in one reported case of acute poisoning. Symptoms included brief loss of consciousness, urinary incontinence, vomiting, muscular hypertonia (an abnormal increase in skeletal or smooth muscle tone), fever, headache and constipation. Workers that entered an area shortly after treatment with 2,4-D experienced weakness, headache, dizziness, stomach pains, nausea, brief loss of consciousness, and moderate leukopenia (an abnormal reduction in the number of white blood cells, often reducing immune system function) (Stevens & Sumner, 1991).

In 1991, the case-control studies showed evidence of a relationship between 2,4-D exposure and non-Hodgkins lymphoma in humans, with some studies showing an increased risk with increased exposure level.

In another study of human exposure, female applicators were found to have a significant increase in cervical cancer associated with 2,4-D application. Due to the many confounding factors that make identification of cause and effect mechanisms difficult, other expert review panels including the EPA, Agriculture and Agri-food Canada, and the World Health Organization concluded that 2,4-D alone is not carcinogenic (Mullison and Bond, 1991).

1.3 Water Treatment Techniques

It is well known fact that clean water is absolutely essential for healthy living. Exactly why a clean and reliable water supply was needed was not known until the second half of the nineteenth century, when the nature of infectious disease was first recognised and the ability of water supplies to transmit diseases such as cholera and typhoid was first demonstrated. After this, concerns about the quality of drinking water focused on disease-causing microorganisms (pathogens) in public water supplies.

Scientists discovered that contaminations in the water that could also indicate a health risk. As a result, drinking water treatment systems were designed to reduce this contaminations, for example removing pathogens that were causing typhoid, dysentery and cholera, or pesticides that were causing cancerogenic effects.

The choice of which treatment methods to use from the great variety of available processes depends on the characteristics of the water, the types of water quality problems likely to be present and the costs of different treatments.

Precipitation, coagulation, sedimentation and flocculation are very effective at removing fine suspended particles. They can remove up to 99.9 percent of the bacteria and 99 percent of the viruses from water supplies. They also remove some of the organic matter that gathers as water travels across the landscape, from raindrop to river.

Ion exchange units can be used to remove any charged (ionic) substance from water, in other words; ions from dilute solutions are exchanged with ions held by electrostatic forces on the exchange resin. Water is pretreated to reduce the suspended solids and total dissolved solids (TDS) load to the ion-exchange unit.

Reverse osmosis is one option for drinking water treatment problems which is an effective method to reduce certain ions and metals, such as nitrate and arsenic. It also can remove certain pesticides, organic and inorganic compounds, though it is not effective for others.

Adsorption occupies an important position among the unit operations in water and wastewater treatment. Adsorption operations exploit the ability of certain solids preferentially to concentrate specific substances from solution onto their surfaces.

The treatment techniques that are used in removal of 2,4-D from water is tabulated with working principles, advantages and disadvantages in Table 1.8.

The comparison of treatment of water by adsorption (potential adsorbents to remove various contaminants such as color, heavy metals, COD, pesticides etc.) is tabulated in Table 1.9.

Table 1.8 Comparison of water treatment techniques that are used in removal of 2,4-D from water

Water Treatment Technique	Advantages & Disadvantages	References
Precipitation	Advantage: *Greater removal efficiency, the feasibility of using higher overflow rates, and more consistent performance. Disadvantages: *Coagulation results in a larger mass of primary sludge that is often more difficult to thicken and dewater. *Entails higher operational costs.	Porras and Talens, 1999 Porras and Talens, 2000
Ion Exchange	Advantages: * In process, like reverse osmosis, can be used with fluctuating flow rates. *Effluent contamination is virtually impossible. *Large variety of specific resins are available from suppliers. Each resin is effective in removing specific contaminants. Disadvantages: *Ion exchange waste is highly concentrated and requires careful disposal. *Potential for unacceptable levels (peaks) of contamination in effluent. *Usually not feasible with high levels of TDS. *Pretreatment required for most surface waters. * Ion exchange units also are sensitive to the presence of competing ions	Kwan and Chu, 2006 Legrouri et al., 2005 Qui et al., 2006
Reverse Osmosis	Advantages: *Removes nearly all contaminant ions and most dissolved non-ions. *Relatively insensitive to flow and TDS level, and thus suitable for small systems with a high degree of seasonal fluctuation in water demand. *RO operates immediately, without any minimum break-in period.	Edwards and Schubert, 1974

	* Low effluent concentration possible. * Bacteria and particles are also removed. • Operational simplicity and automation allow for less operator attention and make RO suitable for small system applications. Disadvantages: *High capital and operating costs. (but less expensive than ion exchange) *Managing the wastewater (brine solution) is a potential problem. *High level of pretreatment is required in some cases. *Membranes are prone to fouling.	Hofman et al., 1997
Adsorption	Advantages: *Low cost (in most biosorbents) *High efficiency Disadvantage: *Possibility of regeneration of adsorbent	Aksu and Kabasakal, 2004 Kim et al., 2002 Goyne et al., 2004

Table 1.9 Comparision of treatment of water by adsorption (potential adsorbents to remove various contaminants such as color, heavy metals, COD, pesticides etc.)

Adsorbent	Adsorbate	Parameter Investigated	Conclusion	References
PAC	Distillery Spent wash	*Initial conc. *Adsorbent dosage	Removal of 18% is noted and when spent was pretreated with polyelectrolyte as a flocculating agent, the color removal was increased up to 99%.	Sekar and Murthy, 1998
PAC	Synthetic dye wastewater of Disperse-red-60	*Effect of contact time *Concentration of PAC.	95-98% of COD removal for 25-200 ppm & 88-98% for various particle sizes. Freundlich, Langmuir, Dziubek & Kowals adsorption isotherms fit well. Film-pore double resistance diffusion model describes the mass transfer. External film mass transfer coefficient increases with decrease in particle size.	Yeh and Thomas, 1995
PAC Activated alumina Molecular Sieves Diatomite	Disperse-red-60	*Contact time *Adsorbent Dosage *Particle size	Decrease in particle size gave only a minor improvement for activated alumina, finer molecular sieve materials reduce the dosage requirement by half. Performance of adsorbents are as PAC> Activated alumina> molecular sieve.	Yeh and Adrian Thomas, 1995
GAC [Industrial grade; Laboratory grade]	Catechol	*Initial Concentration *pH *Adsorbent dosage *Particle Size	Equilibrium studies showed that IGGAC has the maximum adsorption capacity. Diffusion studies showed that initial part of the adsorption is attributed to external mass transfer effects followed by intraparticle diffusion.	Mahesh et al., 1998
Fly ash	Copper (Synthetic)	*Initial conc. *pH *Adsorbent dosage	Maximum efficiency was at the pH of 6.0. The fly ash treatement raises the pH of effluent.	Kapadia et al., 2000

GAC	Nitro phenol	*Bed depths *Flow rates	The experimental half lives are very close to predicted by self-sharpening wave approach and proportional to bed depth-flow rate ratio. Experimental and predicted breakthrough curves are in good agreement.	Chern and Chien, 2002
Lignite	Cr (IV)	*Adsorbent dosage	Kinetic showed the applicability of Lagergren model. The data tend to follow first order rate kinetics.	Balasubramaniam et al., 1998
Blast furnace dust Slag	Raw Paper mill effluent	*Initial COD conc. * pH *Temperature *Adsorbent dosage.	COD removal efficiency of BFD is significantly better than Basic slag.	Das and Patnaik, 2001
PAC	2,4-D	*pH *Temperature *Initial concentration *Capacity vs Kinetics	The max. adsorption capacity occurs at pH=2; adsorption increased with increasing conc., and decreased with increasing temp. up to 45 °C.	Aksu and Kabasakal, 2005
GAC	2,4-D CPA 2,4-DNP	*pH *Kinetics	Adsorption equilibrium capacities of herbicides on GAC increased with decreasing of pH.	Kim et al., 2005
GAC	2,4-D 2,4 DNP	*Type of adsorbent *Capacity vs Kinetics *pH *Temperature	Adsorption capacities of adsorbents; decreased with increasing pH and temperature.	Kim et al., 2002
Fly Ash [Coal]	Petrochemical Effluent (Raw)	*Initial Concentration *Adsorbent dosage *Contact time	Adsorption dose of 3-3.5% shows significant color removal. Contact period of 30-40 minutes gives optimum removal.	Kapadia et al., 2000
PAC, GAC, Carbon soot, Fly ash	Petrochemical Effluent (Raw)	*Bed Height * Particle size.	Batch studies show that flyash also reduces suspended solids, ammoniacal nitrogen, COD, and nitrophenol apart from color. Efficiencies of adsorbents in decreasing order PAC>Carbon soot>GAC> Flyash.	Kapadia et al., 2001

1.4 Adsorption Theory

Adsorption is a surface phenomenon that is defined as the increase in concentration of a particular component at the surface or interface between two phases. In any solid or liquid, atoms at the surface are subject to unbalanced forces of attraction normal to the surface plane. These forces are merely extensions of the forcing acting within the body of the material and are ultimately responsible for the phenomenon of adsorption. In discussing the fundamentals of adsorption, it is useful to distinguish between *physical* adsorption, involving only relatively weak intermolecular forces, and *chemisorption*, which involves essentially the formation of a chemical bond between the sorbate molecule and the surface of the adsorbent. Kumar et al.(2004) were summarized the physical and chemical adsorption characteristics (Table 1.10). Although this distinction is conceptually useful, many cases are intermediate and it is not always possible to categorize a particular system unequivocally (Aly and Faust, 1987).

Table 1.10 Typical characteristics of adsorption processes (Kumar et al., 2004)

Characteristics	Physical Adsorption	Chemical Adsorption
Binding force	Due to physical force of attraction, thus this process is also called as Vanderwaal's adsorption	Due to chemical forces or bonding, thus this process is also called as activated adsorption.
Saturation uptake	Multilayer phenomena	Single layer phenomena
Activation Energy	No activation energy involved	May be involved
Temperature Range (over which adsorption occurs)	Adsorption is appreciable at lower temperature below boiling point of adsorbate	Adsorption can take place even at higher temperature
Nature of sorbate	Amount of adsorbate removed depends more on adsorbate than on adsorbent	Depends on both adsorbent and adsorbate
Crystallographic specificity	Virtually independent of surface atomic geometry	Marked variation between crystal planes
Heat of adsorption	1 Kcal/mole	50 - 100 Kcal/mole

1.4.1 Adsorbent

Adsorbent capacity (or loading) is the most important characteristics of an adsorbent. It is the amount of the adsorbate taken up by the adsorbent, per unit mass or volume of the adsorbent. It depends on the fluid-phase concentration, temperature, and other conditions (especially the initial condition of the adsorbent). For activated carbon, capacity parameters determine loading characteristics. Maximum adsorption capacity of activated carbon is only achieved at equilibrium.

Selectivity is another important parameter of an adsorbent which is related to capacity. It is the ratio of the one component to that of another

at a given fluid concentration. The ratio generally approaches a constant value as concentration drops towards zero. An ideal situation occurs when the major component is not adsorbed much, which leads to a very large selectivity.

All cyclic adsorption applications depend on regenerability, so that the adsorbent can operate in sequential cycles with uniform performance. This means each adsorbable component must be relatively weakly adsorbed. The regenerability of an adsorbent affects the fraction of the original capacity that is retained, and the time, energy, etc. required for regeneration.

Mass transfer kinetics is a catch-all term related to intraparticle mass transfer resistance. It is important because it controls the cycle time of a fixed bed adsorption process. Kinetic parameters only determine the rate of adsorption and have negligible affect on adsorption capacity.

Compatibility covers various possible models of chemical and physical attack that could reduce the life expectancy of the adsorbent. For example the adsorbent should be inert to the carrier or solvent, and should not irreversibly react with (or chemisorb) the adsorbate or contaminants.

Cost is perhaps the most subtle characteristic to understand because it may vary from week to week and from sales rep to sales rep, even for the same exact material.

Adsorbent Materials

Materials that used as adsorbent are organic or inorganic materials.

Most minerals and many synthetic inorganic materials have been tried as adsorbents. Some have been successful, despite being poor adsorbents. Others have turned out to be immensely effective adsorbents. Alumina, silica, zeolite are the most used commercial inorganic adsorbents.

A wide variety of organic materials have been used as for “sorption”. Some might function as solid “adsorbents” rather than adsorbents. Among these are cellulose (the most abundant biopolymer in nature), chitin (the second most abundant biopolymer in nature), collagen, wool, polysaccharides derived from corn, and miscellaneous forms of biomass. The most used commercial organic adsorbents are; activated carbon and polymers.

The some adsorbents that are used in the adsorption process of 2,4-D is tabulated in Table 1.11.

Table 1.11 Some adsorbents that are used in the adsorption process of 2,4-D

Adsorbate	Material Type	Adsorbent Type	Adsorbent	References
2,4-D	Inorganic	Alumina	γ -Alumina	Clausen et al., 2001
			Alumina	Goyne et al., 2004
			Zinc-aluminium-chloride layered double hydroxides	Legrouri et al., 2005
		Silica	Silica-supported β -cyclodextrin derivatives	Phan et al., 2002
			Chemically modified silica gel surface	Prado and Airolidi, 2001
			Silica	Goyne et al., 2004
		Zeolites	Zeolite-supported TiO ₂	Shankar et al., 2006
		Hydrotalcite	Calcinated Hydrotalcite	Pavlovic, 2005
			Sepiolite and DAS	Akçay et al., 2005
	Organic	Polymer	Modified hypercrosslinked polystyrene (NDA-99)	Qui et al., 2003
			Crosslinked Poly(N-vinyl pyrrolidone)	Saraydin and Karadag, 1996
			Waste tyre rubber granules	Alam et al., 2006
			Rubber granules,	Alam et al., 2000
		Carbon	Gac SLS103, WWL	Cho et al., 2003
			H- type Gac 6-16 mesh size	Aksu and Kabasakal, 2004

2,4-D			PAC	Aksu and Kabasakal, 2005
			Gac F400	Chingombe et al., 2006
				Cho et al., 2003
				Kim et al., 2002
			Viz.wood charcoal, bottom ash	Alam et al., 2000
			CH supplied PAC & (CL)(grad 20070D)	Belmouden et al., 2000
		Clay	Organo-clays	Akçay and Yurdakoç, 2000
		Soil	Alfic Dystric Eutrocrept	Morillo et al., 2001
			Sonning Soil I-II-III	Spark and Switf, 2002
			Thirteen Constrasting Field Soils	Boivin et al., 2005
			Sepiolite and DAS	Akçay et al., 2005
	Biological		Macro fungi sajor caju and florida	Alam et al., 2000
			Fertilizer and Steel Industry Wastes	Gupta et al., 2006

Activated Carbon

Activated carbon can be made from many substances containing high carbon content such as *coal*, *wood* and *coconut* shells. The raw material has a very large influence on the characteristics and performance activated carbon (Table 1.12).

Table 1.12 The comparison of some properties of activated carbons made from different raw materials

Property	Coconut Activated Carbon	Coal Activated Carbon	Lignite Activated Carbon	Wood Activated Carbon (Powder)
Micropore	High	High	Medium	Low
Macropore	Low	medium	High	High
Hardness	High	High	Low	n/a
Ash	5%	10%	20%	5%
Water Soluble Ash	High	Low	High	Medium
Dust	Low	medium	High	n/a
Reactivation	Good	good	Poor	None

There are three main forms of activated carbon as granular, powder and pelleted. Granular activated carbon (GAC) has irregular shaped particles with sizes ranging from 0.2 to 5 mm that used in both liquid and gas phase applications. Powder activated carbon (PAC) is pulverized carbon with a size predominantly less than 0.18mm (US Mesh 80).that are mainly used in liquid phase applications and for flue gas treatment. Pelleted activated carbon is extruded and cylindrical shaped with diameters from 0.8 to 5mm that are mainly used for gas phase applications because of their low pressure drop, high mechanical strength

and low dust content. Activated carbon is also available in special forms such as a cloth and fibres.

Comparison of surface area, particle porosity etc. of some adsorbents are tabulated in Table 1.13.

Granular activated carbon is a highly adsorbent material used to remove contamination from water. Granular activated carbon particles are commonly used in municipal and home drinking-water filter systems to remove odors, taste, and excess chlorine.

The type of compound to be removed is effected the adsorption performance of the activated carbon. For example, compounds with high molecular weight and low solubility are better absorbed. And also the concentration of the compound is an influence factor. The higher the concentration, the higher the carbon consumption occurs. The pH of the waste stream is important too. For example, acidic compounds are better removed at lower pH.

Table 1.13 Comparison of surface area, particle porosity etc. of adsorbents

Adsorbent	Adsorbate	Particle Diameter	Particle Density	Particle Porosity	#BET surface area	Micropore Area *Mesopore Volume	Average Pore Diameter	Conclusion	References
Unit		mm	kg/m ³	-	m ² /g	(m ² /g) *(cm ³ /g)	Å		
GAC F400	2,4-D 2,4-DNP	0,37-0,54	682	0,62	800	490	19,02	Although BET area of SLS103 is the max, F400 shows the best adsorption performance. This result may come from the effect of pore size distribution and the surface area and surface properties.	Kim et al., 2002 Cho et al., 2003 Kim et al., 2003
GAC SLS103		0,37-0,54	880	0,47	1040	930	15,11		
GAC WWL		0,37-0,54	707	0,57	670	360	15,44		
ACF-48	Atrazine		345		1061	*0,20		Nevertheless, the experimental results also show that to perform better than GAC, the ACF must be highly activated, in order to have a wide opened microporosity	Gullon and Font, 2001
ACF-58			276		1570	*0,21			
ACF-68			254		1665	*0,89			
GAC1240			495		1062	*0,45			

								with an appreciable contribution of the low size mesopores.	
GAC F400	dye		1300-1400	0,4	1050-1200			A slight variation in D_{eff} was needed to describe variation in carbon particle size ;due to increased tortuosity caused by the relatively large molecular size.	Walker and Weatherley, 1998
Amberlite XAD-2	Beta-lactam antibiotics	20-60 mesh size			330		90	Although Bet area of XAD-16 is the max, XAD4 shows the best adsorption performance. This result may come from the effect of pore size distribution and surface properties.	Dutta et al., 1999
Amberlite XAD-4		20-60 mesh size			725		40		
Amberlite XAD-7		20-60 mesh size			450		90		
Amberlite XAD-16		20-60 mesh size			800		100		

The surface BET measurements of the adsorbents were obtained using BET method with nitrogen gas (N_2) at 77K using surface area analyser

When activated carbon is used as an adsorbent for an adsorption process; firstly molecules from gas or liquid phase will be attached in a physical way to a surface and the adsorption process takes place in three steps as ; (1)macro transport which the movement of organic material through the macro-pore system of the active carbon (macro-pore $>50\text{nm}$) is occurred, (2)micro transport which is the movement of organic material through the meso-pore and micro-pore system of the active carbon (micro-pore $<2\text{nm}$; meso-pore $2\text{-}50\text{nm}$) is occurred, (3)sorption which the physical attachment of organic material on the surface of active carbon in the meso-pores and micro-pores of the active carbon is occurred(Fritz and Schlünder, 1981) (Figure 1.7).

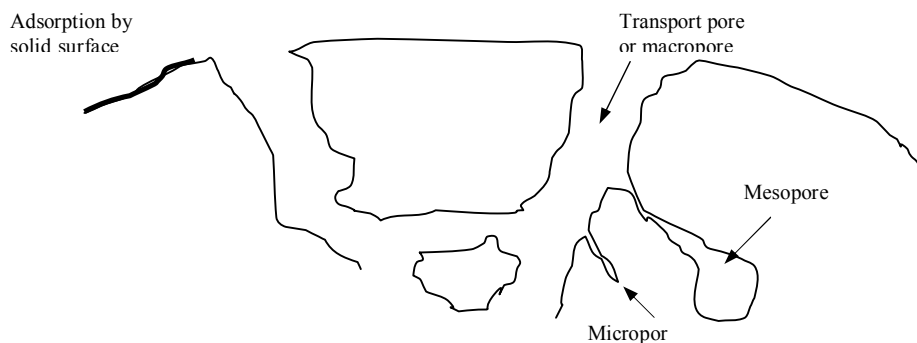


Figure 1.7 Schematic representation of adsorption by activated carbon

1.4.2 Adsorbate

These are the important parameters for the adsorbate; (1) Solubility of adsorbate (Adsorption $\propto$ (1/solubility of solute in solvent)), (2) Chain length of molecules (Adsorption $\propto$ chain length of molecule),

(3) Molecular size of adsorbate (increase in molecular size of solute favors adsorption), (4) Geometry of the molecule(branched lesser tendency to get removed), (5) Degree of ionization (Adsorption $\propto$ (1/ Dissociation constant) (6) Surface tension of the solvent in which they are dissolved become concentrated in surface layer while those substances which raise the surface tension are less concentrated in the surface than in the bulk of solution.

1.4.3 Batch System

In batch contact unit systems, a predetermined amount of adsorbent is mixed with the water for a given contact period and subsequently is separated by sedimentation or filtration. The optimum of application should allow adequate dispersion of the carbon and sufficient contact time to ensure maximum adsorption.

The first step in the evaluation of carbon dosage for determining the contact period. This is determined by adding a known quantity of carbon to a given volume of the water to be treated and placing the mixture in a stirring apparatus. A sample is removed at various time intervals and the carbon is immediately removed by filtration or centrifugation (for powdered forms). The residual concentration of the contaminant subsequently is determined in each sample. The data are plotted to show the change in concentration with time. Adsorption equilibrium is achieved at the contact period where no significant change in concentration is observed with increased time (Faust and Aly, 1987)

The amount of adsorbent adsorbed onto AC at equilibrium was calculated from the following mass balance equation.

$$q = (C_i - C) \frac{V}{W} \quad (1.1)$$

Here q is the equilibrium amount adsorbed on the adsorbent (mg/ g), C_i is the initial concentration of bulk fluid (mg/L), C is the equilibrium concentration of the solution (mg/L), V is the volume of solution (L), and W is the weight of adsorbent (g) (Cho et al., 2003).

Comparison of batch mode studies is tabulated in Table 1.14.

Table 1.14 Comparison of batch mode studies with activated carbon

Adsorbent Form	Adsorbent Size	Adsorbate	Parameter Investigated	Parameter Range	Conclusion	References
GAC	0,055-0,065cm in diameter	2,4-D 2,4 DNP	*Type of adsorbate *Capacity vs Kinetics *pH *Temperature	pH=3,5; 7,0; 10,0 T=288,15K; 298,15K; 313,5K	Adsorption capacities of adsorbents; decreased with increasing pH and temperature.	Kim et al., 2002
AC Polymeric resins	-	Beta-lactam antibiotics	*Type of adsorbent *Capacity *pH	pH=3,5; 5,0; 7,0	AC provides higher adsorption capacity than studied polymeric resins.	Dutta et al., 1999
GAC Biologic adsorbents & rubber granules	0,15-0,30mm	2,4-D Atrazine	*Type of adsorbent *Capacity vs Kinetics	Adsorption capacity	Adsorption capacity of the Activated charcoal is the max compared to other adsorbents.	Alam et al., 2000
GAC AC&AC-S	8-20 mesh size	Lead(II)	*Type of adsorbent *Capacity	Adsorption capacity	Pb(II) adsorption onto AC-S shows about 35% increase respect to adsorption on AC.	Goel et al., 2005
PAC Afsin-elbistan fly ash	-	C.I Reactive Black	*Type of adsorbent *Capacity vs Kinetics *Initial dye concentration *Adsorbent dosage	Adsorption capacity	Afsin-elbistan fly ash shows lower adsorption capacity.	Eren and Acar, 2006

GAC AC-C	*0,6-1.7mm *Cloth	Zn(II)	*Type of adsorbent *pH *Capacity	pH=3-6	GAC shows the min adsorption capacity. Increasing the pH causes decreases Zn(II) ions removal.	Alvarez-Merino et al., 2005
PAC	<0,15mm	2,4-D	*pH *Temperature *Initial concentration * Capacity vs Kinetics	pH=2-8 T=25; 35; 45 °C C=106; 204,1; 416,8; 628,6 mg/L	The max. adsorption capacity occurs at pH=2; adsorption increased with increasing conc., and decreased with increasing temp.up to 45 °C.	Aksu and Kabasakal, 2005
PAC	CH&(CL) (grad 20070D)	2,4-D	*Type of adsorbent *Contact time *Adsorbent concentration *pH	Time=0-180 min pH=1-10	CH shows the max adsorption capacity.The adsorption decreases with the increase in adsorbent conc. Because of aggregation of AC particles.	Belmouden et al., 2000
GAC	F400	2,4-D CPA 2,4-DNP	*pH *Kinetics	pH=3,5; 7,0; 10,0	Adsorption equilibrium capacities of herbicides on GAC increased with decreasing of pH.	Kim et al., 2005

1.4.3.1 Kinetic Modeling of Adsorption in a Batch System

If the movement of organic pollutant molecule from the bulk liquid to the liquid film or boundary layer surrounding the adsorbent is ignored, the following sequence of steps can take place in the adsorption process of porous adsorbent transport of solute molecules from the boundary film to the external surface of the adsorbent (film diffusion), transfer of molecules from the surface to the intraparticle active sites and uptake of molecules by the active sites of sorbent. In the removal of organics from wastewater, it is important for design purposes to investigate the mechanisms of adsorption and potential rate controlling steps which control the adsorption rate. In order to find the contribution of rate controlling steps such as external mass transfer, intraparticle diffusion, and adsorption process and also, mass transfer and kinetic models have been used to test the experimental data.

In the first step of adsorption, the *film diffusion* is an important rate-controlling step and external mass transfer or boundary layer diffusion can be characterized by the initial rate of solute sorption. In this case, adsorption rate is expected to be proportional to the first power of concentration; it means that this step is a first-order process and can be defined as:

$$\frac{dC}{dt} = k_{1,ad} C \quad (1.2)$$

where C is the pollutant concentration in the wastewater remaining at each contact time and $k_{1,ad}$ is the first-order reaction-rate constant. After integration and applying boundary conditions, $t = 0$ to $t = t$ and $C = C_0$ to $C = C$; the integrated form of Eq. (1.2) becomes;

$$\log \frac{C_0}{C} = \frac{1}{2.303} k_{1,ad} t \quad (1.3)$$

where C_0 is the initial pollutant concentration (Chu and Chen, 2002).

If *intraparticle diffusion* is involved in the sorption process, the model developed by Weber and Morris , (1963) can be used to find the region where intraparticle diffusion is rate-limited and to determine intraparticle diffusion rate.

An empirically found functional relationship, common to the most adsorption processes, is that the uptake varies almost proportionally with $t^{1/2}$, the Weber–Morris plot, rather than with the contact time t (Weber and Morris, 1963).

$$q_t = k_{id} t^{1/2} + C \quad (1.4)$$

where k_{id} is the intra-particle diffusion rate constant. According to Eq. (1.4), a plot of q_t versus $t^{1/2}$ should be a straight line with a slope k_{id} and intercept C when adsorption mechanism follows the intra-particle diffusion process. Values of intercept give an idea about the thickness of boundary layer, i.e., larger the intercept with greater is the boundary layer effect (Kannan and Sundaram, 2001).

Assuming spherical geometry for the adsorbent, the time for half adsorption can be correlated to the pore diffusion coefficient (Michelson et al., 1975).

$$t_{1/2} = 0.03 r_0^2 / D_p \quad (1.5)$$

where $t_{1/2}$ is the time for half adsorption (s), r_0 is the radius of the adsorbent particle (cm) and D_p is the diffusion coefficient (cm^2/s). Values of D_p can be calculated for different temperatures etc.

Kinetic data can further be used to check whether pore diffusion is the only rate-controlling step or not in the adsorption system using *Bangham's equation* (Aharoni et al., 1979).

$$\log \log(C_o / (C_o - q_t m)) = \log(k_o m / 2.303V) + \log(t) \quad (1.6)$$

where C_o is the initial concentration of adsorbate in solution (mg/L), V is the volume of solution (mL), m is the weight of adsorbent per liter of solution (g/L), q_t (mg/g) is the amount of adsorbate retained at time t and k_o is constant.

In many cases, the kinetics of adsorption based on overall adsorption rate by adsorbents are described by the first-order Lagergren (Lagergren, 1898) and pseudo second-order (McKay and Ho, 1999) kinetic models.

The sorption kinetics may be described by a pseudo-first-order according to Lagergren (Lagergren, 1898), Ho and McKay (Ho and McKay, 1998), Namasivayam and Kardivelu (Namasivayam and Kardivelu, 1999), *the first-order rate expression of Lagergren* based on the sorption capacity of adsorbent is generally expressed as follows:

$$\frac{dq}{dt} = k_{1,ad} (q_{eq} - q) \quad (1.7)$$

where q_{eq} is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g) , q the amount of solute adsorbed at any time (mg/g) and $k_{l,ad}$ (L/min) is the rate constant of Lagergren first-order adsorption.

After integration and applying boundary conditions, $t = 0$ to

$t = t$ and $q = 0$ to $q = q$; the integrated form of Eq. (1.7) becomes

$$\log(q_{eq} - q) = \log q_{eq} - \frac{k_{l,ad}}{2.303} t \quad (1.8)$$

A straight line of $\log(q_{eq} - q)$ versus t suggests the applicability of this kinetic model. In order to fit Eq. (1.8) to experimental data, the equilibrium sorption capacity, q_{eq} , must be known. In many cases q_{eq} is unknown and as adsorption tends to become unmeasurably slow, the amount sorbed is still significantly smaller than the equilibrium amount. For this reason it is necessary to obtain the real equilibrium sorption capacity, q_{eq} , by extrapolating the experimental data to $t = \infty$ or by using a trial and error method. Furthermore, in most cases the first-order equation of Lagergren does not fit well for the whole range of contact time and is generally applicable over the initial 20–30 min of the sorption process.

The pseudo second-order equation is also based on the sorption capacity of the solid phase. Contrary to the other model it predicts the behaviour over the whole range of adsorption. The sorption kinetics may also be described by a pseudo-second-order according to Ho and McKay (Ho and McKay, 1998;1999) and the pseudo second-order kinetic rate equation is expressed as

$$\frac{dq}{dt} = k_{2,ad} (q_{eq} - q)^2 \quad (1.9)$$

where, q_{eq} is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g) (the equilibrium adsorption capacity), q is the amount of solute adsorbed at any time (mg/g) and $k_{2,ad}$ (g/mg min) is the rate constant of second-order adsorption. For the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q$; the integrated and linear form of Eq. (1.9) becomes

$$\frac{t}{q} = \frac{1}{k_{2,ad} q_{eq}^2} + \frac{1}{q_{eq}} t \quad (1.10)$$

If second-order kinetics are applicable, the plot of t/q against t of Eq. (1.10) should give a linear relationship, from which q_{eq} and $k_{2,ad}$ can be determined from the slope and intercept of the plot and there is no need to know any parameter beforehand.

1.4.3.2 Equilibrium Modeling of Adsorption in a Batch System

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems used for the removal of organic pollutants. The Langmuir, Freundlich are the most frequently used two-parameter models in the literature describing the non-linear equilibrium between adsorbed organic pollutant (adsorbate) on the adsorbant (q_{eq}) and organic pollutant in solution (C_{eq}) at a constant temperature.

The Langmuir Model

The Langmuir equation which is valid for monolayer sorption onto a surface with a finite number of identical sites is given by Eq.(1.11).

$$q_{eq} = \frac{Q_o b C_{eq}}{1 + b C_{eq}} \quad (1.11)$$

where q_{eq} is the amount adsorbed (mg/g), C_{eq} is the equilibrium concentration of the adsorbate (mg/L), and parameters Q_o and b are Langmuir constants related to maximum adsorption capacity (mg/g) (monolayer capacity) and bonding energy of adsorption (L/mg), respectively, which are functions of the characteristics of the system as well as time (Langmuir, 1918).

Plots were obtained from $\left[\frac{1}{q_{eq}} = \frac{1}{Q_o} + \frac{1}{b Q_o C_{eq}} \right]$ which was the linearized form of the Langmuir equation, for $1/q_{eq}$ versus $1/C_{eq}$, for the adsorption of pesticides showing the applicability of the equation. The values of monolayer capacity (Q_o) and Langmuir constant (b) have been evaluated from the intercept and the slope of these plots .

The adsorption capacity can be correlated with the variation of surface area and porosity of the adsorbent. Higher surface area and pore volume will result in higher adsorption capacity. The Langmuir equation is used for homogeneous surfaces.

The essential characteristics of Langmuir model can be expressed by a dimensionless constant called equilibrium parameter R_L , defined by Weber and Chakkravorti (1974); as $R_L = 1/(1+bC_0)$ (where C_0 is the initial concentration of adsorbate in (mg/L), and b is the Langmuir constant). The Langmuir parameters can be used to predict the affinity between the sorbate and sorbent using the dimensionless separation factor (R_L).

This indicates the nature of adsorption as ;

Seperation Factor, R_L	Characteristiscis of Langmuir Models
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The Freundlich Model

The Freundlich model assumes neither homogeneous site energies nor limited levels of sorption. The Freundlich equation has the general form:

$$q_{eq} = K_F C_{eq}^{1/n} \quad (1.12)$$

where q_{eq} is the amount adsorbed (mg/g), C_{eq} is the equilibrium concentration of the adsorbate (mg/L), K_F ((mg/g)*(mg/L)ⁿ) and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively (Freundlich, 1906). Eq. (1.12) can be linearized in logarithmic form.

Plots were obtained from $\left[\ln q_{eq} = \ln K_F + \frac{1}{n} \ln C_{eq} \right]$ which was the linearized form of Freundlich equation. $\ln q_{eq}$ versus $\ln C_{eq}$ linear plots would give the value of $\frac{1}{n}$ as slope and K_F as intercept. The value of K_F can be used as alternative measure of adsorption capacity, while $1/n$ determines the adsorption intensity.

1.4.4 Continuous System

When an organic pollutant containing solution passes through a packed bed column, at the beginning, most of organic pollutant get sorbed on adsorbent so organic pollutant concentration in the effluent remains either very low or in some cases is not detectable. As adsorption continues, organic pollutant concentration in the effluent rises, slowly at first, and then abruptly. When this abrupt rise or breakthrough occurs the flow is stopped.

The performance of continuous packed bed is described through the concept of the breakthrough curve. The time for breakthrough appearance (breakthrough time) and the shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic response of an adsorption column. The general position of the breakthrough curve along the time or volume axis depends on the capacity of the column with respect to the feed concentration and flow rate. The breakthrough curves show the loading behaviour of pollutant to be removed from solution in a fixed bed and is usually expressed in terms of normalized concentration defined as the ratio of effluent pollutant concentration to inlet pollutant concentration (C/C_0) as a function of time or volume of effluent (V_{eff}) for a given bed height (Figure 1.8).

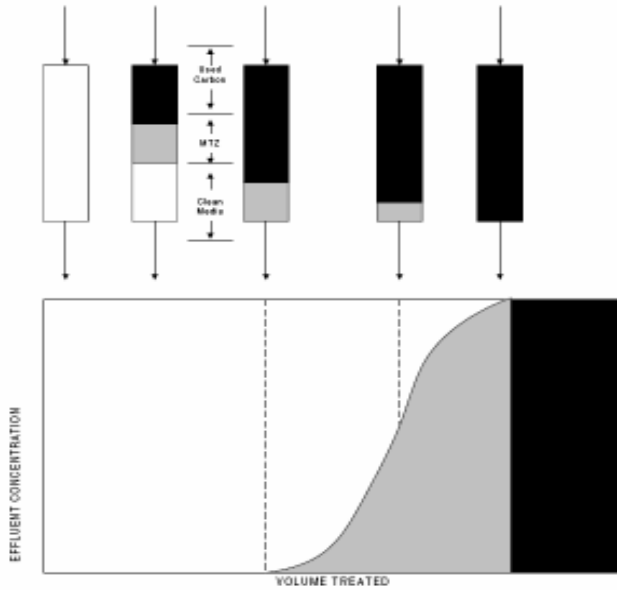


Figure 1.8 Adsorption column mass transfer zone and idealized breakthrough zone

Effluent volume (V_{eff}) can be calculated from Eq. (1.13).

$$V_{\text{eff}} = Qt_{\text{total}} \quad (1.13)$$

where t_{total} and Q are the total flow time (min) and volumetric flow rate (mL min^{-1}). The area under the breakthrough curve (A) obtained by integrating the adsorbed concentration (C_{ad} ; mg L^{-1}) versus t (min) plot can be used to find the total adsorbed adsorbate quantity (maximum column capacity). Total adsorbed adsorbate quantity (q_{total} ; mg) in the column for a given feed concentration and flow rate is calculated from Eq. (1.14):

$$q_{\text{total}} = \frac{QA}{1000} = \frac{Q}{1000} \int_{t=0}^{t=t_{\text{total}}} C_{\text{ad}} dt \quad (1.14)$$

Total amount of adsorbate sent to column (m_{total}) is calculated from Eq. (1.15).

$$m_{total} = \frac{C_o Q_{total}}{1000} \quad (1.15)$$

Total removal percent of adsorbate (column performance) with respect to flow volume can be also found from the ratio of total adsorbed quantity of adsorbate (q_{total}) to the total amount of adsorbate sent to column (m_{total}) Eq. (1.16).

$$Total\ removal\ \% = \frac{q_{total}}{m_{total}} \times 100 \quad (1.16)$$

Adsorption is also a well-known equilibrium separation process for wastewater treatment. Equilibrium studies on adsorption give information about the capacity of the sorbent or the amount required to remove a unit mass of pollutant under the system conditions. As the adsorption isotherms obtained from sorption data in a batch system are not able to represent the column equilibrium, the experimental data from the column experiments should be used to fit isotherm models. Equilibrium adsorbate uptake (q_{eq}) (or maximum capacity of the column) in the column is defined by Eq. (1.17) as the total amount of adsorbate sorbed (q_{total}) per g of sorbent (X) at the end of total flow time.

$$q_{eq} = \frac{q_{total}}{X} \quad (1.17)$$

Unadsorbed adsorbate concentration at equilibrium in the column (C_{eq} ; $mg\ L^{-1}$) can be defined by Eq. (1.18):

$$C_{eq} = \frac{m_{total} - q_{total}}{V_{eff}} \times 1000 \quad (1.18)$$

Successful design of a column adsorption process requires prediction of the concentration-time profile or breakthrough curve for the effluent under given specific operating conditions. Developing a model to accurately describe the dynamic behaviour of adsorption in a fixed bed system is inherently difficult. Since the concentration of the adsorbate as the feed moves through the bed, the process does not operate at steady state. The fundamental transport equations derived to model the fixed bed with theoretical rigor are differential in nature and usually require complex numerical methods to solve. Such a numerical solution is not usually difficult, but often does not fit experimental results especially well. Some solutions for very limiting cases have been reported, but in general, complete time-dependent analytical solutions to differential equation based models of the proposed rate mechanisms are not available. Because of this, various simple mathematical models have been developed to predict the dynamic behaviour of the column and the models used to characterize the fixed bed performance for the removal of organics are presented in the literature (Rao and Viraraghavan, 2002; Volesky, 2001; Aksu 1998; Aksu and Gönen, 2004; Guibal et al., 1995).

Comparison of column mode studies is tabulated in Table 1.15.

Table 1.15 Comparison of column mode studies with activated carbon

Adsorbent Form	Adsorbent Size	Adsorbate	Parameter Investigated	Parameter Range	Conclusion	References
GAC	0,9mm mean diameter	TNT	*Concentration *Temperature *Flowrate *Bed height	C:32,76 to 171 mg/dm ³ T=10-60°C v= 1, 2, 4 dm ³ /h h= 70 mm&135 mm	Adsorption capacity increased with increasing temperature, but decreased with increasing inlet concentration and flow rate.	Kim et al., 2002
GAC	8-20 mesh size	Lead(II)	*Bed height *Hydraulic Loading Rate *Initial feed concentration	h: 0,3-0,5m HLR:3-10,5 m ³ /(h*m ²) C:2-6 mg/L	0,4m is chosen as optimized bed height. Increase in HLR, resulting decrease in the time to achieve breakthrough. Increase in Concentration causes increase in adsorption capacity.	Goel et al., 2005
GAC	*0,6-1.7mm *Cloth	Zn(II)	*Type of adsorbent	Adsorbents: ACC&ACC-ox	oxidizing carbon ions causes decrease in the time to achieve breakthrough...	Alvarez-Merino et al., 2005
GAC ACF	100µm	Atrazine	*Type of adsorbent	3 types of ACF and GAC	Pitch based ACF are more effective than GAC if they are highly activated.	Gullon and Font, 2001

GAC	F400	Acid Dyes	*Bed height *Flow rate *Inlet dye concentration *Adsorbent particle size	$\xi = 0,0762; 0,1524;$ $0,2286; 0,3047; 0,3809$ $\mu = 0,025; 0,1; 0,5$ $\text{dm}^3\text{min}^{-1}$ $c = 100; 200; 300$ mg/dm^3 Particle size = $0,06;$ $0,0425; 0,0303$ cm	By using low linear flow rates and use fine adsorbent particle size ; the optimum bed results are obtained.	Walker and Weatherley, 1998
GAC	F400 SLS103 WWL	2,4-D 2,4-DNP	*Capacity vs Kinetics	Types of Adsorbents	A simple dynamic model (LDFA) successfully simulated the experimental adsorption breakthrough.	Kim et al., 2003
GAC	24-32 mesh	nitro phenol	*Bed depths *Flow rates	$h = 3-6$ cm $v = 21,6-86,4$ cm ³ /h	The experimental half lives are very close to predicted by self-sharpening wave approach and proportional to bed depth-flow rate ratio. Experimental and predicted breakthrough curves are in good agreement.	Chern and Chien, 2002

The sorption capacity parameter obtained from a batch experiment is useful in providing information about effectiveness of adsorbate-adsorbent system. But, batch reactors were easy to use in the laboratory study, less convenient for industrial applications. The data obtained under batch conditions are generally not applicable to most treatment system (such as column operations) where contact time is not sufficient long for the attainment of equilibrium. In batch mode adsorption studies, the same solution remains in contact with a given quantity of adsorbent. The adsorption process continues, however, till equilibrium between the solute concentration in solution, and the solute adsorbed per unit weight of adsorbent is reached. This equilibrium established is static in nature, as it does not change further with time. In continuous column adsorption, solution continuously enters and leaves the column, so that the complete equilibrium is never established, as each time, it meets the fresh concentrations, hence, equilibrium in column mode is termed as dynamic equilibrium. Fixed-bed columns were widely used in various chemical industries because of their operation. Hence, there is a need to perform equilibrium studies using columns.

1.4.4.1 Kinetic Modelling of Adsorption in a Continuous Packed Bed System

The Thomas Model

The data obtained in column in continuous mode studies was used to calculate maximum solid phase concentration of adsorbate on adsorbent and the adsorption rate constant using the kinetic model developed by Thomas (Thomas, 1944). The Thomas solution is one of the most general and widely used methods in column performance

theory. The expression by Thomas for an adsorption column is given as follows:

$$\frac{C_t}{C_o} = \frac{1}{1 + \exp[k_{Th}(q_o x - C_o V_{eff})/v]} \quad (1.19)$$

where k_{Th} is the Thomas rate constant ($\text{mL min}^{-1} \text{mg}^{-1}$), q_o the equilibrium adsorbate uptake per gram of the adsorbent (the maximum solid-phase concentration of the solute) (mg g^{-1}), x the amount of adsorbent in the column (g), V_{eff} the effluent volume (mL), C_o the influent concentration (mg L^{-1}), C_t the effluent concentration at time t (mg L^{-1}) and v the flow rate (mL min^{-1}). The value of C_t/C_o is the ratio of effluent and influent concentrations. The value of t is time (min, $t = V_{eff}/v$).

The linearized form of the Thomas model is as follows:

$$\ln\left(\frac{C_o}{C_t} - 1\right) = \frac{k_{Th} q_o x}{v} - \frac{k_{Th} C_o V_{eff}}{v} \quad (1.20)$$

The kinetic coefficient k_{Th} and the adsorption capacity of the column q_o can be determined from a plot of $\ln[(C_o/C_t)-1]$ against V_{eff} (or t) at a given flow rate (Aksu and Gönen, 2004).

The Thomas or reaction model, which assumes Langmuir kinetics of adsorption-desorption and no axial dispersion is derived with the adsorption that the rate driving force obeys second-order reversible reaction kinetics (Fu and Viraraghavan, 2003; Vijayaraghavan et al., 2005).

Thomas' solution also assumes a constant separation factor but it is applicable to either favorable or unfavorable isotherms. The primary weakness of the Thomas solution is that its derivation is based on second order reaction kinetics. Adsorption is usually not limited by chemical reaction kinetics but is often controlled by interphase mass transfer. This discrepancy can lead some error when this method is used to model adsorption process (Thomas, 1944).

The Yoon and Nelson Model

Yoon and Nelson model is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent. The Yoon and Nelson equation regarding to a single component system is expressed as;

$$\ln \frac{C_t}{C_o - C_t} = k_{YN}t - \tau k_{YN} \quad (1.21)$$

where k_{YN} is the rate constant ($L \min^{-1}$); τ the time required for 50% adsorbate breakthrough (min); t the breakthrough time (min).

The kinetic coefficient k_{YN} and τ can be determined from a plot of $\ln[C_t/(C_o - C_t)]$ against t at a given adsorption conditions. If the theoretical model accurately characterizes the experimental data, this plot will result in a straight line with slope of k_{YN} and intercept τk_{YN} (Aksu and Gönen, 2004).

The Adams–Bohart Model

The fundamental equations describing the relationship between C/C_o and t in a flowing system were established by Adams and Bohart (1920) for the adsorption of chlorine on charcoal. Although the original work by Adams–Bohart was done for the gas–charcoal adsorption system, its overall approach can be applied successfully in quantitative description of other systems. This model assumes that the adsorption rate is proportional to both the residual capacity of the activated carbon and the concentration of the sorbing species.

Adams–Bohart model based on the surface reaction theory and it assumes that equilibrium is not instantaneous; therefore, the rate of the sorption is proportional to the fraction of sorption capacity still remains on the sorbent (Goel et al., 2005).

The Adams–Bohart model is used for the description of the initial part of the breakthrough curve (Aksu and Gönen, 2004; Liao et al., 2004).

The mass transfer rates obey the following equations:

$$\frac{\partial q}{\partial t} = -k_{AB} q C_b \quad (1.22)$$

$$\frac{\partial C_b}{\partial Z} = -\frac{k_{AB}}{U_o} q C_b \quad (1.23)$$

where k_{AB} is the kinetic constant ($L \text{ mg}^{-1} \text{ min}^{-1}$). Some assumptions are made for the solution of these differential equation systems: (i) the concentration field is considered to be low, e.g. effluent concentration

$C < 0.15C_o$; (ii) for $t \rightarrow \infty$, $q \rightarrow N_o$, (where N_o is the saturation concentration (mg L^{-1})). When the differential equation systems solved, the following equation is obtained with parameters k_{AB} and N_o :

$$\ln \frac{C_t}{C_o} = k_{AB} C_o t - k_{AB} N_o \frac{Z}{U_o} \quad (1.24)$$

where C_o and C_t are the inlet and effluent adsorbate concentrations (mg L^{-1}), respectively. Z is the height of the column (cm), U_o is the superficial velocity (cm min^{-1}), N_o is saturation concentration in the Adams–Bohart model (mg L^{-1}) and k_{AB} is the Adams–Bohart kinetic constant (the mass-transfer coefficient) ($\text{L mg}^{-1} \text{ min}^{-1}$). The range of t should be considered from the beginning to the end of breakthrough. A straight line was attained for this system by plotting $\ln(C_t/C_o)$ against t , which gives the value of k_{AB} from the slope of the line (Texier et al., 2002; Bohart and Adams, 1920; Wolborska, 1989; Aksu and Gönen 2004).

The Wolborska Model

The Wolborska model is also used for the description of adsorption dynamics using mass transfer equations for diffusion mechanisms in the range of the low-concentration breakthrough curve. The mass transfer in the fixed bed sorption is described by the following equations:

$$\frac{\partial C_b}{\partial t} + U_o \left(\frac{\partial C_b}{\partial Z} \right) + \left(\frac{\partial q}{\partial t} \right) = D \left(\frac{\partial^2 C_b}{\partial^2 Z} \right) \quad (1.25)$$

$$\frac{\partial q}{\partial t} = -v \left(\frac{\partial q}{\partial Z} \right) = \beta_a (C_b - C_s) \quad (1.26)$$

where C_s is the adsorbate concentration at the solid/liquid interface (mg L^{-1}); D , the axial diffusion coefficient ($\text{cm}^2 \text{min}^{-1}$); $\mathbf{v}$, the migration rate (cm min^{-1}); and β_a is the kinetic coefficient of the external mass transfer (min^{-1}). With some assumptions previously described by Wolborska: $C_s \ll C_b$, $\mathbf{v} \ll U_o$ and axial diffusion negligible $D \rightarrow 0$ as $t \rightarrow 0$, the solution can be approximated to:

$$\ln \frac{C}{C_o} = \frac{\beta_a C_o}{N_o} t - \frac{\beta_a Z}{U_o} \quad (1.27)$$

with

$$\beta_a = \frac{U_o^2}{2D} \left(\sqrt{1 + \frac{4\beta_o D}{U_o^2}} - 1 \right) \quad (1.28)$$

where β_o is the external mass transfer coefficient with a negligible axial dispersion coefficient D . Wolbraska observed that in short beds or at high flow rates of solution through the bed, the axial diffusion is negligible and $\beta_a = \beta_o$. The migration velocity of the steady-state front satisfies the relation, known as Wicke's law:

$$\nu = \frac{U_o C_o}{N_o + C_o} \quad (1.29)$$

The expression of the Wolborska solution is equivalent to the Adams–Bohart relation if the coefficient k_{AB} is equal to β_a / N_o . So the drawing of $\ln C/C_o$ versus t would also give information on this model (Wolborska, 1989; Guibaletal., 1995)

1.5 Measurement Techniques

If a beam of white light passes through a glass container (cuvet) filled with liquid, the emergent radiation is always less powerful than that entering. The diminution of power is generally of different extent for different wavelengths. The loss is due in part to reflections at surfaces and to scattering by any suspended particles present, but in the absence of such particles, it is primarily accounted for by the absorption of radiant energy by the liquid. (Ewing, 1985).

If the energy absorbed is greater for some visible wavelengths than for others, the emergent beam will appear colored. The apparent color of the solution is always the complement of the color absorbed. Thus a solution absorbing in the blue region will appear yellow, one that absorbs green will appear purple, etc. (Ewing, 1985).

Many organic substances found in raw water sources exhibit characteristics property of absorbing light in the ultraviolet (UV) and visible regions, wavelengths 10 to 400 nm and 400 to 800 nm, respectively. Most of the absorbance occurs in the near UV range of 200 to 400 nm. This UV-absorbance, due mainly to the stimulations of π -electrons, is characteristics for substances with carbon-carbon and carbon-oxygen double bonds. The UV absorbance spectra of naturally occurring substances are featureless due to random interactions and the spectra monotonically decreases with increasing wavelength (Sontheimer et al., 1988).

Ultraviolet-visible spectroscopy (UV/VIS)

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometer (UV/ VIS) involves the spectroscopy of photons and spectrophotometer. It uses light in the visible and adjacent near ultraviolet (UV) and near infrared (NIR) ranges. In this region of energy space molecules undergo electronic transitions.

Applications of UV

UV/V is spectroscopy is routinely used in quantitative determination of solutions of transition metal ions and highly conjugated organic compounds.

Solutions of transition metals ions can be colored (i.e., absorb visible light) because d electrons within the metal atoms can be excited from one electronic state to another. The color of metal ion solutions is strongly affected by the presence of other species, such as certain anions or ligands. For instance, the color of a dilute solution of copper sulphate is a very light blue; adding ammonia intensifies the color and changes the wavelength of maximum absorption(λ_{max}).

Organic compounds, especially those with a high degree of conjugation, also absorb light in the UV or visible regions of the electromagnetic spectrum. The solvents for these determinations are often water soluble compounds, or ethanol for organic-soluble compounds. (organic solvents may have significant UV absorption; not all solvents are suitable for use in UV spectroscopy. Ethanol absorbs very weakly at most wavelengths.)

While charge transfer complexes also give rise to colors, the colors are often too intense to be used for quantitative measurements.

Mathematical Theory

The absorption of radiant energy by matter can be described quantitatively through the general principle known as ***Beer's Law***. Consider a glass cuvet with a plane parallel faces traversed by monochromatic radiation. Losses by reflection at the surfaces and absorption by the glass will be neglected for the moment. Suppose that the cuvet is filled with an absorbing species dissolved in a non-absorbing solvent. The radiation diminishes in power the further it penetrates into the solution and the greater the concentration of solute. More generally stated, the diminution in power is proportional to the number of absorbing molecules in the path of the beam. The quantitative statement of this relation is ***Beer's Law(or Beer-Lambert Law)***. (Ewing, 1985).

Beer-Lambert Law

The method is most often used in a quantitative way to determine concentrations of an absorbing species in solutions, using the Beer-Lambert Law:

$$A = \log_{10}(I/I_o) = \varepsilon \cdot c \cdot L$$

Where A is the measured absorbance, I_o is the intensity of the incident light at a given wavelength, I is the transmitted intensity, L the path length through the sample, and c the concentration of the absorbing species (Figure 1.9). For each species and wavelength, ε is a constant

known as the molar absorptivity or extinction coefficient. This constant is a fundamental molecular property in a given solvent, at a particular temperature and pressure, and has units of l / M^*cm or often AU / M^*cm .

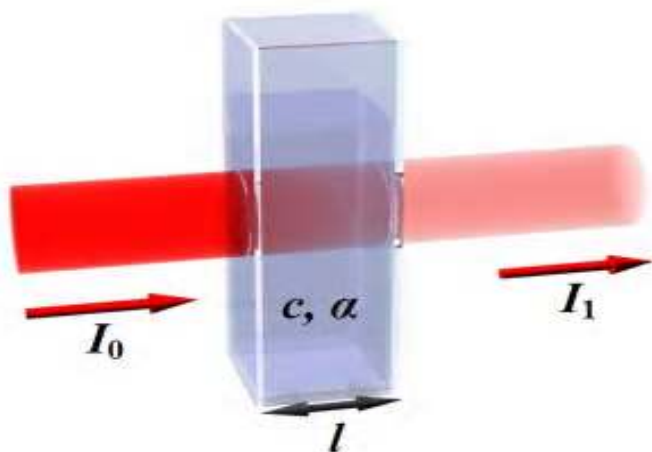


Figure 1.9 Figure of Beer-Lambert Law

In spectroscopy, the absorbance A is defined as;

$$A_{\lambda} = \log_{10}(I_0/I)$$

where I is the intensity of light at a specified wavelength λ that has passed through a sample (transmitted light intensity) and I_0 is the intensity of the light before it enters the sample or incident light intensity. Absorbance measurements are often carried out in analytical chemistry, since the absorbance of a sample is proportional to the thickness of the sample and the concentration of the absorbing species in the sample, in

contrast to the transmittance I/I_o of a sample, which varies exponentially with thickness and concentration.

The absorbance and extinction ϵ are sometimes defined in terms of the natural logarithm instead of the base 10 logarithm.

The Beer-Lambert Law is useful for characterizing many compounds but does not hold as a universal relationship for the concentration and absorption of all substances.

Comparison of UV/V, HPLC, Gas Chromatography

UV/V spectroscopy is routinely used in the quantitative determination of solutions of transition metal ions can be colored, organic compounds, especially those with a high degree of conjugation. Less volatile and larger samples can be used with HPLC. It was discovered that better separation of the components of the mixture occurs if the particles in the stationary phase are very small. However, it was also found that if very small particles were used in the column, then the liquid passed very slowly through the column. Therefore, a pump is used to force the liquid through the column. This is not necessary in GC but a shorter column can be used in HPLC because the separation is more efficient.

The used measurement techniques of different adsorbates (especially pesticides) on some adsorbents are tabulated in Table 1.16.

Table 1.16 The used measurement techniques of some adsorbate on adsorbents

Adsorbate	Adsorbent	Measurement Techniques	References
Acid dyes	GAC	UV	Walker and Weatherley, 1997
2,4D Carbofuran	Fertilizer industry waste & Steel industry waste	UV	Gupta et al., 2006
2,4D	PAC	UV	Aksu and Kabasakal, 2005
2,4D	PAC	UV	Belmouden et al., 2000
2,4D 2,4DB 2,4DP 2,4,5 T MCPA	Organo-clays	UV	Akçay and Yurdakoc, 2000
Cr(VI) (Chromium)	Pomace (Olive oil industry waste)	UV	Malkoç et al., 2006
2,4D	GAC	UV	Kim et al., 2003
Isoproturon	Alumina(with and without sodium dodecyl sulfate)	UV	Gawade et al., 2004
Thiazafluron Metamitron	Soil –Clay suspensions	UV & HPLC	Cox et al., 1997
2,4D	Dodecylammonium sepiolite (DAS)	UV	Akçay et al., 2004
TNT(trinitrotoluene)	GAC	HPLC	Marinovic et al., 2005
Atrazine	Activated carbon fibres(ACF)	HPLC	Gullon and Font, 2001
2,4D Atrazine	Waste Tyre Rubber Granules	GC	Alam et al., 2004
Atrazine Simazine Terbutryn Diuron Sandy	Different soil samples	GC	Csutoras and Kiss, 2007

2.0 MATERIALS AND METHODS

2.1 Chemicals and Equipments

The used chemicals in the experiments were; 2,4-dichlorophenoxyacetic acid (Sigma Aldrich), GAC (Aqualine), C_2H_5OH (Kimetsan), HCl (Emir Kimya), NaOH (pure pellets, Merck), $CaCl_2$ (pure, Merck), pH=4 and pH=7 buffer (WTW), NaCl (Merck), TSA-Tryptic Soy Agar (Merck), TSB-Tryptic Soy Broth (Criterion).

The used equipments in the experiments were; glass column (ID=1.1cm), shaker (Memmert WNB 7-45), peristaltic pump (Watson-Marlow 430-VM4 (10rpm)), power supply (Makelsan 2006-1000VA), tubing (Watson-Marlow marprene grey 1.29mm), micropipette (Socorex Acura Manual 825), pH meter (WTW pH 330/set), autoclave (HMC HIRAYAMA Hiclave HV-50L), magnetic stirrer (IKAMAG RO5 power, Selectra multimatic-5N), scale (AND HM-200), vacuum (Sartorius Glass Vacuum Filter Holder), vacuum filter (cellulose filter pore size=0.45 μ m), vortex (Bio Vortex V-1 plus), microwave (Bosh 812-c), incubator (Nuve), petri dishes (Isolab disposal) and spectrophotometer (Jasco Model 7800 UV/VIS Spectrophotometer).

The stock solution of 2,4-D (200ppm stock solution of 2,4-D) was prepared in 10^{-2} M $CaCl_2$ (was prepared by dissolving 1.11g $CaCl_2$ in distilled water and diluted to 1L) in order to promote the flocculation and to have a constant background electrolyte concentration in order to overcome the solubility difficulties of 2,4D in water, 5 mL ethanol were used to provide complete solutions. The required amount of 2,4-D (0.2g 2,4-D for 1 Liter solution) is dissolved in 5mL ethanol. Then

(ethanol+2,4-D) solution is added slowly into 10^{-2} M CaCl_2 . The pH value of the solution was adjusted in the range of 6.5–7 by using dilute (0.1N) NaOH solution. The dilute NaOH (0.1 N NaOH) solution was prepared by dissolving 0.4g NaOH in 100 mL distilled water. The samples of required concentrations were prepared by diluting the stock solution with distilled water.

There are two types of culture mediums. The contents of the mediums are tabulated in Table 2.1.

Table 2.1 Contents of culture mediums

TSB (Tryptic Soy Broth)	TSA (Tryptic Soy Agar)
Casein peptone (17g)	Casein peptone (17g)
Soy peptone (3 g)	Soy peptone (3 g)
Sodium chloride (5 g)	Sodium chloride (5 g)
Dipotassium Hydrogen phosphate (2.5g)	Agar agar (15g)
Glucose (2.5 g)	

TSB (Tryptic Soy Broth) medium was prepared as 30 g (broth)/liter distilled water where TSA (Tryptic Soy Agar) medium was prepared as 40 g (agar)/liter distilled water. Then either two mediums were autoclaved for 15min at 121°C . The medias' pH should be 7.3 ± 0.2 at 25°C . After preparation both medias were clear and yellowish-brown.

0.86% NaCl solution was prepared by dissolving 0.86 g NaCl in 100 mL distilled water.

2.2 Methods

2.2.1 Activated Carbon

Aqualine labeled activated carbon was purchased from Esli and PWG Co., Turkey. It was ground and sieved into desired particle size (1-2mm). Before using, the carbon washed with distilled water a few times to remove carbon powder and impurities, oven dried at 110°C unless obtain stable weight. The GAC was stored in a sealed bottle along a silica gel to prevent the readsorption of moisture before use. GACs characteristics are summarized in Table 2.2.

Table 2.2 Properties of Aqualine Coal Activated Carbon

Particle Size	8 * 30 (2.36-0.6 mm)
Total Surface Area (Min)	1000 m ² /g
Iodine Number (Min)	1050 mg/g
Moisture Content	4 %
Ash Content	12 %
Mass Density	450 ± 20 kg/m ³
Methylene Blue	160 mg/g
CTC (Min)	60 %
Pore Volume	0.8 cm ³ / g
Hardness	97 %
pH Liquid	8-10
Dechlorination Value	5 cm ³

2.2.2 Biological Contamination

In biological contamination studies, The “Acidovorax avenae subsp. Avenae LMG 17238” bacteria was used as biological

contamination where it was purchased from BCCMTM/LMG bacteria collection at the Gent university (Gent/Belgium). This bacteria is produced for the biodegradation of the synthetic-based polyester based plastics, poly ϵ -caprolactone(PCL), poly(butylene succinate-cobutylene adipate) and a starch –PCL blend.

2.2.3 Analysis of 2,4-dichlorophenoxyacetic Acid

Absorbance of samples were measured at $\lambda_{\max}$ = 228 nm by means of Jasco Model 7800 UV/VIS Spectrophotometer.

Before beginning measurement of absorbances of the samples, the absorbances of 1.0, 5.0, 10.0, 15.0 and 20.0 mg 2,4-D / L of standart solutions were measured to obtain the calibration curve (Figure 2.1). The calibration curve was obtained before every measurement. After the calibration curve was determined, absorbances of samples were measured.

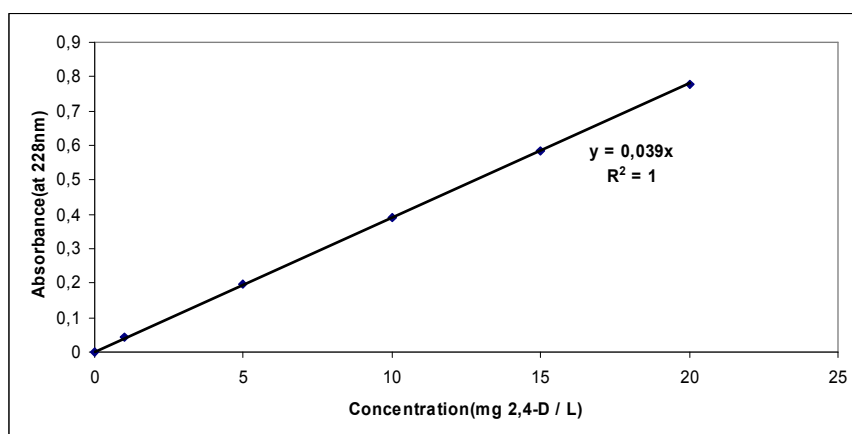


Figure 2.1 Calibration curve adsorbate 2,4-dichlorophenoxyacetic acid

2.2.4 Inoculation Methods

Two different techniques are advised for the bacteria inoculation from the biologist in the literature. One of them is the inoculating bacteria in TSB, other is inoculating bacteria on TSA.

Inoculating Bacteria Cultures with TSB and TSA

After preparation TSB medium, the cultures (going to be inoculate and culture that inoculum taken from) were taken in front of bunsen burner to sterile (Fig 2.2a). The inoculating wire loop was heated and to be sured that the entire wire was sterilized (Fig 2.2.b). The inoculum was picked from the bacterial culture (Fig 2.2.c). The sterile inoculation wire loop was kept in hand, both tube caps were removed with little finger. The sterilized tube tops (to eliminate potential air contamination) was replaced. The bacterial culture was inoculated into TSB (TSB is in liquid form at room conditions). The sterilized tube tops (to eliminate potential air contamination again) were replaced again. The tubes were incubated in 27-30 °C incubator with 48 hour hold.

The differences in inoculating bacteria with TSA are; after preparation TSA medium, 7mL TSA was discharged to 16x150mL test tube and autoclaved (15 min at 121 °C). Tubes filled with TSA was taken out from the autoclave and slope agar was obtained at room temperature. The same sterilization procedure in TSB was applied. The only difference of TSA is solid even if TSB is liquid at room conditions so the bacterial culture was inoculated onto TSA. After incubated the tubes in 27-30 °C incubator with 48 hour hold, sterile saline water (0.86%NaCl) (approximately 4mL) was added to the inoculated bacterial culture that

were grown on TSA, which was suspended with a glass rod. The bacterial suspension was homogenized using a vortex mixer (Fig 2.2d)

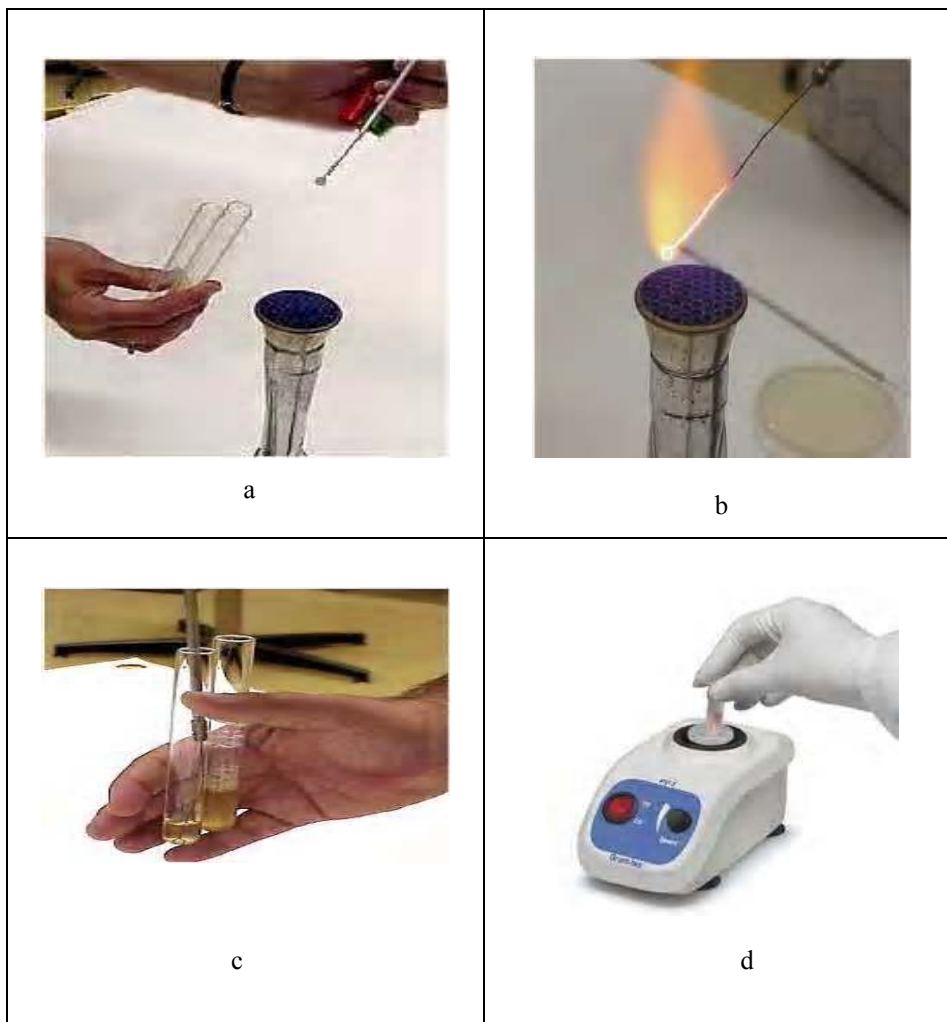


Figure 2.2 Figures of inoculating bacteria

Bacteria Count Methods

Many of the bacteria present in a sample may grow on the medium used at the pH and the temperature employed or in the time inoculated. It is often necessary to report on the size of bacterial population in sample, in every inoculation. Accuracy is often demanded where it is not needed. And it should be said that, in viable count methods, it is recognized that large errors are inevitable, even if numbers of replicate plates are used. (Collins and Lyne, 1976)

There are many ways to count the bacteria. The most known, used ones are pour plate count and viable plate count techniques.

• Pour Plate Method



Figure 2.3 Procedure for pour plate count technique

Figure 2.3 shows the procedure of pour plate count.

• Viable Plate Count Method

Firstly, dilution tubes were prepared. 9mL sterile 0.86 NaCl-H₂O solution was repipetted into each of sterile 16x150mm capped tubes. The tubes were labeled as 1, 2, 3, 4, 5, 6, 7, 8 for the 10², 10³, 10⁴, 10⁵, 10⁶, 10⁷, 10⁸ dilutions(Fig 2.4a). Then 10⁻⁸ serial dilution of the suspension was performed and used a fresh pipette for each solution as ; 1 mL of the original bacteria suspension was delivered into first tube, vortex to mix. 1 mL from #1 was delivered into #2 tube, vortex to mix. Dilution was made from 1st to 8th tubes (Fig 2.4b). Labeled numbered empty petri dish was inoculated with the diluted bacteria solution that was taken from the same number of dilution tube (Fig 2.4c). 15 mL of melted TSA (at 25-30°C) was poured into the inoculated petri dish (Fig 2.4d). By gentle tilting and swirling, the petri dish was covered and mixed thoroughly. The agar was placed on a flat surface, undisturbed for about 10 minutes to allow the agar to *completely* gel. The agar was completely gelled and the surface was "smooth as glass" (Fig 2.4e). The agar was inverted and incubated at 27-30° for 48 hours (Fig 2.4f) and counted, recorded. Each colony represents a "colony forming unit" (CFU).

For optimum accuracy of a count, the preferred range for total CFU/plate is between 30 to 300 colonies/plate (Collins and Lyne, 1976).

Figure 2.5 shows the procedure for the viable count method for bacteria studies.

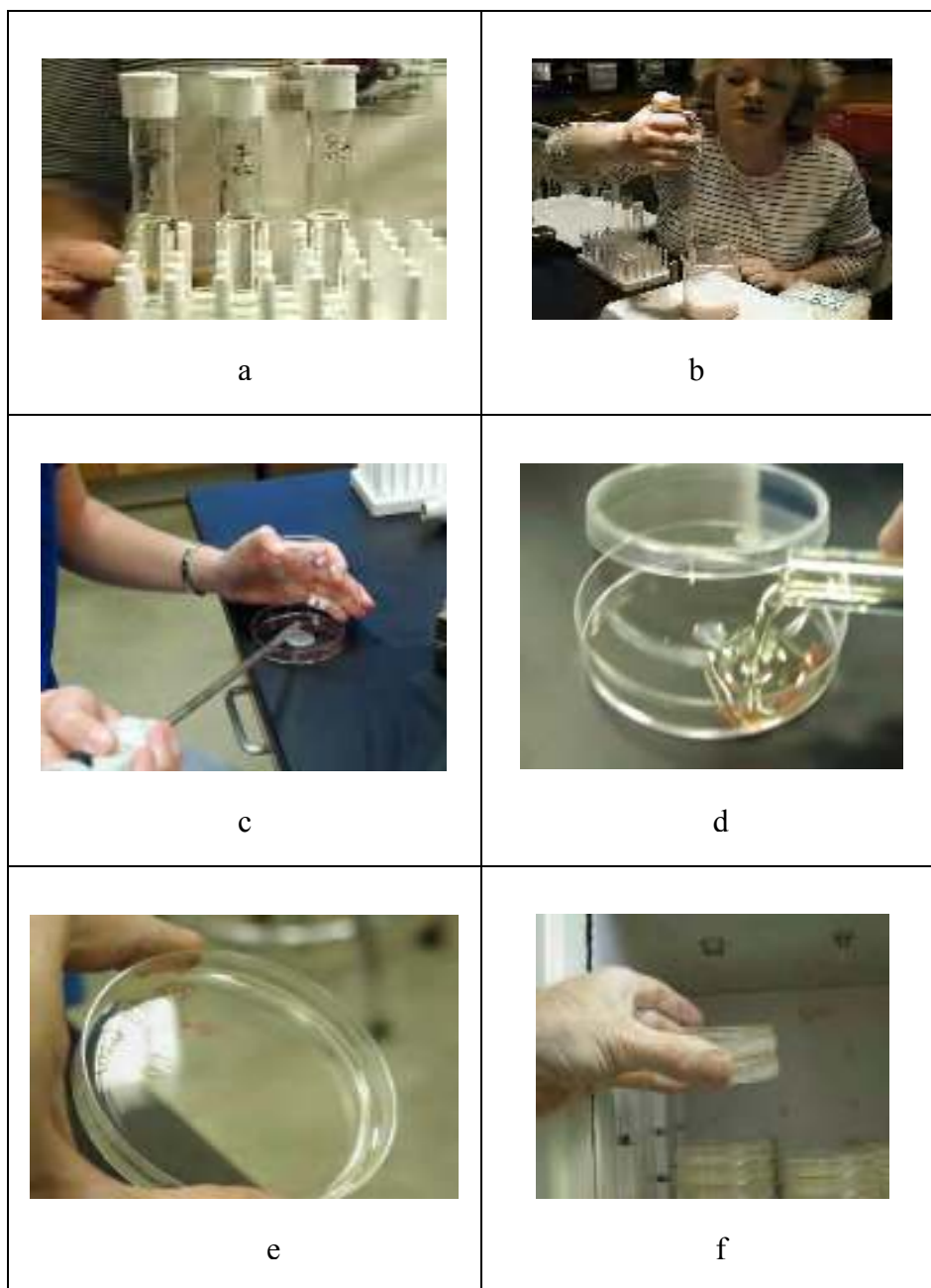


Figure 2.4 Figures for viable plate count technique

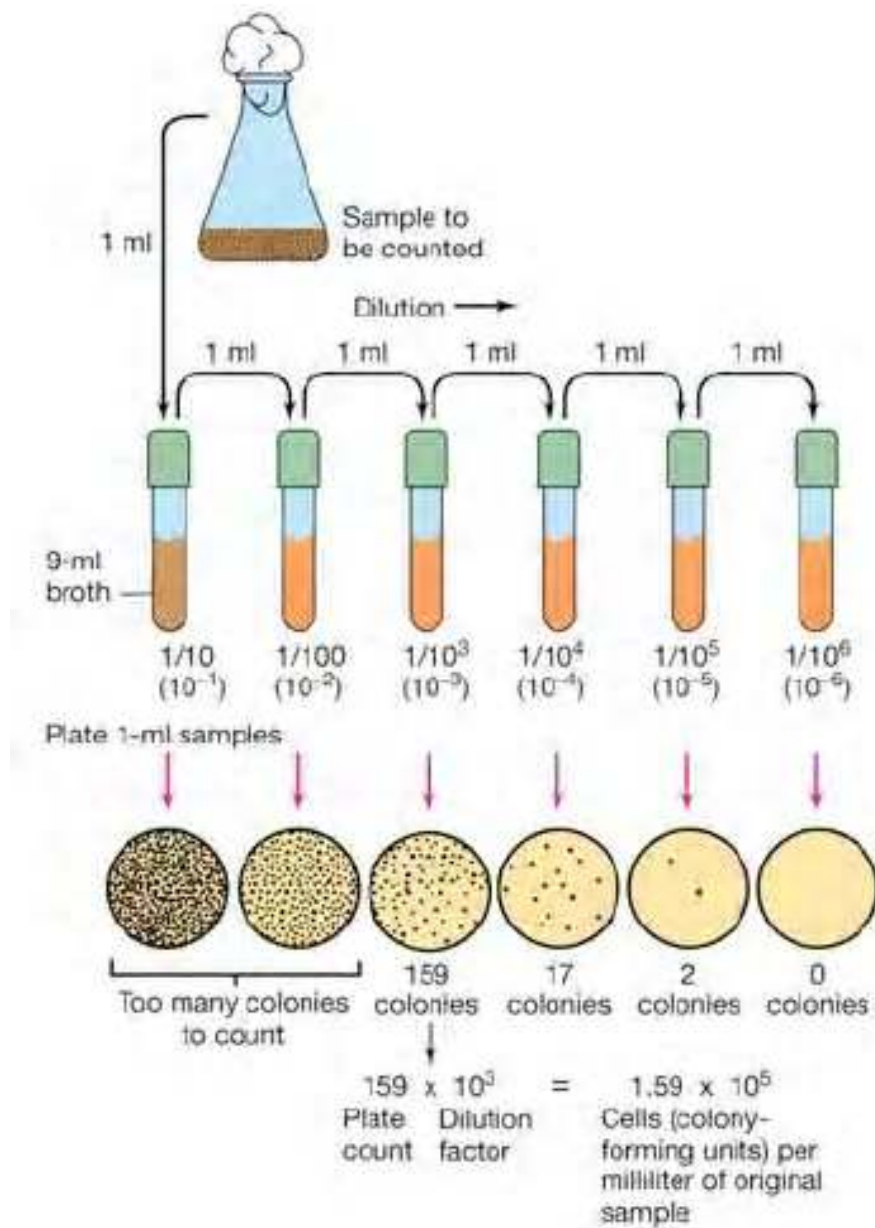


Figure 2.5 Procedure for viable plate count technique

2.3. Experimental Programme

2.3.1 Batch Mode Adsorption Studies

Time Dependent/Kinetic Study

The adsorption kinetic study was carried out in batch mode. 100 mL conical flasks were used in kinetic experiments. 50 mL of 100 ppm 2,4-D solutions were taken in set of bottles and the adsorbent were added to these as 0.01g. The sample bottles were shaken on a mechanical shaker at 90 rpm. The experiments were carried out for duration of 48 h at 25°C and the samples were collected every 1 hour up to 6 hours, and then every 8 hours. Blanks without GAC prepared in the same way showed no adsorption of pesticides on the flask wall. The studies were conducted in duplicate for all samples to ensure the reproducibility of results and the average value is reported in all the cases. The amount of 2,4-D adsorbed by GAC was calculated from the difference between the initial and equilibrium 2,4-D concentration in solution.

Concentration-dependent/Isotherm Study

Concentration dependent studies were carried out in 100 mL conical flasks. 2,4-D sample concentrations (50 mL) were in the range of 20-100 ppm. Each sample consisted of 0.01g GAC. The sample bottles were shaken on a mechanical shaker at 90 rpm at 25°C. Blanks without GAC prepared in the same way showed no adsorption of pesticides on the flask wall. The studies were conducted in duplicate for all samples to ensure the reproducibility of results and the average value is reported in

all the cases. The amount of 2,4-D adsorbed by GAC was calculated from the difference between the initial and equilibrium 2,4-D concentration in solution.

2.3.2 Continuous Mode Adsorption Studies

In order to get information about column performance of GAC on removal of 2,4-D, continuous mode adsorption studies were performed. Figure 2.6 and 2.7 show the flowsheet of the column studies and the photograph of continuous mode studies that used in the laboratory.

In these studies, a glass column with an internal diameter of 1.1 cm is used. The column was operated in upflow mode at room temperature using a peristaltic pump with no effluent recycle. The GAC in the 1-2 mm of particle size range were used for the column studies. The column was cleaned with dilute chromic acid and rinsed with distilled water before the experiments. Distilled water was pumped in an upflow mode to remove any trapped air from the bed.

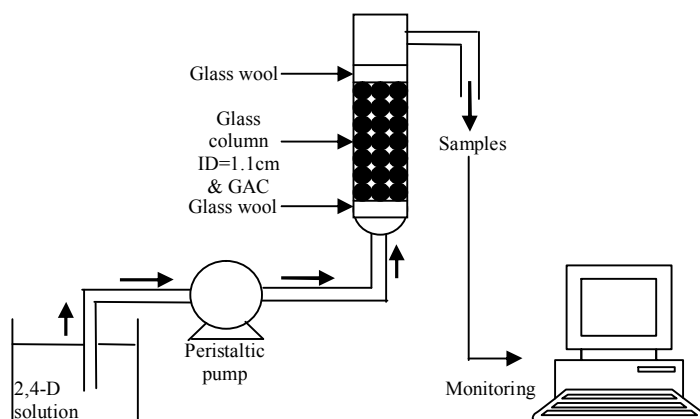


Figure 2.6 Flowsheet of continuous mode studies



Figure 2.7 Photograph of continuous mode studies that used in the laboratory

Effect of Influent Concentration

50ppm, 100ppm, 150ppm, 200ppm influent concentrations were studied with 3 different flowrates (0.2; 0.3; 0.4mL/min) in column mode with 2cm bed height. In Table 2.3, characteristics and operational parameters for the effect of influent concentration experiments are tabulated.

Table 2.3 Characteristics and operational parameters for the effect of influent concentration and flowrate experiments in continuous mode.

Flow Rate (v) (mL/min)	0.2 ; 0.3; 0.4
Column Height (cm)	2.5
Initial Concentration (C_o) (ppm)	50; 100; 150; 200
Internal diameter (cm)	1,1
Area of Column (cm²)	3.8
Column Material	Glass
Bed Height (h) (cm)	2
Adsorbent	GAC
Mass of Adsorbent (g)	~ 0.85-1
Particle Size Range(mm)	1-2
Type of pump	Watson Marlow/Peristaltic Pump
Retention Time (min)	9.0min for v=0.2mL/min 6.0min for v=0.3mL/min 4.5min for v=0.4mL/min
Mode of Flow	Upflow

Effect of Flowrate

0.2mL/min; 0.3 mL/min; 0.4mL/min flowrates were studied with 4 different concentrations (50; 100; 150; 200ppm) in column mode with 2cm bed height. In Table 2.3, characteristics and operational parameters for the effect of flowrate experiments are tabulated.

Effect of Bed Height

2.0cm; 2.5cm; 3.0cm; 3.5cm bed heights were studied with influent concentration of 200ppm and flowrate of 0.4mL/min. In Table 2.4, characteristics and operational parameters for the effect of flowrate experiments are tabulated.

Table 2.4 Characteristics and operational parameters for the effect of bed height experiments in continuous mode.

Flow Rate (v) (mL/min)	0.4
Column Height (cm)	2.5-4.0
Initial Concentration (C_o) (ppm)	200
Internal diameter (cm)	1.1
Area of Column (cm²)	3.8
Column Material	Glass
Bed Height (h)(cm)	2.0; 2.5; 3.0; 3.5
Adsorbent	GAC
Mass of Adsorbent (g)	~ 1; 1.2, 1.4; 1.6
Particle Size Range(mm)	1-2
Type of pump	Watson Marlow/Peristaltic Pump
Retention Time (min)	4.5min for h=2.0cm 8.0 min for h=2.5cm 10 min for h=3.0cm 12 min for h=3.5cm
Mode of Flow	Upflow

2.3.3 Biological Contamination Studies

Effect of Biological Contamination in Batch Mode Concentration-dependent Study

The adsorbed concentration studies were carried out with 0.0050; 0.010; 0.015; 0.020 (mL bacteria/mL 2,4-D solution) in batch mode. 2,4-D sample concentrations (50 mL) were in the range of 20-100 ppm. Each sample consisted of 0.01g GAC. The sample bottles were shaken on a mechanical shaker at 90 rpm at 25°C. Blanks without GAC prepared in the same way showed no adsorption of pesticides on the flask wall. The studies were conducted in duplicate for all samples to ensure the reproducibility of results and the average value is reported in all the cases. The sample solution that contained bacteria solution was filtered by vacuum pump using cellulose filter with pore size (0.45 μ m) . The amount of 2,4-D adsorbed by GAC was calculated from the difference between the initial and equilibrium 2,4-D concentration in solution.

Effect of Biological Contamination Load in Continuous Mode Study

In order to get information about column performance of GAC with bacteria on removal of 2,4-D , continuous mode adsorption studies with bacteria were performed.

In these studies, a glass column with an internal diameter of 1.1 cm and bed height 2cm is used. The column was operated in upflow mode at room temperature. The GAC in the 1-2 mm of particle size range was used for the column study with bacteria. The column was cleaned with

dilute chromic acid and rinsed with distilled water before the experiments. Distilled water was pumped in an upflow mode to remove any trapped air from the bed. 0.020 (mL bacteria/mL 2,4-D solution) was loaded for 20 hour, 44 hour and 68 hour time intervals using a peristaltic pump with flowrate of 0.4mL/min and no effluent bacteria recycle. After loading column with bacteria, 200 ppm 2,4-D was pumped with flowrate 0.4 mL/min.

3. RESULTS AND DISCUSSION

3.1 Batch Mode Adsorption Studies

3.1.1 Kinetic Modeling of Adsorption of 2,4-D in a Batch system

If the movement of organic pollutant molecule from the bulk liquid to the liquid film or boundary layer surrounding the adsorbent is ignored, the following sequence of steps can take place in the adsorption process of a porous adsorbent: transport of solute molecules from the boundary film to the external surface of the adsorbent (film diffusion), transfer of molecules from the surface to the intraparticle active sites and uptake of molecules by the active sites of sorbent. In the removal of organics from wastewater, it is important for design purposes to investigate the mechanisms of adsorption and potential rate controlling steps which control the adsorption rate. In order to find the contribution of rate controlling steps such as external mass transfer, intraparticle diffusion, and adsorption process and also, mass transfer and kinetic models have been used to test the experimental data.

Application of the Film Diffusion Model

In Figure 3.1, the film diffusion graph of GAC(1-2mm) for adsorption of 2,4-D is shown. Results were tabulated in Appendix-I. As seen from the integrated form of the film diffusion equation, $\left[\log \frac{C_0}{C} = \frac{1}{2.303} k_{1,ad} t \right]$ where $C_0(\text{mg/L})$ is the initial pollutant concentration and $k_{1,ad} (\text{mg/L})$ is the first-order reaction-rate constant; if

the film diffusion would be the rate controlling step, the line must be passed through the origin and a linear trendline should be obtained from the experimental data. But in the film diffusion graph in Figure 3.1, it is seen that the obtained trendline was logarithmic not linear and did not pass through the origin. As result, it can be said that the film diffusion was not the controlling step in the GAC (1-2mm) adsorption process and the adsorption rate was not proportional to the first order power of concentration.

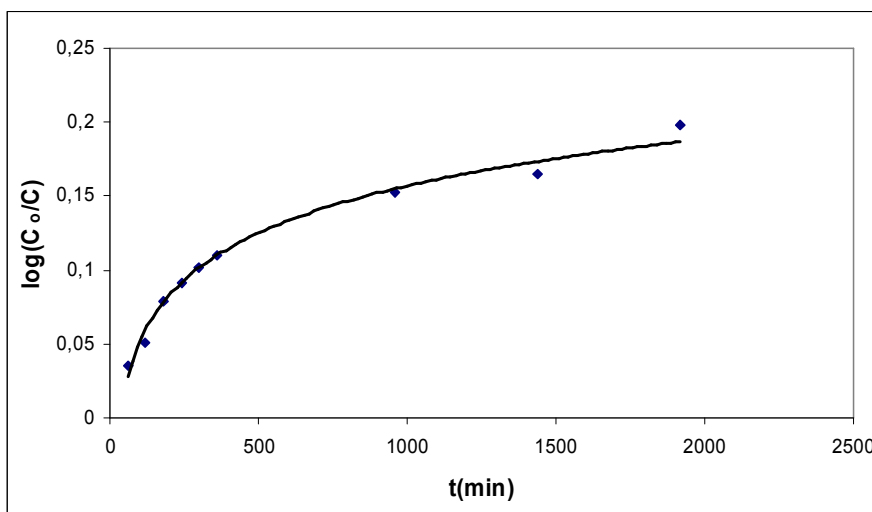


Figure 3.1 The film diffusion graph for GAC (1-2mm) ($x=0.01g$, $C_0=100ppm$ 2,4-D, equilibrium time=40hours)

Application of the Intraparticle Diffusion Model

The intraparticle diffusion graph of GAC(1-2mm) for adsorption of 2,4-D is shown in Figure 3.2. Results are tabulated in Appendix-I. The linear plot of the intraparticle diffusion equation $[q_t = k_{id}t^{1/2} + C]$;

where k_{id} ($\text{mg/g.min}^{0.5}$) is the intra-particle diffusion rate constant] was attributed to the pore diffusion (probably macropore) that is accessible sites of adsorption. This is attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface. From the slope of the line, the k_{id} value was found as $3.628 \text{ mg/ (gxmin}^{0.5} \text{)}$, and the value of intercept “C” was found to be 29.58. It can be said that the boundary layer effect was great or in other words the thickness of the boundary layer was high. Ahmaruzzaman and Sharma, 2005 investigated the k_{id} values for phenol adsorption onto samla coal and activated carbon as 0.0353 and $0.0268 \text{ mg/ (gxmin}^{0.5} \text{)}$, respectively. When k_{id} values of 2,4-D adsorption onto GAC(1-2mm) compared respect to phenol adsorption onto samla coal and activated carbon, it can be said that in 2,4-D adsorption, intraparticle diffusion occurred faster. And also by assuming the spherical geometry for the active carbon particle and the diameter was taken as 0.15cm, from the pore diffusion equation [$t_{1/2} = 0.03r_0^2 / D_p$, where $t_{1/2}$ is the time for half adsorption (s), r_0 is the radius of the adsorbent particle (cm) and D_p is the diffusion coefficient (cm^2/s)], the pore diffusion coefficient was calculated as $2.344 \times 10^{-9} \text{ cm}^2/\text{s}$ where Ahmaruzzaman and Sharma (2005) found as $1.36 \times 10^{-10} \text{ cm}^2/\text{s}$, $3.72 \times 10^{-11} \text{ cm}^2/\text{s}$ for samla coal and activated carbon, respectively. The value of the pore diffusion rate constant was found to be on the order of $10^{-9} \text{ cm}^2/\text{s}$ indicating that the pore diffusion was significant in 2,4-D adsorption on GAC(1-2mm) whereas in phenol adsorption not because of 10^{-10} - $10^{-11} \text{ cm}^2/\text{s}$ orders as proved by Faust and Alay (1986) for phenol adsorption onto active carbon.

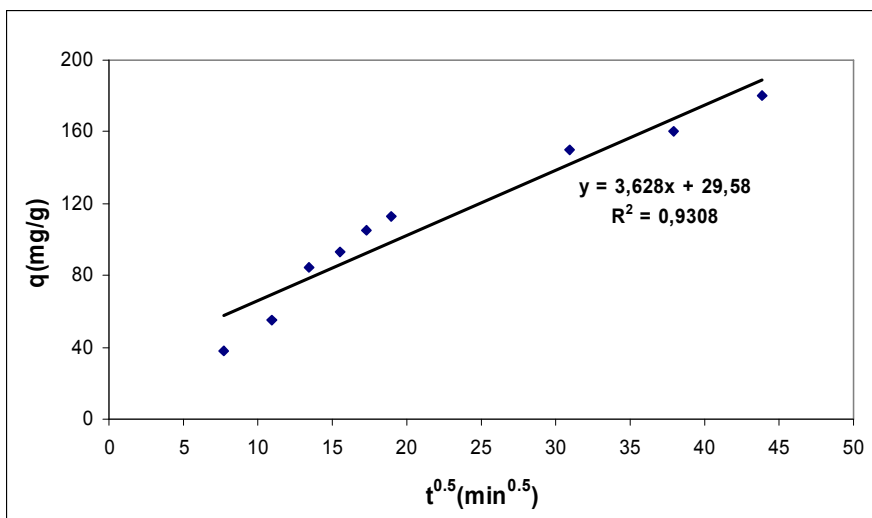


Figure 3.2 The intraparticle diffusion graph for GAC (1-2mm) ($x=0.01\text{g}$, $C_o=100\text{ppm}$ 2,4-D, equilibrium time=40hours)

Application of the Bangham's Equation

The applicability of the following Bangham equation $[\log \log(C_o / (C_o - q_t m)) = \log(k_o m / 2.303V) + \log(t)]$, where C_o is the initial concentration of adsorbate in a solution (mg/L), V is the volume of solution (mL), m is the weight of adsorbent per liter of solution (g/L), q_t (mg/g) is the amount of adsorbate retained at time t , and α (less than 1) and k_o are constants] was studied in the present study and the graph is shown in Figure 3.3. Results were tabulated in Appendix-I. It can be seen from the figure that the double logarithmic plot according to Bangham's equation yielded a very good linear curve (correlation coefficient value was obtained as 0.95) for the linear regression values for 2,4-D removal by carbon. The linearity of this plot confirms the applicability of the Bangham equation and indicates that diffusion of pesticides into pores of the adsorbent mainly controls the adsorption process as by Aharoni et al.

(1979) proved for colloid ioncoated alumina in adsorption of phosphate ions and as proved by Tutem et al. (1998) for bituminous shale in adsorption of chlorophenols.

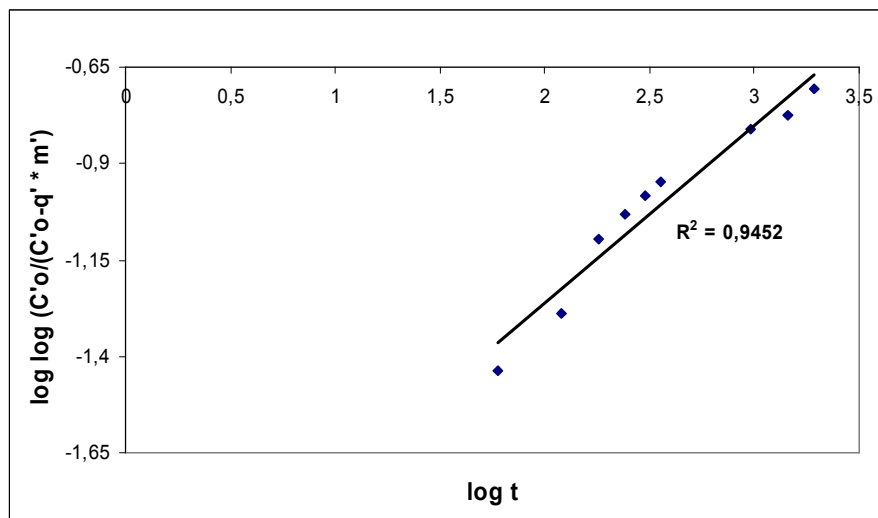


Figure 3.3 The Bangham's Equation graph for GAC (1-2mm) ($x=0.01\text{g}$, $C_o=100\text{ppm}$ 2,4-D, equilibrium time=40hours)

Application of the First Order and the Second Order Kinetic Models

The obtained kinetic data was fitted to the sorption kinetics using the pseudo first order and pseudo second order kinetic model equations for GAC (1-2mm). Figure 3.4 was plotted in order to observe first order reaction orders by plotting $\log (q_e - q)$ versus time and Figure 3.5 was plotted in order to observe second order reaction orders by plotting t/q versus time. Predicted q_e values were also calculated from the graphs. Theoretical and experimental comparisons are given in the Figure 3.6 for

first order and second order kinetics. Related data were tabulated in the Appendix-I.

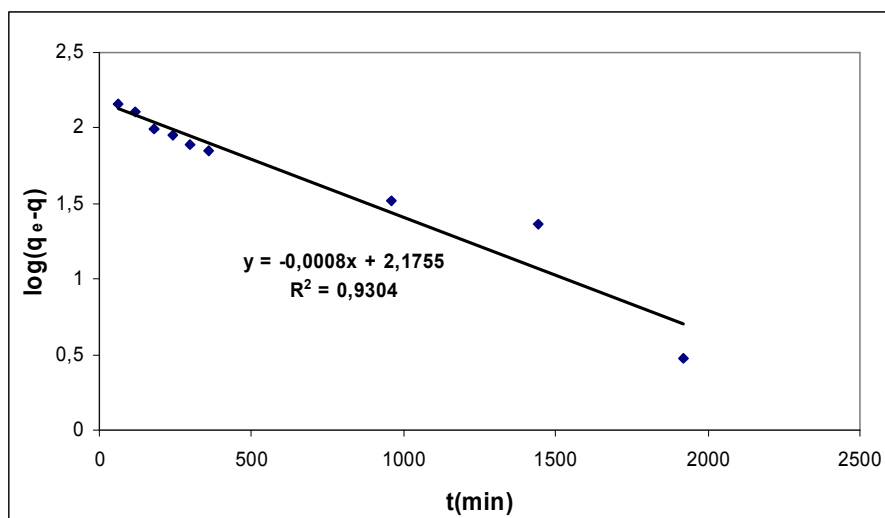


Figure 3.4 Linearized form of pseudo-first-order kinetics for 2,4-D adsorption on GAC (1-2mm)

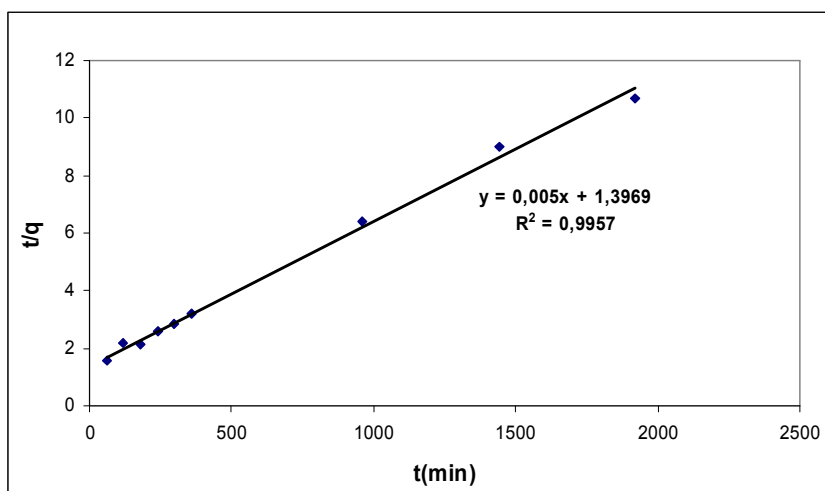


Figure 3.5 Linearized form of pseudo-second-order kinetics for 2,4-D adsorption on GAC (1-2mm)

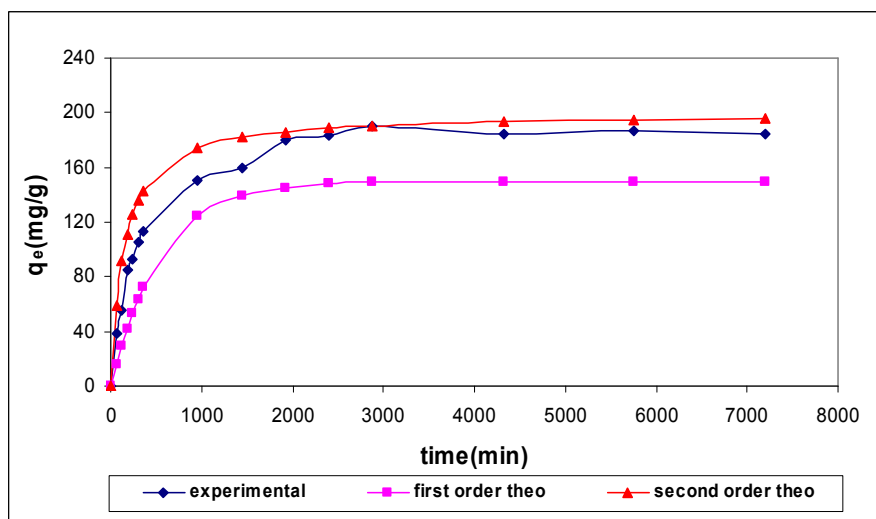


Figure 3.6 Comparison of first and second order kinetic model with predicted and experimental q_t values for 2,4-D adsorption on GAC (1-2mm)

Sorption kinetics reaction orders for GAC (1-2mm) ($R^2 = 0.9304$ for first order and 0.9957 for second order kinetics) greatly fit to pseudo-second-order mechanism.

The comparison of the experimental and theoretical curves for second order kinetics showed similarity as a proof of the fitting to the Ho pseudo-second-order mechanism.

With the comparison of obtained results from different adsorption processes of 2,4-D, the first and second order kinetic constants are tabulated in Table 3.1 and Table 3.2, respectively.

Table 3.1 The comparison of the pseudo first order kinetic constants

Adsorbent	$q_{e,calc}$ (mg/g)	$k_{1,ads}$ (1/min)	Reference
GAC (1.19-3.36mm)	96.60	39.12×10^{-4}	Aksu and Kabasakal, 2004
PAC (<0.15mm)	50.8	15.34×10^{-2}	Aksu and Kabasakal, 2005
DAS	4.46	15.40×10^{-3}	Gawede et al., 2005
Carbonaceous adsorbent	48.67	31.9×10^{-3}	Gupta et al., 2006
GAC (1-2mm)	149.77	18.42×10^{-4}	Thesis

As seen in Table 3.1, although rate constant of GAC(1,19-3,36mm) was nearly half of the GAC(1-2mm), the amount of solute adsorbed at equilibrium (q_e) was nearly 100 mg/g because of the studied pH. The obtained constant values for “DAS” was not a surprise because it was investigated that DAS showed non-favourable adsorption for 2,4-D .

Table 3.2 The comparison of the pseudo second order kinetic constants

Adsorbent	$q_{e,calc}$ (mg/g)	$k_{2,ads}$ [g/(mg × min)]	Reference
GAC (1,19-3,36mm)	102.00	18.29×10^{-5}	Aksu and Kabasakal, 2004
PAC (<0,15mm)	102.00	0.86×10^{-5}	Aksu and Kabasakal, 2005
Carbonaceous adsorbent	81.96	2.18×10^{-3}	Gupta et al., 2006
GAC (1-2mm)	200.00	1.790×10^{-5}	Thesis

As seen in Table 3.2, $k_{2,ads}$ (rate constant) and the amount of solute adsorbed at equilibrium (q_e) of PAC were nearly the half of the GAC(1-2mm) even if PAC had more surface area than GAC. Rate constant of GAC(1,19-3,36mm) was nearly ten times of the GAC(1-2mm), but q_e value was not too small when compared with the rate constants ratio. The reason for this result might be the studied pH.

3.1.2 Equilibrium Modeling of Adsorption of 2,4-D in a Batch System

Equilibrium data was obtained for 2,4-D adsorption onto GAC (1-2mm). The results are tabulated in Appendix-II. The equilibrium relationship for GAC (1-2mm) was shown in Figure 3.7. The linearized fitting curves of for GAC (1-2mm)) are given for Langmuir and Freundlich models in Figure 3.8 and Figure 3.9, respectively. The comparison of experimental and theoretical curves of Langmuir and Freundlich models is shown in Figure 3.10.

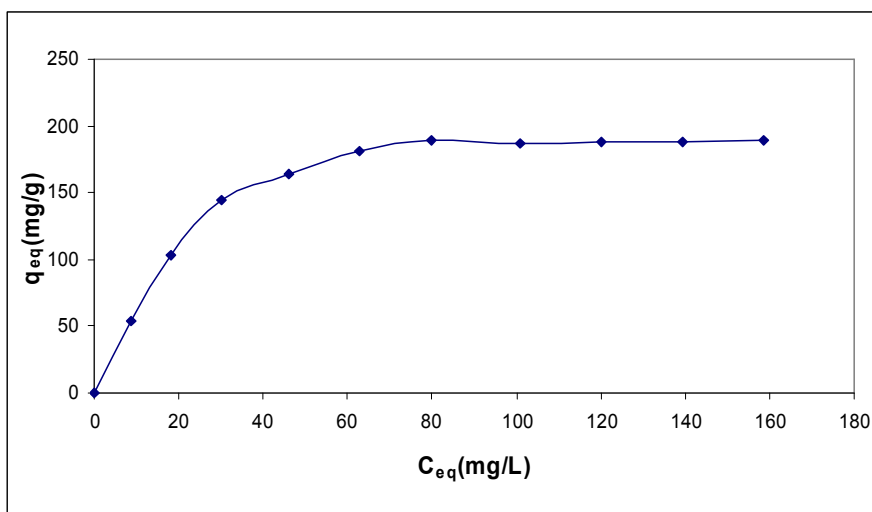


Figure 3.7 Equilibrium isotherm of GAC(1-2 mm) for adsorption of 2,4-D

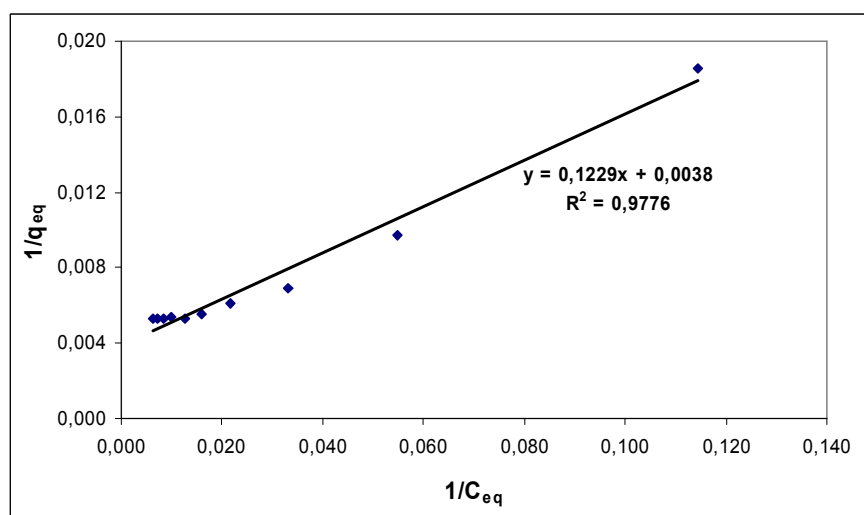


Figure 3.8 Linearized form of Langmuir model of GAC(1-2mm) for adsorption of 2,4-D

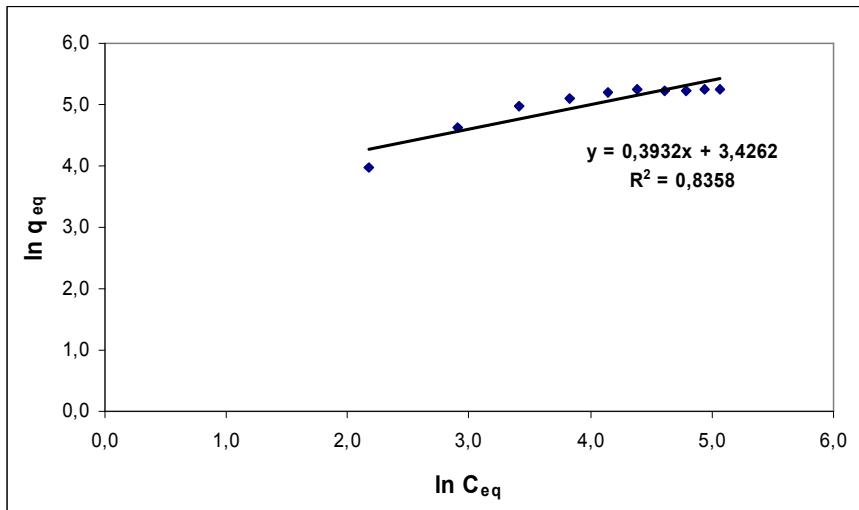


Figure 3.9 Linearized form of Freundlich model of GAC (1-2 mm) for adsorption of 2,4-D

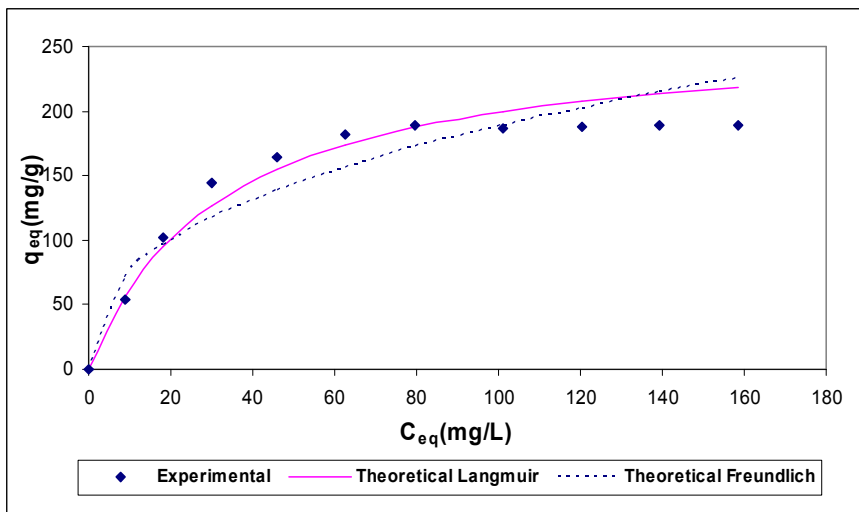


Figure 3.10 The comparison of the experimental and theoretical curves for Langmuir & Freundlich models of GAC (1-2 mm) for adsorption of 2,4-D

The correlation coefficients for the linear regression fit of Langmuir and Freundlich model were found to be 0.9776 and 0.8358 for GAC (1-2 mm), respectively. The adsorbent showed a better fit for the Langmuir model than the Freundlich model. The theoretical curve for Langmuir shows similarity with the equilibrium curve indicates that there is a strong relationship for the data and the Langmuir model mechanism. All the results show that the Langmuir model fitted the results quite well suggesting that the surface of the sorbent is homogeneous.

The Langmuir parameter can be used to predict the affinity between the sorbent and sorbate using the dimensionless separation factor (R_L). Figure 3.11 shows that the values of R_L ($R_L = 1/(1+bC_0)$ where C_0 is the initial concentration of adsorbate in (mg/L), and b is the Langmuir constant) for the adsorption of 2,4-D. R_L values were between 0 and 1, which indicates the favourable adsorption of 2,4-D on GAC (1-2mm). as Ahmaruzzaman and Sharma (2005) found for adsorption of phenols from wastewater and Vadivelan and Kumar (2005) found for sorption of methylene blue onto rice husk. And also it can be said that higher R_L values at lower concentrations showed that the adsorption was more favourable at lower 2,4-D concentrations.

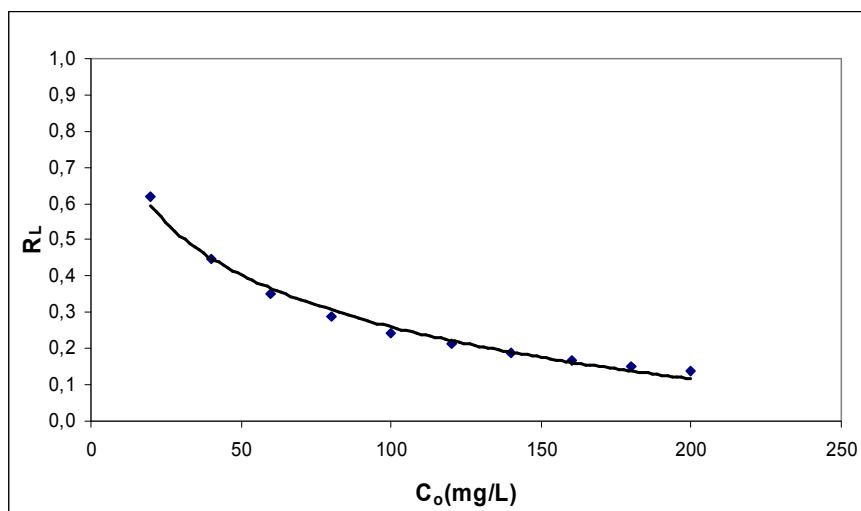


Figure 3.11 Separation factor of 2,4-D sorbed on GAC (1-2 mm).

The comparison of Langmuir and Freundlich parameters from different references and the thesis are tabulated in Tables 3.3-3.4, respectively.

As seen from the Table 3.3, Q_0 (maximum adsorption capacity (mg/g)) of PAC was higher than GAC(1-2mm) as a result of high studied pH even if b (bonding energy of adsorption (L/mg)) was nearly the same. Although the bonding energy of adsorption values (b) of GAC F400 (55-65mm) and GAC SLS103 (55-65mm) were higher than GAC(1-2mm), maximum adsorption capacities (Q_0) were lower because of the particle size, in spite of the same pH was studied. It was not a surprise that maximum adsorption capacity of organo-clay was very low respect to activated carbon because of the surface area, even if the optimum pH level was studied for 2,4-D adsorption onto organo clays.

Table 3.3 Langmuir parameters (Q_0 and b) of different adsorbents that used in removal of 2,4-D

pH	Adsorbent	Q_0 (mg/g)	b (L/mg)	Reference
2.0	GAC (1.19-3.36mm)	555	28.00×10^{-3}	Aksu and Kabasakal, 2004
2.0	PAC (<0.15mm)	333.3	29.00×10^{-3}	Aksu and Kabasakal, 2005
7.0	GAC F400 (55-65mm)	135.915	40.69×10^{-3}	Kim et al., 2005; Kim et al., 2002; Cho et al., 2003
7.0	GAC SLS103 (55-65mm)	142.766	38.32×10^{-3}	Kim et al., 2005; Kim et al., 2002; Cho et al., 2003
7.0	GAC WWL (55-65mm)	126.191	6.502×10^{-3}	Kim et al., 2005; Kim et al., 2002; Cho et al., 2003
6.5-7.5	Carbonaceous adsorbent	322.5	22.5×10^{-3}	Gupta et al., 2006
2.8	Organo-clays	4.604	0.136×10^{-3}	Akçay and Yurdakoç, 2000
6.5-7	Calcinated Hydrotalcite	179.673	12.67×10^{-3}	Pavlovic et al., 2005
7	Zinc-aluminium-chloride layered double hydroxides	(115.8±11.05) (735.93±6.63) (587.86±6.63)	(57.1±0.361) $\times 10^{-3}$ (56.6±0.361) $\times 10^{-3}$ (55.8±0.361) $\times 10^{-3}$	Legrouri et al., 2005
6.5-7	GAC (1-2mm)	263.158	30.919×10^{-3}	Thesis

As seen in Table 3.4, adsorption intensity, n values of DAS, 13 contrasting field soils, organo-clays were smaller than 1 which suggested that adsorption capacity, K_F values were to be less than other adsorbents.

Table 3.4 Freundlich parameters (K_F and n) of different adsorbents that used in removal of 2,4-D

pH	Adsorbent	K_F [(mg/g)X(mg/L) ⁿ]	n	Reference
2.0	GAC (1.19-3.36mm)	42.48[(mg/g)X(mg/L) ⁿ]	2.06	Aksu and Kabasakal, 2004
2.0	PAC (<0.15mm)	43.93[(mg/g)X(mg/L) ⁿ]	2.91	Aksu and Kabasakal, 2005
7.0	GAC F400 (55-65mm)	0.771[(mol/kg)X(mol/m ³) ⁿ]	4.45	Kim et al., 2005; Kim et al., 2002; Cho et al., 2003
7.0	GAC SLS103 (55-65mm)	0.898[(mg/g)X(mg/L) ⁿ]	3.56	Kim et al., 2005; Kim et al., 2002; Cho et al., 2003
7.0	GAC WWL (55-65mm)	0.696[(mg/g)X(mg/L) ⁿ]	1.99	Kim et al., 2005; Kim et al., 2002; Cho et al., 2003
2.8	Organo-clays	0.519(μmol/g)	0.96	Akçay and Yurdakoç, 2000
-	DAS	2.44(mol/g)	0.97	Akçay et al., 2005
3.0	13 constrasting field soils	3.3-8.7[(mg/kg)X(mg/L) ⁿ]	0.85-0.94	Boivin et al., 2005
6.5-7	GAC (1-2mm)	30.76[(mg/g)X(mg/L) ⁿ]	2.54	Thesis

3.2 Continuous Mode Adsorption Studies

3.2.1 Kinetic Modelling of Adsorption of 2,4-D in a Continuous Packed Bed System

The column performance of GAC (1-2mm) was investigated in a fixed bed column (column diameter ID=1.1cm). The effect of important

parameters, such as influent concentration, flowrate and bed height was studied.

3.2.1.1 Effect of Influent Concentration and Flowrate

In order to examine the change in influent 2,4-D concentration and flowrate as well as their effects on pesticide adsorption in the column, influent concentration and flowrate experiments were done at three different flowrates (0.2 mL/min, 0.3 mL/min, and 0.4 mL/min) and four different 2,4-D influent concentrations (50ppm, 100ppm, 150ppm, and 200ppm) with a bed height of 2cm. Breakthrough curves are shown in Figures 3.12 -3.18. Related data were tabulated in the Appendix-III.

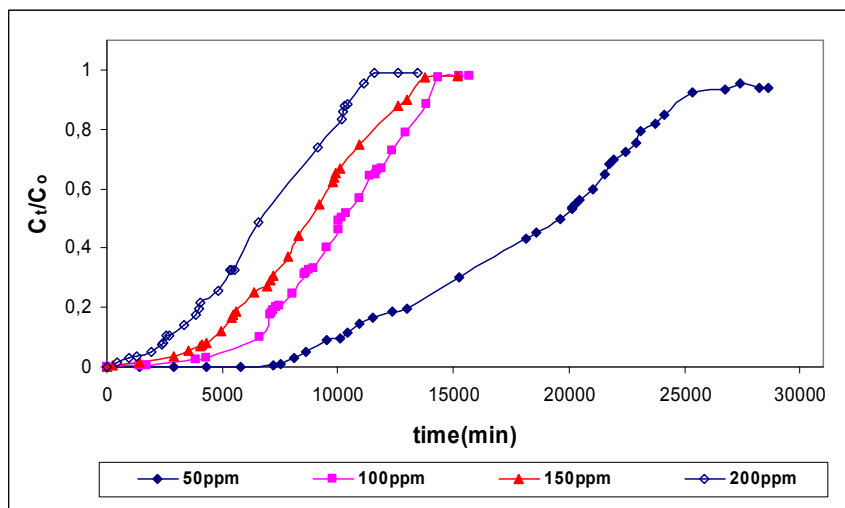


Figure 3.12 Breakthrough curves of GAC (1-2mm) obtained at different concentrations for adsorption of 2,4-D ($v = 0.2$ mL/min, bed height= 2cm)

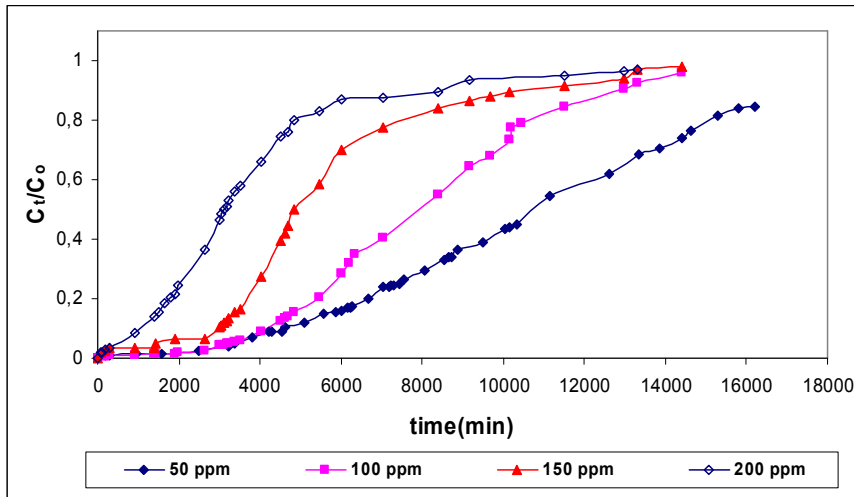


Figure 3.13 Breakthrough curves of GAC (1-2mm) obtained at different concentrations for adsorption of 2,4-D ($v = 0.3$ mL/min, bed height= 2cm)

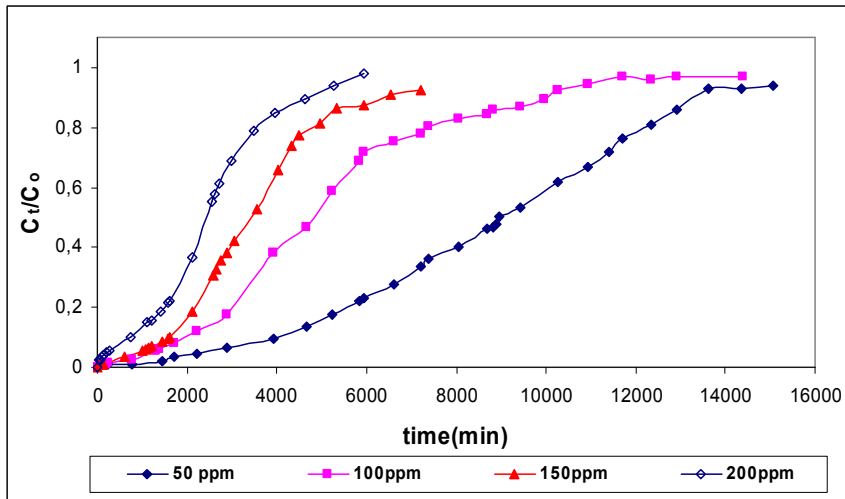


Figure 3.14 Breakthrough curves of GAC (1-2mm) obtained at different concentrations for adsorption of 2,4-D ($v = 0.4$ mL/min, bed height= 2cm)

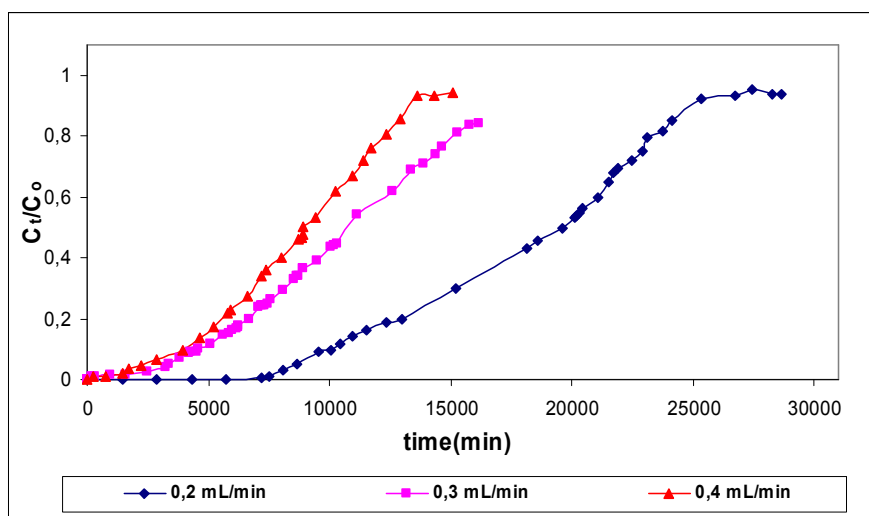


Figure 3.15 Breakthrough curves of GAC (1-2mm) obtained at different flowrates for adsorption of 2,4-D ($C_0 = 50\text{ppm}$, bed height= 2cm)

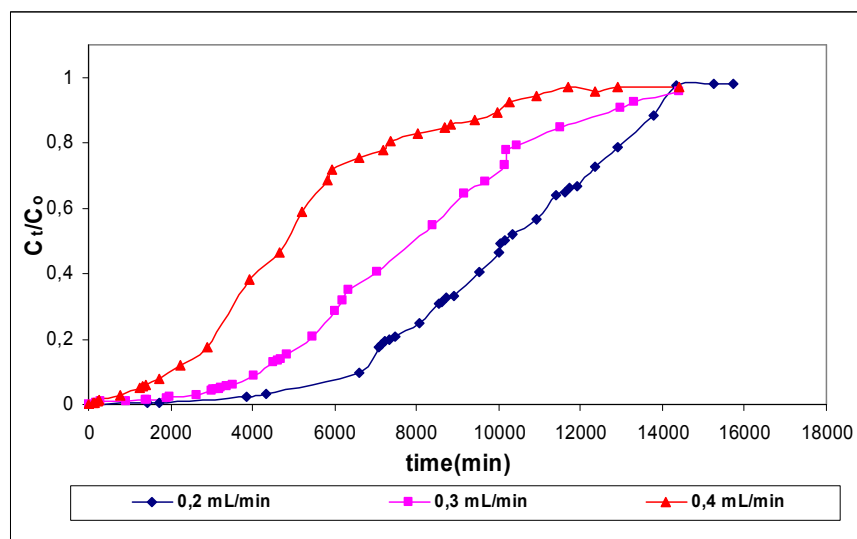


Figure 3.16 Breakthrough curves of GAC (1-2mm) obtained at different flowrates for adsorption of 2,4-D ($C_0 = 100\text{ppm}$, bed height= 2cm)

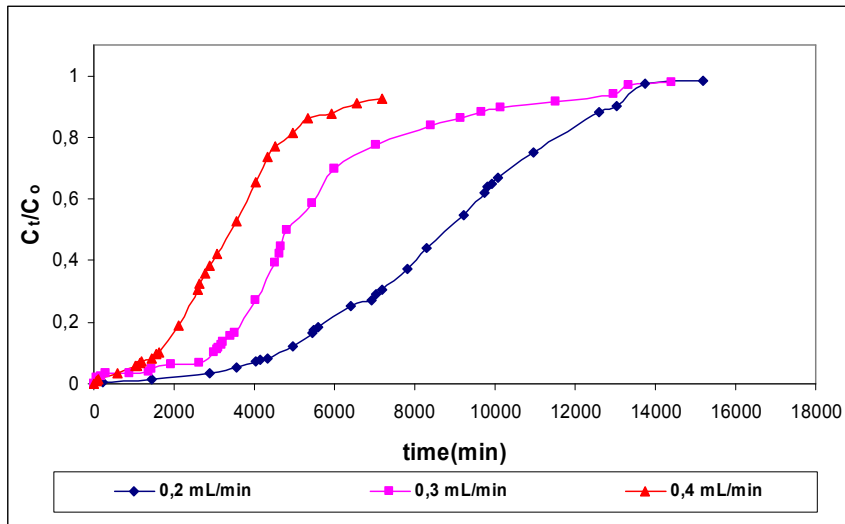


Figure 3.17 Breakthrough curves of GAC (1-2mm) obtained at different flowrates for adsorption of 2,4-D ($C_0=150$ ppm, bed height= 2cm)

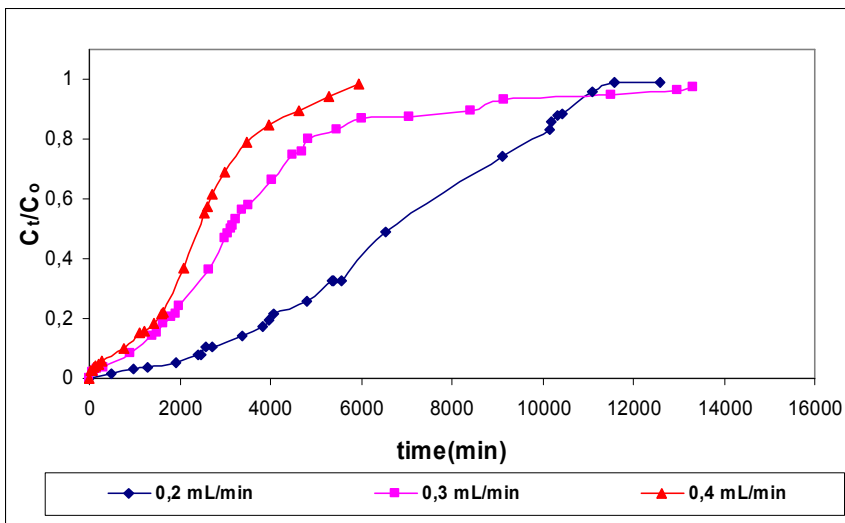


Figure 3.18 Breakthrough curves of GAC (1-2mm) obtained at different flowrates for adsorption of 2,4-D ($C_0=200$ ppm, bed height= 2cm)

As shown in the breakthrough curves from Figures 3.12-3.14, the larger the influent concentration, the steeper is the slope of the breakthrough curve and the smaller is the breakthrough time. These results demonstrate that the change of concentration gradient affects the saturation rate and breakthrough time or in other words, the diffusion process is concentration dependent. As the influent concentration increases, 2,4-D loading rate increases, but so does the driving force for mass transfer, which in a decrease in the adsorption zone length. The net effect is an appreciable increase in adsorption capacity as proved by Goel et al. (2005) for the removal of lead(II) by adsorption using treated granular activated carbon in column studies.

It was shown in breakthrough curves from Figures 3.15 to 3.18 that breakthrough generally occurred faster with faster flow rate. Breakthrough time reaching saturation was increased significantly with a decrease in the flow rate. At a low rate of influent, pesticide ions had more time to contact with carbon that resulted in higher removal of 2,4-D ions in column. While increasing the flow rate, the results indicated that the adsorption capacity would reach the equilibrium value faster, which may cause a negative effect on the mass transfer efficiency of 2,4-D ions. In other word, as the flowrate increased, the breakthrough curve becomes steeper. The break point time and adsorbed ion concentration decreases. The reason for this behavior can be explained in the following way: if the residence time of the solute in the column is not long enough for adsorption equilibrium to be reached at that flowrate, the pesticide solution leaves the column before the equilibrium occurs.

To sum up; it can be said that for reaching the maximum adsorption capacity in the column, it should be studied with lower flowrate and higher influent concentration and higher flowrate and lower influent concentration have disadvantage to adsorption of 2,4-D on GAC column.

The effect of influent concentration and flowrate on the column adsorption parameters were investigated by the kinetic modeling adsorption by the Thomas, Yoon and Nelson, Adams-Bohart, and Wolborska models.

The breakthrough curves in the application of models showed the superposition of experimental results (points) and the theoretical calculated points (lines). Linear regression coefficients (R^2) showed the fit between experimental data and linearized forms of model (Thomas Yoon–Nelson, Adams-Bohart, and Wolborska) equations. Data used in the models were tabulated in Appendix III.

Application of the Thomas Model

The column data were fitted to the Thomas model to determine the Thomas rate constant, ($k_{Th} = \text{ml min}^{-1} \text{ mg}^{-1}$), and the adsorption capacity of the bed maximum ($q_0 = \text{mg g}^{-1}$). Table 3.5 shows the parameters together with the correlation coefficients. k_{Th} and q_0 can be determined from a plot of $\ln[(C_0/C_t)-1]$ against t at a given flow rate where is the linearized form of the Thomas model is as

$$\ln\left(\frac{C_o}{C_t} - 1\right) = \frac{k_{Th} q_o x}{v} - \frac{k_{Th} C_o V_{eff}}{v}.$$

Table 3.5 Parameters predicted from Thomas model of 2,4-D adsorption at different influent concentrations and flowrates

C_o (mg/L)	v (mL/min)	k_{Th} (mL/minXmg)	q_o (g/g)	R^2
50	0.2	4.00×10^{-6}	222.943	0.994
	0.3	6.00×10^{-6}	216.206	0.992
	0.4	8.00×10^{-6}	190.686	0.998
100	0.2	5.00×10^{-6}	231.661	0.998
	0.3	5.94×10^{-6}	228.423	0.987
	0.4	7.00×10^{-6}	206.889	0.962
150	0.2	3.33×10^{-6}	276.928	0.997
	0.3	5.33×10^{-6}	247.306	0.958
	0.4	6.66×10^{-6}	233.818	0.995
200	0.2	2.50×10^{-6}	282.373	0.996
	0.3	5.00×10^{-6}	250.483	0.995
	0.4	6.50×10^{-6}	238.544	0.993

As seen in Table 3.5, as concentration increased, the values of k_{Th} decreased and the values of q_o increased and as flowrate increased, the values of k_{Th} increased and the values of q_o decreased. These results were expected because; increasing flowrate causes decreasing in retention time so pesticide ions do not have more time to contact with carbon as a result bed capacity decreases and increasing concentration causes increasing the opportunity of come across of the pesticide ion and adsorbate so bed capacity increases. The maximum bed adsorption capacity (q_o) was observed at minimum flowrate and maximum influent concentration. The minimum bed adsorption capacity (q_o) was observed at maximum flowrate and minimum influent concentration. Those results were evidences for validity of the mechanism of flowrate and concentration differences. The same conclusions were found by Han et al. (2005) for

the sorption of the copper(II) and lead(II) from aqueous solutions by chaff in a fixed bed column and by Malkoc and Nuhoglu (2006) for the removal of Ni(II) ions from aqueous solutions using waste of tea factory.

The comparison of the experimental and predicted breakthrough curve obtained at different concentrations and flowrates according to the Thomas model are shown from Figures 3.19-3.25.

It is clear from the figures that there is good agreement between the experimental and the predicted values at experimented concentrations. And also, the all correlation coefficients for the linear regression fit to the Thomas equation are very high as an evidence of validity.

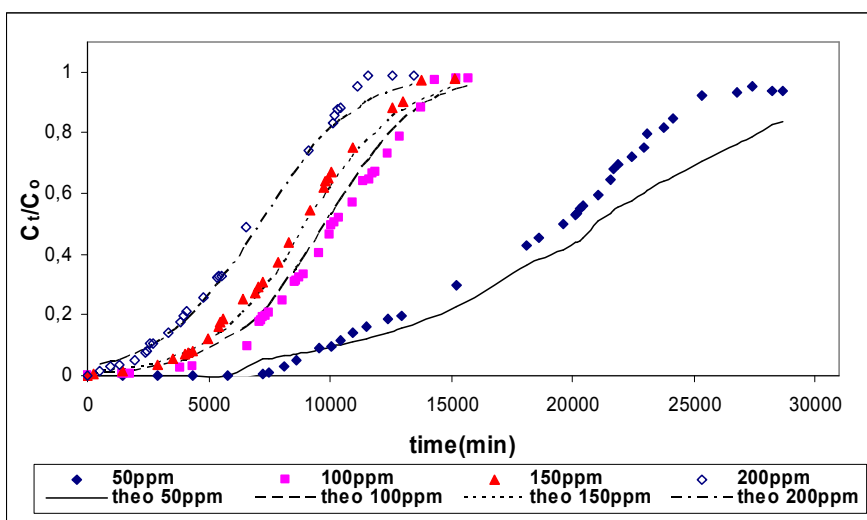


Fig. 3.19 Comparison of the experimental and predicted breakthrough curves obtained at different concentrations according to the Thomas model ($v = 0.2$ mL/min, bed height = 2 cm)

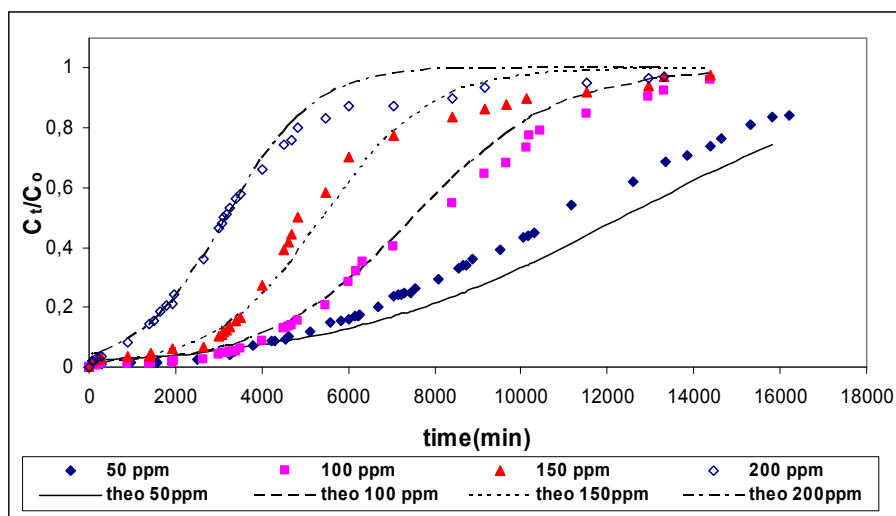


Fig. 3.20 Comparison of the experimental and predicted breakthrough curves obtained at different concentrations according to the Thomas model ($v = 0.3$ mL/min, bed height = 2 cm)

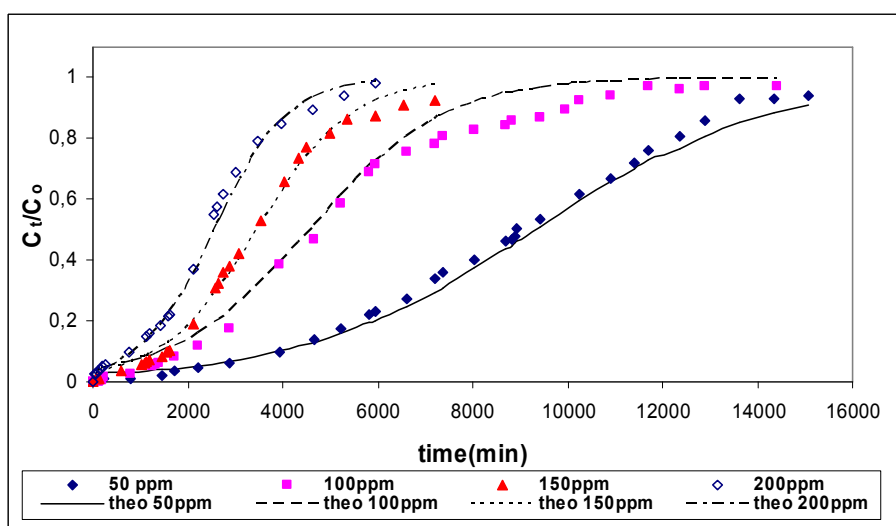


Fig. 3.21 Comparison of the experimental and predicted breakthrough curves obtained at different concentrations according to the Thomas model ($v = 0.4$ mL/min, bed height = 2 cm)

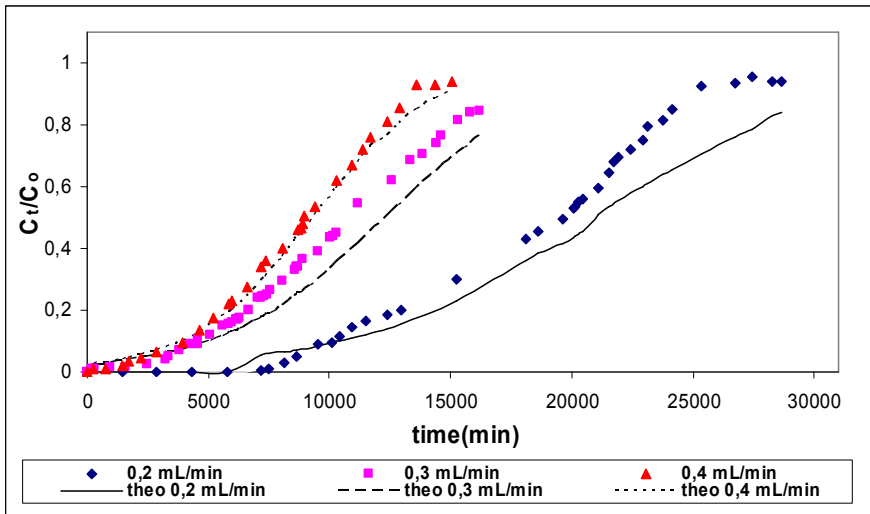


Fig. 3.22 Comparison of the experimental and predicted breakthrough curves obtained at different flowrates according to the Thomas model ($C_0=50\text{ppm}$, bed height = 2 cm)

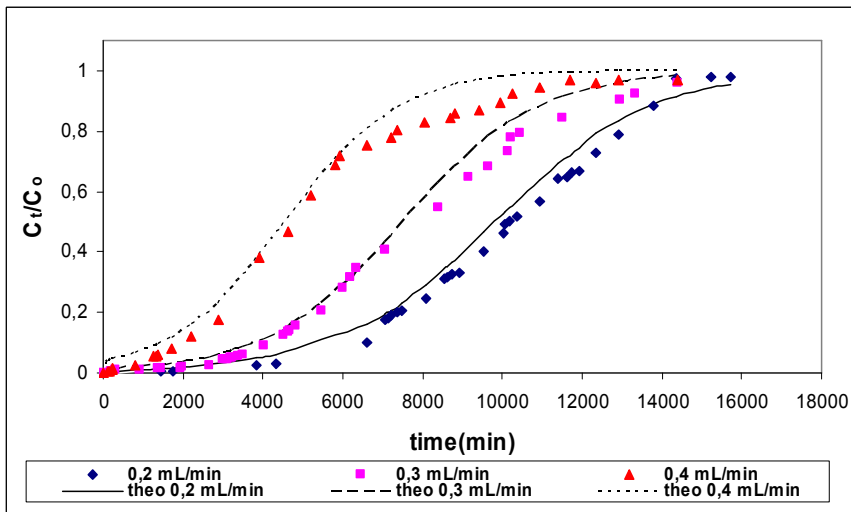


Fig. 3.23 Comparison of the experimental and predicted breakthrough curves obtained at different flowrates according to the Thomas model ($C_0=100\text{ppm}$, bed height = 2 cm)

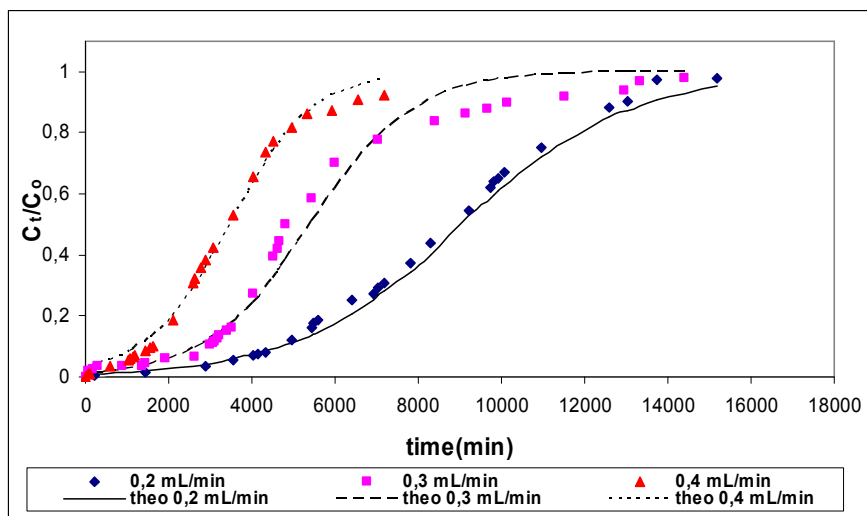


Fig. 3.24 Comparison of the experimental and predicted breakthrough curves obtained at different flowrates according to the Thomas model ($C_0 = 150 \text{ ppm}$, bed height = 2 cm)

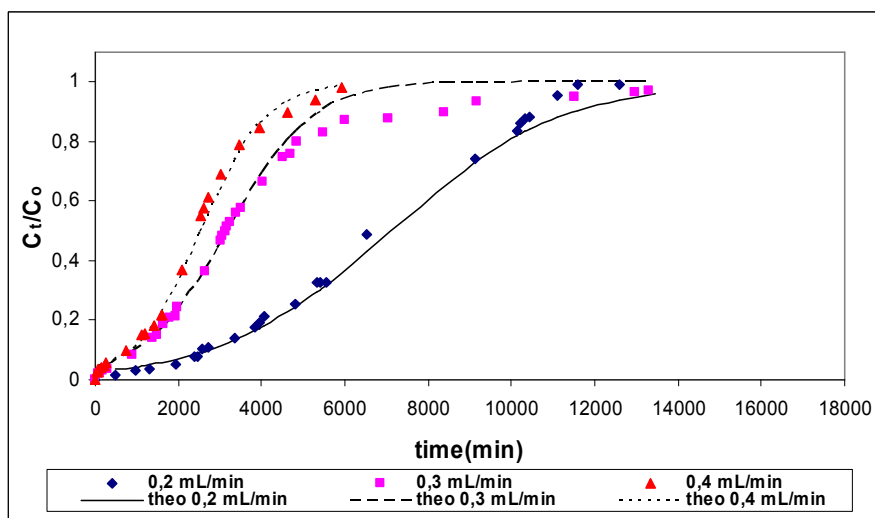


Fig. 3.25 Comparison of the experimental and predicted breakthrough curves obtained at different flowrates according to the Thomas model ($C_0 = 200 \text{ ppm}$, bed height = 2 cm)

Application of the Yoon–Nelson Model

The column data were fitted to the Yoon and Nelson model $\left[\ln \frac{C_i}{C_o - C_i} = k_{YN}t - \tau k_{YN} \right]$ to determine the Yoon and Nelson rate constant ($k_{YN} = \text{L min}^{-1}$) and the time required for 50% adsorbate breakthrough ($\tau = \text{min}$). Table 3.6 shows the parameters of Yoon-Nelson together with the correlation coefficients. k_{YN} and τ can be determined from a plot of $\ln[C_i/(C_o - C_i)]$ against t at given adsorption conditions.

Table 3.6 Parameters predicted from the Yoon-Nelson model of 2,4-D adsorption at different influent concentrations and different flowrates

C_o (mg/L)	v (mL/min)	k_{YN} (L/min)	τ (min)	R^2
50	0.2	0.0002	23402	0.981
	0.3	0.0003	12188	0.995
	0.4	0.0004	9809	0.996
100	0.2	0.0006	9427	0.990
	0.3	0.0006	8375	0.983
	0.4	0.0006	5720	0.960
150	0.2	0.0006	8125	0.989
	0.3	0.0009	5426	0.969
	0.4	0.0012	3494	0.987
200	0.2	0.0006	6363	0.987
	0.3	0.0010	3188	0.986
	0.4	0.0013	2478	0.994

As seen in Table 3.6, generally the values of k_{YN} increased and the values of τ decreased both with increasing in the influent concentration and flowrate. The time required for 50% adsorbate breakthrough (τ) was

minimum at operational parameters of 200 ppm influent concentration and 0.4mL/min flowrate. Because of (1) the high flowrate, the retention time of the pesticide solution in column was decreased; (2) the high concentration, the opportunity of the encounter of the adsorbate and the pesticide solution was increased so bed capacity filled steeper. And τ was maximum at operational parameters of 50 ppm concentration and 0.2mL/min. . Because of (1) the low flowrate, the retention time of the pesticide solution in column was increased; (2) the low concentration, the opportunity of the encounter of the adsorbate and the pesticide solution was decreased so bed capacity filled slower. The same conclusions were obtained by Malkoc et al. (2006) for Cr(VI) adsorption onto waste acorn in fixed beds and by Aksu and Gönen (2004) for phenol sorption by immobilized activated sludge.

The comparison of the experimental and predicted breakthrough curve obtained at different concentrations and different flowrates according to the Yoon and Nelson model are shown in Figures 3.26-3.32.

As shown in figures , the experimental breakthrough curves were very close to the calculated ones according to Yoon–Nelson model. And also from the all correlation coefficients for the linear regression fit to the Yoon–Nelson equation (are higher than 0.95), the model proposed by Yoon–Nelson provided a very good correlation at tested ranges.

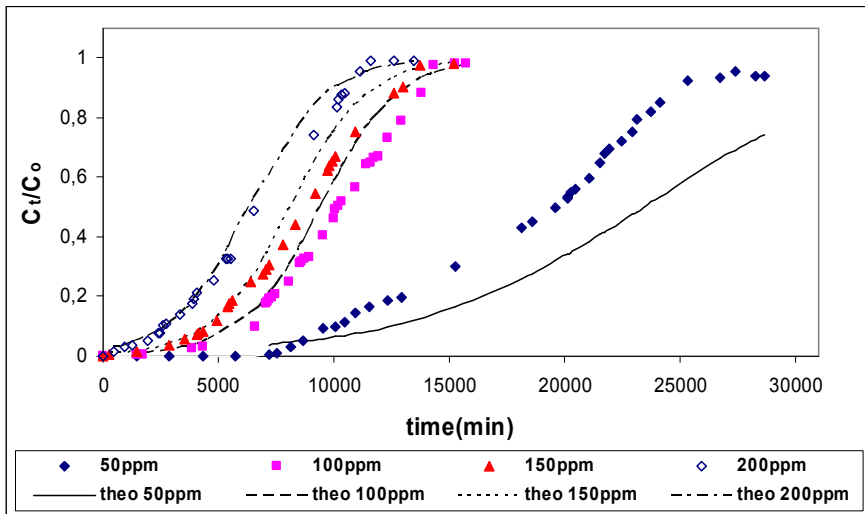


Fig. 3.26 Comparison of the experimental and predicted breakthrough curves obtained at different concentrations according to the Yoon-Nelson model ($v = 0.2$ mL/min, bed height = 2 cm)

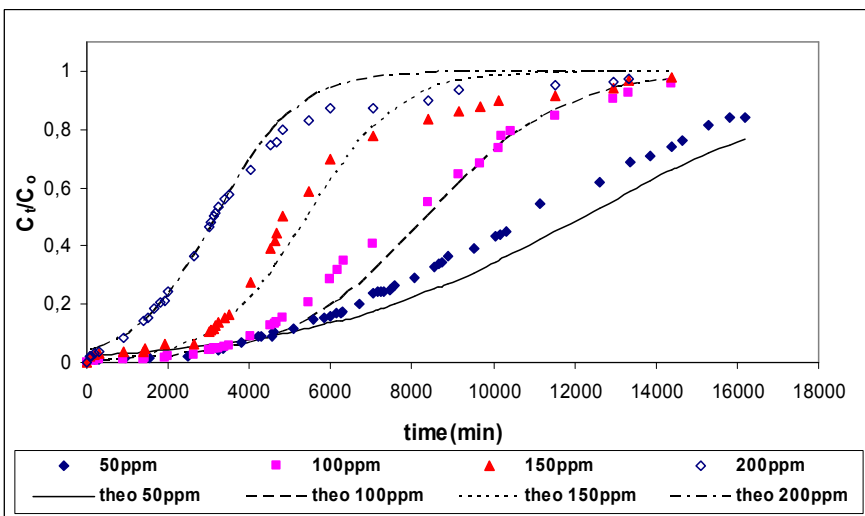


Fig. 3.27 Comparison of the experimental and predicted breakthrough curves obtained at different concentrations according to the Yoon-Nelson model ($v = 0.3$ mL/min, bed height = 2 cm)

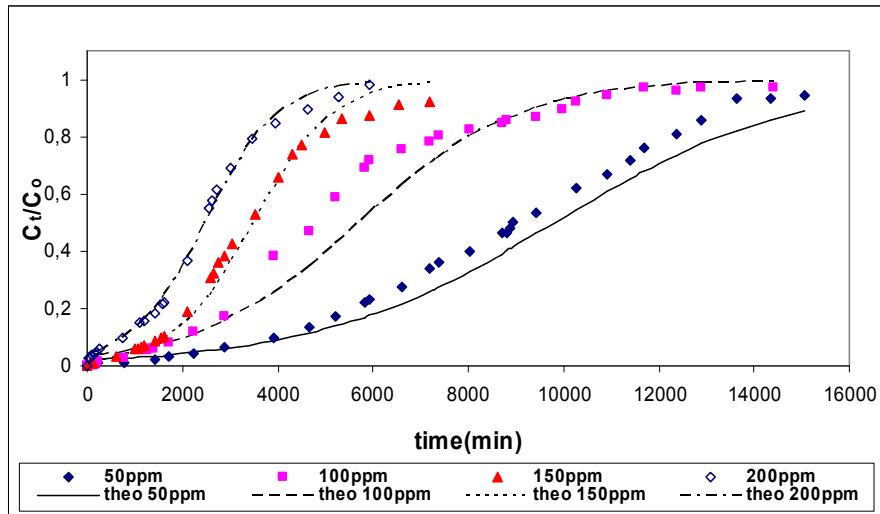


Fig. 3.28 Comparison of the experimental and predicted breakthrough curves obtained at different concentrations according to the Yoon-Nelson model ($v = 0.4$ mL/min, bed height = 2 cm)

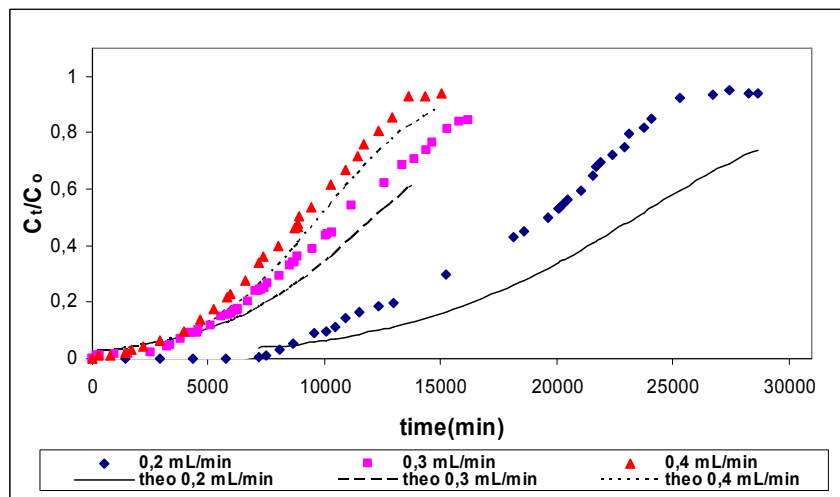


Fig. 3.29 Comparison of the experimental and predicted breakthrough curves obtained at different flowrates according to the Yoon-Nelson model ($C_0 = 50$ ppm, bed height = 2 cm)

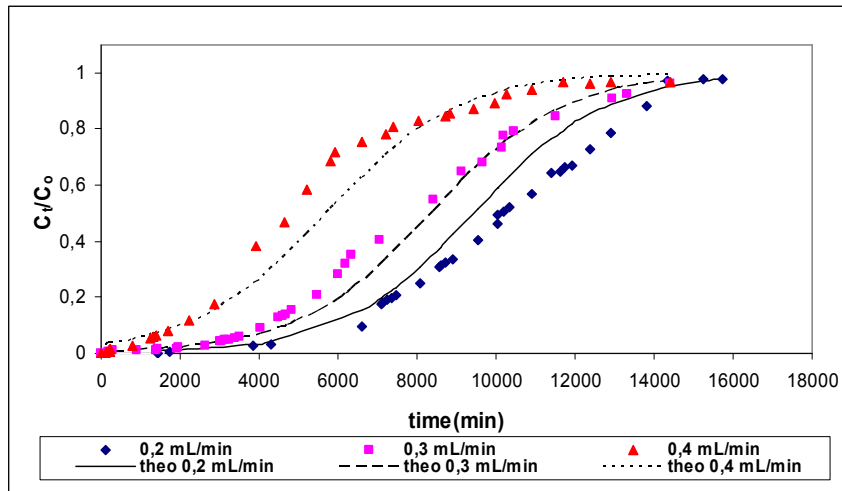


Fig. 3.30 Comparison of the experimental and predicted breakthrough curves obtained at different flowrates according to the Yoon -Nelson model ($C_0= 100\text{ppm}$, bed height = 2 cm)

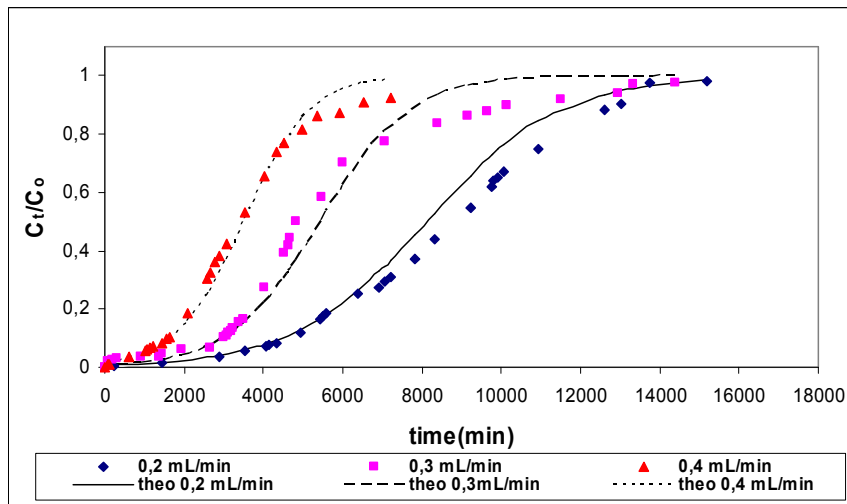


Fig. 3.31 Comparison of the experimental and predicted breakthrough curves obtained at different flowrates according to the Yoon -Nelson model ($C_0= 150\text{ppm}$, bed height = 2 cm)

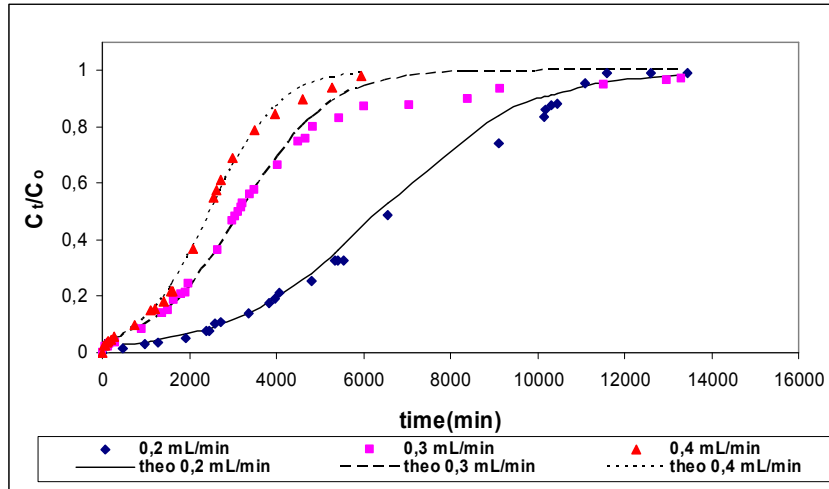


Fig. 3.32 Comparison of the experimental and predicted breakthrough curves obtained at different flowrates according to the Yoon -Nelson model ($C_o = 200\text{ppm}$, bed height = 2 cm)

Application of the Adams–Bohart and the Wolborska Models

The Adams–Bohart (or Wolborska) sorption model was applied to experimental data for the description of the initial part of the breakthrough curve. This approach was focused on the estimation of characteristic parameters, such as maximum adsorption capacity ($N_o = \text{mg L}^{-1}$) and kinetic constant ($k_{AB} = \text{L mg}^{-1} \text{min}^{-1}$) from Adams–Bohart model and kinetic coefficient of the external mass transfer (β_a) from the Wolborska model. After applying $\ln \frac{C_t}{C_o} = k_{AB} C_o t - k_{AB} N_o \frac{Z}{U_o}$ to the experimental data for varying concentrations and flowrates, a linear relationship between $\ln C/C_o$ and t was obtained for the relative concentration region up to 0.5, i.e. up to 50% breakthrough, for all breakthrough curves ($R^2 > 0.95$). Respective values of N_o , k_{AB} , β_a

calculated from the $\ln C_t/C_0$ versus t plots studied are presented in Table 3.7 together with the correlation coefficients.

Table 3.7 Parameters predicted from the Adams-Bohart and Wolborska models of 2,4-D adsorption at different influent concentrations and different flowrates

C_0 (mg/L)	v (mL/min)	Adams-Bohart		Wolborska		R^2
		k_{AB} (L/minXmg)	N_0 (g/L)	β_a (l/min)	γ (cm/min)	
50	0.2	4.00×10^{-6}	108.240	0.432	10.02×10^{-5}	0.981
	0.3	6.00×10^{-6}	105.230	0.782	16.89×10^{-5}	0.975
	0.4	8.00×10^{-6}	99.144	0.793	21.22×10^{-5}	0.976
100	0.2	3.00×10^{-6}	141.483	0.424	14.86×10^{-5}	0.996
	0.3	6.00×10^{-6}	128.525	0.771	24.55×10^{-5}	0.986
	0.4	7.00×10^{-6}	113.316	0.793	37.12×10^{-5}	0.969
150	0.2	2.00×10^{-6}	174.908	0.349	18.03×10^{-5}	0.994
	0.3	6.00×10^{-6}	129.139	0.774	36.53×10^{-5}	0.993
	0.4	6.66×10^{-6}	118.429	0.789	53.26×10^{-5}	0.996
200	0.2	1.50×10^{-6}	188.270	0.282	22.00×10^{-5}	0.958
	0.3	3.50×10^{-6}	133.550	0.463	47.00×10^{-5}	0.984
	0.4	5.50×10^{-6}	130.098	0.715	64.62×10^{-5}	0.988

As seen in Table 3.7, the values of the kinetic constant was influenced by the flowrate, increased with increasing flowrate. This showed that the overall system kinetics is dominated by external mass transfer in the initial part of the adsorption in column. β_a is also an effective coefficient which reflects the effect of both mass transfer in liquid phase and axial dispersion. Wolborska observed that in short beds or at high flowrates of solution through the bed, the axial dispersion is negligible $\beta_a = \beta_0$, the external mass transfer coefficient. Increasing in

flowrate increased the β_a value since increased turbulence reduces film boundary layer surrounding the carbon particle. As expected, maximum adsorption capacity (N_o) decreased with increasing flowrate. Increasing the flow rate from 0.2 to 0.4 mL/min increased the β_a value since increased turbulence reduces the film boundary layer surrounding the particle. As expected, maximum adsorption capacity (N_o) increased with increasing influent concentration. This was the reason for obtaining the maximum adsorption capacity at minimum flowrate 0.2mL/min and maximum influent concentration 200ppm as proved by Aksu and Gönen (2004) for phenol sorption by immobilized activated sludge.

The comparison of the experimental and predicted breakthrough curve obtained at different concentrations with the flowrates of 0.2 mL/min, 0.3 mL/min, 0.4 mL/min according to the Adams–Bohart and the Wolborska models are shown in Figure 3.33- 3.39, respectively.

The predicted and experimental breakthrough curves with respect to influent 2,4-D concentration show that there is a good agreement between the experimental and predicted values, suggesting that the Adams–Bohart (or Wolborska) model is valid for the relative concentration region up to 0.5 where as large discrepancies were found between the experimental and predicted curves above this level for the 2,4-D adsorption column.

Although the Adams–Bohart (or Wolbraska) model provides a simple and comprehensive approach to running and evaluating sorption-column tests, its validity is limited to the range of conditions used.

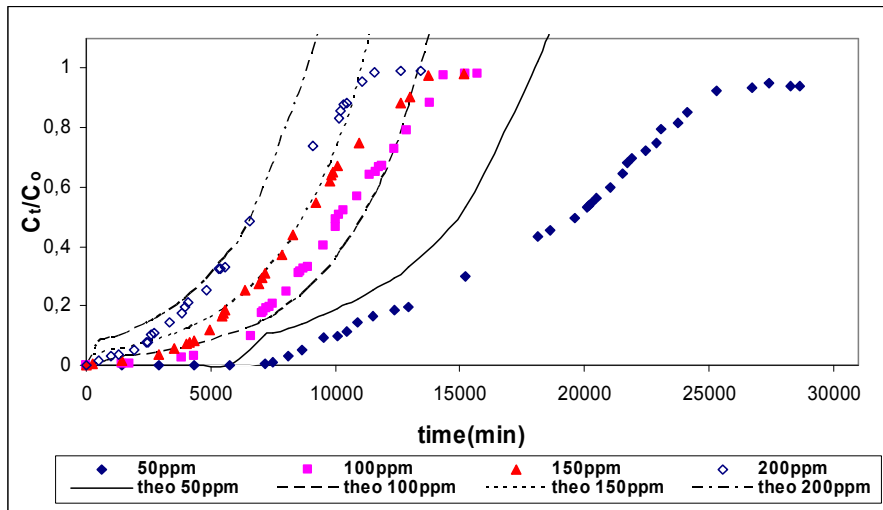


Fig. 3.33 Comparison of the experimental and predicted breakthrough curves obtained at different concentrations according to the Adams–Bohart model ($v = 0.2$ mL/min, bed height = 2 cm)

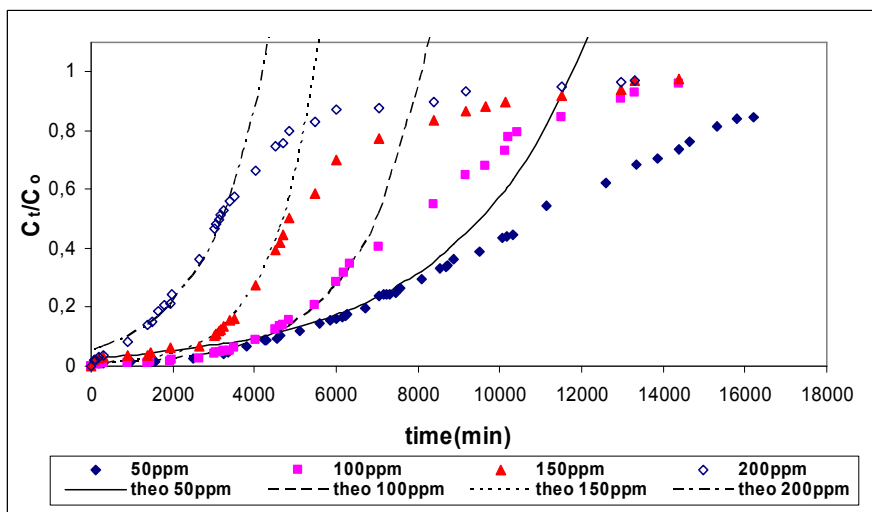


Fig. 3.34 Comparison of the experimental and predicted breakthrough curves obtained at different concentrations according to the Adams–Bohart model ($v = 0.3$ mL/min, bed height = 2 cm)

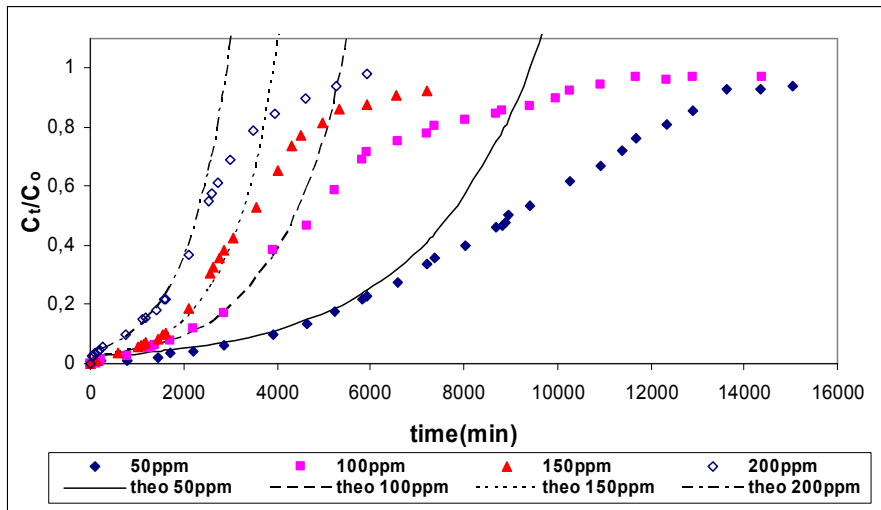


Fig. 3.35 Comparison of the experimental and predicted breakthrough curves obtained at different concentrations according to the Adams–Bohart model ($v = 0.4$ mL/min, bed height = 2 cm)

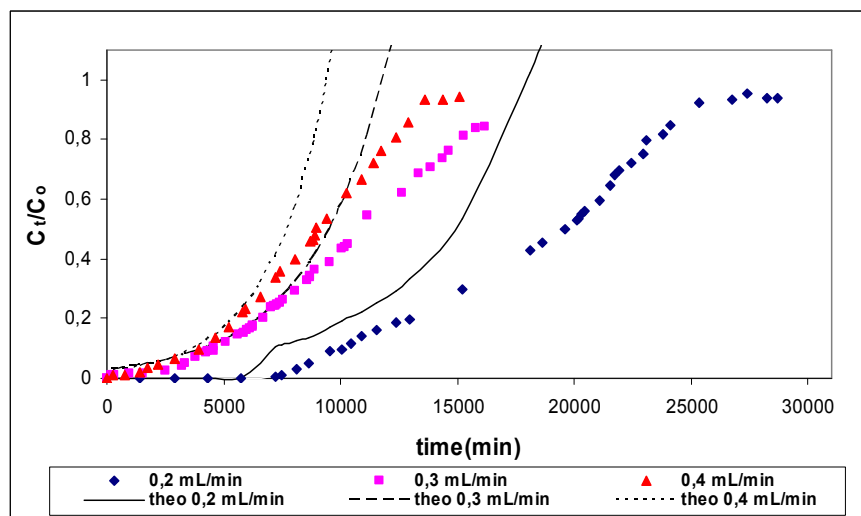


Fig. 3.36 Comparison of the experimental and predicted breakthrough curves obtained at different flowrates according to the Adams–Bohart model ($C_0 = 50$ ppm, bed height = 2 cm)

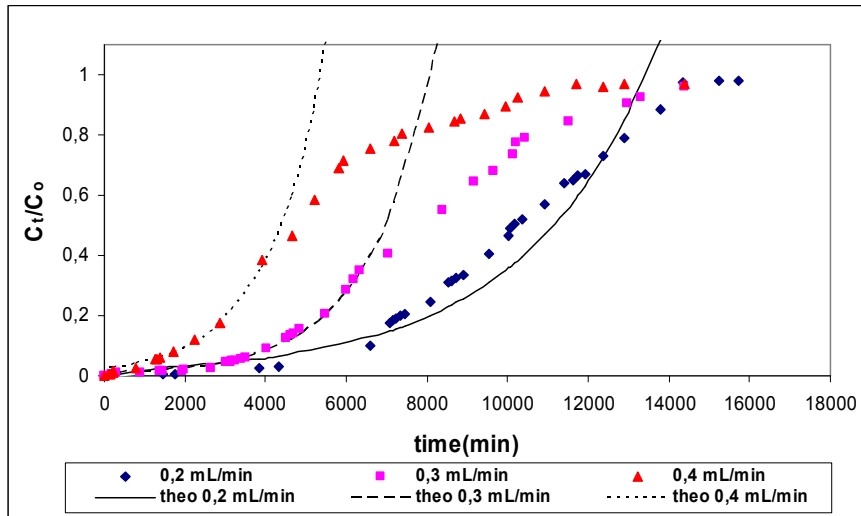


Fig. 3.37 Comparison of the experimental and predicted breakthrough curves obtained at different flowrates according to the Adams–Bohart model ($C_0 = 100$ ppm, bed height = 2 cm)

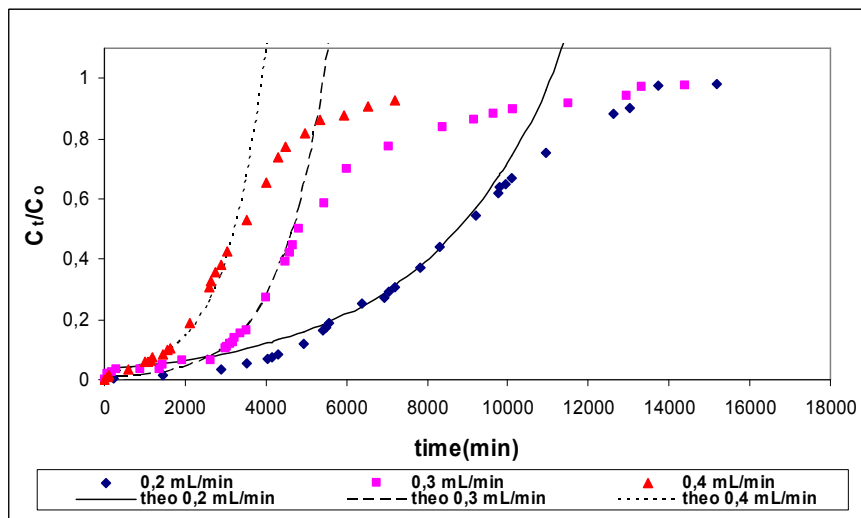


Fig. 3.38 Comparison of the experimental and predicted breakthrough curves obtained at different flowrates according to the Adams–Bohart model ($C_0 = 150$ ppm, bed height = 2 cm)

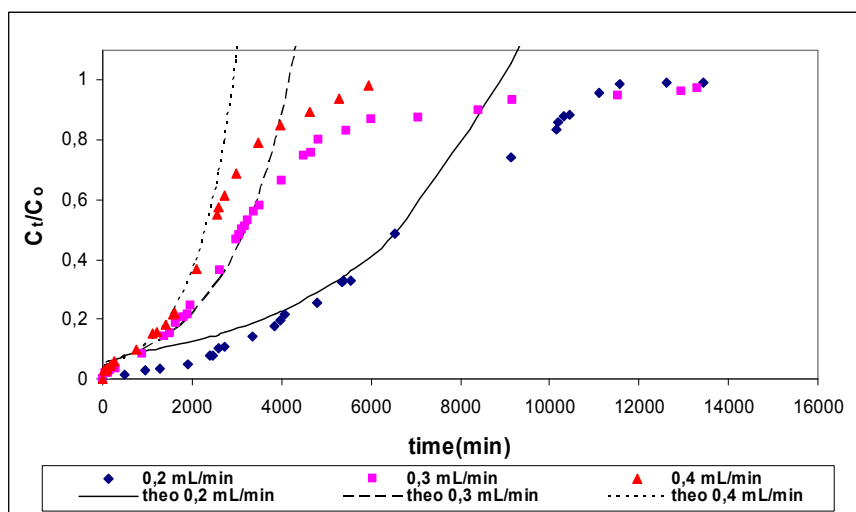


Fig. 3.39 Comparison of the experimental and predicted breakthrough curves obtained at different flowrates according to the Adams–Bohart model ($C_o = 200\text{ppm}$, bed height = 2 cm)

The kinetic rate constants that are obtained from the applied continuous models at different influent concentrations and different flowrates are tabulated in Table 3.8 for comparison.

Table 3.8 Comparison of kinetic rate constants predicted from the continuous models of 2,4-D adsorption at different influent concentrations and different flowrates

C_o (mg/L)	v (mL/min)	Thomas	Yoon-Nelson	Adams-Bohart	Wolborska
		k_{Th} (mL/minXmg)	k_{YN} (L/min)	k_{AB} (L/minXmg)	β_a (1/min)
50	0.2	4.00×10^{-6}	0.0002	4.00×10^{-6}	0.432
	0.3	6.00×10^{-6}	0.0003	6.00×10^{-6}	0.782
	0.4	8.00×10^{-6}	0.0004	8.00×10^{-6}	0.793
100	0.2	5.00×10^{-6}	0.0006	3.00×10^{-6}	0.424
	0.3	5.94×10^{-6}	0.0006	6.00×10^{-6}	0.771
	0.4	7.00×10^{-6}	0.0006	7.00×10^{-6}	0.793
150	0.2	3.33×10^{-6}	0.0006	2.00×10^{-6}	0.349
	0.3	5.33×10^{-6}	0.0009	6.00×10^{-6}	0.774
	0.4	6.66×10^{-6}	0.0012	6.66×10^{-6}	0.789
200	0.2	2.50×10^{-6}	0.0006	1.50×10^{-6}	0.282
	0.3	5.00×10^{-6}	0.0010	3.50×10^{-6}	0.463
	0.4	6.50×10^{-6}	0.0013	5.50×10^{-6}	0.715

3.2.1.2 Effect of Bed Height

To investigate the effect of bed height on the adsorption of 2,4-D by GAC (1-2mm), the bed height was changed from 2 cm to 3.5cm, while the influent 2,4-D concentration and the flowrate was held constant at 200ppm and 0.4 mL/min, respectively. Breakthrough curves of different bed heights with the same influent concentration of 2,4-D and flowrate are shown in Figure 3.40. Related data were tabulated in the Appendix III.

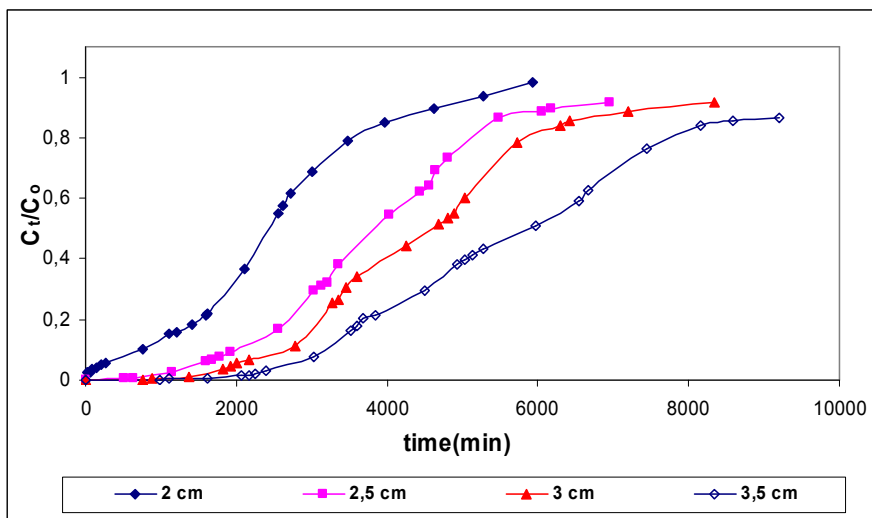


Figure 3.40 Breakthrough curves of GAC (1-2mm) obtained at different bed heights for adsorption of 2,4-D ($C_0 = 200\text{ppm}$, $v = 0.4\text{ mL/min}$)

It was shown in Figure 3.40 that breakthrough generally occurred steeper with smaller bed height. Increasing the bed height was resulted in the increase in the breakthrough time. Because of the increasing in bed height, absorbate weight increases. Not only the total bed capacity and also retention time increases. Because of these reasons, longer breakthrough times and larger bed capacities were obtained with higher bed heights.

The effect of bed height of 2,4-D on the column adsorption parameters was investigated by the kinetic modeling adsorption by the Thomas, Yoon and Nelson, Adams-Bohart, and Wolborska models.

The breakthrough curves in the application of models showed the superposition of experimental results (points) and the theoretical calculated points (lines). Linear regression coefficients (R^2) showed the

fit between experimental data and linearized forms of model (Thomas Yoon–Nelson, Adams-Bohart, and Wolborska) equations. Data that used in the models were tabulated in the Appendix III.

Application of the Thomas Model

The column data were fitted to the linearized form of the Thomas model $\left[\ln\left(\frac{c_o}{c_t} - 1\right) = \frac{k_{Th} q_o x}{v} - \frac{k_{Th} c_o V_{eff}}{v} \right]$ to determine the Thomas rate constant, $(k_{Th} = \text{ml min}^{-1} \text{ mg}^{-1})$ and the adsorption capacity of the bed maximum $(q_o = \text{mg g}^{-1})$. The parameters of the Thomas Model is tabulated in Table 3.9 together with the correlation coefficients. k_{Th} and q_o can be determined from a plot of $\ln[(C_o/C_t)-1]$ against t at a given flow rate.

Table 3.9 Parameters predicted from Thomas model of 2,4-D adsorption at different bed heights

C_o (mg/L)	v (mL/min)	Bed Height (cm)	k_{Th} (mL/minXmg)	q_o (g/g)	R^2
200	0.4	2.00	6.50×10^{-6}	238.544	0.993
		2.50	6.00×10^{-6}	256.604	0.996
		3.00	5.00×10^{-6}	269.934	0.977
		3.50	3.50×10^{-6}	304.921	0.947

As seen from the table, as bed height increased, the values of k_{Th} decreased and the values of q_o increased. Maximum adsorption capacity (q_o) was obtained at maximum bed height with the lowest rate constant

of Thomas because of the increase in the adsorbate weight and retention time.

The comparison of the experimental and predicted breakthrough curves obtained at different bed heights with the influent concentration 200ppm and flowrate 0.4 mL/min according to the Thomas model is shown in Figure 3.41.

It is clear from figure that there is good agreement between the experimental and the predicted values at bed heights studied. And also, the all correlation coefficients for the linear regression fit to the Thomas equation are higher than 0.95 as an evidence of the Thomas model is valid for 2,4-D adsorption onto GAC .

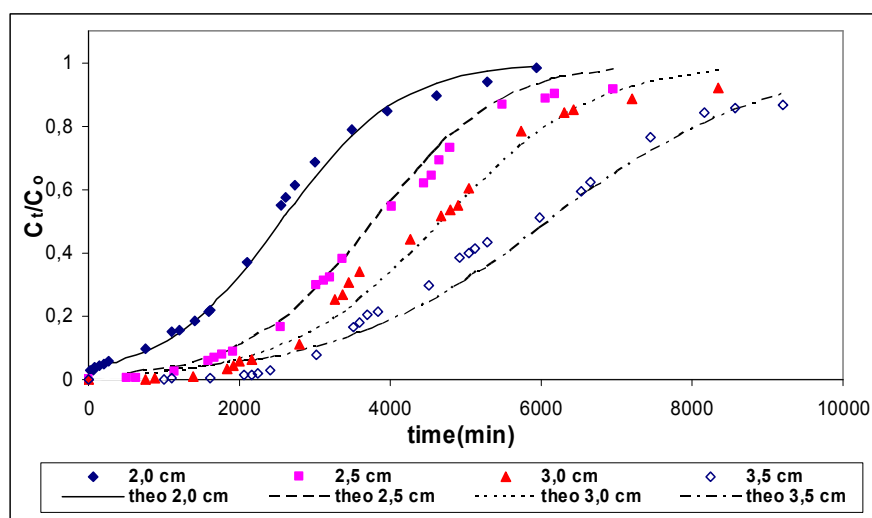


Fig. 3.41 Comparison of the experimental and predicted breakthrough curves obtained at different bed heights according to the Thomas model ($C_0=200\text{ppm}$, $v=0.4\text{ mL/min}$)

Application of the Yoon–Nelson Model

The column data were fitted to the Yoon and Nelson model $\left[\ln \frac{C_i}{C_o - C_i} = k_{YN}t - \tau k_{YN} \right]$ to determine the Yoon and Nelson rate constant ($k_{YN} = \text{L min}^{-1}$) and the time required for 50% adsorbate breakthrough ($\tau = \text{min}$). Table 3.10 shows the parameters of Yoon-Nelson together with the correlation coefficients. k_{YN} and τ can be determined from a plot of $\ln[Ct/(C_0 - C_t)]$ against t at a given adsorption conditions.

Table 3.10 Parameters predicted from Yoon-Nelson model of 2,4-D adsorption at different bed heights

C_o (mg/L)	N (mL/min)	Bed Height (cm)	k_{YN} (L/min)	τ (min)	R^2
200	0.4	2.00	0.0013	2478	0.994
		2.50	0.0012	3765	0.996
		3.00	0.0010	4327	0.958
		3.50	0.0007	5522	0.990

As seen in Table 3.10, as bed height increased, the values of k_{YN} decreased and the values of τ increased. Maximum value of the time required for 50% adsorbate breakthrough τ was obtained in a maximum bed height with the lowest rate constant

The comparison of the experimental and predicted breakthrough curves obtained at different bed heights with the influent concentration 200ppm and flowrate 0.4 mL/min according to the Yoon and Nelson model are shown in Figure 3.42.

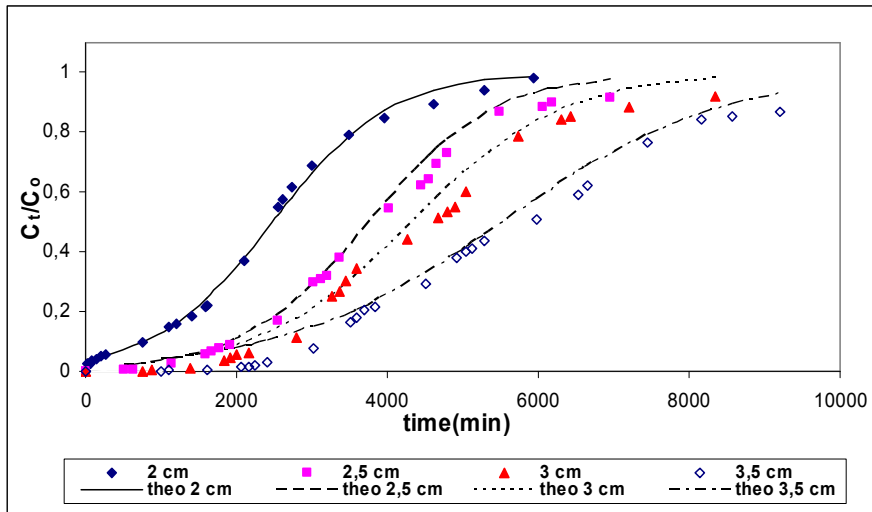


Fig. 3.42 Comparison of the experimental and predicted breakthrough curves obtained at different bed heights according to the Yoon-Nelson model ($C_0 = 200\text{ppm}$, $v = 0.4\text{ mL/min}$)

As shown Figure 3.42, experimental breakthrough curves were very close to calculated ones according to Yoon–Nelson model. And also from the all correlation coefficients for the linear regression fit to the Yoon–Nelson equation (are higher than 0.95), the model proposed by Yoon–Nelson provided a very good correlation at studied bed heights.

Application of the Adams–Bohart and the Wolborska Models

In Table 3.11, the parameters of the Adams–Bohart and the Wolborska Models are tabulated together with the correlation coefficients.

Table 3.11 Parameters predicted from Adams-Bohart and Wolborska model of 2,4-D adsorption at different bed heights

C_o (mg/L)	v (mL/min)	Bed Height (cm)	Adams-Bohart		Wolborska		R^2
			k_{AB} (L/minXmg)	N_o (g/L)	β_a (min ⁻¹)	γ (cm/min)	
200	0.4	2.00	5.50×10^{-6}	130.098	0.716	64.62×10^{-5}	0.988
		2.50	4.00×10^{-6}	162.180	0.649	51.86×10^{-5}	0.960
		3.00	2.00×10^{-6}	192.946	0.386	43.60×10^{-5}	0.996
		3.50	1.50×10^{-6}	225.442	0.338	37.30×10^{-5}	0.960

As seen in Table 3.11, the parameters were influenced by bed heights. Maximum adsorption capacity (N_o) from Adams–Bohart model increased, kinetic constant (k_{AB}) from Adams–Bohart model and kinetic coefficient of the external mass transfer (β_a) from Wolborska model decreased with increasing bed heights as expected. Maximum adsorption capacity was obtained by the highest bed height with the lowest k_{AB} , β_a values.

According to the Adams–Bohart and the Wolborska models, the comparison of the experimental and predicted breakthrough curves obtained at different bed heights is shown in Figure 3.43.

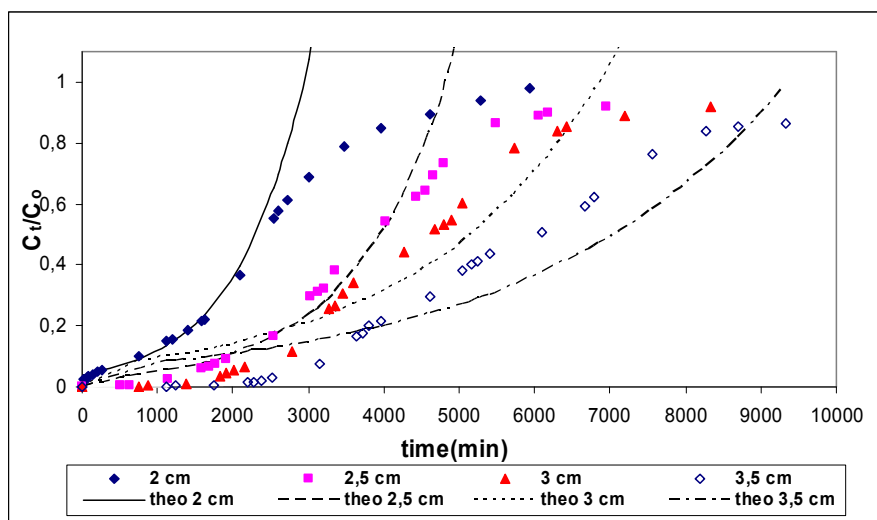


Fig. 3.43 Comparison of the experimental and predicted breakthrough curves obtained at different bed heights according to the Adams–Bohart model ($C_0 = 200\text{ppm}$, $v = 0.4\text{mL/min}$)

The predicted and experimental breakthrough curves with respect to bed height show that there is a good agreement between the experimental and predicted values, suggesting that the Adams–Bohart (or Wolborska) model is valid for the process. But different from the influent concentration and flowrate effects; as the bed height increases, the large discrepancies were decreased between the experimental and predicted curves above the relative concentration region “0.5”. Because, although studied with the highest flowrate, the beds’ height was high enough to prevent the turbulence.

The kinetic rate constants that are obtained from the applied continuous models at different bed heights are tabulated in Table 3.12 for comparison.

Table 3.12 Comparison of kinetic rate constants predicted from the continuous models of 2,4-D adsorption at different bed heights

C_o (mg/L)	v (mL/min)	Bed Height (cm)	Thomas	Yoon- Nelson	Adams- Bohart	Wolborska
			k_{Th} (mL/minXmg)	k_{YN} (L/min)	k_{AB} (L/minXmg)	β_a (min ⁻¹)
200	0.4	2.00	6.50×10^{-6}	0.0013	5.50×10^{-6}	0.716
		2.50	6.00×10^{-6}	0.0012	4.00×10^{-6}	0.649
		3.00	5.00×10^{-6}	0.0010	2.00×10^{-6}	0.386
		3.50	3.50×10^{-6}	0.0007	1.50×10^{-6}	0.338

3.3 Biological Contamination Studies

Granular activated-carbon (GAC) filters have been used for 35 years to remove dissolved organic matter by adsorption. More recently, it has been shown that, in addition to adsorption of organic matter, GAC is also a good material for the development of attached bacteria. The colonization of GAC filters by bacteria has been observed in some industrial treatment plants by various techniques: scanning electron microscopy (Weber et al. 1978). Studies have shown that GAC columns continue to yield effective organic matter removal far beyond the point where adsorption capacity would normally be exhausted (Rittmann and Snoeyink 1984; McFeeters et al. 1987). Also addition to advantage of the microbiological removal of organic matter, biological GAC filters need no regeneration of the GAC.

In biological contamination studies, The “*Acidovorax avenae* subsp. *Avenae* LMG 17238” bacteria was used as biological contamination where it was purchased from BCCMTM/LMG bacteria collection at the Gent university (Gent/Belgium). It was the first time,

LMG bacteria ,which was produced for PCL, had been used with the activated carbon.

3.3.1 Bacteria Count Results

Repetition and monitoring is very important in the experiments. So bacteria were counted in every inoculation.

The disadvantage of the pour plate technique is that embedded colonies will be much smaller than those which happen to be on the surface. Because of this reason, viable count technique was used for the bacteria experiments.

TSB was chosen as inoculation medium because the higher results were obtained in the counts. The viable plate count results of inoculated bacteri with TSB are tabulated in Table 3.13 and figured in Figure 3.44.

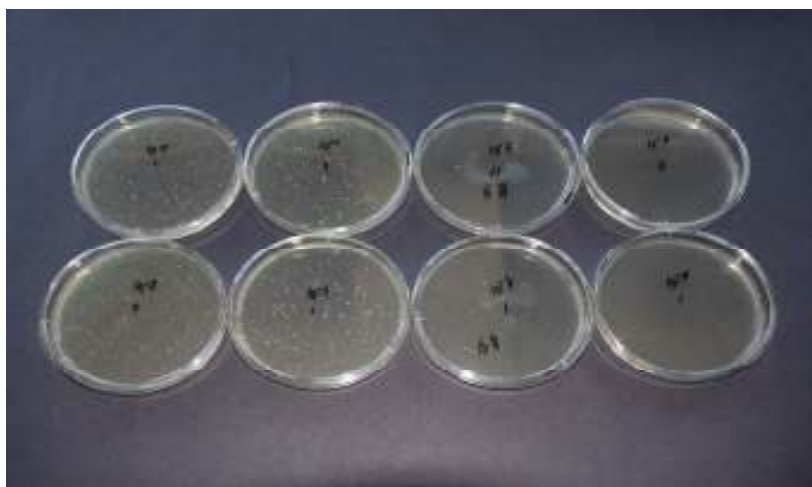


Figure 3.44 Photograph of one of viable plate count technique

Table 3.13 Viable plate count technique results of bacteria

# of inoculation	Inoculated bacteria with TSB (unit: cfu / mL)
1.	8.25×10^8
2.	3.30×10^8
3.	1.12×10^9
4.	1.18×10^9
5.(1 st day)	1.33×10^9
5.(2 nd day)	1.60×10^9
5.(3 rd day)	1.35×10^9
5.(4 th day)	1.40×10^9
5.(5 th day)	1.62×10^9
6.	6.80×10^8
7.	7.70×10^7

3.3.2 Effect of Biological Contamination in Batch Mode Concentration-dependent Study

The adsorption concentration study was carried out with 0.0050; 0.010; 0.015; 0.020 (mL bacteria/mL 2,4-D solution) and the equilibrium data were obtained for 2,4-D adsorption onto GAC (1-2mm). Results were tabulated in Appendix IV. The equilibrium relationship is shown in Figure 3.45.

As seen from the figure; as the removal percentage of 2,4-D decreased with increasing bacteria concentration and lastly in 0.020 (mL bacteria/mL 2,4-D solution) equilibrium study , no 2,4-D removal was observed.

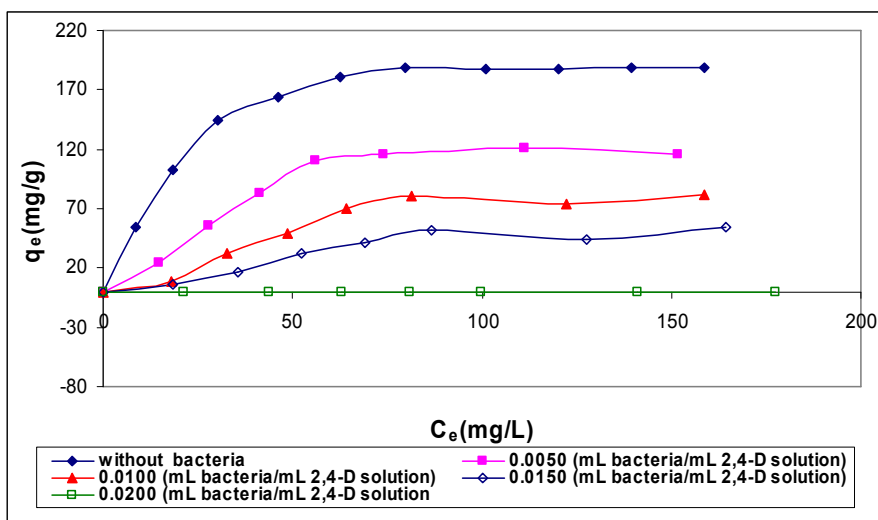


Figure 3.45 The comparison of equilibrium isotherm of GAC (1-2 mm) with and without biological contamination for adsorption of 2,4-D

The decrease in the removal of 2,4-D was occurred because of the surface of the carbon particle was covered with biofilm. In batch mode adsorption studies, the same solution remains in contact with a given quantity of adsorbent, so the bacteria solution contacted the carbon particle during shaking time. When the particle surface is covered with the solution, also mesopores and micropores of carbon were filled with bacteria solution and by the time biofilm occurred. So the number of adsorption sites decreased. As a result, removal of 2,4-D was decreased. When the bacteria-2,4-D solution ratio is increased, the start up time of occurring biofilm decreases. This is the reason, why no removal in 0.020 (mL bacteria/mL 2,4-D solution) ratio was observed.

3.3.3 Effect of Biological Contamination Load in Continuous Mode Study

To investigate the effect of the bacteria load on the adsorption of 2,4-D by GAC (1-2mm), the load time was changed from 20 to 68 hour, while the 0.020 (mL bacteria/mL 2,4-D solution) ratio biological contaminant was held constant. The influent concentration of 2,4-D was 200ppm with flowrate of 0,4 mL/min. Breakthrough curves of 2,4-D, after loading 20 hour , 44 hour and 68 hour bacteria and the comparison of breakthrough curves of bacteria loading is shown in Figure 3.46. Related data was tabulated in Appendix IV.

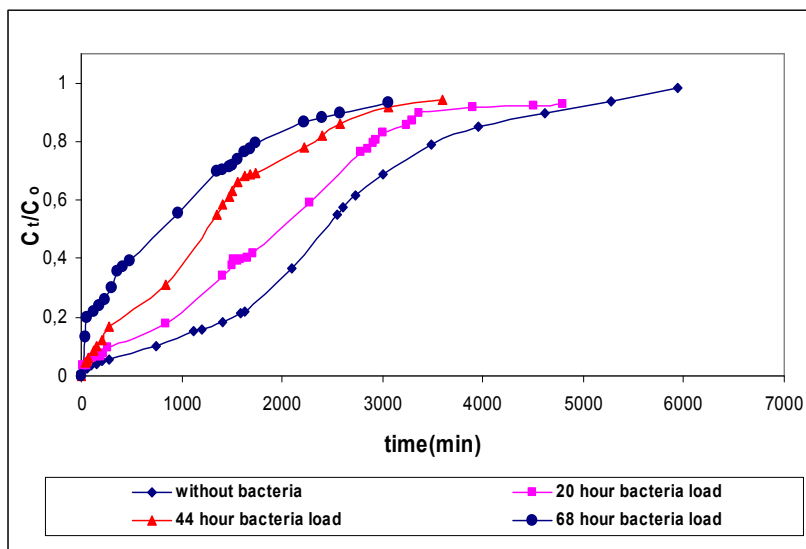


Fig.3.46 Comparison of the breakthrough curves obtained at different bacteria load times for adsorption of 2,4-D ($C_0 = 200\text{ppm}$, $v = 0.4\text{ mL/min}$)

In column studies, solution continuously enters and leaves the column. As a result, as seen from the figures, after loading, bacterias were drifted with the effluent 2,4-D solution within 20 hour. This showed that bacterias could not hang on to the surface because of the stable structure of the carbon particle. But it is clear from the breakthrough curves that although bacterias could not hang on to the particle surface completely, they filled the mesapores and micropores of the carbon particle which caused the breakthrough time decreased in respect to a without bacteria study. Although in batch study at 0.020 (mL bacteria/mL 2,4-D solution) ratio, no 2,4-D removal was observed, in column study 2,4-D removal was seen because of being dynamic. When the bacteria loading time was increased, the bacteri had more opportunity to hang on the carbon surface, so probability of occurring biofilm was increased. To sum up, increasing the bacteria load time, causes decrease in breakthrough time.

4. CONCLUSIONS

Water sources are going to be distinct and water pollution by organic and inorganic chemical pollutants has become a primary public concern in the last few years.

In this thesis, removal of 2,4-D -a member of the phenoxy herbicide group, has been widely applied to control broad leaf weeds- by using adsorption technique was investigated. The adsorbent was aqualine labeled GAC(1-2mm).

In batch mode kinetic studies, in order to film diffusion, intraparticle diffusion was significant. It could be said by the obtained pore diffusion coefficient that the pore diffusion was significant and also diffusion of pesticides into pores of the adsorbent mainly controls the adsorption process by applying Bangham equation to the kinetic data.

Sorption kinetics reaction order fits to H_0 pseudo-second-order mechanism in with correlation coefficient 0.99. The theoretical curve for second order kinetics showed similarity respect to experimental curve as a proof of H_0 pseudo-second-order mechanism was valid for the adsorption of GAC(1-2mm) for 2,4-D.

In equilibrium modeling of batch mode, better Langmuir fits were obtained from the equilibrium data than Freundlich fit with correlation coefficients of 0.98 and 0.84, respectively. And also the theoretical curve for Langmuir model showed similarity respect to experimental isotherm as a proof of validity.

In continuous mode experiments, when concentration was increased, capacity of the bed was increased. Whereas when the flowrate was increased, capacity of the bed was decreased. It can be said that for reaching the maximum adsorption capacity in the column, it should be studied with lower flowrate and higher influent concentration. Higher flowrate and lower influent concentration have disadvantage to adsorption of 2,4-D on GAC column. Bed capacity increased with increasing bed height. The experimental data were analyzed to fitting to the continuous mathematical models, the Thomas, Yoon-Nelson, Adams-Bohart, Wolborska. From the theoretical curve of models and the correlation coefficients, models are fitted the obtained data well.

When the column performances for the adsorption study are compared respect to pesticide standarts; with minimum flowrate, minimum influent concentration and maximum bed height operational parameters, better results are obtained. The comparison of columns with minimum effluent concentration and time reaching to those concentrations are tabulated in Table 4.1.

Table 4.1 Comparison of columns respect to pesticide standarts with minimum effluent concentration and time reaching for min effluent concentration

C _o (mg/L)	v (mL/min)	Bed Height (cm)	EU pesticide standarts (1998)	WHO 2,4-D standart (1993)	Time reaching min eff.conc. (min)	Min effluent Conc. (mg/L)
50	0.2	2.00	0,1 µg/L for individual pesticides and of 0,5 µg/L for total of all pesticides present	30 µg/L	0-7200	0
	0.3				180	0.487
	0.4				240	0.515
100	0.2	2.00			1440	0.260
	0.3				180	0.332
	0.4				120	0.258
150	0.2	2.00			240	0.464
	0.3				60	3.120
	0.4				30	1.675
200	0.2	2.00			480	3.179
	0.3				60	4.015
	0.4				30	5.412
	0.4	2.50			510	0.865
	0.4	3.00			750	0.407
	0.4	3.50			990	0.305

In biological contamination studies, The “*Acidovorax avenae* subsp. *Avenae* LMG 17238” bacteria was used as biological contaminant where it was purchased from BCCMTM/LMG bacteria collection at the Gent university (Gent/Belgium).

In batch mode of the biological contamination studies, it was observed that when the bacteria-2,4-D ratio was increased, the efficiency of the adsorption process decreased. Decreasing in the removal of 2,4-D was increasing with the volume of bacteria in the solution. Because, if more bacteria contacted with the carbon, the thickness of the biofilm was increased.

In continuous mode studies of biological contamination experiments, bacteria could not hang on to surface because of the stable structure of the carbon particle. But it is clear from the breakthrough curves that although bacteria could not hang on the particle surface completely, they filled the mesopores and micropores of the carbon particle. The breakthrough time decreased with increase in the bacteria load time. When the bacteria load time was increased, the bacteria had more opportunity to hang on the carbon surface, so probability of occurring biofilm was increased.

The bacteria –LMG 17238- could not hang on the carbon surface. Because this bacteria is produced for the biodegradation of the synthetic-based polyester based plastics, poly ϵ -caprolactone(PCL), poly(butylene succinate-cobutylene adipate) and a starch –PCL blend. So there should be an external bond effect applied to attach the LMG bacteria on carbon surface. And in the further studies, the column studies of PCL and the effect of biological contamination on PCL column should be investigated .

APPENDIX-

Appendix-I (Batch-Mode-Kinetic Studies)

Table A.1 Results of film and intraparticle diffusion model for GAC (1-2 mm)

Time (min)	Time ^{0.5} (min ^{0.5})	log(C _o /C)	q _e (mg/g)
0	0,000	0,036	0,000
60	7,746	0,050	37,981
120	10,954	0,079	55,291
180	13,416	0,091	84,416
240	15,492	0,102	93,305
300	17,321	0,110	105,439
360	18,974	0,153	113,154
960	30,984	0,165	150,000
1440	37,947	0,198	160,006
1920	43,818	0,036	180,078

Table A.2 Results of Bangham equation for GAC (1-2 mm)

Time (min)	log t	log log (C' _o /(C' _o -q' * m'))
0	1,778	-1,438
60	2,079	-1,289
120	2,255	-1,095
180	2,380	-1,033
240	2,477	-0,983
300	2,556	-0,948
360	2,982	-0,810
960	3,158	-0,776
1440	3,283	-0,707
1920	1,778	-1,438

Table A.3 Results of First Order and Second Order Kinetic Model for GAC (1-2 mm)

Time (min)	$\log(q_e/q)$	t/q
0	0,000	0,000
60	2,162	7,746
120	2,106	10,954
180	1,994	13,416
240	1,953	15,492
300	1,890	17,321
360	1,844	18,974
960	1,519	30,984
1440	1,362	37,947
1920	0,471	43,818

Appendix-II (Batch-Mode-Equilibrium Studies)

Table A.4 Data for Langmuir isotherm

$1/q_e$	$1/C_e$	R_L	$q_{e,theoretical}$ (mg/g)
0,019	0,114	0,618	56,020
0,010	0,055	0,447	95,050
0,007	0,033	0,350	127,027
0,006	0,022	0,288	154,568
0,006	0,016	0,244	173,569
0,005	0,013	0,212	187,259
0,005	0,010	0,188	199,340
0,005	0,008	0,168	207,365
0,005	0,007	0,152	213,597
0,005	0,006	0,139	218,576

Table A.5 Data for Freundlich isotherm

$\ln q_e$	$\ln C_e$	$q_{e,theoretical}$ (mg/g)
3,985	2,169	72,163
4,632	2,906	96,438
4,976	3,407	117,436
5,101	3,829	138,647
5,201	4,138	156,515
5,241	4,379	172,122
5,231	4,615	188,850
5,235	4,789	202,211
5,239	4,937	214,332
5,243	5,066	225,478

Appendix-III (Continuous-Mode-Kinetic Studies)

Table A.6 Results of continuous-mode studies of GAC (1-2mm) for adsorption of 2,4-D ($C_0=50\text{ppm}$, $v=0.2\text{mL/min}$, bed height=2cm)

Time (min)	C_t/C_0	$\ln[(C_0/C_t)-1]$	$\ln[C_t/(C_0-C_t)]$	$\ln(C_t/C_0)$
0	0,000	0,000	0,000	0,000
1440	0,000	0,000	0,000	0,000
2880	0,000	0,000	0,000	0,000
4320	0,000	0,000	0,000	0,000
5760	0,000	0,000	0,000	0,000
7200	0,005	5,291	-5,291	-5,296
7500	0,010	4,572	-4,572	-4,582
8100	0,030	3,465	-3,465	-3,495
8640	0,051	2,926	-2,926	-2,978
9540	0,091	2,303	-2,303	-2,398
10080	0,096	2,237	-2,237	-2,339
10440	0,114	2,048	-2,048	-2,170
10920	0,143	1,789	-1,789	-1,943
11520	0,164	1,631	-1,631	-1,810
12360	0,185	1,482	-1,482	-1,687
12960	0,198	1,399	-1,399	-1,620
15240	0,300	0,847	-0,847	-1,204
18120	0,431	0,276	-0,276	-0,841
18600	0,454	0,185	-0,185	-0,790
19620	0,497	0,010	-0,010	-0,698
20100	0,531	-0,123	0,123	-0,634
20160	0,536	-0,143	0,143	-0,624
20280	0,548	-0,194	0,194	-0,601
20460	0,561	-0,246	0,246	-0,578
21060	0,597	-0,393	0,393	-0,516
21540	0,647	-0,605	0,605	-0,436
21720	0,682	-0,761	0,761	-0,383
21900	0,697	-0,831	0,831	-0,362
22440	0,721	-0,951	0,951	-0,327
22920	0,751	-1,105	1,105	-0,286
23100	0,796	-1,362	1,362	-0,228
23760	0,818	-1,500	1,500	-0,202
24120	0,850	-1,735	1,735	-0,163
25320	0,923	-2,480	2,480	-0,080
26760	0,933	-2,628	2,628	-0,070
27420	0,953	-3,001	3,001	-0,049
28260	0,939	-2,727	2,727	-0,063
28650	0,939	-2,727	2,727	-0,063

Table A.7 Results of theoretical C_t/C_o values of the Thomas, Yoon-Nelson, Adams-Bohart and Wolborska models ($C_o=50\text{ppm}$, $v=0.2\text{mL/min}$, bed height=2cm, $x=0.97\text{g}$)

Time (min)	C_t/C_o	$C_t/C_{o,\text{theo}}$ (Thomas)	$C_t/C_{o,\text{theo}}$ (Yoon-Nelson)	$C_t/C_{o,\text{theo}}$ (Adams-Bohart)
0	0,000	0,000	0,000	0,000
1440	0,000	0,000	0,000	0,000
2880	0,000	0,000	0,000	0,000
4320	0,000	0,000	0,000	0,000
5760	0,000	0,000	0,000	0,000
7200	0,005	0,054	0,038	0,101
7500	0,010	0,058	0,040	0,107
8100	0,030	0,064	0,045	0,121
8640	0,051	0,071	0,050	0,135
9540	0,091	0,086	0,059	0,162
10080	0,096	0,095	0,065	0,180
10440	0,114	0,102	0,070	0,193
10920	0,143	0,110	0,076	0,213
11520	0,164	0,122	0,085	0,240
12360	0,185	0,139	0,099	0,284
12960	0,198	0,155	0,110	0,320
15240	0,300	0,228	0,164	0,505
18120	0,431	0,361	0,258	0,899
18600	0,454	0,384	0,277	0,989
19620	0,497	0,413	0,319	1,213
20100	0,531	0,437	0,341	1,335
20160	0,536	0,440	0,343	1,351
20280	0,548	0,446	0,349	1,384
20460	0,561	0,455	0,357	1,435
21060	0,597	0,510	0,385	1,618
21540	0,647	0,535	0,408	1,781
21720	0,682	0,544	0,417	1,846
21900	0,697	0,553	0,425	1,914
22440	0,721	0,578	0,452	2,132
22920	0,751	0,602	0,476	2,347
23100	0,796	0,610	0,485	2,433
23760	0,818	0,640	0,518	2,776
24120	0,850	0,657	0,536	2,984
25320	0,923	0,707	0,595	3,793
26760	0,933	0,762	0,662	5,059
27420	0,953	0,786	0,691	5,772
28260	0,939	0,828	0,725	6,828
28650	0,939	0,840	0,741	7,382

Table A.8 Results of continuous-mode studies of GAC (1-2mm) for adsorption of 2,4-D ($C_o=100\text{ppm}$, $v=0.2\text{mL/min}$, bed height=2cm)

Time (min)	C_t/C_o	$\ln[(C_o/C_t)-1]$	$\ln[C_t/(C_o-C_t)]$	$\ln(C_t/C_o)$
0	0,000	0,000	0,000	0,000
1440	0,003	5,943	-5,943	-5,945

1740	0,006	5,064	-5,064	-5,070
3840	0,025	3,668	-3,668	-3,693
4320	0,032	3,396	-3,396	-3,429
6600	0,098	2,218	-2,218	-2,321
7080	0,177	1,539	-1,539	-1,734
7140	0,183	1,497	-1,497	-1,699
7230	0,192	1,438	-1,438	-1,651
7350	0,198	1,396	-1,396	-1,617
7470	0,207	1,342	-1,342	-1,574
8070	0,247	1,113	-1,113	-1,397
8550	0,310	0,802	-0,802	-1,172
8610	0,315	0,778	-0,778	-1,156
8730	0,325	0,730	-0,730	-1,123
8910	0,333	0,695	-0,695	-1,100
9540	0,404	0,391	-0,391	-0,907
10020	0,464	0,146	-0,146	-0,769
10050	0,492	0,031	-0,031	-0,709
10170	0,504	-0,015	0,015	-0,685
10350	0,519	-0,077	0,077	-0,655
10920	0,568	-0,273	0,273	-0,566
11400	0,642	-0,584	0,584	-0,443
11610	0,648	-0,612	0,612	-0,433
11730	0,664	-0,680	0,680	-0,410
11910	0,669	-0,703	0,703	-0,402
12360	0,729	-0,991	0,991	-0,316
12900	0,788	-1,312	1,312	-0,239
13800	0,884	-2,026	2,026	-0,124
14340	0,975	-3,651	3,651	-0,026
15240	0,980	-3,876	3,876	-0,021
15720	0,980	-3,876	3,876	-0,021

Table A.9 Results of theoretical C_t/C_o values of the Thomas, Yoon-Nelson, Adams-Bohart and Wolborska models ($C_o=100\text{ppm}$, $v=0.2\text{mL/min}$, bed height=2cm, $x=0.86\text{g}$)

Time (min)	C_t/C_o	$C_t/C_{o,theo}$ (Thomas)	$C_t/C_{o,theo}$ (Yoon-Nelson)	$C_t/C_{o,theo}$ (Adams-Bohart)
0	0,000	0,000	0,000	0,000
1440	0,003	0,015	0,008	0,027
1740	0,006	0,017	0,010	0,030
3840	0,025	0,048	0,034	0,056
4320	0,032	0,060	0,045	0,065
6600	0,098	0,162	0,155	0,128
7080	0,177	0,198	0,197	0,148
7140	0,183	0,201	0,202	0,151
7230	0,192	0,208	0,211	0,155
7350	0,198	0,218	0,223	0,161
7470	0,207	0,229	0,236	0,167
8070	0,247	0,293	0,307	0,200
8550	0,310	0,345	0,371	0,231
8610	0,315	0,352	0,380	0,235
8730	0,325	0,365	0,397	0,243
8910	0,333	0,387	0,423	0,257

9540	0,404	0,468	0,517	0,310
10020	0,464	0,528	0,588	0,358
10050	0,492	0,532	0,592	0,362
10170	0,504	0,547	0,610	0,375
10350	0,519	0,569	0,635	0,396
10920	0,568	0,638	0,710	0,469
11400	0,642	0,691	0,766	0,542
11610	0,648	0,713	0,787	0,577
11730	0,664	0,726	0,799	0,599
11910	0,669	0,743	0,816	0,632
12360	0,729	0,793	0,853	0,723
12900	0,788	0,835	0,889	0,850
13800	0,884	0,888	0,932	1,114
14340	0,975	0,912	0,950	1,310
15240	0,980	0,943	0,970	1,716
15720	0,980	0,955	0,978	1,981

Table A.10 Results of continuous-mode studies of GAC (1-2mm) for adsorption of 2,4-D ($C_0=150\text{ppm}$, $v=0.2\text{mL/min}$, bed height=2cm)

Time (min)	C_t/C_0	$\ln[(C_0/C_t)-1]$	$\ln[C_t/(C_0-C_t)]$	$\ln(C_t/C_0)$
0	0,000	0,000	0,000	0,000
240	0,003	5,784	-5,784	-5,787
1440	0,015	4,162	-4,162	-4,178
2880	0,035	3,327	-3,327	-3,363
3540	0,056	2,831	-2,831	-2,889
4050	0,070	2,579	-2,579	-2,652
4140	0,077	2,488	-2,488	-2,567
4320	0,083	2,407	-2,407	-2,493
4950	0,120	1,988	-1,988	-2,117
5430	0,164	1,630	-1,630	-1,809
5490	0,175	1,547	-1,547	-1,740
5580	0,186	1,476	-1,476	-1,682
6390	0,251	1,091	-1,091	-1,381
6930	0,273	0,982	-0,982	-1,300
7050	0,292	0,884	-0,884	-1,230
7200	0,307	0,813	-0,813	-1,180
7830	0,372	0,525	-0,525	-0,990
8310	0,440	0,242	-0,242	-0,821
9210	0,546	-0,186	0,186	-0,604
9750	0,621	-0,493	0,493	-0,477
9810	0,639	-0,569	0,569	-0,448
9930	0,651	-0,625	0,625	-0,429
10080	0,670	-0,708	0,708	-0,400
10950	0,751	-1,103	1,103	-0,287
12600	0,881	-1,998	1,998	-0,127
13020	0,902	-2,214	2,214	-0,104
13740	0,975	-3,646	3,646	-0,026
15180	0,981	-3,963	3,963	-0,019

Table A.11 Results of theoretical C_t/C_o values of the Thomas, Yoon-Nelson, Adams-Bohart and Wolborska models ($C_o=150\text{ppm}$, $v=0.2\text{mL/min}$, bed height=2cm, $x=0.99\text{g}$)

Time (min)	C_t/C_o	$C_t/C_{o,theo}$ (Thomas)	$C_t/C_{o,theo}$ (Yoon-Nelson)	$C_t/C_{o,theo}$ (Adams-Bohart)
0	0,000	0,000	0,000	0,000
240	0,003	0,012	0,009	0,039
1440	0,015	0,021	0,018	0,056
2880	0,035	0,042	0,041	0,086
3540	0,056	0,058	0,060	0,104
4050	0,070	0,074	0,080	0,121
4140	0,077	0,077	0,084	0,125
4320	0,083	0,084	0,093	0,132
4950	0,120	0,110	0,130	0,159
5430	0,164	0,136	0,166	0,184
5490	0,175	0,140	0,171	0,187
5580	0,186	0,145	0,178	0,192
6390	0,251	0,206	0,261	0,245
6930	0,273	0,254	0,328	0,288
7050	0,292	0,265	0,344	0,299
7200	0,307	0,280	0,365	0,312
7830	0,372	0,344	0,456	0,377
8310	0,440	0,400	0,528	0,436
9210	0,546	0,528	0,657	0,571
9750	0,621	0,587	0,726	0,672
9810	0,639	0,594	0,733	0,684
9930	0,651	0,609	0,747	0,709
10080	0,670	0,627	0,764	0,741
10950	0,751	0,720	0,845	0,963
12600	0,881	0,850	0,936	1,579
13020	0,902	0,873	0,950	1,791
13740	0,975	0,909	0,967	2,223
15180	0,981	0,954	0,986	3,424

Table A.12 Results of continuous-mode studies of GAC (1-2mm) for adsorption of 2,4-D ($C_o=200\text{ppm}$, $v=0.2\text{mL/min}$, bed height=2cm)

Time (min)	C_t/C_o	$\ln[(C_o/C_t)-1]$	$\ln[C_t/(C_o-C_t)]$	$\ln(C_t/C_o)$
0	0,000	0,000	0,000	0,000
480	0,016	4,129	-4,129	-4,145
960	0,031	3,437	-3,437	-3,469
1290	0,036	3,291	-3,291	-3,327
1920	0,051	2,930	-2,930	-2,982
2400	0,077	2,488	-2,488	-2,568
2460	0,079	2,459	-2,459	-2,541
2580	0,104	2,155	-2,155	-2,265
2730	0,108	2,113	-2,113	-2,227
3360	0,143	1,793	-1,793	-1,947
3840	0,175	1,550	-1,550	-1,742
3960	0,195	1,421	-1,421	-1,637

4080	0,214	1,301	-1,301	-1,542
4800	0,255	1,070	-1,070	-1,365
5340	0,324	0,734	-0,734	-1,126
5400	0,327	0,722	-0,722	-1,118
5550	0,329	0,713	-0,713	-1,112
6540	0,488	0,049	-0,049	-0,718
9120	0,741	-1,050	1,050	-0,300
10140	0,833	-1,609	1,609	-0,182
10200	0,859	-1,807	1,807	-0,152
10320	0,877	-1,964	1,964	-0,131
10440	0,885	-2,037	2,037	-0,123
11100	0,956	-3,067	3,067	-0,045
11580	0,989	-4,460	4,460	-0,012
12600	0,991	-4,713	4,713	-0,009
13440	0,991	-4,713	4,713	-0,009

Table A.13 Results of theoretical C_t/C_o values of the Thomas, Yoon-Nelson, Adams-Bohart and Wolborska models ($C_o=200\text{ppm}$, $v=0.2\text{mL/min}$, bed height=2cm, $x=1.00\text{ g}$)

Time (min)	C_t/C_o	$C_t/C_{o,theo}$ (Thomas)	$C_t/C_{o,theo}$ (Yoon-Nelson)	$C_t/C_{o,theo}$ (Adams-Bohart)
0	0,000	0,000	0,000	0,000
480	0,016	0,035	0,029	0,079
960	0,031	0,044	0,038	0,091
1290	0,036	0,051	0,046	0,101
1920	0,051	0,069	0,065	0,122
2400	0,077	0,086	0,085	0,140
2460	0,079	0,088	0,088	0,143
2580	0,104	0,093	0,094	0,148
2730	0,108	0,100	0,102	0,155
3360	0,143	0,134	0,142	0,187
3840	0,175	0,165	0,181	0,216
3960	0,195	0,174	0,192	0,224
4080	0,214	0,182	0,204	0,233
4800	0,255	0,242	0,283	0,289
5340	0,324	0,295	0,353	0,339
5400	0,327	0,302	0,361	0,345
5550	0,329	0,318	0,382	0,361
6540	0,488	0,428	0,528	0,486
9120	0,741	0,731	0,840	1,055
10140	0,833	0,820	0,907	1,432
10200	0,859	0,825	0,910	1,458
10320	0,877	0,833	0,915	1,512
10440	0,885	0,842	0,921	1,567
11100	0,956	0,880	0,945	1,910
11580	0,989	0,903	0,958	2,206
12600	0,991	0,940	0,977	2,996
13440	0,991	0,959	0,986	3,854

Table A.14 Results of continuous-mode studies of GAC (1-2mm) for adsorption of 2,4-D ($C_o=50\text{ppm}$, $v=0.3\text{mL/min}$, bed height=2cm)

Time (min)	C_t/C_o	$\ln[(C_o/C_t)-1]$	$\ln[C_t/(C_o-C_t)]$	$\ln(C_t/C_o)$
0	0,000	0,000	0,000	0,000
180	0,010	4,624	-4,624	-4,634
300	0,012	4,420	-4,420	-4,432
960	0,014	4,258	-4,258	-4,272
1560	0,017	4,054	-4,054	-4,071
2490	0,024	3,723	-3,723	-3,747
3240	0,042	3,126	-3,126	-3,169
3360	0,049	2,961	-2,961	-3,011
3810	0,070	2,591	-2,591	-2,663
4230	0,088	2,342	-2,342	-2,434
4290	0,090	2,317	-2,317	-2,411
4545	0,091	2,298	-2,298	-2,394
4605	0,104	2,158	-2,158	-2,268

5100	0,119	2,002	-2,002	-2,129
5580	0,148	1,753	-1,753	-1,913
5850	0,153	1,709	-1,709	-1,875
6000	0,160	1,655	-1,655	-1,830
6150	0,168	1,599	-1,599	-1,783
6240	0,171	1,580	-1,580	-1,768
6270	0,176	1,544	-1,544	-1,738
6690	0,199	1,390	-1,390	-1,612
7050	0,239	1,155	-1,155	-1,429
7170	0,242	1,144	-1,144	-1,421
7230	0,244	1,133	-1,133	-1,412
7290	0,246	1,122	-1,122	-1,404
7440	0,250	1,097	-1,097	-1,385
7560	0,263	1,028	-1,028	-1,334
8070	0,293	0,879	-0,879	-1,226
8550	0,330	0,706	-0,706	-1,107
8670	0,339	0,667	-0,667	-1,082
8730	0,341	0,658	-0,658	-1,076
8880	0,363	0,562	-0,562	-1,013
9510	0,390	0,446	-0,446	-0,941
10050	0,434	0,264	-0,264	-0,834
10170	0,441	0,239	-0,239	-0,820
10320	0,448	0,208	-0,208	-0,803
11160	0,545	-0,179	0,179	-0,608
12600	0,621	-0,493	0,493	-0,477
13350	0,687	-0,786	0,786	-0,375
13860	0,707	-0,883	0,883	-0,346
14400	0,738	-1,035	1,035	-0,304
14640	0,763	-1,171	1,171	-0,270
15300	0,813	-1,470	1,470	-0,207
15810	0,838	-1,646	1,646	-0,176
16200	0,843	-1,684	1,684	-0,170

Table A.15 Results of theoretical C_t/C_o values of the Thomas, Yoon-Nelson, Adams-Bohart and Wolborska models ($C_o=50\text{ppm}$, $v=0.3\text{mL/min}$, bed height=2cm, $x=0.86\text{ g}$)

Time (min)	C_t/C_o	$C_t/C_{o,\text{theo}}$ (Thomas)	$C_t/C_{o,\text{theo}}$ (Yoon-Nelson)	$C_t/C_{o,\text{theo}}$ (Adams-Bohart)
0	0,000	0,000	0,000	0,000
180	0,010	0,025	0,027	0,030
300	0,012	0,026	0,027	0,031
960	0,014	0,032	0,033	0,038
1560	0,017	0,038	0,040	0,046
2490	0,024	0,049	0,052	0,061
3240	0,042	0,061	0,064	0,076
3360	0,049	0,063	0,066	0,079
3810	0,070	0,071	0,075	0,090
4230	0,088	0,080	0,084	0,102
4290	0,090	0,081	0,086	0,104
4545	0,091	0,087	0,092	0,112
4605	0,104	0,089	0,093	0,114

5100	0,119	0,102	0,107	0,133
5580	0,148	0,116	0,121	0,153
5850	0,153	0,124	0,130	0,166
6000	0,160	0,129	0,135	0,174
6150	0,168	0,134	0,140	0,182
6240	0,171	0,137	0,144	0,187
6270	0,176	0,140	0,145	0,189
6690	0,199	0,156	0,161	0,214
7050	0,239	0,171	0,176	0,238
7170	0,242	0,176	0,182	0,247
7230	0,244	0,179	0,184	0,252
7290	0,246	0,182	0,187	0,256
7440	0,250	0,188	0,194	0,268
7560	0,263	0,192	0,200	0,278
8070	0,293	0,217	0,225	0,324
8550	0,330	0,243	0,251	0,374
8670	0,339	0,249	0,258	0,387
8730	0,341	0,253	0,262	0,394
8880	0,363	0,261	0,270	0,413
9510	0,390	0,299	0,309	0,498
10050	0,434	0,335	0,345	0,586
10170	0,441	0,343	0,353	0,608
10320	0,448	0,353	0,363	0,636
11160	0,545	0,413	0,424	0,818
12600	0,621	0,520	0,531	1,260
13350	0,687	0,576	0,586	1,577
13860	0,707	0,613	0,623	1,838
14400	0,738	0,650	0,660	2,161
14640	0,763	0,667	0,676	2,323
15300	0,813	0,712	0,718	2,831
15810	0,838	0,742	0,748	3,300
16200	0,843	0,764	0,769	3,709

Table A.16 Results of continuous-mode studies of GAC (1-2mm) for adsorption of 2,4-D ($C_o=100\text{ppm}$, $v=0.3\text{mL/min}$, bed height=2cm)

Time (min)	C_t/C_o	$\ln[(C_o/C_t)-1]$	$\ln[C_t/(C_o-C_t)]$	$\ln(C_t/C_o)$
0	0,000	0,000	0,000	0,000
180	0,003	5,703	-5,703	-5,706
300	0,009	4,651	-4,651	-4,660
900	0,010	4,547	-4,547	-4,558
1380	0,013	4,346	-4,346	-4,359
1440	0,015	4,161	-4,161	-4,177
1920	0,017	4,065	-4,065	-4,082
1980	0,021	3,826	-3,826	-3,847
2640	0,026	3,605	-3,605	-3,631
3000	0,043	3,104	-3,104	-3,148
3060	0,044	3,067	-3,067	-3,113
3120	0,047	3,020	-3,020	-3,068
3180	0,048	2,986	-2,986	-3,035
3240	0,050	2,942	-2,942	-2,993
3390	0,054	2,864	-2,864	-2,919
3510	0,060	2,756	-2,756	-2,818

4020	0,089	2,321	-2,321	-2,415
4500	0,127	1,932	-1,932	-2,067
4620	0,134	1,869	-1,869	-2,012
4680	0,139	1,826	-1,826	-1,975
4830	0,154	1,707	-1,707	-1,874
5460	0,206	1,347	-1,347	-1,578
6000	0,283	0,928	-0,928	-1,261
6180	0,318	0,763	-0,763	-1,145
6330	0,349	0,625	-0,625	-1,054
7050	0,405	0,386	-0,386	-0,905
8400	0,550	-0,199	0,199	-0,599
9150	0,646	-0,603	0,603	-0,436
9660	0,682	-0,763	0,763	-0,383
10140	0,733	-1,009	1,009	-0,311
10200	0,776	-1,243	1,243	-0,253
10440	0,791	-1,333	1,333	-0,234
11520	0,845	-1,697	1,697	-0,168
12960	0,906	-2,267	2,267	-0,099
13320	0,926	-2,533	2,533	-0,076
14400	0,959	-3,162	3,162	-0,041

Table A.17 Results of theoretical C_t/C_o values of the Thomas, Yoon-Nelson, Adams-Bohart and Wolborska models ($C_o=100\text{ppm}$, $v=0.3\text{mL/min}$, bed height=2cm, $x=0.99\text{ g}$)

Time (min)	C_t/C_o	$C_t/C_{o,\text{theo}}$ (Thomas)	$C_t/C_{o,\text{theo}}$ (Yoon-Nelson)	$C_t/C_{o,\text{theo}}$ (Adams-Bohart)
0	0,000	0,000	0,000	0,000
180	0,003	0,012	0,007	0,008
300	0,009	0,013	0,008	0,009
900	0,010	0,019	0,011	0,013
1380	0,013	0,025	0,015	0,017
1440	0,015	0,026	0,015	0,018
1920	0,017	0,034	0,020	0,024
1980	0,021	0,036	0,021	0,025
2640	0,026	0,052	0,031	0,037
3000	0,043	0,064	0,038	0,046
3060	0,044	0,066	0,040	0,047
3120	0,047	0,068	0,041	0,049
3180	0,048	0,070	0,042	0,051
3240	0,050	0,073	0,044	0,053
3390	0,054	0,079	0,048	0,058
3510	0,060	0,085	0,051	0,062
4020	0,089	0,111	0,068	0,084
4500	0,127	0,143	0,089	0,113
4620	0,134	0,152	0,095	0,121
4680	0,139	0,157	0,098	0,125
4830	0,154	0,170	0,107	0,137
5460	0,206	0,230	0,148	0,200
6000	0,283	0,292	0,194	0,277
6180	0,318	0,311	0,211	0,308
6330	0,349	0,330	0,227	0,338
7050	0,405	0,431	0,311	0,520

8400	0,550	0,628	0,504	1,169
9150	0,646	0,725	0,614	1,833
9660	0,682	0,782	0,684	2,489
10140	0,733	0,827	0,742	3,320
10200	0,776	0,832	0,749	3,441
10440	0,791	0,851	0,775	3,975
11520	0,845	0,914	0,868	7,598
12960	0,906	0,962	0,940	18,028
13320	0,926	0,969	0,951	22,374
14400	0,959	0,983	0,974	42,773

Table A.18 Results of continuous-mode studies of GAC (1-2mm) for adsorption of 2,4-D ($C_o=150\text{ppm}$, $v=0.3\text{mL/min}$, bed height=2cm)

Time (min)	C_t/C_o	$\ln[(C_o/C_t)-1]$	$\ln[C_t/(C_o-C_t)]$	$\ln(C_t/C_o)$
0	0,000	0,000	0,000	0,000
60	0,021	3,853	-3,853	-3,874
180	0,025	3,676	-3,676	-3,701
300	0,033	3,381	-3,381	-3,415
900	0,035	3,304	-3,304	-3,340
1380	0,037	3,260	-3,260	-3,298
1440	0,048	2,994	-2,994	-3,043
1920	0,063	2,699	-2,699	-2,764
2640	0,066	2,656	-2,656	-2,724
3000	0,104	2,156	-2,156	-2,265
3060	0,111	2,082	-2,082	-2,200
3120	0,118	2,014	-2,014	-2,140
3180	0,126	1,934	-1,934	-2,069
3240	0,136	1,845	-1,845	-1,992
3390	0,154	1,705	-1,705	-1,872
3510	0,163	1,638	-1,638	-1,816
4020	0,273	0,980	-0,980	-1,299
4500	0,393	0,434	-0,434	-0,933
4620	0,420	0,321	-0,321	-0,867
4680	0,444	0,225	-0,225	-0,812
4830	0,501	-0,003	0,003	-0,691
5460	0,586	-0,348	0,348	-0,534
6000	0,700	-0,848	0,848	-0,356
7050	0,775	-1,237	1,237	-0,255
8400	0,838	-1,640	1,640	-0,177
9150	0,865	-1,854	1,854	-0,145
9660	0,880	-1,991	1,991	-0,128
10140	0,897	-2,162	2,162	-0,109
11520	0,917	-2,403	2,403	-0,087
12960	0,941	-2,765	2,765	-0,061
13320	0,970	-3,461	3,461	-0,031
14400	0,978	-3,795	3,795	-0,022

Table A.19 Results of theoretical C_t/C_o values of the Thomas, Yoon-Nelson, Adams-Bohart and Wolborska models ($C_o=150\text{ppm}$, $v=0.3\text{mL/min}$, bed height=2cm, $x=0.99\text{g}$)

Time (min)	C_t/C_o	$C_t/C_{o,\text{theo}}$ (Thomas)	$C_t/C_{o,\text{theo}}$ (Yoon-Nelson)	$C_t/C_{o,\text{theo}}$ (Adams-Bohart)
0	0,000	0,000	0,000	0,000
60	0,021	0,013	0,008	0,008
180	0,025	0,015	0,009	0,009
300	0,033	0,016	0,010	0,010
900	0,035	0,026	0,017	0,017
1380	0,037	0,038	0,026	0,026
1440	0,048	0,039	0,027	0,027
1920	0,063	0,057	0,041	0,042
2640	0,066	0,097	0,075	0,080
3000	0,104	0,125	0,101	0,110
3060	0,111	0,130	0,106	0,116
3120	0,118	0,136	0,112	0,123
3180	0,126	0,142	0,117	0,129
3240	0,136	0,148	0,123	0,137
3390	0,154	0,163	0,138	0,156
3510	0,163	0,176	0,151	0,174
4020	0,273	0,243	0,220	0,275
4500	0,393	0,321	0,303	0,424
4620	0,420	0,342	0,326	0,473
4680	0,444	0,353	0,338	0,499
4830	0,501	0,386	0,369	0,571
5460	0,586	0,510	0,508	1,007
6000	0,700	0,617	0,626	1,637
7050	0,775	0,789	0,812	4,211
8400	0,838	0,917	0,936	14,192
9150	0,865	0,953	0,966	27,874
9660	0,880	0,968	0,978	44,111
10140	0,897	0,978	0,986	67,945
11520	0,917	0,992	0,996	235,262
12960	0,941	0,998	0,999	859,800
13320	0,970	0,998	0,999	1188,800
14400	0,978	0,999	1,000	3142,268

Table A.20 Results of continuous-mode studies of GAC (1-2mm) for adsorption of 2,4-D ($C_o=200\text{ppm}$, $v=0.3\text{mL/min}$, bed height=2cm)

Time (min)	C_t/C_o	$\ln[(C_o/C_t)-1]$	$\ln[C_t/(C_o-C_t)]$	$\ln(C_t/C_o)$
0	0,000	0,000	0,000	0,000
60	0,020	3,889	-3,889	-3,909
120	0,021	3,820	-3,820	-3,842
180	0,030	3,484	-3,484	-3,515
300	0,035	3,305	-3,305	-3,341
900	0,083	2,405	-2,405	-2,491
1380	0,142	1,796	-1,796	-1,950
1500	0,153	1,713	-1,713	-1,878

1650	0,187	1,473	-1,473	-1,679
1800	0,205	1,354	-1,354	-1,583
1920	0,214	1,302	-1,302	-1,542
1980	0,243	1,135	-1,135	-1,414
2640	0,363	0,563	-0,563	-1,014
3000	0,467	0,131	-0,131	-0,761
3060	0,483	0,070	-0,070	-0,729
3120	0,501	-0,003	0,003	-0,692
3180	0,512	-0,049	0,049	-0,669
3240	0,532	-0,126	0,126	-0,632
3390	0,561	-0,246	0,246	-0,578
3510	0,578	-0,316	0,316	-0,548
4020	0,662	-0,674	0,674	-0,412
4500	0,745	-1,073	1,073	-0,294
4680	0,758	-1,142	1,142	-0,277
4830	0,798	-1,377	1,377	-0,225
5460	0,832	-1,599	1,599	-0,184
6000	0,870	-1,904	1,904	-0,139
7050	0,875	-1,947	1,947	-0,133
8400	0,897	-2,162	2,162	-0,109
9150	0,934	-2,646	2,646	-0,069
11520	0,949	-2,930	2,930	-0,052
12960	0,963	-3,266	3,266	-0,037
13320	0,972	-3,551	3,551	-0,028

Table A.21 Results of theoretical C_t/C_o values of the Thomas, Yoon-Nelson, Adams-Bohart and Wolborska models ($C_o=200\text{ppm}$, $v=0.3\text{mL/min}$, bed height=2cm, $x=0.85\text{g}$)

Time (min)	C_t/C_o	$C_t/C_{o,theo}$ (Thomas)	$C_t/C_{o,theo}$ (Yoon-Nelson)	$C_t/C_{o,theo}$ (Adams-Bohart)
0	0,000	0,000	0,000	0,000
60	0,020	0,042	0,042	0,055
120	0,021	0,044	0,044	0,058
180	0,030	0,047	0,047	0,060
300	0,035	0,052	0,053	0,065
900	0,083	0,092	0,092	0,099
1380	0,142	0,140	0,141	0,139
1500	0,153	0,155	0,156	0,151
1650	0,187	0,176	0,177	0,168
1800	0,205	0,199	0,200	0,187
1920	0,214	0,219	0,220	0,203
1980	0,243	0,231	0,230	0,212
2640	0,363	0,368	0,366	0,336
3000	0,467	0,455	0,453	0,432
3060	0,483	0,470	0,468	0,451
3120	0,501	0,485	0,483	0,470
3180	0,512	0,500	0,498	0,491
3240	0,532	0,515	0,513	0,512
3390	0,561	0,552	0,550	0,568
3510	0,578	0,577	0,580	0,618
4020	0,662	0,695	0,697	0,883
4500	0,745	0,786	0,788	1,236

4680	0,758	0,815	0,816	1,402
4830	0,798	0,838	0,838	1,557
5460	0,832	0,907	0,906	2,420
6000	0,870	0,943	0,943	3,532
7050	0,875	0,979	0,979	7,365
8400	0,897	0,995	0,995	18,950
9150	0,934	0,997	0,997	32,034
11520	0,949	1,000	1,000	168,309
12960	0,963	1,000	1,000	461,185
13320	0,972	1,000	1,000	593,359

Table A.22 Results of continuous-mode studies of GAC (1-2mm) for adsorption of 2,4-D ($C_o=50\text{ppm}$, $v=0.4\text{mL/min}$, bed height=2cm)

Time (min)	C_t/C_o	$\ln[(C_o/C_t)-1]$	$\ln[C_t/(C_o-C_t)]$	$\ln(C_t/C_o)$
0	0,000	0,000	0,000	0,000
240	0,010	4,580	-4,580	-4,590
780	0,011	4,531	-4,531	-4,541
1440	0,021	3,839	-3,839	-3,861
1710	0,034	3,351	-3,351	-3,386
2220	0,044	3,076	-3,076	-3,121
2880	0,064	2,690	-2,690	-2,755
3930	0,097	2,229	-2,229	-2,331
4650	0,137	1,844	-1,844	-1,991
5220	0,174	1,558	-1,558	-1,749
5820	0,220	1,266	-1,266	-1,514
5940	0,230	1,207	-1,207	-1,469
6600	0,274	0,974	-0,974	-1,294
7200	0,338	0,674	-0,674	-1,086
7380	0,360	0,577	-0,577	-1,023
8040	0,401	0,401	-0,401	-0,914
8700	0,462	0,154	-0,154	-0,773
8820	0,466	0,138	-0,138	-0,764
8880	0,478	0,087	-0,087	-0,737
8940	0,504	-0,015	0,015	-0,686
9420	0,534	-0,138	0,138	-0,627
10260	0,618	-0,482	0,482	-0,481
10920	0,668	-0,701	0,701	-0,403
11400	0,720	-0,943	0,943	-0,329
11700	0,761	-1,160	1,160	-0,273
12360	0,808	-1,438	1,438	-0,213
12900	0,857	-1,792	1,792	-0,154
13620	0,931	-2,607	2,607	-0,071
14340	0,931	-2,607	2,607	-0,071
15060	0,941	-2,778	2,778	-0,060

Table A.23 Results of theoretical C_t/C_o values of the Thomas, Yoon-Nelson, Adams-Bohart and Wolborska models ($C_o=50\text{ppm}$, $v=0.4\text{mL/min}$, bed height=2cm, $x=0.99\text{g}$)

Time (min)	C_t/C_o	$C_t/C_{o,theo}$ (Thomas)	$C_t/C_{o,theo}$ (Yoon-Nelson)	$C_t/C_{o,theo}$ (Adams-Bohart)
0	0,000	0,000	0,000	0,000
240	0,010	0,025	0,021	0,025
780	0,011	0,031	0,026	0,032
1440	0,021	0,039	0,034	0,041
1710	0,034	0,044	0,038	0,046
2220	0,044	0,053	0,046	0,056
2880	0,064	0,068	0,059	0,073
3930	0,097	0,101	0,087	0,111
4650	0,137	0,130	0,113	0,148
5220	0,174	0,158	0,138	0,186
5820	0,220	0,193	0,169	0,237
5940	0,230	0,201	0,175	0,249
6600	0,274	0,247	0,217	0,324
7200	0,338	0,295	0,260	0,412
7380	0,360	0,310	0,275	0,442
8040	0,401	0,373	0,330	0,576
8700	0,462	0,438	0,391	0,750
8820	0,466	0,450	0,402	0,787
8880	0,478	0,456	0,408	0,806
8940	0,504	0,462	0,414	0,826
9420	0,534	0,510	0,461	1,001
10260	0,618	0,594	0,545	1,400
10920	0,668	0,657	0,609	1,823
11400	0,720	0,699	0,654	2,209
11700	0,761	0,731	0,681	2,491
12360	0,808	0,767	0,735	3,243
12900	0,857	0,806	0,775	4,025
13620	0,931	0,851	0,821	5,368
14340	0,931	0,884	0,860	7,160
15060	0,941	0,911	0,891	9,550

Table A.24 Results of continuous-mode studies of GAC (1-2mm) for adsorption of 2,4-D ($C_o=100\text{ppm}$, $v=0.4\text{mL/min}$, bed height=2cm)

Time (min)	C_t/C_o	$\ln[(C_o/C_t)-1]$	$\ln[C_t/(C_o-C_t)]$	$\ln(C_t/C_o)$
0	0,000	0,000	0,000	0,000
120	0,003	5,974	-5,974	-5,976
150	0,005	5,278	-5,278	-5,283
210	0,008	4,870	-4,870	-4,878
240	0,015	4,169	-4,169	-4,185
780	0,026	3,617	-3,617	-3,644
1260	0,053	2,887	-2,887	-2,941
1320	0,057	2,803	-2,803	-2,862
1380	0,062	2,720	-2,720	-2,784
1710	0,080	2,438	-2,438	-2,522

2220	0,119	2,000	-2,000	-2,127
2880	0,173	1,562	-1,562	-1,752
3930	0,384	0,474	-0,474	-0,958
4650	0,467	0,133	-0,133	-0,762
5220	0,587	-0,351	0,351	-0,533
5820	0,688	-0,791	0,791	-0,374
5940	0,716	-0,925	0,925	-0,334
6600	0,753	-1,116	1,116	-0,283
7200	0,780	-1,266	1,266	-0,248
7380	0,806	-1,422	1,422	-0,216
8040	0,827	-1,567	1,567	-0,190
8700	0,845	-1,698	1,698	-0,168
8820	0,857	-1,789	1,789	-0,155
9420	0,870	-1,897	1,897	-0,140
9960	0,895	-2,144	2,144	-0,111
10260	0,923	-2,488	2,488	-0,080
10920	0,943	-2,806	2,806	-0,059
11700	0,969	-3,445	3,445	-0,031
12360	0,959	-3,162	3,162	-0,041
12900	0,970	-3,461	3,461	-0,031
14400	0,970	-3,461	3,461	-0,031

Table A.25 Results of theoretical C_t/C_o values of the Thomas, Yoon-Nelson, Adams-Bohart and Wolborska models ($C_o=100\text{ppm}$, $v=0.4\text{mL/min}$, bed height=2cm, $x=0.89\text{g}$)

Time (min)	C_t/C_o	$C_t/C_{o,\text{theo}}$ (Thomas)	$C_t/C_{o,\text{theo}}$ (Yoon-Nelson)	$C_t/C_{o,\text{theo}}$ (Adams-Bohart)
0	0,000	0,000	0,000	0,000
120	0,003	0,042	0,034	0,025
150	0,005	0,042	0,034	0,026
210	0,008	0,044	0,035	0,027
240	0,015	0,045	0,036	0,027
780	0,026	0,065	0,049	0,040
1260	0,053	0,088	0,064	0,056
1320	0,057	0,092	0,067	0,058
1380	0,062	0,095	0,069	0,061
1710	0,080	0,118	0,083	0,076
2220	0,119	0,160	0,109	0,109
2880	0,173	0,233	0,154	0,173
3930	0,384	0,389	0,255	0,362
4650	0,467	0,514	0,345	0,599
5220	0,587	0,613	0,426	0,892
5820	0,688	0,707	0,515	1,358
5940	0,716	0,725	0,533	1,477
6600	0,753	0,807	0,629	2,345
7200	0,780	0,865	0,708	3,569
7380	0,806	0,879	0,730	4,048
8040	0,827	0,921	0,801	6,425
8700	0,845	0,949	0,857	10,198
8820	0,857	0,953	0,865	11,092
9420	0,870	0,968	0,902	16,881
9960	0,895	0,978	0,927	24,636

10260	0,923	0,982	0,938	30,393
10920	0,943	0,989	0,958	48,241
11700	0,969	0,993	0,973	83,279
12360	0,959	0,996	0,982	132,185
12900	0,970	0,997	0,987	192,905
14400	0,970	0,999	0,995	551,256

Table A.26 Results of continuous-mode studies of GAC (1-2mm) for adsorption of 2,4-D ($C_o=150\text{ppm}$, $v=0.4\text{mL/min}$, bed height=2cm)

Time (min)	C_t/C_o	$\ln[(C_o/C_t)-1]$	$\ln[C_t/(C_o-C_t)]$	$\ln(C_t/C_o)$
0	0,000	0,000	0,000	0,000
60	0,011	4,487	-4,487	-4,498
90	0,011	4,487	-4,487	-4,498
120	0,013	4,369	-4,369	-4,382
600	0,034	3,345	-3,345	-3,379
1020	0,057	2,799	-2,799	-2,858
1080	0,060	2,753	-2,753	-2,815
1140	0,066	2,657	-2,657	-2,724
1200	0,073	2,545	-2,545	-2,620
1440	0,085	2,379	-2,379	-2,468
1560	0,098	2,222	-2,222	-2,325
1620	0,103	2,167	-2,167	-2,275
2100	0,188	1,462	-1,462	-1,671
2580	0,307	0,816	-0,816	-1,182
2640	0,325	0,732	-0,732	-1,125
2760	0,359	0,579	-0,579	-1,024
2880	0,382	0,480	-0,480	-0,962
3060	0,424	0,307	-0,307	-0,858
3540	0,529	-0,118	0,118	-0,636
4020	0,656	-0,644	0,644	-0,422
4320	0,736	-1,027	1,027	-0,306
4500	0,771	-1,216	1,216	-0,260
4980	0,816	-1,487	1,487	-0,204
5340	0,862	-1,830	1,830	-0,149
5940	0,875	-1,944	1,944	-0,134
6540	0,909	-2,303	2,303	-0,095
7200	0,925	-2,507	2,507	-0,078

Table A.27 Results of theoretical C_t/C_o values of the Thomas, Yoon-Nelson, Adams-Bohart and Wolborska models ($C_o=150\text{ppm}$, $v=0.4\text{mL/min}$, bed height=2cm, $x=0.89\text{g}$)

Time (min)	C_t/C_o	$C_t/C_{o,theo}$ (Thomas)	$C_t/C_{o,theo}$ (Yoon-Nelson)	$C_t/C_{o,theo}$ (Adams-Bohart)
0	0,000	0,000	0,000	0,000
60	0,011	0,032	0,016	0,021
90	0,011	0,033	0,017	0,021
120	0,013	0,034	0,017	0,022
600	0,034	0,054	0,030	0,036
1020	0,057	0,080	0,049	0,054

1080	0,060	0,084	0,052	0,057
1140	0,066	0,089	0,056	0,061
1200	0,073	0,094	0,060	0,065
1440	0,085	0,117	0,078	0,082
1560	0,098	0,129	0,089	0,093
1620	0,103	0,136	0,095	0,098
2100	0,188	0,203	0,158	0,159
2580	0,307	0,291	0,250	0,257
2640	0,325	0,304	0,264	0,273
2760	0,359	0,330	0,293	0,308
2880	0,382	0,357	0,324	0,347
3060	0,424	0,402	0,373	0,416
3540	0,529	0,521	0,514	0,672
4020	0,656	0,638	0,653	1,086
4320	0,736	0,709	0,729	1,466
4500	0,771	0,741	0,770	1,755
4980	0,816	0,822	0,856	2,835
5340	0,862	0,869	0,902	4,064
5940	0,875	0,923	0,950	7,405
6540	0,909	0,956	0,975	13,493
7200	0,925	0,978	0,988	26,107

Table A.28 Results of continuous-mode studies of GAC (1-2mm) for adsorption of 2,4-D ($C_o=200\text{ppm}$, $v=0.4\text{mL/min}$, bed height=2cm)

Time (min)	C_t/C_o	$\ln[(C_o/C_t)-1]$	$\ln[C_t/(C_o-C_t)]$	$\ln(C_t/C_o)$
0	0,000	0,000	0,000	0,000
30	0,027	3,584	-3,584	-3,611
60	0,027	3,584	-3,584	-3,611
90	0,037	3,265	-3,265	-3,302
150	0,042	3,128	-3,128	-3,171
210	0,049	2,962	-2,962	-3,013
270	0,057	2,808	-2,808	-2,867
750	0,100	2,200	-2,200	-2,305
1110	0,151	1,730	-1,730	-1,893
1200	0,157	1,681	-1,681	-1,851
1410	0,183	1,493	-1,493	-1,696
1590	0,216	1,292	-1,292	-1,534
1620	0,219	1,269	-1,269	-1,516
2100	0,369	0,537	-0,537	-0,997
2550	0,551	-0,203	0,203	-0,597
2610	0,575	-0,304	0,304	-0,553
2730	0,614	-0,466	0,549	-0,487
3000	0,688	-0,789	0,789	-0,374
3480	0,790	-1,328	1,328	-0,235
3960	0,848	-1,722	1,722	-0,164
4620	0,896	-2,151	2,151	-0,110
5280	0,940	-2,743	2,743	-0,062
5940	0,982	-3,996	3,996	-0,018

Table A.29 Results of theoretical C_t/C_o values of the Thomas, Yoon-Nelson, Adams-Bohart and Wolborska models ($C_o=200\text{ppm}$, $v=0.4\text{mL/min}$, bed height=2cm, $x=0.86$)

Time (min)	C_t/C_o	$C_t/C_{o,theo}$ (Thomas)	$C_t/C_{o,theo}$ (Yoon-Nelson)	$C_t/C_{o,theo}$ (Adams-Bohart)
0	0,000	0,000	0,000	0,000
30	0,027	0,036	0,040	0,041
60	0,027	0,037	0,041	0,042
90	0,037	0,039	0,043	0,044
150	0,042	0,042	0,046	0,047
210	0,049	0,045	0,050	0,050
270	0,057	0,049	0,054	0,053
750	0,100	0,087	0,096	0,090
1110	0,151	0,132	0,144	0,134
1200	0,157	0,146	0,159	0,148
1410	0,183	0,184	0,199	0,187
1590	0,216	0,222	0,239	0,228
1620	0,219	0,229	0,247	0,235
2100	0,369	0,357	0,379	0,399
2550	0,551	0,499	0,523	0,654
2610	0,575	0,519	0,542	0,699
2730	0,614	0,557	0,581	0,798
3000	0,688	0,640	0,663	1,074
3480	0,790	0,768	0,786	1,820
3960	0,848	0,861	0,873	3,087
4620	0,896	0,936	0,942	6,380
5280	0,940	0,972	0,974	13,185
5940	0,982	0,988	0,989	27,251

Table A.30 Results of continuous-mode studies of GAC (1-2mm) for adsorption of 2,4-D ($C_o=200\text{ppm}$, $v=0.4\text{mL/min}$, bed height=2.5cm)

Time (min)	C_t/C_o	$\ln[(C_o/C_t)-1]$	$\ln[C_t/(C_o-C_t)]$	$\ln(C_t/C_o)$
0	0,000	0,000	0,000	0,000
510	0,004	5,438	-5,438	-5,442
630	0,007	4,918	-4,918	-4,925
1140	0,026	3,619	-3,619	-3,645
1590	0,059	2,767	-2,767	-2,828
1680	0,066	2,650	-2,650	-2,718
1770	0,076	2,501	-2,501	-2,580
1920	0,090	2,314	-2,314	-2,409
2550	0,168	1,603	-1,603	-1,787
3030	0,297	0,862	-0,862	-1,214
3120	0,311	0,796	-0,796	-1,168
3210	0,321	0,749	-0,749	-1,136
3360	0,381	0,487	-0,487	-0,966
4020	0,545	-0,180	0,180	-0,607
4440	0,620	-0,491	0,491	-0,477
4560	0,643	-0,589	0,589	-0,441
4650	0,694	-0,817	0,817	-0,366

4800	0,731	-1,002	1,002	-0,313
5490	0,866	-1,868	1,868	-0,144
6060	0,887	-2,057	2,057	-0,120
6180	0,898	-2,176	2,176	-0,107
6960	0,917	-2,405	2,405	-0,086
8640	0,949	-2,925	2,925	-0,052
8910	0,954	-3,035	3,035	-0,047

Table A.31 Results of theoretical C_t/C_o values of the Thomas, Yoon-Nelson, Adams-Bohart and Wolborska models ($C_o=200\text{ppm}$, $v=0.4\text{mL/min}$, bed height=2.5 cm, $x=1.16\text{g}$)

Time (min)	C_t/C_o	$C_t/C_{o,\text{theo}}$ (Thomas)	$C_t/C_{o,\text{theo}}$ (Yoon-Nelson)	$C_t/C_{o,\text{theo}}$ (Adams-Bohart)
0	0,000	0,000	0,000	0,000
510	0,004	0,019	0,020	0,032
630	0,007	0,022	0,023	0,035
1140	0,026	0,040	0,041	0,053
1590	0,059	0,067	0,069	0,076
1680	0,066	0,074	0,076	0,081
1770	0,076	0,082	0,084	0,087
1920	0,090	0,096	0,099	0,098
2550	0,168	0,185	0,189	0,163
3030	0,297	0,288	0,293	0,240
3120	0,311	0,310	0,316	0,258
3210	0,321	0,334	0,340	0,277
3360	0,381	0,375	0,381	0,312
4020	0,545	0,566	0,576	0,523
4440	0,620	0,683	0,692	0,731
4560	0,643	0,713	0,722	0,804
4650	0,694	0,734	0,743	0,864
4800	0,731	0,768	0,776	0,974
5490	0,866	0,886	0,888	1,726
6060	0,887	0,939	0,940	2,725
6180	0,898	0,947	0,948	3,000
6960	0,917	0,979	0,979	5,603
8640	0,949	0,997	0,997	21,521
8910	0,954	0,998	0,998	26,717

Table A.32 Results of continuous-mode studies of GAC (1-2mm) for adsorption of 2,4-D ($C_o=200\text{ppm}$, $v=0.4\text{mL/min}$, bed height=3cm)

Time (min)	C_t/C_o	$\ln[(C_o/C_t)-1]$	$\ln[C_t/(C_o-C_t)]$	$\ln(C_t/C_o)$
0	0,000	0,000	0,000	0,000
750	0,002	6,194	-6,194	-6,196
870	0,003	5,787	-5,787	-5,790
1380	0,011	4,491	-4,491	-4,502
1830	0,036	3,293	-3,293	-3,330
1920	0,045	3,065	-3,065	-3,110
2010	0,056	2,819	-2,819	-2,877
2160	0,064	2,688	-2,688	-2,754

2790	0,114	2,048	-2,048	-2,170
3270	0,254	1,078	-1,078	-1,371
3360	0,266	1,012	-1,012	-1,322
3450	0,305	0,826	-0,826	-1,189
3600	0,343	0,652	-0,652	-1,071
4260	0,441	0,236	-0,236	-0,818
4680	0,516	-0,063	0,063	-0,662
4800	0,533	-0,134	0,134	-0,628
4890	0,549	-0,195	0,195	-0,600
5040	0,603	-0,417	0,417	-0,506
5730	0,786	-1,301	1,301	-0,241
6300	0,841	-1,664	1,664	-0,173
6420	0,854	-1,762	1,762	-0,158
7200	0,887	-2,057	2,057	-0,120
8340	0,918	-2,422	2,422	-0,085

Table A.33 Results of theoretical C_t/C_o values of the Thomas, Yoon-Nelson, Adams-Bohart and Wolborska models ($C_o=200\text{ppm}$, $v=0.4\text{mL/min}$, bed height=3 cm, $x=1.39$)

Time (min)	C_t/C_o	$C_t/C_{o,theo}$ (Thomas)	$C_t/C_{o,theo}$ (Yoon-Nelson)	$C_t/C_{o,theo}$ (Adams-Bohart)
0	0,000	0,000	0,000	0,000
750	0,002	0,019	0,027	0,086
870	0,003	0,022	0,031	0,091
1380	0,011	0,036	0,050	0,111
1830	0,036	0,055	0,076	0,133
1920	0,045	0,059	0,083	0,138
2010	0,056	0,065	0,090	0,143
2160	0,064	0,074	0,103	0,152
2790	0,114	0,131	0,177	0,195
3270	0,254	0,196	0,258	0,237
3360	0,266	0,211	0,275	0,245
3450	0,305	0,226	0,294	0,254
3600	0,343	0,254	0,326	0,270
4260	0,441	0,393	0,483	0,349
4680	0,516	0,496	0,587	0,413
4800	0,533	0,526	0,616	0,433
4890	0,549	0,548	0,637	0,449
5040	0,603	0,584	0,671	0,477
5730	0,786	0,742	0,803	0,635
6300	0,841	0,836	0,878	0,797
6420	0,854	0,852	0,890	0,837
7200	0,887	0,926	0,946	1,144
8340	0,918	0,975	0,982	1,805

Table A.34 Results of continuous-mode studies of GAC (1-2mm) for adsorption of 2,4-D ($C_o=200\text{ppm}$, $v=0.4\text{mL/min}$, bed height=3.5cm)

Time (min)	C_t/C_o	$\ln[(C_o/C_t)-1]$	$\ln[C_t/(C_o-C_t)]$	$\ln(C_t/C_o)$
0	0,000	0,000	0,000	0,000
990	0,002	6,482	-6,482	-6,483
1110	0,003	5,921	-5,921	-5,924
1620	0,006	5,156	-5,156	-5,162
2070	0,013	4,340	-4,340	-4,353
2160	0,015	4,200	-4,200	-4,215
2250	0,020	3,905	-3,905	-3,925
2400	0,030	3,478	-3,478	-3,509
3030	0,076	2,496	-2,496	-2,575
3510	0,165	1,622	-1,622	-1,802
3600	0,178	1,532	-1,532	-1,728
3690	0,203	1,367	-1,367	-1,594
3840	0,216	1,291	-1,291	-1,534
4500	0,295	0,871	-0,871	-1,221
4920	0,382	0,481	-0,481	-0,962
5040	0,400	0,407	-0,407	-0,917
5130	0,414	0,349	-0,349	-0,883
5280	0,435	0,261	-0,261	-0,832
5970	0,510	-0,038	0,038	-0,674
6540	0,592	-0,374	0,374	-0,524
6660	0,624	-0,507	0,507	-0,471
7440	0,764	-1,177	1,177	-0,269
8160	0,841	-1,664	1,664	-0,173
8580	0,855	-1,773	1,773	-0,157
9210	0,866	-1,868	1,868	-0,144

Table A.35 Results of theoretical C_t/C_o values of the Thomas, Yoon-Nelson, Adams-Bohart and Wolborska models ($C_o=200\text{ppm}$, $v=0.4\text{mL/min}$, bed height=3.5 cm, $x=1.60\text{g}$)

Time (min)	C_t/C_o	$C_t/C_{o,theo}$ (Thomas)	$C_t/C_{o,theo}$ (Yoon-Nelson)	$C_t/C_{o,theo}$ (Adams-Bohart)
0	0,000	0,000	0,000	0,000
990	0,002	0,027	0,040	0,084
1110	0,003	0,030	0,044	0,087
1620	0,006	0,042	0,061	0,101
2070	0,013	0,056	0,082	0,116
2160	0,015	0,060	0,087	0,119
2250	0,020	0,063	0,092	0,122
2400	0,030	0,070	0,101	0,128
3030	0,076	0,105	0,149	0,155
3510	0,165	0,140	0,196	0,179
3600	0,178	0,148	0,207	0,184
3690	0,203	0,156	0,217	0,189
3840	0,216	0,171	0,236	0,197
4500	0,295	0,244	0,328	0,239
4920	0,382	0,302	0,396	0,271

Table A.36 Results of batch mode equilibrium isotherms of biological contamination of GAC (1-2mm) for adsorption of 2,4-D [*represents (mg bacteria /mg 2,4D solution) ratio]

[illegible]

Table A.37 Results of continuous-mode biological contamination load studies of GAC (1-2mm) for adsorption of 2,4-D ($C_o=200\text{ppm}$, $v=0.4\text{mL/min}$, bed height=2cm, $x=0.93\text{ g}$)

Time (min) for 20 hour load	C_i/C_o (filtered) for 20 hour load	Time (min) for 44 hour load	C_i/C_o (filtered) for 44 hour load	Time (min) for 68 hour load	C_i/C_o (filtered) for 68 hour load
0	0,000	0	0,000	0	0,000
15	0,034	45	0,044	45	0,133
60	0,037	60	0,052	60	0,199
75	0,044	75	0,060	120	0,217
105	0,060	120	0,085	180	0,238
165	0,064	150	0,103	240	0,257
195	0,066	210	0,124	300	0,299
225	0,074	270	0,166	360	0,359
255	0,099	840	0,312	420	0,373
840	0,176	1350	0,550	480	0,390
1410	0,342	1410	0,588	960	0,553
1500	0,377	1470	0,609	1350	0,698
1515	0,395	1500	0,629	1410	0,704
1560	0,391	1560	0,663	1470	0,711
1590	0,399	1620	0,681	1500	0,720
1650	0,404	1680	0,685	1560	0,739
1710	0,417	1740	0,694	1620	0,762
2280	0,593	2220	0,780	1680	0,772
2790	0,763	2400	0,819	1740	0,793
2850	0,775	2580	0,862	2220	0,866
2910	0,792	3060	0,917	2400	0,880
2940	0,806	3600	0,943	2580	0,897
3000	0,828			3060	0,930
3240	0,856				
3300	0,870				
3360	0,898				
3900	0,915				
4500	0,923				
4800	0,926				

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