

**EGE UNIVERSITY GRADUATE SCHOOL OF
APPLIED AND NATURAL SCIENCES**

PhD THESIS

**DETECTION OF SOME ENDOCRINE DISRUPTING
COMPOUNDS IN WATER BY ADVANCED
ANALYTICAL TECHNIQUES AND THEIR
REMOVAL BY POLYMER ADSORBENTS**

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Sayın **SEYHAN SOLAK** tarafından **Doktora tezi** olarak sunulan “**Detection of some Endocrine Disrupting Compounds in Water by Advanced Analytical Techniques and their Removal by Polymer Adsorbents**” başlıklı bu çalışma EÜ Lisansüstü Eğitim ve Öğretim Yönetmeliği ile EÜ Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi’nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

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ÖZET**SULARDA BULUNAN BAZI HORMON BOZUCULARIN İLERİ
ANALİTİK YÖNTEMLERLE TAYİNİ VE POLİMER
ADSORBANLARLA GİDERİLMESİ**

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Hormon bozucu bileşikler (EDCs), gıda, su ve toprakta dünya çapında bir sorun haline gelmiştir. Hormon bozucu bileşikler (EDCs) düşük derişimlerde aktiftirler ve hormonların faaliyetlerini bozmaktadırlar. İnsanlar hormon bozucu bileşiklere, diğer çevresel kirleticilerde olduğu gibi, su, hava, toprak ya da gıda yoluyla, ağızdan, soluma ve deriden emilim yoluyla maruz kalabilirler. Son 20 yılda, hormon bozucu etkileri konusunda bazı kimyasal bileşiklere karşı duyulan endişe artmaktadır.

Bu tez çalışmasında, bazı hormon bozucu bileşiklerin (triklosan, 2,4 dikloro fenol, 2,3,4 trikloro fenol, estron, 17 β -estradiol, 17- α -etinil estradiol, clofibrik asit, klofibret, klofibret metil ester, karbamazepin, ftalatlar (DEP ve DMP)) ileri analitik yöntemlerle (Katı faza özütleme (SPE) ile GC/MS ve Katı faza mikro-özütleme (SPME) ile GC/MS) ve uv-vis spektrometre ile tayinleri incelenmiştir.

Ayrıca, bazı hormon bozucu bileşiklerin (triklosan, 2,4 dikloro fenol, 2,3,4 trikloro fenol, estron, 17 β -estradiol, 17- α -etinil estradiol, clofibrik asit, klofibret, klofibret metil ester, karbamazepin) yüksek çapraz bağlı polimerik adsorbanlarla

(Diaion SP207 (Mitsubishi Chem), Diaion SP825 (Mitsubishi Chem) ve Dowex L493 (Dow Chem)) giderimleri araştırılmıştır.

Ftalatların (DEP ve DMP) giderimleri için yüksek çapraz bağlı adsorbanlar (PAD400 (Purolite International Limited), (Diaion SP207 (Mitsubishi Chem), Diaion SP825 (Mitsubishi Chem) and Dowex L493 (Dow Chem)) kullanılarak kesikli adsorpsiyon çalışmaları, izoterm ve kinetik çalışmaları yapılmıştır. Elde edilen izoterm test sonuçlarının Freundlich, Langmuir ve Temkin izoterm modellerine uygunluğu incelenmiştir. Kinetik çalışma sonuçları kullanılarak 1. ve 2. mertebe kinetik modelleri ve difüzyon kinetik modellerine uyum incelenmiştir.

DEP ve DMP giderimi için DowexL493 adsorbanı ile adsorpsiyon-membran filtrasyon hibrit çalışmaları yapılmıştır. Çalışmalarda adsorban miktarı, doymuş ve taze adsorbanın yer değiştirme hızı, besleme ve süzöntü akış hızı ve adsorban tanecik boyutunun etkisi gibi parametreler incelenmiştir.

Anahtar sözcükler: Hormon Bozucu Bileşikler, Ftalatlar, Katı Faza Özütleme, Katı faza mikro-özütleme, Gaz Kromatografisi-Kütle Spektrometresi, uv-vis Spektrofotometresi, Adsorban.

ABSTRACT**DETECTION OF SOME ENDOCRINE DISRUPTING
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BY POLYMER ADSORBENTS**

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PhD in Chemistry

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Endocrine disrupting compounds (EDCs) in food, water, and soil has been problem in worldwide. Endocrine disrupting compounds (EDCs) are active even at low concentrations and they disturb hormone activities in mammals. It is known that endocrine disrupting compounds can expose to human via food, soil, water or air, by the way of ingestion, dermal absorption and inhalation. The impacts of exposure to endocrine disrupting compounds in the environment have been increased, especially over the last 2 decades.

In this study, determination of some EDCs (2,4-dichloro phenol, triclosan, estrone, 17- β -estradiol, clofibrate methyl ester, 2,3,4-trichloro phenol, 17- α -ethinylestradiol, clofibric acid, clofibrate, carbamazepine, phthalates (DEP and DMP)) in water by using advanced analytical techniques (GC/MS coupled with solid-phase micro-extraction (SPME) and solid-phase extraction methods) and uv-vis spectrophotometer was studied.

Also, removal of some EDCs (triclosan, 2,4-dichloro phenol, 2,3,4-trichloro phenol, estrone, 17- β -estradiol, 17- α -ethinylestradiol, clofibric acid, clofibrate, clofibrate methyl ester, carbamazepine) from water using highly cross-linked polymeric adsorbents (Diaion SP207 (Mitsubishi Chem), Diaion SP825 (Mitsubishi Chem) and Dowex L493 (Dow Chem)) was investigated.

For removal of phthalates (DEP and DMP), batch adsorption tests, isotherm tests, kinetic tests (using highly cross-linked polymeric adsorbents PAD400 (Purolite International Limited), (Diaion SP207 (Mitsubishi Chem), Diaion SP825 (Mitsubishi Chem) and Dowex L493 (Dow Chem)) were performed. Isotherm test data were evaluated using Freundlich, Langmuir and Temkin isotherm models. The kinetic results obtained were evaluated using pseudo first-second order and diffusional kinetic models.

Adsorption-membrane filtration hybrid tests using Dowex L493 (Dow Chem) were performed for DEP and DMP removal. In these studies, some parameters such as effect of adsorbent amount, effect of rate of replacement of saturated and fresh adsorbent, effect of flow rate of permeate and feed and effect of adsorbent particle size were investigated. To decrease of DMP and DEP concentration 4 g/L adsorbent is determined as an optimum amount. From the results it can be said that DMP and DEP removal was higher by using higher amount of adsorbent. However, it showed that when the rate of saturated and fresh adsorbent replacement was increased or when the flow rate of permeate and feed was decreased, DMP and DEP concentration was decreased.

Keywords: Endocrine Disruptors Compounds, Solid Phase Extraction (SPE), Solid Phase Micro-extraction (SPME), Phthalates, Gas Chromatography-Mass Spectrometer (GC/MS), uv-vis Spectrophotometer, Adsorbent.

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1. INTRODUCTION

1.1 Endocrine Disrupting Compounds (EDCs)

The endocrine system is defined as one of the main systems for the body's activities like communication, control and coordination (Ying et al., 2004). The neural system helps the hormonal system to put in order principal body functions which include propagation, osmoregulation, growth and development, energy metabolism and homeostasis. Skeletal development and reproductive processes are regulated by this system (Olujimi et al., 2010).

In recent years, some unnatural compounds have been gained importance in some organisms which are living because of their disrupting effects. An endocrine disrupting compounds (EDCs) is defined as external agent that blocks the carry, synthesis, binding, excretion, action and elimination of native hormones in the body, which are responsible for the maintenance of propagation, homeostasis, development and behavior (Gultekin et al., 2007).

Endocrine disrupting compounds (EDCs) include a structurally various chemicals that may negatively influence the health of man, nature life and sea life, or their progenies, by interplay with the hormonal structure. It is known that endocrine disrupting compounds can expose to human via food, soil, water or air, by the way of ingestion, dermal absorption and inhalation. Endocrine disrupting compounds (EDCs) are active even at lower doses and they disturb hormone activities in mammals (Zhao et al., 2004). In this class chemicals, organic compounds especially in industry and farming, such as alkylphenols-ethionylates, organochloride pesticides, alkyl phenols and polychlorinated biphenyls (PCBs). Some of them are dichlorodiphenyl, polychlorinated dibenzo-p-dioxins, dichloroethylene, nonylphenols, polychlorinated dibenzofurans, steroid hormones and phthalates (Olujimi et al., 2010; Campbell et al., 2006; Fuerhacker et al., 2001). Plasticizers and surfactants are also known as EDCs (Fuerhacker et al., 2001).

Endocrine disrupting compounds disrupt the hormones using the following mechanisms (Olujimi et. al., 2010):

- Endocrine disruptors effects the hormones by imitating or they do not give permission to bind.
- Their amounts are increased original hormone's amount so they do not allow the synthesis or growing of nature hormones.
- Endocrine disruptors do not allow to give notice between the hypothalamus-pituitary-endocrine gland axes.
- They change the hormone receptor's number in a cell.

Endocrine disrupting compounds can be taken via air, food, soil or water, through ingestion, inhalation and absorption by dermal, as with every other environmental contaminant. Young infants and children can expose by the chemicals, milk, contaminated environment such as water, food, surface and dirt, children's play and apparatus used in medicinal via the oral way by ingestion directly (Huang et al., 2008).

EDCs have an impact on human sexual and cognitive development that they may being induced by exposure of EDC (Suliman, 2006; Campbell, 2006; Solomon and Schettler, 2000). They cause immunological and neurologic troubles (Patandin et al., 1999) and they may be decreased in low sperm number and quality of sperm (Van Wyk et al., 2003).

Chemicals are said that they have endocrine effects in the wildlife and man, ever since the last 20 years. These chemicals effect were first recorded in the 1930s. Researches of these chemicals were started at 1970s and 1980s about human and nature life health (Moder et al., 2007). These compounds can expose even at very low concentrations so some of phthalates and phenols have been concerned about their disrupting effects at quantifiable concentrations in all water samples, sediments and even potable water in some countries (Huang et. al., 2008).

1.1.1 Phthalates

Phthalates, are also called phthalates are dialkyl or alkyl esters of 1,2 benzene carboxylic acid (Alatrisme-Mondragon et al., 2003; Adeniyi et al., 2008; Luks-Betlej et al., 2001). The convenient esters occur with a lot of alkyl chains, for example, dibutyl (DBP), diethyl (DEP), dimethyl phthalate (DMP) and di (2-ethylhexyl) phthalate (DEHP). Their structure are hydrophilic in disposition and other natural ambiance. Generally, their melt points are between from -4.6°C to 5.5°C and their molecular weight are ranges from 194 to 396.

Phthalates have many usage area in industries like production of plastics that is used as plasticizers especially to protect polyvinyl chloride (PVC) base plastics (Rudel and Perovich, 2009). Phthalates are also used in production of pesticide, plumbing, non-ionic surface active agent, vinyl upholstery and building materials (Yuan et al., 2002; Huang et al., 2008). They develop the mechanic of plastic resin's properties, its elasticity and suppleness (Rudel and Perovich 2009; Kayali et al., 2006; Alatrisme-Mondragon et al., 2003; Ling et al., 2007; Luks-Betlej et al., 2001; Cortazar et al., 2005; Yuan et al., 2008). For production of plasticizers for acrylic, resins and manufacturing of building materials, cleaners, cosmetics and paint sectors, phthalates includes carboxyl groups between C1 and C4, in alcohols are usually used (Kabdashli et. al., 2009). Of late years, residual point has been about both the production of phthalates and their applications significantly (Castillo et al., 1999; Cortazar et al., 2005). Phthalates bound to the polymer only physically, not chemically, so they may be leached into the environment during the use, production and incineration of the polymeric materials containing these substances (Holadov'a et al., 1995; Castillo et al., 1997).

Humans are subjugated to phthalates from food that has been contaminated during agricultural activities, processing, package or holding. Certain phthalates together with their metabolites and degradation products have been determined in the kidney, liver, and testicles of humans (Arcadi et al., 1998). Many studies have shown that existence of phthalates and their metabolites leads to reproductive and development problems in laboratory animals (Saillanfait et al., 2008). These compounds may also have adverse effects on human health (Matsumoto et al.,

2008) and current research indicates that measurable concentrations of phthalate metabolites can be found in almost all urine samples taken from most children (Sathyaanarayana, 2008).

One of the low molecular weight phthalates is diethyl phthalate (DEP). It is also used as a plasticizer to increase the elasticity of high molecular weight polymer at different type of industries, including automotive sector, herbicides, children's play, cosmetics, medical treatment tubing, plastic packing films, and as an aspirin ingredient (Cheng, 2012). DEP is used also in various cosmetics like deodorants, perfumes and odor products as denaturing agent and fixative. The Research Institute for Fragrance Materials explained that approximately 4000 tons of DEP have been used in cosmetic sector in 1995–1996. In a quantitative analytical experiments has shown that DEP has found at 34 perfumes out of 36 by Greenpeace, it is used commonly in 2003–2004. Their levels are between from 9.4% (94 mg/kg) to % 1 (0.1 mg/kg). Also, studies shows that DEP have been used in different medical equipment, e.g. intestinal tubing and tubing which is used dialysis (Pereira et al., 2007).

Dimethyl phthalate (DMP) is the most basic and generally utilized chemical in latex, cellulose acetate film and plastics, among the different plasticizers known in the plastic industrial. DMP contaminates to the environment from many uses such as papers, tubings or general plastic uses (Brar et al., 2009). DMP may affect the animals and humans. Their development and reproductive system may be affected and testosterone production can reduce, sperm concentrations may decrease (Brar et. al., 2009).

Phthalates are let out natural and eating by evaporation or leaching. They may also migrate through environment. So, phthalates spread through the nature life and eating. Eventually, the human take phthalates into their body persistently (Sioen et al., 2012). Phthalates and their degradation midlevel are toxic, mutagenic and they are known that they have endocrine disrupting effects, also classified as priority pollutants. Because of that, the removal of phthalates from the water and soil is gained importance in last years (Brar et al., 2009).

Nowadays, phthalates are known as pollutants for environmental life because of their large amount of usage. They are leached from polymer matrix easily to environment. Because they are connected to the polymer physically, not chemically. So, people are exposed to them by ingestion or inhalation. Also, they may be taken from PVC blood bags during blood transferring (Seredio and Nogueira, 2006). Phthalates has been caused negative influence which are predicted to be endocrine disrupting substances indicating carcinogenic effect for human, this is increasing social problem. Some phthalates have been classified as priority pollutant because of the healthy effect and risks for human (David et al., 2003). Some phthalate esters are di-(2-ethylhexyl) phthalate, diethyl phthalate (DEP), dibutyl phthalate, dimethyl phthalate (DMP), butyl benzyl phthalate (BBP) and dioctyl phthalate (DOP). They have been established by US Clean Water Act (Feas et al., 2008). Determination of these trace substances from environment are essential for human and their life (Liang et al., 2008).

Phthalates are studied for their environmental effect and biological migration. They have low solubility in water and they can be mentioned about their bioavailability, so they can be classified as toxic. On the other hand, the phthalates which have lower molecular weight are both seriously and chronically toxic at concentrations below their solubility level has been reported. Their toxicity are increasing with their alkyl chain. Phthalates have been established teratogenic if they are at high dosages by several investigators. Also, there are some indications about the phthalates that to be carcinogenic especially low molecular weight phthalates effect liver (Staples et al., 1997).

The biological and environmental effects of phthalates have been designated that maximum remains levels would be found at mid-levels rather than at the top of the food chain. Therefore, phthalates put up with biological transformation in mammal hormonal system. These chemicals' effects in environmental life has occurred in consequently of their endocrine-disrupting properties, this is really great concern. A lots of researches have been shown that these chemicals are also effected the sea life especially on the reproductive system of fish and on their genital structures (Kapanen et al., 2007).

To prevent the intake of the phthalates through the body of human, some environmental regulations have been provided. Where by these regulations research and interest have been increased control and effect of phthalates. Even so, the scientific research has been inadequate about the phthalates treatability in the aquatic life (Kabdashlı et al., 2009). For the treatability of phthalates dissolved in the water two methods have been tested that they are adsorption and chemical oxidation. Biological treatments or photo catalytic techniques may eliminate the phthalate esters. But, degradation and removal efficiency of biological processes are not very-well. Therefore, non-destructive techniques seem to be attractive. Adsorption process has an advantages among the various treatment methods, they are it is not include sludge, it is clean and it removes all of them from the dilute solutions (Mohan et al., 2007).

1.1.2 Hormones

A lots of EDCs are said estrogenic, affecting especially reproduction systems. It is now generally known that endocrine-disrupting chemicals (EDCs) are that they are disrupt the wild life partially reproductive and development system (Porte et al., 2006). They have ecological contamination and they may be observed. Also, the natural female sex hormones 17β -estradiol, estriol and estrone are known as an endocrine disruptors (Fuerhacker et al., 2001).

Estrone naturally occurs in human body and it is one of the most persuasive estrogenic hormones. It may be toxic even at low amount of it and it is carcinogenic and it prevents growth strongly. Estrone has been reported that it may have effects of reproduction system like suppression of spermatogenesis and impotence, inhibition of egg implantation. Estrone is normally mixed through sewage effluent from the human body. It is reported to be powerless than that of 17β -estradiol. It is also found to be more abundant in the sewage effluents and river waters. So, it is required that they should be monitored and improved. Estrogenic hormones in water are generally determined by instrumental analysis such as high performance liquid chromatography (HPLC), high performance liquid chromatography coupled with gas chromatography (HPLC-MS), gas chromatography-mass spectrometry (GC-MS), GC-MS/MS and HPLC-MS/MS (Li et al., 2004).

Estrogenic chemicals, especially the synthetic steroid which is 17 α -ethynylestradiol (EE2) and natural steroid estrone (E1) and 17 β -estradiol (E2), have gained importance because of presence of them in waters samples like surface or wastewater treatment plants, recently. Also, they have remarkable effects on the development and reproductive system of sea life, environment and human (Zhang et al., 2005).

Estrogenic compounds have been found in many sewage treatment plant effluents in some countries and in Asia, Europe. Estrogenic compounds found in domestic sewage effluents. They can occur naturally (E1 and E2) or synthetic (EE2). Their concentrations have been detected at the low levels. Estrogenic steroids, especially 17 α -ethynylestradiol, have physiological activity even at low amount. They may affect reproductive and the growth success of sea and wildlife. Because of that, studies can be essential for sensitive measurement, reliable and appropriate analytical technique to determine the presence, transportation, biologic effects and consequence of steroids (Zhang et al., 2005).

Many immunoassay and chromatographic methods have been used for determination of these chemicals from water. Some of them are gas chromatography (GC), gas chromatography–mass spectrometry (GC–MS), liquid chromatography (LC), and liquid chromatography–mass spectrometry (LC–MS) (Zhang, 2005).

1.1.3 Synthetic Chemicals

Triclosan has an antibacterial and antifungal agent properties. It is used in production of care products such as soaps, dust cloth, dentifrice and plastics. Triclosan is said that it is strongly toxic for aquatic life of alive; especially to algae. Chao and Metcalfe, 2006, have explained that they change thyroid function in amphibians at even low concentrations such as 0.15 $\mu\text{g/L}$. Gas chromatography, gas chromatography–mass spectrometry and high-pressure liquid chromatography can be used to determination of triclosan (Safavi, 2003).

Chlorophenols (CPs) are being used as disinfectants and protector for wood, dyes, vegetative fibers and leather because they are broad-spectrum antimicrobial (Karci et al., 2012). Wastewaters occur with CPs and their derivatives at high

concentrations because of their big amount production and large consumption. Most of them are considerably toxic to microorganisms like bacteria is found in sludge. They should be removed but they have inhibitor effect and they do not allow biodegradation so removal of them is not suitable with biological treatment processes. They can be removed from wastewaters with conventional wastewater treatment methods (Karci et al., 2012). If wastewaters included chlorophenols are being drained through natural water they may give serious toxicological problems such as carcinogenic and mutagenic. Because of these results, in the US Clean Water Act and EU Directive 2455/2001/EC have listed CPs as priority toxic chemicals (Karci et al., 2012).

Carbamazepine is used as human medicine which is used as psychomotor epilepsy, grand mal, trigeminal neuralgia and bipolar depression. Carbamazepine is taken with a daily dosage of 100–2000 mg. Because of the high amount of consumption and its chronic management, it is produced large quantity around the world (Jones et al., 2002). It is guessed that this substances have been produced 43 000 kg in 2000, and 35000 kg in 2003 in the United States (Thacker, 2005). Nearly half of carbamazepine and its metabolites let off urine towards municipal wastewater treatment plants as and influent (Lienert et al., 2007). Its degradation is difficult in WWTPs, so it does not answer treatment processes and leaches environmental water systems like surface, drinking and irrigation water (Ternes, 1998). So, this compound can be said that one of the mostly detected pharmaceutical in wastewater treatment effluents and in environmental water samples. It has been determined in wastewater effluents (Ternes, 1998), groundwater (Ternes et al., 2007), surface waters (Zhang et al., 2007a) and even in drinking water (Zhang, 2010).

Clofibric acid is one of the clofibrate metabolite. It is a drug used as a lipid regulator. It is known that it stays in environment for extended period of time (Buser and Müller, 1998). It has polar property, so clofibric acid isn't adsorbed in soil so much and it can easily leach in surface and groundwater. Biological effects of clofibric acid are not known clearly, but it can be said that it has endocrine disrupting effect, it doesn't allow to synthesis of cholesterol (Pfluger and Dietrich, 2001). Clofibric acid in German WWTP has been determined by Ternes that

measured up to 1.6 µg/L in effluent (Ternes et al., 1998). Clofibric acid is also determined in drinking water samples in Berlin 270 ng/L of concentration (Heberer and Stan, 1997; Heberer 2002; Rosal et al., 2009).

1.2 Way of Exposing of EDCs to the Aquatic Environment

Importance of water quality is increased day by day; so we are faced to industry around the world from various sources against the continuous and safety drinking water to the challenge. In addition to this, urbanization, population increment, associated changes and technological development in cultivation and soil implementation have contributed markedly to reduce the quality of water through naturally occurring and anthropogenic pollution. Metals, carcinogens, synthetic substances and vet, medical and illegal drugs are occurred surface water pollutants. Also, production of personal cleaning, food supplements converted products are the others (Falconer et al., 2006; Brasher and Wolff, 2004; Cortazar et al., 2005). Some of these substances and their metabolites are classified as endocrine disruptors and enter water directly drain of households, substances, pharmaceuticals, industrial wastes and agricultural wastes (Huang et al., 2008). Agrochemicals that are used to improve crop can be contaminated drinking water sources (Falconer et al., 2006). Endocrine disrupting compounds can be concentrated in the environment by the way of biogeochemical and these chemicals can be removed by using adsorptive materials (Segner, 2005; Luks-Betlej et al., 2001; Suliman et al., 2006). Aquatic life is polluted by many compounds which are active hormonally such as industrial compounds, drugs, organo-chlorides, estrogens and pesticides (Yuan et al., 2002; Alatrisme-Mondragon et al., 2003; Xue and Xu, 2006; Li et al., 2006). Many aquatic ecosystems hang by a thread danger ranges and permanent complex of EDCs because of the pollution of industrial compounds (Schmidt et al., 2005). The environment, especially aquatic life, chemicals are released into rivers, lakes and the sea and chemicals are released through runoff, wastewater (Sanchez-Avila et al., 2009; Luks-Betlej et al., 2001; Sumpter, 2005).

1.3 Detection of EDCs

There are some analytical methods for detection of endocrine disrupting compounds. For analyzing pesticides, industrial compounds, metals and polychlorine biphenyls in environmental and food samples, chemical and biological analytical methods have been designated by some countries like the US and EU. There are some methods for analysis of these compounds (endocrines, medicine and cosmetics), but some analytical techniques and analysis methods are not enough.

Certain phthalates and their metabolites and degradation products can cause negative health effects on human body including kidney, liver and testicles. Potential endocrine disrupting properties have also been reported so that phthalates have become a major public health problem. There are various analytical methods for determination of them in water (Zhang, 2011). For assessing the occurrence, distribution and characterization of phthalates and phenols, there are various some methods and they are summarized in Table 1.1.

Table 1.1: Methods for determination of endocrine disrupting chemicals (phenols and phthalate esters) (Olujimi et al., 2010)

Country	Environmental matrix	Method	Concentration/ Detection range	Compound	Reference
China	Water	GC-FID	0.05-3.91 $\mu\text{g}\cdot\text{t}^{-1}$	phthalate esters	Li et al., 2006
Taiwan	Water	GC-MS/ GC-ECD	50 -100 $\mu\text{g}\cdot\text{t}^{-1}$	phthalate esters	Yuan et al., 2002
China	Water	HPLC-UV	3.1-5.8 $\mu\text{g}\cdot\text{t}^{-1}$	phthalate esters	Cai et al., 2003
South Africa	Water	GC-FID	0.03-2309 $\mu\text{g}\cdot\text{t}^{-1}$	phthalate esters	Fatoki and Noma, 2002
Poland and Germany	Water	GC-MS	0.015-0.06 $\mu\text{g}\cdot\text{m}\cdot\text{t}^{-1}$	phthalate esters	Luks-Betlej et al., 2001
Spain	Water	SPME/HPLC	9-22 $\mu\text{g}\cdot\text{t}^{-1}$	phthalate esters	Kayali et al., 2006
China	Water	HPLC-UV	1.0-3.8 $\mu\text{g}\cdot\text{t}^{-1}$	phthalate esters	Ling et al., 2007
Spain	Water	DSPME/ HS-SPME/GC-MS	< LOD to 6172 $\text{pg}\cdot\text{m}\cdot\text{t}^{-1}$	phthalate esters	Polo et al., 2005
China	Water Sediment Particulate matter	GC-FID	3.99×10^{-3} - 45.45×10^{-3} $\text{mg}\cdot\text{kg}^{-1}$	phthalate esters	Sha et al., 2007
		GC-FID	40.56 -94.22 $\text{mg}\cdot\text{kg}^{-1}$	phthalate esters	Sha et al., 2007
		GC-FID	30.52 -63.96 $\text{mg}\cdot\text{kg}^{-1}$	phthalate esters	Sha et al., 2007
South Africa	Soil	GC-FID	3.8-48.89 $\text{ng}\cdot\text{kg}^{-1}$	phthalate esters	Adeniyi et al., 2008
Italy	Breast milk	LC/LC – MS/MS	8.4-18.8 $\mu\text{g}\cdot\text{t}^{-1}$	phthalate esters	Latini et al., 2009
Taiwan		GC-MS	0.05-46.5 $\text{mg}\cdot\text{kg}^{-1}$	phthalate esters	Huang et al., 2008
			1.4-253 $\text{mg}\cdot\text{kg}^{-1}$	phthalate esters	Huang et al., 2008
Oman	Water	RP-HPLC	0.1-0.9 $\mu\text{g}\cdot\text{t}^{-1}$	Phenols	Suliman et al., 2006;
	Water	GC-MS	5-22 $\text{ng}\cdot\text{t}^{-1}$	Phenol	Bagheri et al., 2007
Spain	Water	HPLC	3-76 $\mu\text{g}\cdot\text{t}^{-1}$	Phenol	Cledra-castro et al., 2006
	Sediment	GC-MS			
Italy	Leachate	SPME/GC-MS	0.005-2.4 $\mu\text{g}\cdot\text{t}^{-1}$	Phenol	Ribeiro et al., 2002
China	Sediment	GC-MS	0.6-664.5 $\text{ng}\cdot\text{g}^{-1}$	Phenol	Peng et al., 2006
China	Wastewater	GC-FID	0.47-9.01 $\mu\text{g}\cdot\text{t}^{-1}$	Phenol	Zhou et al., 2005
China	Water	GC-NCI-MS	17-685 $\text{ng}\cdot\text{t}^{-1}$	Phenol	Zhao et al., 2009
Japan	Soil	GC-MS	1.0 $\text{ng}\cdot\text{g}^{-1}$	Phenol	Helaleh et al., 2001
China	Water	SPE/GC-FID	0.02-0.701 $\mu\text{g}\cdot\text{t}^{-1}$	Phenol	Wang et al., 2006
Germany	Urine	HPLC/MS/MS	0.1-13.6 $\text{ng}\cdot\text{kg}^{-1}\cdot\text{b.w}$	Phthalate esters	Seckin et al., 2009
Sweden	Breast milk	GC-MS	0.06-305 $\text{ng}\cdot\text{m}\cdot\text{t}^{-1}$	Phthalate esters	Hogberg et al., 2008
	Blood	GC-MS	0.06-305 $\text{ng}\cdot\text{m}\cdot\text{t}^{-1}$	Phthalate esters	Hogberg et al., 2008
	Urine	GC-MS	0.06-305 $\text{ng}\cdot\text{m}\cdot\text{t}^{-1}$	Phthalate esters	Hogberg et al., 2008
China	Soil	GC-MS	ND-293 $\mu\text{g}\cdot\text{g}^{-1}$	Phthalate esters	Zeng et al., 2009
South Africa	Water	GC-MS	ND-119 $\mu\text{g}\cdot\text{t}^{-1}$	Phthalate esters/p-NP	Mahomed et al., 2008

Key: GC-FID = Gas Chromatography Flame Ionization Detector; GC-MS = Gas Chromatography Mass Spectrometer;
GC-ECD = Gas Chromatography Electron Capture Detector; HPLC = High Performance Liquid Chromatography

Phenols and phthalates have been determined in environmental samples using many analytical techniques, for example, HPLC coupled with detectors such as fluorescence, ultraviolet, mass spectrometer (MS) and also gas chromatography (GC) coupled with mass spectrometer (MS) (Liu et al., 2004; Huang et al., 2008; Zeng et al., 2009). Especially, for determination of phthalates and phenolic compounds, GC-MS is widely used (Rompa et al., 2003). Some EDCs that include hydroxyl groups are usually analyzed by using gas chromatography (Liu et al., 2004). Hydroxyl groups have oxygen atom, they have poor nucleophilicity based on its low electron density is well known. Gas Chromatography with electron capture detector or mass spectrometer can analyze derivatized compounds which have hydroxyl groups need high temperatures and longer reaction periods (Zhao et al., 2009).

1.4 Pre-concentration of Endocrine Disrupting Compounds in Samples

For detection of endocrine disrupting compounds in water samples, Gas chromatography (GC) and high-performance liquid chromatography (HPLC) have been used. At the same time, if the concentrations of EDCs are too low, some techniques to enrich their concentrations can be used. The pre-concentration techniques, which are used for monitoring EDCs in liquid samples are depending on liquid liquid extraction (LLE) and for their determination, chromatographic techniques such as column, gas or high performance liquid chromatography coupled with sensitive detectors are used (Zhou et al., 2005). Liquid liquid extraction method has many advantages such as well-advanced, effective and accuracy; at the same time it has some disadvantages like time and consumption of organic solvents which is used at large amounts (Ling et al., 2007; Zhou et al., 2005). EDCs can find in various environmental media at different concentration and they are risky for ecology (Cai et al., 2003; Santana et al., 2009). However, usage of organic solvents largely that they are usually toxic and they are quickly light, emulsions occur. In addition, solvents may be lost at cleanup step (Piug and Barcelo, 1996). Because of the some disadvantages, instead of LLE, some extraction methods for liquid samples like solid phase extraction (SPE), microwave accelerated extraction (MAE) and solid phase micro-extraction (SPME) can be used (Polo et al., 2005; Santana et al., 2005).

SPE provides pre-concentration of EDCs which are found seldom for determination in peripheral, medicine and biologic samples. It has advantages like higher concentration factors, a faster and easier manipulation, and uses low volume of dissolvent (Zhou et al., 2005). SPE cartridges have been used for more than 20 years. For reducing of solvent usage, particularly methylene chloride which is known to be carcinogen effect, SPE method has became important, instead of LLE (Eberlin and Cesar de Silva, 2008).

To obtain repeatable and high recovery of analytes for environmental samples, SPE cartridges are chosen importantly because specific sorbent materials are very effective for recovery of analytes at low concentration. Most sorbents which include particles bounded with C-18 or strene-divinyl benzene are used for

SPE. Enrichment of chemicals for SPE is highly dependent on the polarity of the eluent (Patrolecco et al., 2004).

Solid phase micro-extraction (SPME) has been important for the detection of phthalates in some natural samples like water, wine, and vegetable oil in late 1990s. Recently, phthalates in milk and human milk samples have been pre-concentrated by using this method. Solid-phase micro-extraction (SPME) is introduced by Arthur and Pawliszyn (Arthur and Pawliszyn, 1990) that has received increasing attention and is now widely accepted as a reliable technique. SPME has been used for detection of various organic substances from environmental matrices (Peñalver et al., 1999). SPME has important advantages over the traditional extraction methods, because dissolvent is not used, it is quick, mobile and simple to use (Farahani et al., 2007). This method has low detection limit like sub-ppb levels so it can be said that SPME method is efficient for determination of phthalates in foods. However, for extraction of phthalates, optimum SPME method and optimum conditions of extraction (such as usage of salt) should be determined found according to investigations. Also most SPME methods for pre-concentration of phthalates in water which were investigated have been shown that direct immersion have used rather than headspace method. For simple matrix like water, direct immersion applications are found basic with SPME methods. On the other hand, headspace method for water samples are found wide applications because of the easy adaptation for other complex matrix. Phthalates may be analyzed with different SPME fibers at several extraction conditions, because each phthalates show different volatilization and polarization and optimum SPME fibers can find for each phthalates sensitively.

Cao et al. (2008) investigated SPME fibers which are used widely for eight phthalates. They tried several extraction conditions and they determined headspace SPME methods with optimum conditions and they have used for determination of the phthalates in bottled water samples (Cao et al., 2008).

1.5 Removal of EDCs

Removal methods of EDCs from water, such as electrochemical methods (Wintgens et al., 2002; Nakata et al., 2001) and a method using a biological membrane (Boscoletto et al., 1994; Araki et al., 2002) have been reported. The removal performance for EDCs by activated carbon has also been reported (Nakanishi et al., 2002). Asada et al. (2004) have also reported the relationship between the carbonization temperature of woody carbon, such as sugi charcoal, bamboo charcoal and the removal performance (Asada et al., 2004).

Some EDCs can be removed in coagulation while surface water are turning into drinking water. For organic micro-pollutants and its removal mechanism, coagulation and including flocculation is found as removing method, coagulation by iron chloride demonstrated useless at degrading phthalate (Thebault et al., 1981; Zhang et al., 2007b).

There are some literatures to remove phthalates from an aquatic life. One of them is microbial degradation which is usually an applied method. For removing phthalates, biodegradation under aerobic and anaerobic conditions have been applied (Chang et al., 2004; Chao et al., 2006; Martinen et al., 2003).

Adsorption is the other method for removing phthalates from wastewater. For adsorption, a whole commercial adsorptive materials (carbon molecular sieves, active carbon, active coke, ion exchange resins, carbon fabrics, magnesium hydroxide and others) are evaluated for removal of phthalates (Ayranci and Bayram, 2005; Fang and Huang, 2010; Mohan et al., 2007).

On the other hands, traditional wastewater treatment methods (coagulation, filtration etc.) are not so effective methods. Alternatively, advanced oxidation processes (AOPs) have been used for removal of phthalates. This method was found effective for their removal. The UV oxidation or ozone oxidation process frequently include the generation and usage of hydroxyl radicals ($\bullet\text{OH}$) which are best oxidants. Hydroxyl radicals can oxidize all the reduced materials in treated effluents and they can do all classes or groups of substances. The UV/ H_2O_2 oxidation process forms hydroxyl radicals that can oxidize organic contaminations quickly and without selection. In addition, the UV/ H_2O_2 oxidation can degrade

the endocrine disrupting chemicals effectively (Park et al., 2010). Photochemical degradation of diethyl phthalate or via UV/ H_2O_2 (Xu et al., 2007; Chen, 2010); oxidative degradation of diethyl phthalate by a photo chemically enhanced Fenton reaction (Yang et al., 2005) are described by researches. For dimethyl phthalate photochemical degradation, oxidation in an Fe(VI)TiO_2 -UV reaction system, degradation by UV/Si- $\text{FeOOH/H}_2\text{O}_2$, photo-catalytic ozonation with TiO_2 are defined by literatures (Yuan et al., 2008; Zhao et al., 2004; Jing et al., 2011; Yuan et al., 2011).

Removal of phthalates by hybrid processes has been the subject of many researchers. For this, different separation techniques are combined to make hybrid systems investigate their removal efficiencies. Cases et al. (2011) investigated the removal of endocrine disrupting compounds (EDCs) in a conventional activated sludge plant connected with a tertiary treatment (CAS-TT). They used two membrane bioreactor. One of them is pilot plant installed with flat sheet (MBR-FS) and other is hollow fiber (MBR-HF) modules.

Removal and degradation of phthalates can be done by abiotic processes such as hydrolysis and photo decomposition but they are known as to be slow and insignificant processes. Breakdown by microorganisms is used for environmental degradation. Degradation of several phthalates by microbes under aerobic conditions in soil, natural water and wastewater has been investigated and it has been successful. Some studies shows the biodegradation of phthalates, but there are some literatures in sufficient on degradation of phthalates. Wastes coming from industry mostly involve phthalate esters and therefore it is significant to research on the biodegradation of their mixtures rather than individual phthalates. Some investigators took as a goal to show biodegradation of individual phthalates but at the same time biodegradation of their mixture in aquatic media using isolated bacterial strain (Prasad and Suresh, 2012).

There are some environmental regulations not to permit phthalate uptake by human being. Because of that, researches and interests have been important to control the phthalates in the environment. But, there is no sufficient scientific research on the treatability of the phthalates (Kabdaslı et al., 2009). For removal of phthalates, biological treatments or photo catalytic techniques may be used. But

biological processes are not enough for their degradation. For the treatability of phthalates dissolved in the water, adsorption and chemical oxidation can be used. Therefore, instead of destruction, some methods can be effective. Among these methods, adsorption process has advantages according to the others. One of advantages is that it does not give sludge and it is clean method. Removal of phthalates from the dilute solutions by adsorption is performed completely (Mohan et al., 2007).

In recent years, membrane processes for removal of endocrine disrupting chemicals has gained increased importance. The reasons can be categorized in three steps; firstly, due to EDCs' physicochemical properties, rejection by membrane is effective. Secondly, influence of membrane module on the rejection of EDCs by membranes is high. Thirdly, the membrane fouling or including of removal water the organic solvent. Studies have shown that EDCs' physicochemical properties affect the rejection of EDCs by membranes. Their molecular weight, K_{ow} , solubility in water, electrostatic property can be assumed as their physicochemical properties. Some estrogenic compounds (Estrone, estradiol and Ethyl estradiol etc.) were effectively remove using the membrane processes (Liu et al., 2009).

1.6 Aim of the Thesis

The aim of this thesis is the determination of some EDCs (clofibrate, triclosan, 2,3,4-trichloro phenol, 17- β -estradiol, 17- α -ethinylestradiol, clofibric acid, 2,4-dichloro phenol, clofibrate methyl ester, estrone, phthalates (DEP and DMP) and carbamazepine) in water by using some advanced analytical techniques such as GC/MS coupled with solid phase extraction (SPE), solid phase micro-extraction (SPME) and spectrophotometric methods. Also, removal of some EDCs (triclosan, 2,3,4-trichloro phenol, 17- α -ethinylestradiol, clofibric acid, 2,4-dichloro phenol, clofibrate, estrone, 17- β -estradiol, clofibrate methyl ester, carbamazepine) from water using highly cross-linked polymeric adsorbents (Dowex L493, Diaion SP207 and Diaion SP825) was investigated. For removal of phthalates (DEP and DMP) batch adsorption tests, isotherm tests and kinetic tests (using highly cross-linked polymeric adsorbents (PAD400, Diaion SP207, Diaion

SP825 and Dowex L493) and adsorption-membrane filtration hybrid tests using Dowex L493 are performed.



2. EXPERIMENTAL

2.1 Materials

For batch, kinetic, isotherm and hybrid studies, diethyl phthalate (DEP) and dimethyl phthalate (DMP) (Merck, < %99 purity) were used for preparation of model solutions in ultrapure water. 2,3,4 trichloro phenol (Supelco (Germany)), clofibric methyl ester (Dr.Ehrenstorfer (Germany)), 2,4 dichloro phenol (Supelco (Germany)), clofibrate (Dr.Ehrenstorfer (Germany)), clofibric acid (Sigma Aldrich (Germany)), triclosan (Dr.Ehrenstorfer (Germany)), Carbamazepine (Sigma Aldrich (Germany)), estrone (Dr.Ehrenstorfer (Germany)), 17- β -Estradiol (Dr.Ehrenstorfer (Germany)), 17- α -ethynl estradiol (Dr. Ehrenstorfer (Germany)) were prepared for standard solutions to perform batch tests and determination by GC/MS coupled with SPME. The working standard solutions of clofibrate, clofibric acid, 2,4-dichloro phenol, clofibric methyl ester, 2,3,4-trichloro phenol, triclosan and carbamazepine were prepared by diluting stocks in methanol (purity of > % 99.8, Sigma Aldrich). Also, the working standard solutions of estrone, 17- β -estradiol and 17- α -ethynlestradiol were prepared by diluting stocks in acetonitrile (>%99, MERCK). NaCl (MERCK), fiber (Polyacrylate, Supelco) and vials were used for solid phase micro extraction method (SPME).

SampliQ C18 (500 mg, 3 mL, Agilent Technologies) SPE Cartridges, Hexane (Lab-scan, %95), Methanol (Lab-scan, %99.9), Dichloromethane (Lab-scan, %99) and Acetone (Merck, >99.9%) were used for solid phase extraction.

The polymeric adsorbents, Diaion SP825, Diaion SP207, Dowex L493 and PAD400 were used for batch, kinetic, isotherm and hybrid studies. Properties of adsorbents are given in Table 2.1.

Table 2.1: Properties of polymer adsorbents

Properties \ Adsorbents	Diaion SP825	Diaion SP207	Dowex L493	Purosorb PAD400
Surface area (m²/g)	900	650	>1100	720
Particle size (μm)	250-840	250-840	297-840	350-1200
Chemical structure	Polystyrene-DVB	Brominated Polystyrene-DVB	Polystyrene-DVB	Polystyrene-DVB
Pore radius (Å)	50-60	105	46	400

2.2 Analyses

2.2.1 Spectrophotometric analysis of phthalates

The concentrations of DEP and DMP were detected by a spectrophotometer (Shimadzu UV-1800 Model) at 229.0 and 243.0 nm, respectively. DEP and DMP (Merck, < %99 purity) were used for preparation of model solutions in ultrapure water (50 mg/L). A 0.892 mL DEP for 1 L stock solution (1000 mg/L) was used and dissolved in 30 mL ethanol (%99 purity). To prepare 1000 mg/L of DMP stock solution, 0.845 mL DMP solution was dissolved in 20 mL of ethanol. Standard DEP and DMP solutions (0.5, 1.0, 2.5, 5.0, 10.0, 25.0 and 50.0 mg/L) were prepared using these stock solutions. The concentrations of the standard solutions and their absorbance values were given in Table 2.2. The calibration curve of DEP analysis was shown in Figure 2.1.

Table 2.2: Absorbance values for standard DEP solutions at 229 nm.

DEP Concentration (mg/L)	Absorbance
0	0
0.5	0.016
1	0.033
2.5	0.091
5	0.193
10	0.375
25	0.941
50	1.879

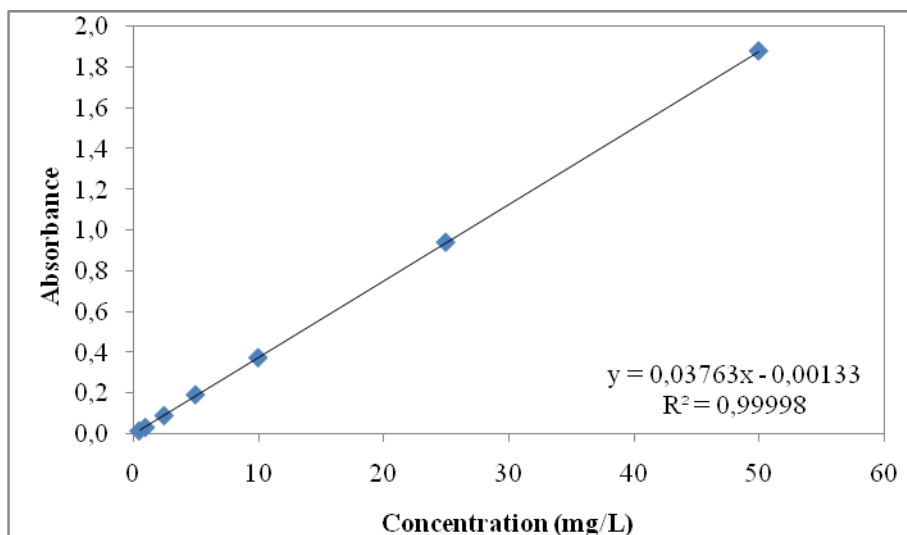


Figure 2.1: Calibration curve obtained at 229 nm for DEP analysis

The concentrations of the standard DMP solutions and their absorbance values were given in Table 2.3. The calibration curve of DMP analysis was shown in Figure 2.2.

Table 2.3: Absorbance values for standard DMP solutions at 243 nm

DMP Concentration (mg/L)	Absorbance
0	0
0.5	0.013
1	0.027
2.5	0.072
5	0.137
10	0.264
25	0.669
50	1.323

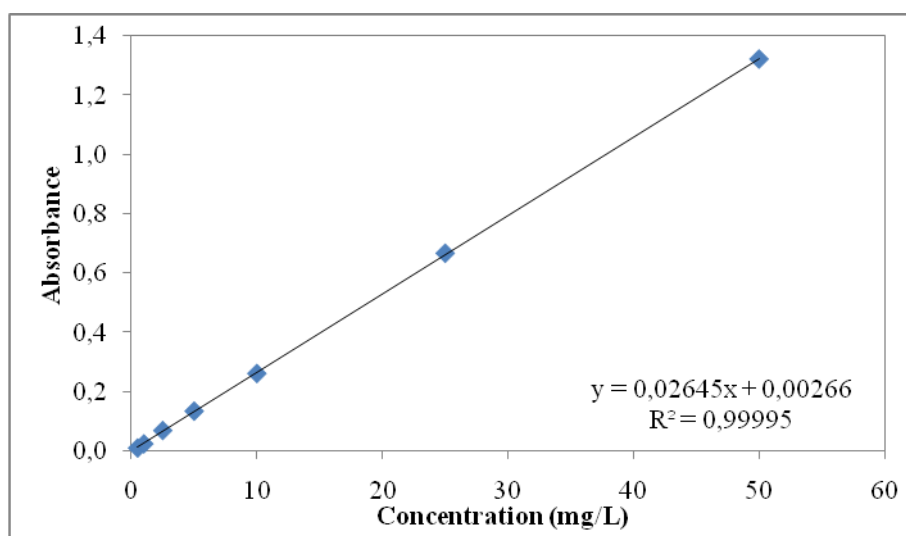


Figure 2.2: Calibration curve obtained at 243 nm for DMP analysis

2.2.2 Analysis of EDCs by using gas chromatography/mass spectrometer (GC-MS)

The analyses of EDCs (triclosan and its metabolites such as 2,4-dichloro phenol and 2,3,4-trichloro phenol), some pharmaceuticals (clofibric acid, clofibrate, clofibrate methyl ester, carbamazepine) and estrogens (estrone, 17- β -estradiol and 17- α -ethinylestradiol) were pre-concentrated by solid phase micro-extraction (SPME) and they were detected using Gas Chromatography-Mass Spectrometry (Shimadzu 17 A Model GC and Shimadzu QP5050A model MS detector). These analyses were carried out at Crete Technical University in Chania, Greece in the framework of TUBITAK-GSRT project.

Capillary column (Sigma-Aldrich Supelco SLBTM 5 MS fused silica) (30 m $\times$ 0.25 mm $\times$ 0.25 μ m of film thickness) was used as analytical column. Splitless mode was used for injections and helium which was carrier gas of flow rate was at 1.0 mL/min.

2.2.2.1 Solid-phase micro extraction (SPME) method

The holder for SPME and fiber settings that were used for the SPME method were taken from Supelco. 10 mL water sample was taken into a vial (15 mL, Supelco) closed with screw-cap and PTFE-silicon septa. An enough amount

of standard solution was added in sample solution and also 2.3 g sodium chloride was added into it. The sample vials were put in a water bath, in order to keep temperature constant. The needle of the SPME apparatus was stayed in water-bath for 60 min at 50°C by stirring sample solution using a magnetic stirrer. The fiber was taken into the needle and immediately injection was done into the GC injector. After, injection of fiber through the inlet, samples were analyzed.

2.2.3 Analysis of phthalates by using GC-MS

7890A Model GC (Agilent Technologies)-5975C VL MSD model MS detector was used for DEP and DMP Solid Phase Extraction (SPME) coupled with gas chromatography/mass spectrometer at Chemical Engineering Department of Ege University. HP5MS Fused Silica capillary column, (30 m×0.25 mm×0.25 µm film thickness (Sigma-Aldrich Supelco)) was used as an analytical column. Splitless mode was used for analyzing. The carrier gas (helium) flow rate was determined as 1.2 mL/min. The oven temperature was programmed from 60°C to 280°C (5 min) at 20°C/min. While Injector temperature was 250 °C, detector temperature was 280°C.

2.2.3.1 Solid phase extraction (SPE) method

For conditioning of SampliQ C18 (500 mg, 3 mL, Agilent Technologies) SPE cartridges, 10 mL of hexane after that 10 mL of dichloromethane, 10 mL of methanol and 15 mL of water was passed from cartridges. Flow rate was 5 mL min⁻¹. While 50 mL sample was passed through the cartridges, flow rate was 10 mL min⁻¹. To rinse cartridge, 5 mL water was used and for drying, vacuum was applied during 30 min. Elution was made with 10 mL CH₂Cl₂ and hexane mixture (1:1) and after 10 mL CH₂Cl₂:acetone (1:1) mixture. Evaporation of extract was done at 25°C under nitrogen. The extract was reconstituted with 250 µL with acetone.

Recovery by SPE method

In order to calculate percent recovery of SPE method for DEP and DMP pre-concentration, DEP/DMP concentration was measured by GC/MS. Their concentrations were measured by GC/MS directly and also after pre-concentration by using SPE. Following equation was used to calculate percent recovery:

$$\text{Recovery (\%)} = \frac{\text{DEP-DMP concentration (without pre-concentration)}}{\text{DEP-DMP concentration (with SPE)}} \times 100$$

Relative Standard Deviation

The following equations were used to calculate values of relative standard deviation (Sawant and Mohan, 2011):

$$\bar{x} = \frac{x_1 + x_2 + x_3 + x_4 + \dots}{n} \quad \text{standard deviation, } S = \sqrt{\frac{(x_1 - \bar{x})^2 + (x_2 - \bar{x})^2 + (x_3 - \bar{x})^2 + \dots}{n - 1}}$$

$$\text{Relative standard deviation} = (S / \bar{x}) * 100$$

s = sample standard deviation

RSD = relative standard deviation

$\bar{x}$ = mean value of the sample data set

$x_1, \dots, x_N$ = the sample data set

n = size of the sample data set

2.3 Removal of EDCs

2.3.1 Adsorption tests

To determine the optimum adsorbent amount for DMP and DEP removal, polymeric adsorbents, PAD400 (0.355-0.500 mm), SP207 (0.500-0.710 mm), SP825 (0.500-0.710 mm) and DOWEXL493 (0.500-0.710 mm) were used. Various amounts of adsorbents (0.005, 0.01, 0.015, 0.02, 0.03, 0.04, 0.06, 0.08,

0.10, 0.15, 0.20, 0.30, 0.40, 0.60 g) were contacted with 50 mL of model solution (50 mg/L) by shaking in a shaker (Membert) at 25°C for 24 hours.

For other EDCs (triclosan, 2,3,4-trichloro phenol, carbamazepine, estrone, clofibrate methyl ester, 17- β -estradiol and 17- α -ethinylestradiol, 2,4-dichloro phenol, clofibric acid, clofibrate) adsorption tests were carried out by contacting various amounts of polymer adsorbents (0.0005, 0.0025, 0.0050, 0.0100, 0.015, 0.0200, 0.0300, 0.0400, 0.0500, 0.060, 0.0800, 0.1000, 0.1200 g) with 100 mL of EDCs (25 μ g/L) for 2 h of shaking at 25°C.

2.3.2 Isotherm tests

Isotherm studies were performed with 50 ml of model solution. Various concentrations of DEP and DMP solution (100, 200,300, 400, 600 mg/L) were contacted with constant amount of polymer adsorbents by shaking in a shaker (Membert) at 25°C for 24 hours.

Adsorbents amounts which were used for isotherm studies are given in Table 2.4.

Table 2.4: Adsorbent amounts used in isotherm studies

Polymer Adsorbent	Adsorbent Amount (g/50 mL)	
	DEP	DMP
PAD400	0.02	0.04
SP207	0.03	0.06
SP825	0.02	0.04
Dowex L493	0.4	0.3

2.3.3 Kinetic tests

Kinetic tests were performed with 750 mL of model solution using polymeric adsorbents. All of the tests were performed at 25°C for 24 hours by using a water bath with a mechanical stirrer. The stirring rate was adjusted to 250 rpm. Samples of 5 mL were collected at a defined time interval of 0, 5, 10, 15, 20, 30, 40, 60, 90, 120, 180, 240, 300, 360, 420, 480 minutes and 24 hours DEP and DMP concentrations were monitored.

Adsorbent amounts used for kinetic studies are given in Table 2.5.

Table 2.5: Adsorbent amounts used in kinetic studies

Polymer Adsorbent	Adsorbent amount (g/750 mL)	
	DEP	DMP
PAD400	0.6	2.25
SP207	0.6	1.5
SP825	9.0	1.2
Dowex L493	9.0	9.0

2.3.4 Adsorption-membrane filtration hybrid tests

This system combines the delivery of feed and fresh resin suspensions with subsequent removal of the loaded sorbent by filtration with a submerged hollow fiber membrane.

For adsorption-membrane filtration hybrid system experiments, a constant volume of solution (1200 mL) was put into the main tank with adsorbent. Ultrafiltration membrane module ZW-1 was submerged into the main tank. During all the experiments, fresh resin was delivered into the main tank at a constant flow rate. To keep the amount of the resin in the main tank constant, the flow rates of the fresh resin and the saturated resin were adjusted as the same. Because of same reason, flow rate of feed and permeate were adjusted as equal to each other. To prevent accumulation of resin on the surface of the membrane, the

air flow was supplied by the compressor and it was kept constant as 4 L/min for all tests.

Permeate samples were generally taken at time intervals of 0, 5, 10, 15, 20, 25, 30, 40, 60, 80, 100, 120, 140, 160 and 180 minutes. DMP and DEP concentrations of permeate samples were analyzed by a spectrophotometer. Experiments were repeated twice to check the reliability of the system. Schematic diagram of the adsorption-ultrafiltration hybrid system is shown in Figure 2.3.

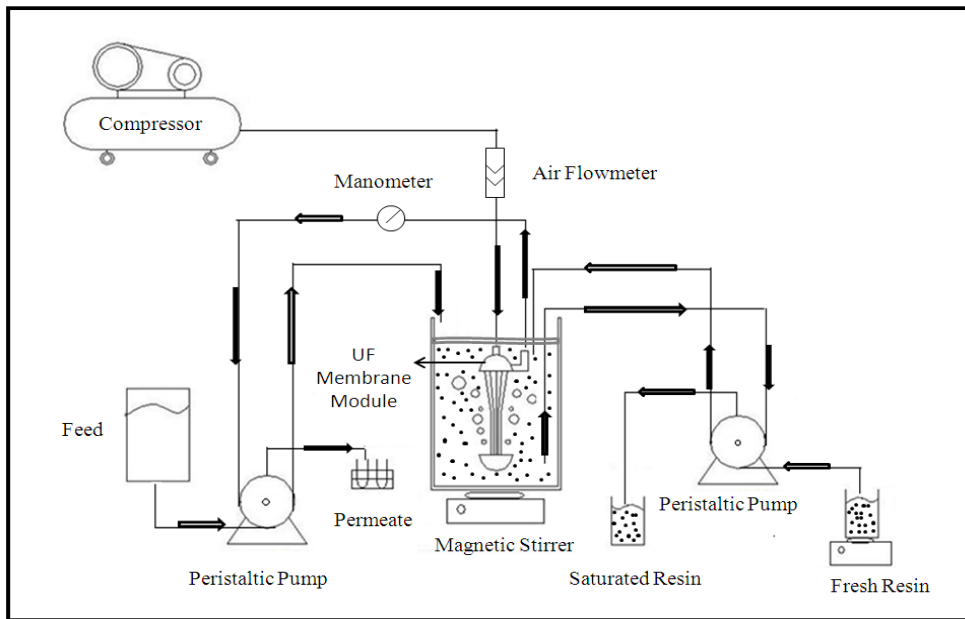


Figure 2.3: Schematic diagram of adsorption-ultrafiltration hybrid system

At this system, parameters such as adsorbent concentration, particle size, rate of replacement of saturated/fresh adsorbents, permeate and feed flow rates were investigated. The investigated parameters were summarized in Table 2.6.

Table 2.6: Investigated parameters in adsorption-membrane filtration hybrid system

DMP and DEP concentration	50 mg/L
Adsorbent amounts (g/L)	2-3-4-6
Particle size of adsorbent (μm)	25-50, 50-100, 100-250
Solution volume (mL)	1200
$Q_{\text{permeate}} = Q_{\text{feed}}$ (mL/min)	3-5
$Q_{\text{sat}} = Q_{\text{fresh}}$ (mL/min)	6-9
Q_{air} (L/min)	4

Operational parameters were given in Tables 2.7 and 2.8 for DMP and DEP removal, respectively.

Table 2.7: Operational parameters for DMP removal in adsorption-membrane filtration hybrid system

Fresh adsorbent concentration (g/L)	Rate of replacement of saturated and fresh sorbent $Q_{\text{sat}} = Q_{\text{fresh}}$ (mL/min)	Flow rate of permeate and feed ($Q_{\text{feed}} = Q_{\text{permeate}}$) (mL/min)	Adsorbent Particle Size Range (μm)
2	6	5	100-250
3	6	5	100-250
4	6	5	100-250
4	6	5	50-100
4	6	5	25-50
4	9	5	50-100
4	6	3	50-100
6	6	5	100-250

Table 2.8: Operational parameters for DEP removal in adsorption-membrane filtration hybrid system

Fresh adsorbent concentration (g/L)	Rate of replacement of saturated and fresh sorbent $Q_{sat}=Q_{fresh}$ (mL/min)	Flowrate of permeate and feed ($Q_{feed}=Q_{permeate}$) (mL/min)	Adsorbent Particle Size Range (μm)
2	6	5	100-250
3	6	5	100-250
4	6	5	100-250
4	6	5	50-100
4	6	5	25-50
4	6	5	100-250
4	9	5	100-250
4	6	3	100-250
6	6	5	100-250

ZeeWeed[®]-1 (ZW-1) Module:

The ultrafiltration module ZeeWeed[®]-1 (ZW-1) supplied by General Electrics, Israel was used in the studies of adsorption-membrane filtration hybrid system. The module has a nominal pore size of 0.04 μm and an effective membrane surface area of 0.047 m². Characteristics of ultrafiltration membrane module ZeeWeed[®]-1 (ZW-1) were given in Table 2.9.

Table 2.9: Characteristics of ultrafiltration membrane module ZeeWeed[®]-1 (ZW-1)

General Type	Supported non-ionic hydrophilic
Effective membrane surface area	0.047 m ²
Nominal pore diameter	0.04 µm
Hold up volume	10 mL
Maximum permeation pressure	0.6 bar
Operating transmembrane pressure	0.07-0.55 bar
Permeate flow range	5-25 mL/min
Maximum scouring air flow	1.8 m ³ /h
Maximum operating (cleaning) temperature	40°C
Operating pH range	5-9
Cleaning pH range	2-10.5

3. RESULTS AND DISCUSSION

3.1 Analysis of Some EDCs by Using GC/MS

Triclosan, carbamazepine, 2,3,4-trichloro phenol, estrone, clofibrate methyl ester, 17- β -estradiol clofibric acid, 17- α -ethinylestradiol, 2,4-dichloro phenol and clofibrate were analysed by GC/MS and their calibration curves are obtained (Figures 3.1-3.10).

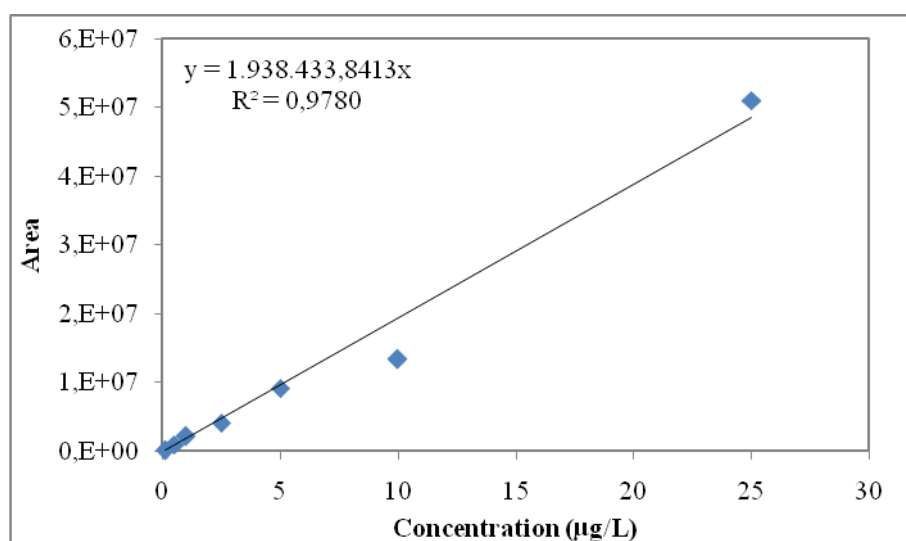


Figure 3.1: Calibration curve for 2,4 dichloro phenol using GC/MS

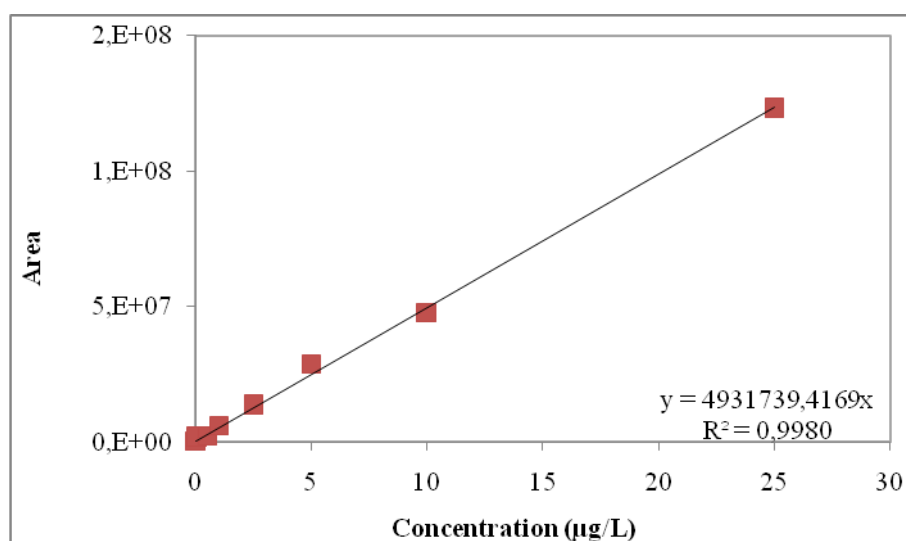


Figure 3.2: Calibration curve for 2,3,4 trichloro phenol using GC/MS

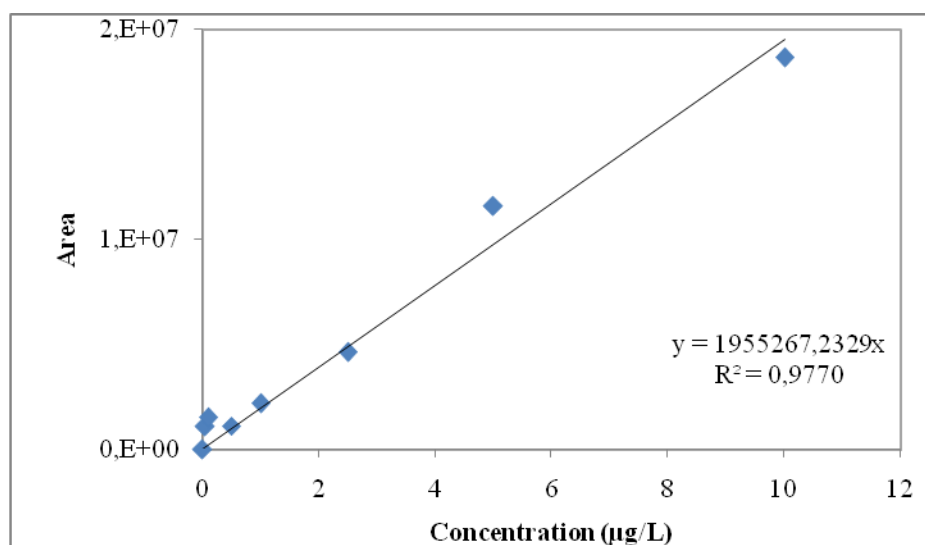


Figure 3.3: Calibration curve for clofibrate methyl ester using GC/MS

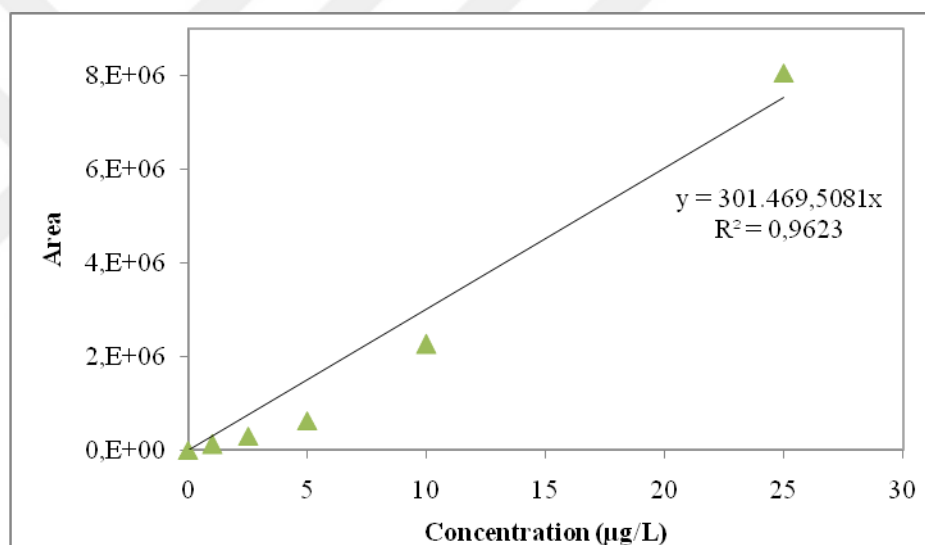


Figure 3.4: Calibration curve for clofibric acid using GC/MS

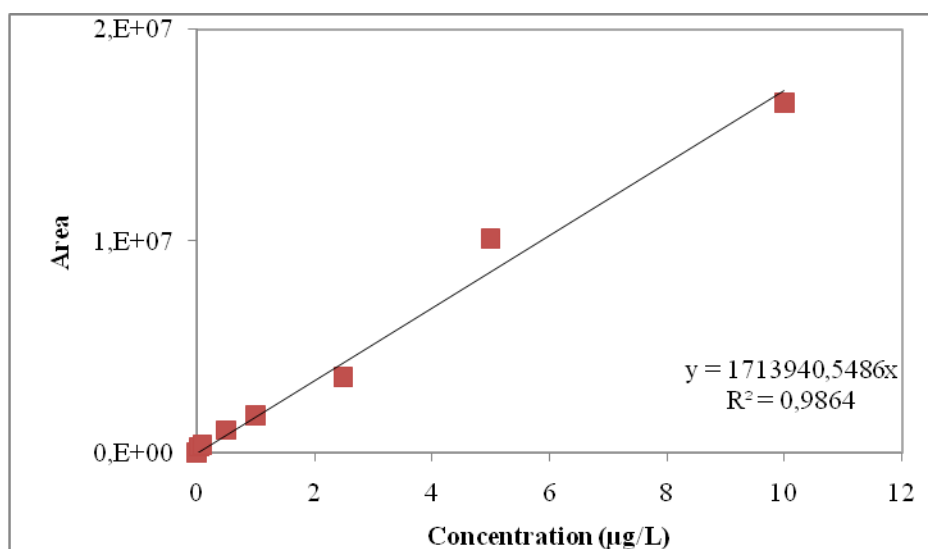


Figure 3.5: Calibration curve for clofibrate using GC/MS

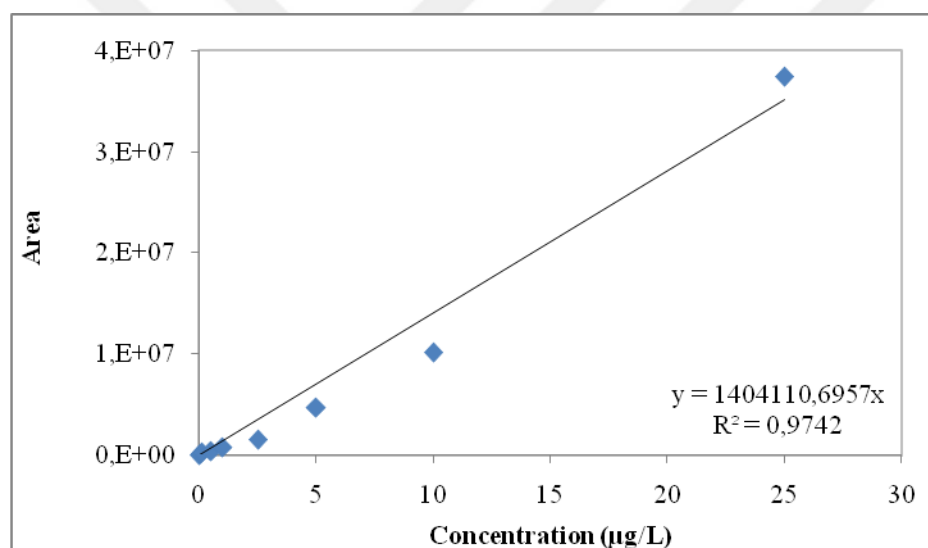


Figure 3.6: Calibration curve for triclosan using GC/MS

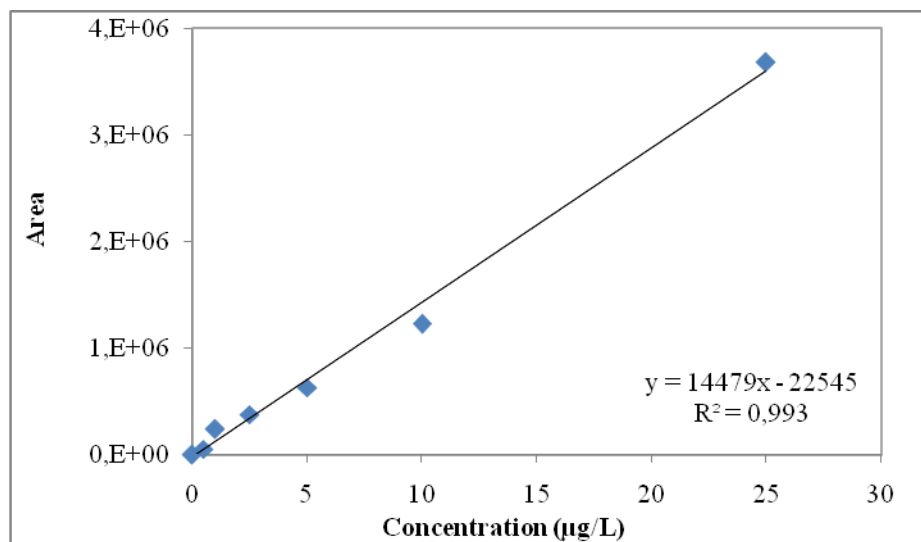


Figure 3.7: Calibration curve for carbamazepine using GC/MS

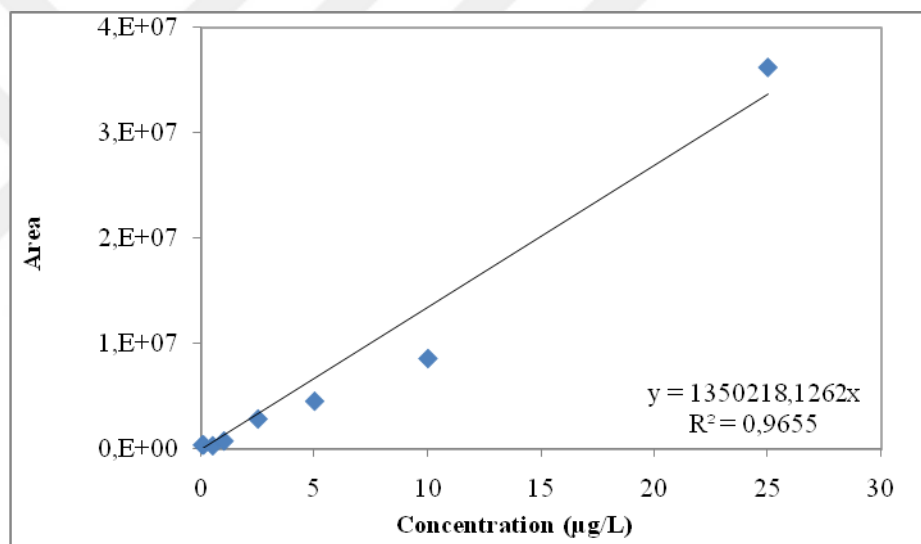


Figure 3.8: Calibration curve for estrone (E1) using GC/MS

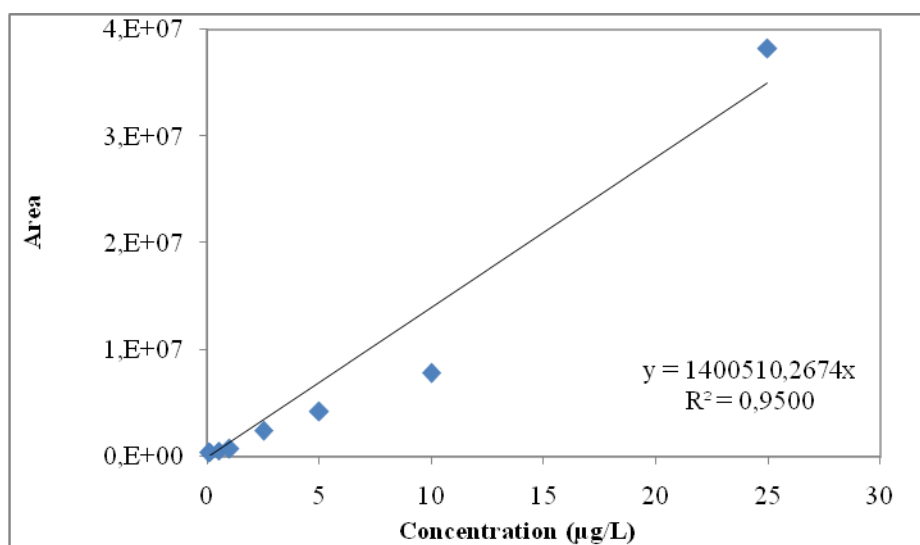


Figure 3.9: Calibration curve for 17β-estradiol (E2) using GC/MS

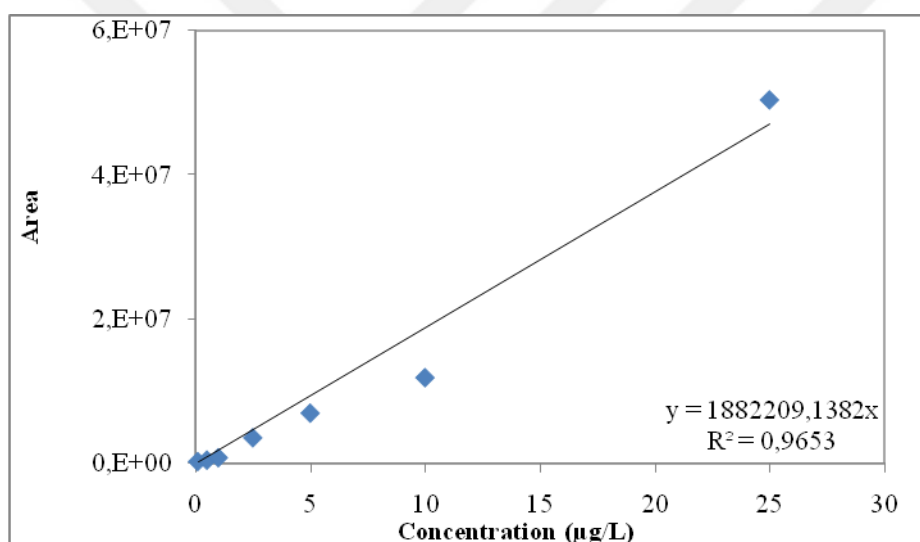


Figure 3.10: Calibration curve for 17-Ethnyl estradiol (EE2) using GC/MS

3.2 Determination of DEP by Using SPE Coupled with GC-MS

Different concentrations of DEP standards (0.5, 1, 2.5, 5, 10, 25 and 50 μg/L) were prepared. Calibration curve was drawn for these concentrations. Table 3.1 shows DEP concentrations and their response values obtained from GC-MS. Calibration curves of DEP standards are given in Figure 3.11. SPE methods used provides the phthalates to be concentrated 200 times, theoretically. According to SPE procedure (is given part 2.2.3.1), sample volume is 50 mL at the beginning, after pre-concentration, volume is 25 μL, because that, volume is enriched 200

times by SPE method theoretically. In figure 3.11, one axis shows the concentrations of DEP as mg/L, it means without pre-concentration, second axis shows the DEP concentrations with pre-concentration by using SPE method.

Table 3.1: DEP concentrations and their response data

DEP concentration (µg/L)	Response (1)	Response (2)	Response (3)	Response (average)
0.5	6569	6978	6985	6844
1	12909	13978	13832	13578
2.5	34505	35102	34033	34547
5	70108	70024	69642	69930
10	146789	147657	147531	147326
25	280090	279890	279017	279665
50	539056	538870	538369	538765

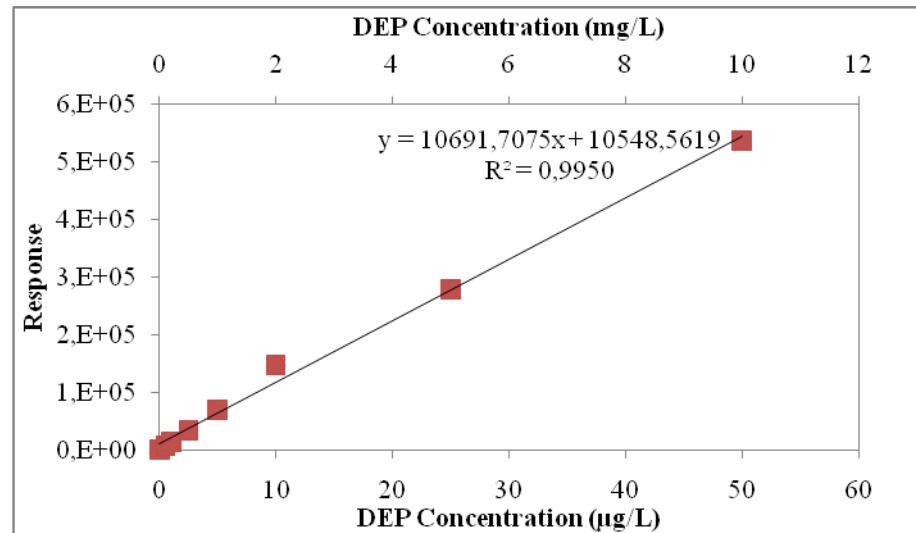


Figure 3.11: Calibration curve for DEP (with SPE)

3.2.1 Determination of DEP by GC-MS (without pre-concentration)

DEP standards (0.1-10 mg/L) were measured by GC-MS and calibration curve was drawn for these concentrations. This calibration curve was drawn to calculate percent recovery by SPE and enrichment factor of DEP extraction. Table 3.2 shows DEP concentrations and their response values. Calibration curves of DEP standards were given in Figure 3.12.

Table 3.2: DEP concentrations and their response data

DEP concentration (mg/L)	Response (1)	Response (2)	Response (3)	Response (average)
0.1	8562	8454	8403	8473
0.2	16796	16587	16565	16649
0.5	40201	40037	40956	40398
1.0	85213	84846	84123	84727
2.0	157655	159341	159987	158994
5.0	312568	312145	312013	312242
10.0	695236	698369	697962	697189

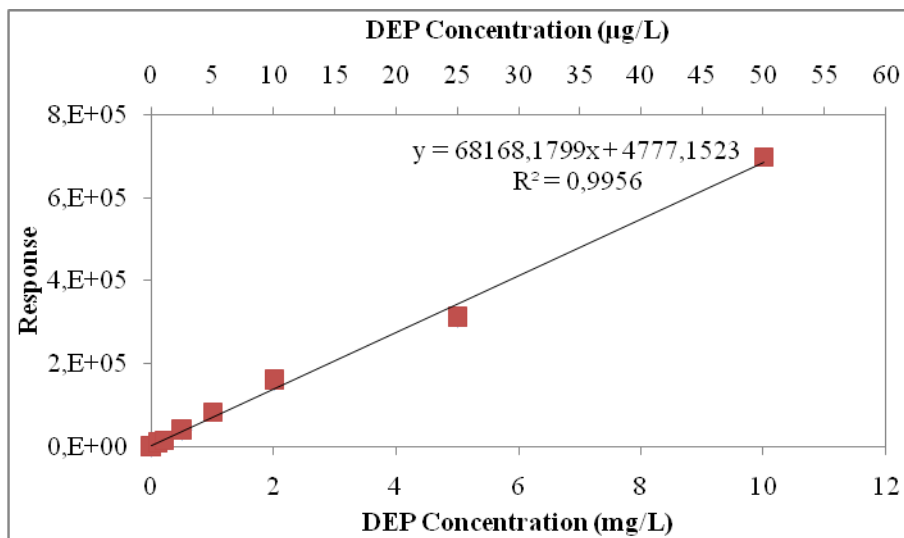


Figure 3.12: Calibration curve for DEP (without SPE)

3.2.2 Calculation of percent recovery for DEP

For percent recovery, 5 µg/L DEP solution was prepared. Its concentration was measured directly by GC/MS and calculated as 4.18 µg/L. After solid phase extraction, concentration was found as 5.03 µg/L. Thus, percent recovery was calculated using equation as follows:

$$\text{percent recovery}(\%) = \frac{4.18}{5.03} \times 100 = \% 83.10$$

Enrichment factor:

It was calculated using equation as follows:

$$\frac{4.18}{5.03} = 0.83 \quad \text{Enrichment factor} = \frac{0.83 \times 1000 (\mu\text{g/L})}{5 (\mu\text{g/L})} = 166$$

SPE methods used provides the phthalates to be concentrated 200 times, theoretically. To calculate enrichment factor, 5 µg/L was used as DEP concentration. Because of the 200 times enrichment of SPE method theoretically, that value was multiplied by 1000. Experimentally, enrichment factor was calculated as 166 for DEP pre-concentration.

3.2.3 Determination of limit of detection (LOD)

In order to determine LOD for DEP by GC-MS, DEP solutions were prepared at different concentrations. These solutions were measured by GC-MS after pre-concentration (SPE method). The increased instrumental response was confirmed and resulted in a decrease of the calculated LODs to 0.4 µg/L for DEP.

3.2.4 Calculation of relative standard deviation (R.S.D.)

For this, 5 different DEP solutions (10 µg/L) were prepared. These solutions were measured by GC/MS after SPE. Table 3.3 shows DEP concentrations and $(X_i - \bar{X}_{ave})^2$ values. The RSD value was calculated using following equation:

$$\text{R. S. D.} = \frac{S}{\bar{X}_{ave}} \times 100 = \frac{0.4750}{10.23} \times 100 = \% 4.64$$

Table 3.3: DEP concentrations and $(X_i - \bar{X}_{ave})^2$ values

DEP concentration ($\mu\text{g/L}$) (X_i)	$(X_i - \bar{X}_{ave})^2$
10.93	0.5457
9.72	0.2262
10.39	0.0392
9.89	0.1527
10.22	0.0009
Average=10.23	S=0.4750

3.3 Determination of DMP by Using SPE Coupled with GC-MS

Different concentrations of DMP standards (0.5-50 $\mu\text{g/L}$) were pre-concentrated using SPE method. Calibration curve was drawn for these concentrations. Table 3.4 shows DMP concentrations and their response values. Calibration curve of DMP standards is given in Figure 3.13. SPE methods used provides the phthalates to be concentrated 200 times, theoretically. According to SPE procedure (is given part 2.2.3.1), sample volume is 50 mL at the beginning, after pre-concentration, volume is 25 μL , because that, volume is enriched 200 times by SPE method theoretically. In figure 3.13, one axis shows the concentrations of DMP as mg/L, it means without pre-concentration, second axis shows the DMP concentrations with pre-concentration by using SPE method.

Table 3.4: DMP concentrations and their response data

DMP concentration (µg/L)	Response (1)	Response (2)	Response (3)	Response (average)
0.5	16756	16546	16987	16763
1	32249	32455	32246	32317
2.5	75157	75601	76568	75775
5	155875	156060	155946	155960
10	294033	297454	297649	296379
25	677817	677376	675010	676734
50	1301382	1296177	1295026	1297528

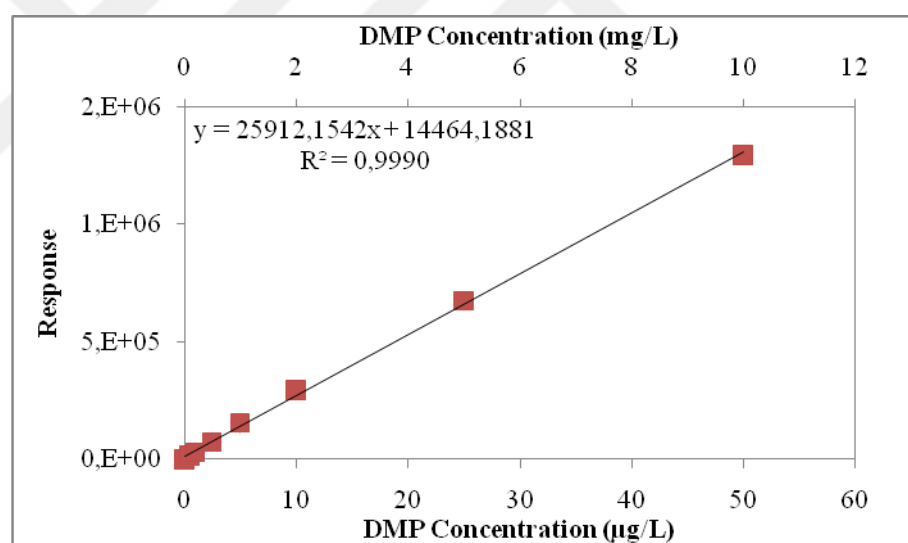


Figure 3.13: Calibration curve for DMP (with SPE)

3.3.1 Determination of DMP concentration by GC-MS (without pre-concentration)

Different concentrations of DMP standards (0.1-10 mg/L) were prepared. Calibration curve was drawn for these concentrations. This calibration curve was drawn to calculate percent recovery of DMP by SPE and enrichment factor of

DMP extraction. Table 3.5 shows DMP concentrations and their response values. Calibration curves of DMP standards were given in Figure 3.14.

Table 3.5: DMP concentrations and their response data

DMP concentration (mg/L)	Response (1)	Response (2)	Response (3)	Response (average)
0.1	18246	18508	18102	18285
0.2	40618	41233	41683	41178
0.5	96955	99392	96286	97544
1.0	170925	168046	171082	170018
2.0	342290	338605	339695	340197
5.0	797682	793620	796910	797071
10.0	1479604	1440725	1487589	1469306

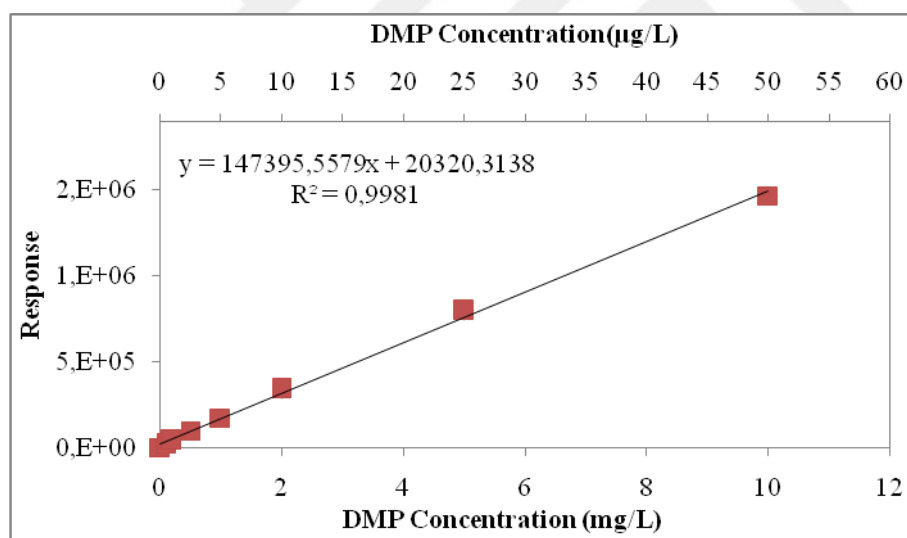


Figure 3.14: Calibration curve for DMP (without SPE)

3.3.2 Calculation of percent recovery for DMP

A 5 µg/L DMP solution was prepared. Its concentration was measured by GC/MS and calculated as 4.36 µg/L without pre-concentration. After solid phase extraction, concentration was found as 5.06 µg/L. For pre-concentration of DMP recovery in the optimized conditions was calculated as follows:

$$\text{percent recovery} = \frac{4.36}{5.06} \times 100 = \% 86.16$$

Enrichment factor:

It was calculated as follows;

$$\frac{4.36}{5.06} = 0.86 \quad \text{Enrichment factor} = \frac{0.86 \times 1000}{5} = 172$$

SPE methods used provides the phthalates to be concentrated 200 times, theoretically. Enrichment factor was found as 172 for DMP pre-concentration, experimentally.

3.3.3 Determination of limit of detection (LOD)

In order to determine LOD, DMP solutions were prepared at different concentrations. These solutions were measured by GC/MS after pre-concentration (SPE method). The increased instrumental response was confirmed and resulted in a decrease of the calculated LODs to 0.07 µg/L for DMP.

3.3.4 Calculation of relative standard deviation for DMP

5 different DMP solutions (10 µg/L) were prepared. These solutions were measured by GC/MS after SPE. Table 3.6 shows DMP concentrations and $(X_i - \bar{X}_{ave})^2$ values. R.S.D. value was calculated using equation.

Table 3.6: DMP concentrations and $(X_i - \bar{X}_{ave})^2$ values

DMP concentration (µg/L) (X_i)	$(x_i - \bar{x}_{ave})^2$
9.63	0.3995
10.78	0.3038
10.27	0.0013
10.24	0.0001
10.26	0.0012
Average=10.24	S=0.4080

$$\text{RSD} = \frac{S}{\bar{X}_{ave}} \times 100 = \frac{0.4080}{10.24} \times 100 = \% 3.98$$

3.3.5 Determination of phthalates (DMP+DEP) mixture by using SPE coupled with GC-MS

DMP and DEP mixture were prepared and SPE procedure was performed for these mixture to see if they could be determined while they are in the same mixture. DMP and DEP were determined in a mixture by GC-MS at different DEP and DMP concentrations. Concentration values and measured data are given in Table 3.7.

Table 3.7: DMP and DEP concentrations measured by GC-MS

DMP + DEP concentrations (µg/L)	Measured concentration (DMP) (µg/L)	Measured concentration (DEP) (µg/L)
50 + 0.5	48.21	0.65
0.5 + 50	0.56	50.79
5 + 5	5.07	4.87
0.5 + 0.5	0.54	0.48

3.3.6 Determination of DEP and DMP in real samples by using SPE coupled with GC-MS

For this, desalinated seawater samples using NF-270, NF-90, SW-30 and BW-30 membranes were obtained from Urla desalination laboratory. Their DEP and DMP concentrations were determined by GC-MS after SPE method. In addition, DMP and DEP concentrations of treated wastewater samples (MBR+NF and MBR+RO) were measured. Table 3.8 shows the results obtained.

Table 3.8: DMP/DEP concentrations measured by GC-MS following SPE in real samples

Samples	DMP concentration (µg/L)	DEP concentration (µg/L)
Seawater (Natural)	4.48	1.07
Desalinated Seawater -NF270	4.23	0.76
Desalinated Seawater-SW30	4.16	1.75
Desalinated Seawater-NF90	4.29	0.88
Desalinated Seawater-NF270+SW30	3.04	0.96
Desalinated Seawater-NF90+SW30	3.27	0.47
Desalinated Seawater-NF270+BW30	3.49	0.70
Desalinated Seawater-NF90+BW30	2.47	0.97
MBR treated wastewater	6.80	5.64
MBR treated wastewater -BW30	<0.07	<0.4
MBR treated wastewater -NF90	6.19	1.17
MBR treated wastewater –BW30	2.65	0.76
MBR treated wastewater –BW30	2.75	1.03
MBR treated wastewater –NF90	4.73	1.18
MBR treated wastewater –NF90	5.24	2.58
MBR treated wastewater -NF90+BW30	2.26	<0.4

3

As seen in Figure 3.8, while DEP and DMP concentrations were higher in seawater, their concentration were lower after desalination using NF270, SW30 and NF90 membranes. Combined systems (NF270+SW30, NF90+SW30, NF270+BW30, NF90+BW30) were able to decrease DEP and DMP concentrations, as seen in Figure 3.8. DEP and DMP concentrations were decreased after treatment of wastewater using NF90, BW30 and NF90+BW30 membranes.

3.4 Removal of EDCs by Polymeric Adsorbents

To determine optimum adsorbent amount for removing of EDCs (triclosan, 2,3,4-trichloro phenol, carbamazepine, estrone, clofibrate methyl ester, 17- β -estradiol and 17- α -ethinylestradiol, 2,4-dichloro phenol, clofibric acid, clofibrate) batch-mode tests were performed. As an adsorbents, high cross linked polymer adsorbents including Diaion SP207 (250-500 μm), Dowex L493 (250-500 μm) and Diaion SP825 (250-500 μm) were used.

3.4.1 Batch tests

As seen in Figure 3.15, the removal of 2,4-dichloro phenol, triclosan and 2,3,4-trichloro phenol increased with increased amount of adsorbent. For removal of triclosan, 0.6 g/L of adsorbent was found as optimum amount (Figure 3.15). As an optimum dosage, 1.2 g/L was determined for both 2,4-dichloro phenol removal and 2,3,4-trichloro phenol removal.

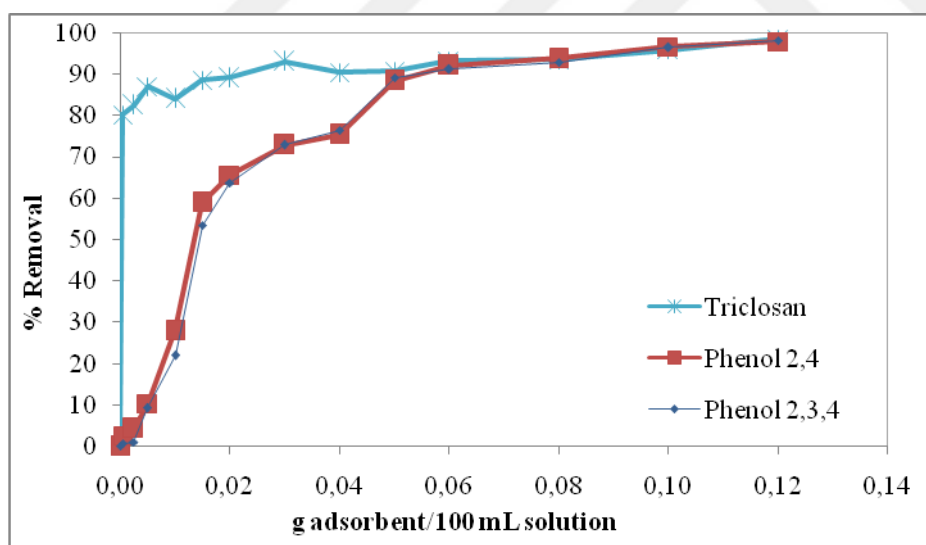


Figure 3.15: Batch studies for 2,4-dichloro phenol, 2,3,4-trichloro phenol and triclosan removal by Diaion SP207 (250-500 μm)

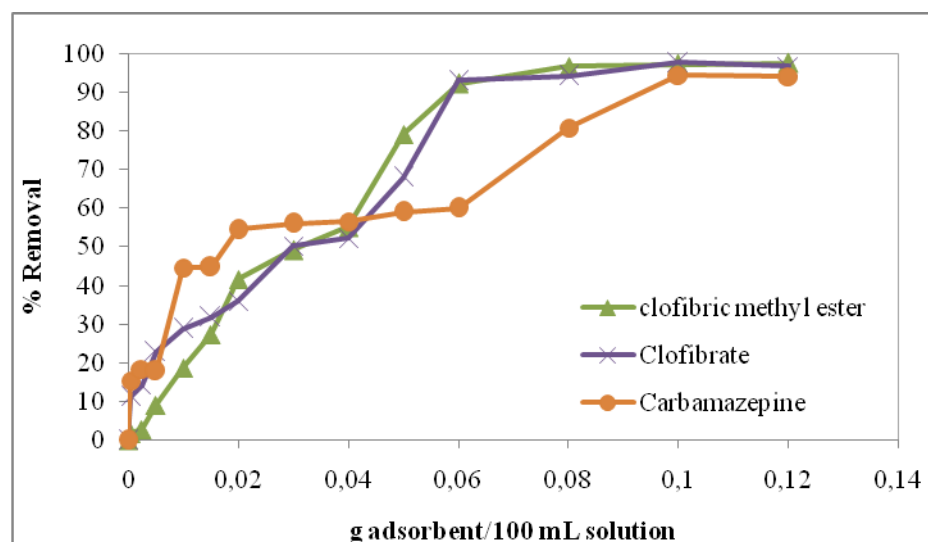


Figure 3.16: Batch studies for clofibrate, clofibric methyl ester and carbamazepine removal by Diaion SP207 (250-500 μm)

The optimum dosage of polymer adsorbents was 1.0 g-adsorbent/L for removal of clofibric methyl ester, clofibrate and carbamazepine using Diaion SP207 (Figure 3.16).

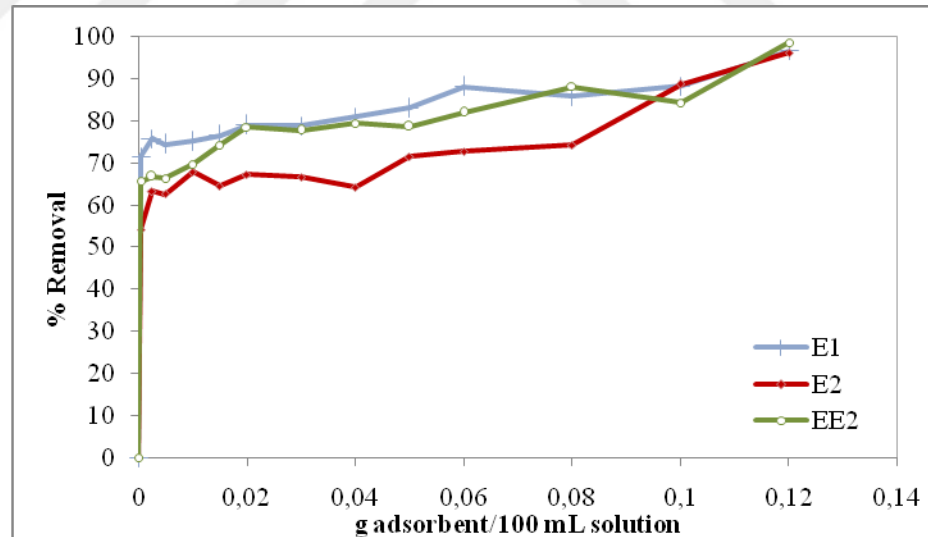


Figure 3.17: Batch studies for estrone (E1), 17- β -estradiol (E2) and 17- α -ethinylestradiol (EE2) removal by Diaion SP207 (250-500 μm)

As shown in Figure 3.17, for estrone (E1), 17- β -estradiol (E2) and 17- α -ethinylestradiol (EE2) removal, 1.2 g- adsorbent/L was determined as an optimum adsorbent dosage using Diaion SP207 adsorbent.

For removal of triclosan, 1.0 g/L adsorbent was determined as optimum amount as seen in Figure 3.18. For 2,4-dichloro phenol and 2,3,4-trichloro phenol removal using Diaion SP825, 1.2 g-polymer adsorbent/L was optimum amount.

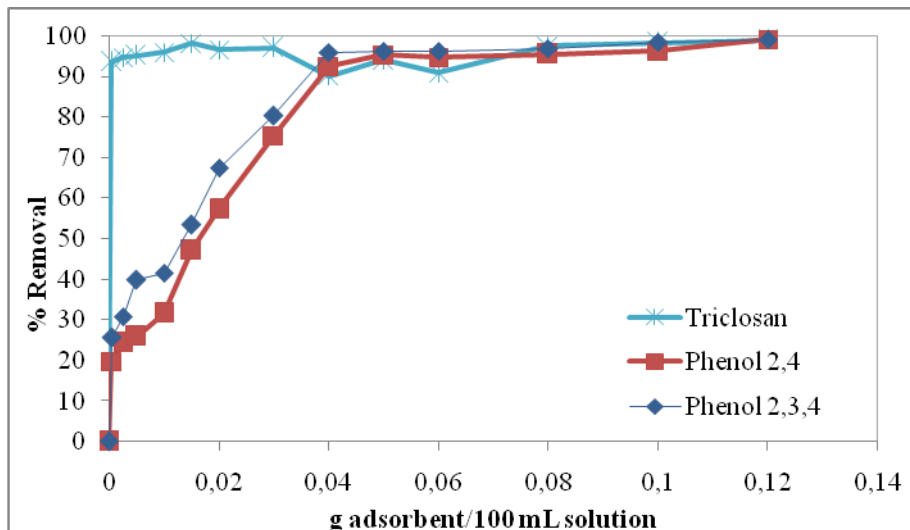


Figure 3.18: Batch studies for triclosan, 2,4-dichloro phenol and 2,3,4-trichloro phenol removal by Diaion SP825 (250-500 μm)

As seen in Figures 3.19 and 3.20, for removal of clofibrate, clofibric methyl ester, clofibric acid and carbamazepine, estrone (E1), 17- β -estradiol (E2) and 17- α -ethinylestradiol (EE2), adsorbent dosages were determined as 1.0, 0.5, 1.0, 1.0, 1.2, 0.8 and 1.2 g/L, respectively.

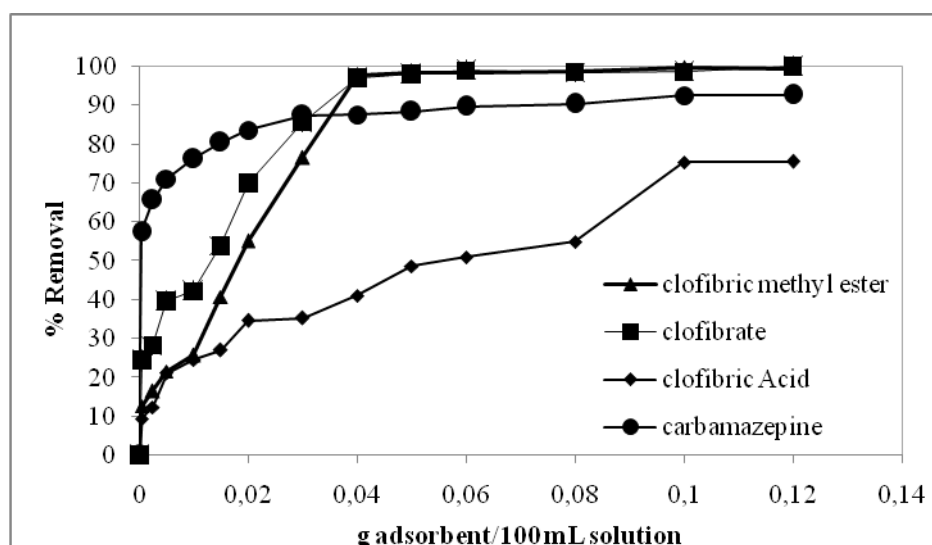


Figure 3.19: Batch studies for clofibric methyl ester, clofibrate, clofibric acid and carbamazepine removal by Diaion SP825 (250-500 μm)

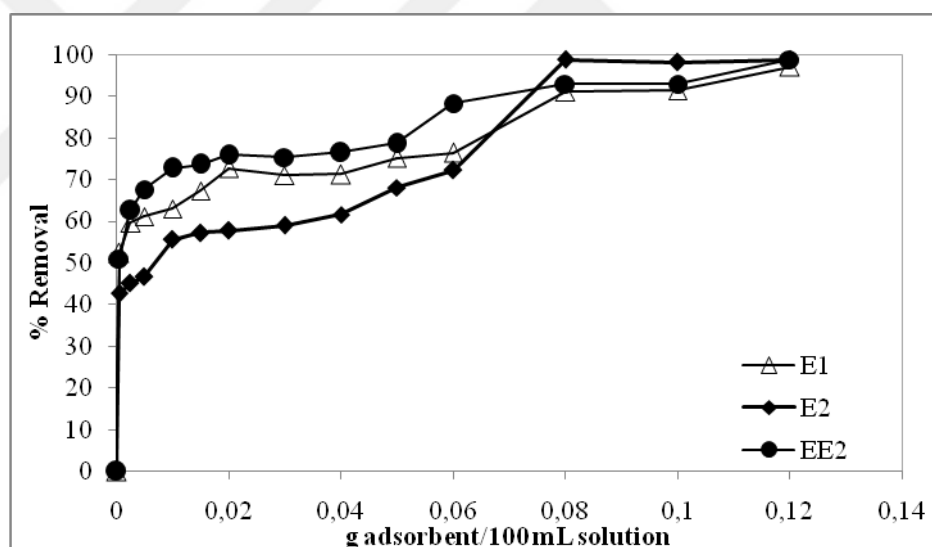


Figure 3.20: Batch studies for estrone (E1), 17- β -estradiol (E2) and 17- α -ethinyl estradiol (EE2) removal by Diaion SP825 (250-500 μm)

According to Figures 3.21-3.23, for 2,4-dichloro phenol and 2,3,4-trichloro phenol, estrone (E1), 17- β -estradiol(E2) removal, optimum dosages were found as 0.5 g/L. Optimum adsorbent dosage was determined as 0.6 g/L for clofibrate, clofibric methyl ester, clofibric acid. For carbamazepine, triclosan and 17- α -ethinylestradiol (EE2), the highest removal was found using 0.8 g/L of Dowex L493.

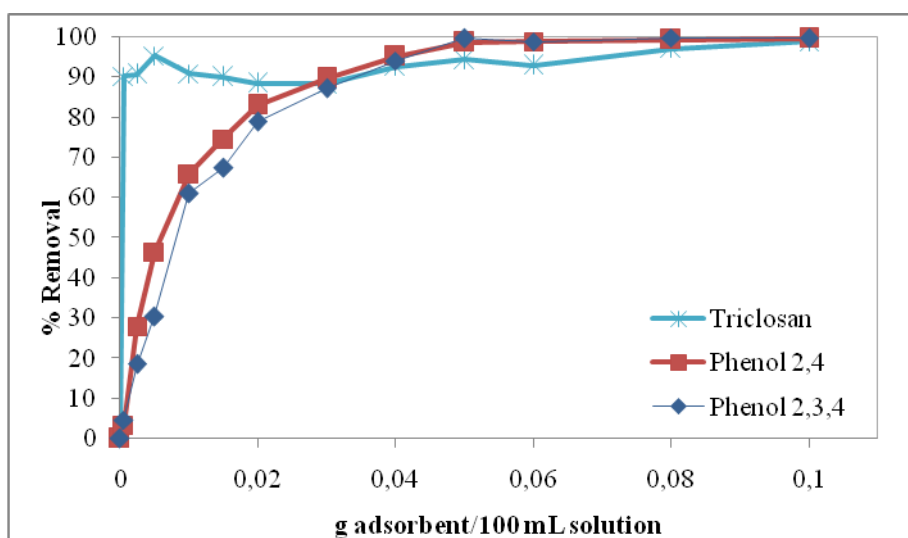


Figure 3.21: Batch studies for triclosan, 2,4-dichloro phenol and 2,3,4-trichloro phenol removal by Dowex L493 (250-500 μm)

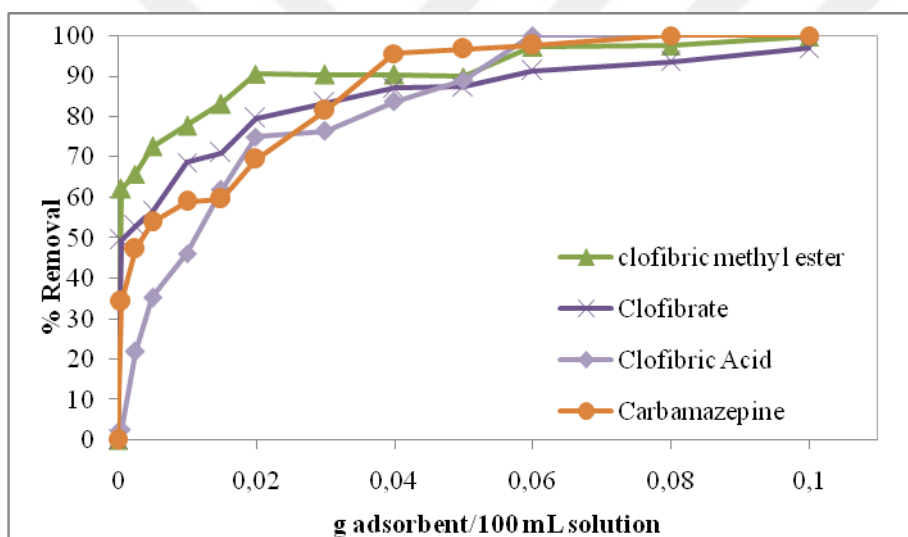


Figure 3.22: Batch studies for clofibrate, carbamazepine, clofibric methyl ester, clofibric acid removal by Dowex L493 (250-500 μm)

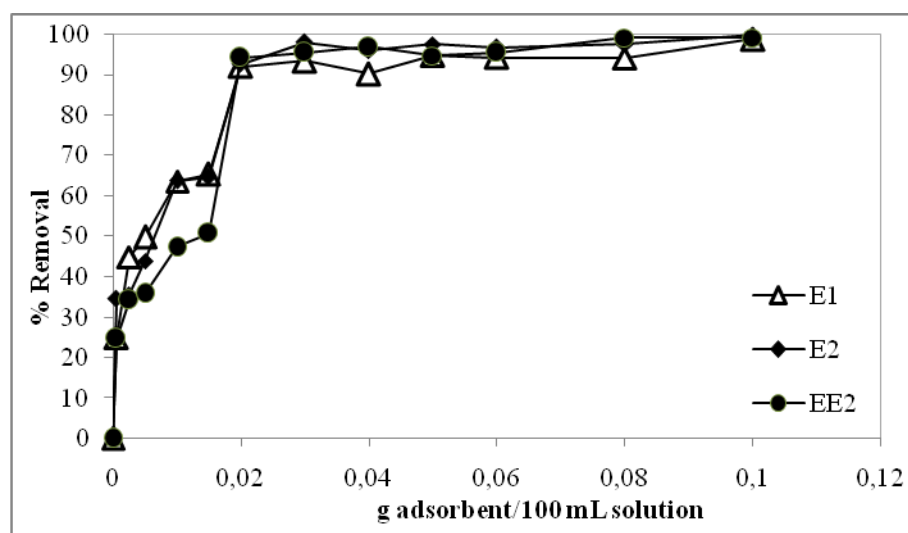


Figure 3.23: Batch studies for Estrone (E1), 17- β -estradiol (E2) and 17- α -ethinyl estradiol (EE2) removal by Dowex L493 (250-500 μ m)

3.5 Removal of DMP from Water

To remove of DMP from water, batch, isotherm, and kinetic tests were performed using high cross-linked polymer adsorbents (Diaion SP207, Diaion SP825, Dowex L493, Purolite PAD400).

3.5.1 Batch Tests

As seen in Figure 3.24, the removal of DMP increases by the increase in concentration of adsorbent in the solution. The highest removal of DMP was obtained at an adsorbent dosage of 0.15 g/50 mL.

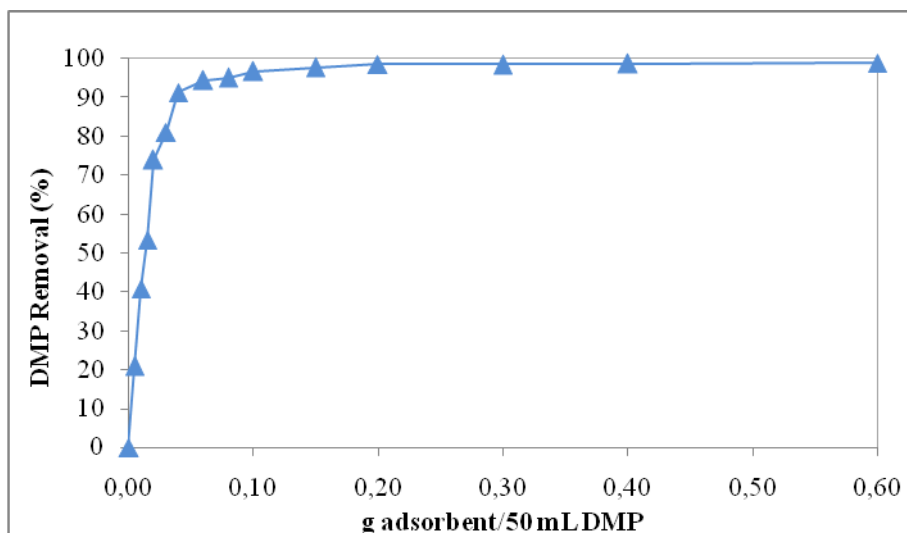


Figure 3.24: Batch study for DMP removal by PAD400 adsorbent (355-500 μm)

In Figure 3.25, for a complete removal of DMP using SP207 adsorbent, 0.10 g/50 mL adsorbent was determined as the optimum dosage of adsorbent.

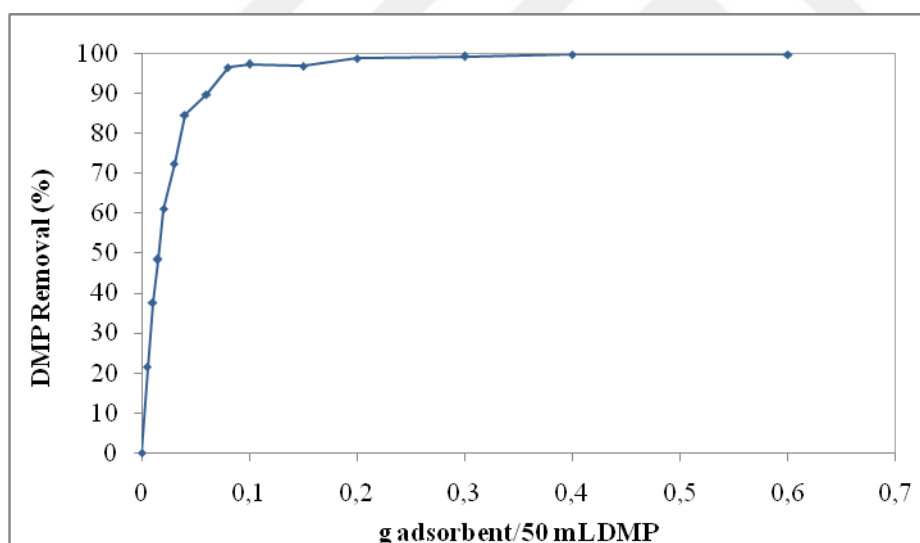


Figure 3.25: Batch study for DMP removal by SP207 adsorbent (500-710 μm)

In Figure 3.26, for DMP removal, 0.08 g-polymer adsorbent/50 mL using Diaion SP825 was obtained as the optimum amount.

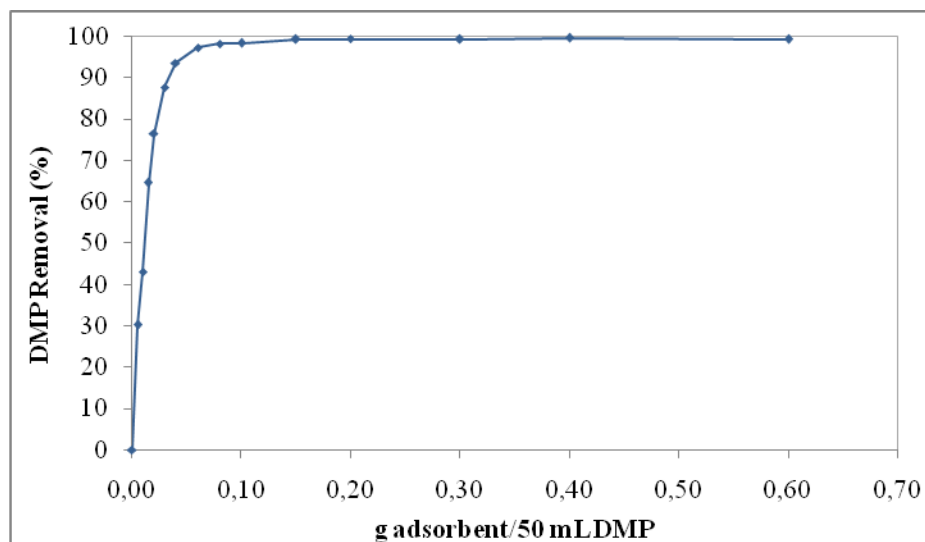


Figure 3.26: Batch study for DMP removal by Diaion SP825 (500-710µm)

As seen in Figure 3.27, the removal of DMP increased when increased amount of adsorbent was used. The highest percentage of DMP was determined at an adsorbent dosage of 0.6 g/50 mL.

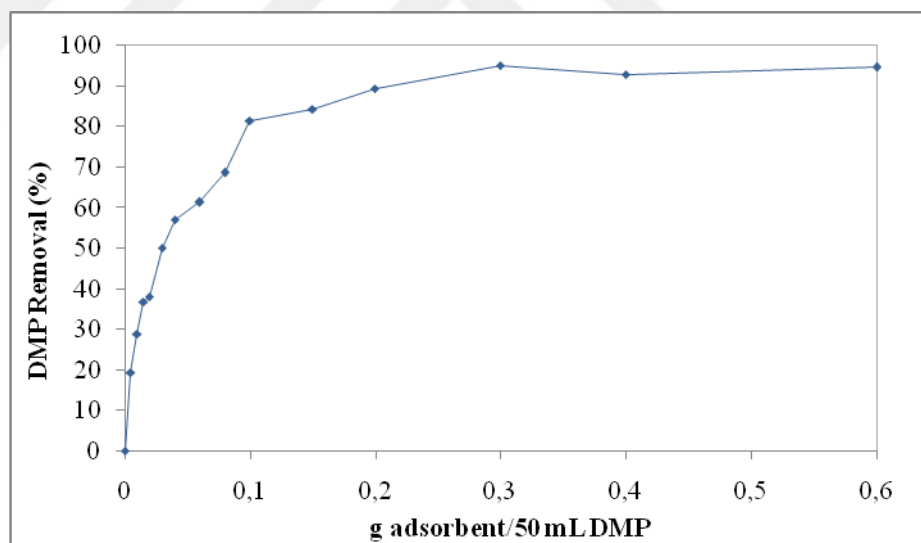


Figure 3.27: Batch study for DMP removal by Dowex L493 (500-710 µm)

3.5.2. Isotherm tests

3.5.2.1 Adsorption isotherms

Langmuir Isotherm;

The Langmuir isotherm hypothesizes that adsorption onto surface including measurable mark of adsorption position of uniform strategies with no transmigration of adsorbate in the plane surface. After position is full, another suction can take place at this site. It means that the surface achieves the maximum adsorption and it arrives saturated point. In ion exchange or adsorption model, a solid phase of the transmission type liquid equilibrium concentration can be modeled using an adsorption isotherm (Ozcaar and Sengil, 2004). The linear form of the Langmuir isotherm is defined by Equation (Perju et al., 2012):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e}$$

q_m is monolayer sorption capacity of saturation (mg/g),

K_L is the Langmuir constant (L/mg) means the energy of adsorption, it shows closeness between the sorbent and sorbate. C_e is the equilibrium concentration (mg/L), Q_e the amount adsorbed at equilibrium (mg/g)

Freundlich isotherm;

Freundlich isotherm theorizes heterogeneous surface with a nonuniform distribution of heat of adsorption, and is explained by the equation below (Perju et al., 2012):

$$\log q_e = \log K_F + N \log C_e$$

K_F , Freundlich constant.

N , a measure of the nature and strength of the adsorption process and of the distribution of active sites. C_e is the equilibrium concentration (mg/L), Q_e the amount adsorbed at equilibrium (mg/g).

Temkin isotherm:

The Temkin isotherm has commonly been applied in the following form (Perju et al., 2012):

$$q_e = \frac{RT}{b_T} \ln a_T + \left(\frac{RT}{b_T} \right) \ln C_e$$

Where b_T is the Temkin constant which is the heat of sorption (kJ/mol) and a_T is the equilibrium binding constant corresponding to the maximum binding energy (L/mg). From the plot of q_e against $\ln C_e$, the Temkin constants a_T and b_T are obtained as intercept and slope.

3.5.2.2 Results for isotherm tests

Adsorption of DMP was investigated using different kinds of adsorbents (Diaion SP207, Mitsubishi Chem, Diaion SP825, Mitsubishi Chem, Dowex L493, Dow Chem and PAD400, Purolite). The Langmuir, Freundlich and Temkin isotherms have been used to describe the adsorption of DMP onto the adsorbents.

Figures 3.28-3.31 were obtained for Langmuir, Freundlich and Temkin isotherms of PAD400 adsorbent.

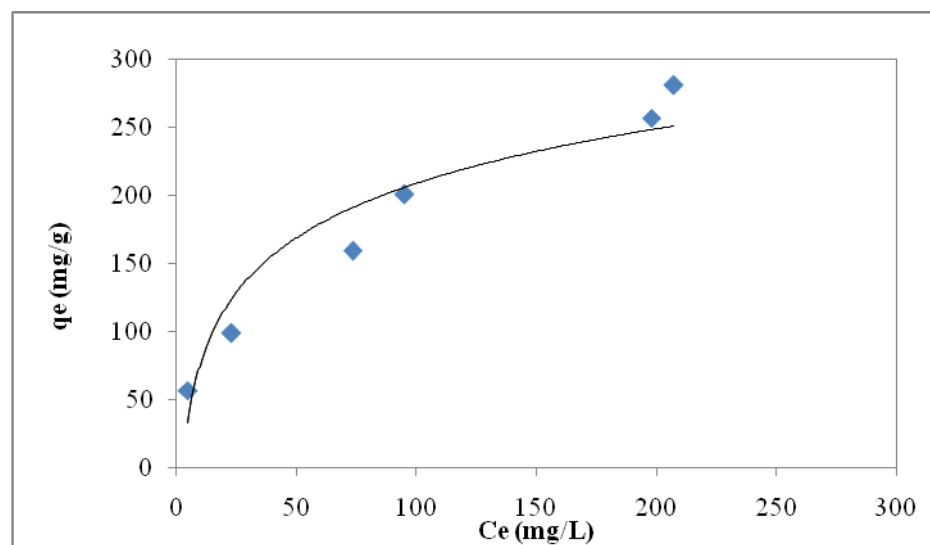


Figure 3.28: Adsorption isotherms of DMP

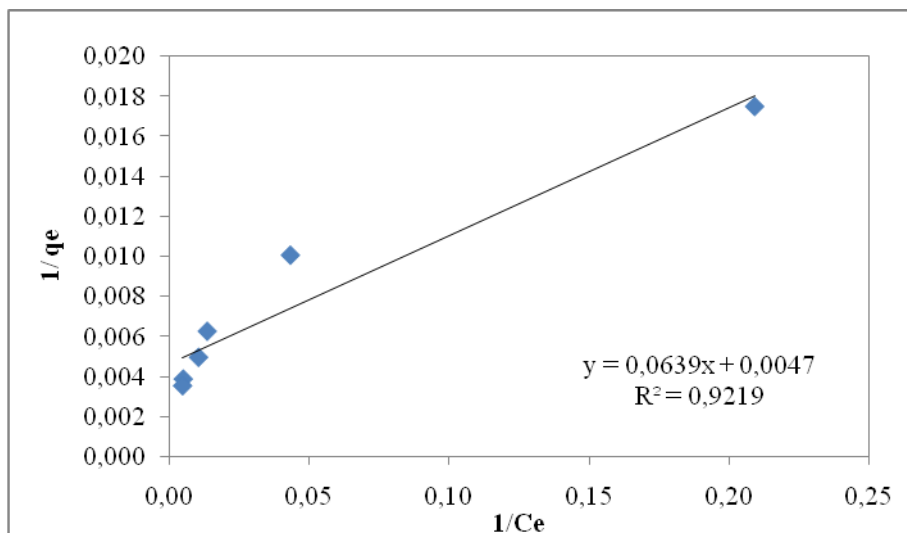


Figure 3.29: Linear form of Langmuir isotherm of DMP for Purolite PAD400 adsorbent

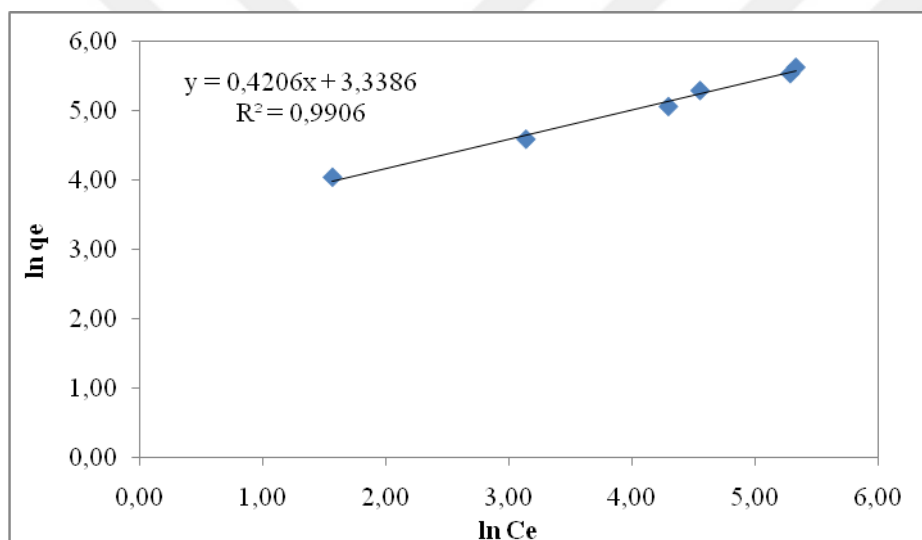


Figure 3.30: Linear form of Freundlich isotherm of DMP for Purolite PAD400 adsorbent

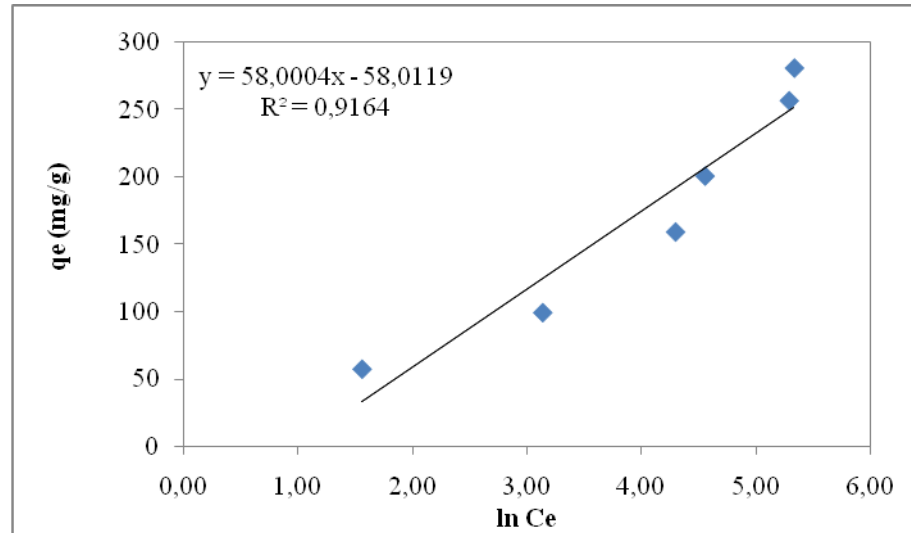


Figure 3.31: Temkin isotherm of DMP for PAD400 adsorbent

Calculated Langmuir equilibrium constant, K_L , L/mg and the theoretical monolayer saturation capacity, q_m , mg/g, Freundlich constant K_F , mg/g, N, g/L, Temkin constant, b_T , J/mol, equilibrium binding constant, a_T , (L/g) and correlation coefficients of isotherms, R^2 values are given in Table 3.9. The correlation coefficients of the Freundlich isotherm ($R^2 = 0.9906$) is higher than those obtained for Langmuir isotherm equation ($R^2 = 0.9219$) and Temkin isotherm ($R^2 = 0.9164$) for DMP adsorption for PAD400 adsorbent. From those results, it was considered that Langmuir isotherm fit well more fitted for DMP adsorption by PAD400 adsorbent.

Table 3.9: Correlation coefficients and constants of isotherms for adsorption of DMP onto Purolite
PAD400

Isotherm \ Adsorbent		Purolite PAD400
Langmuir	R^2	0.9219
	q_m (mg/g)	250
	K_L (L/mg)	0.063
Freundlich	R^2	0.9906
	K_F (mg/g)	28.17
	N (g/L)	2.38
Temkin	R^2	0.9164
	b_T (kJ/mol)	58.00
	a_T (L/g)	0.36

Figures 3.32-3.35 were obtained for Langmuir, Freundlich and Temkin isotherms of Diaion SP207 adsorbent.

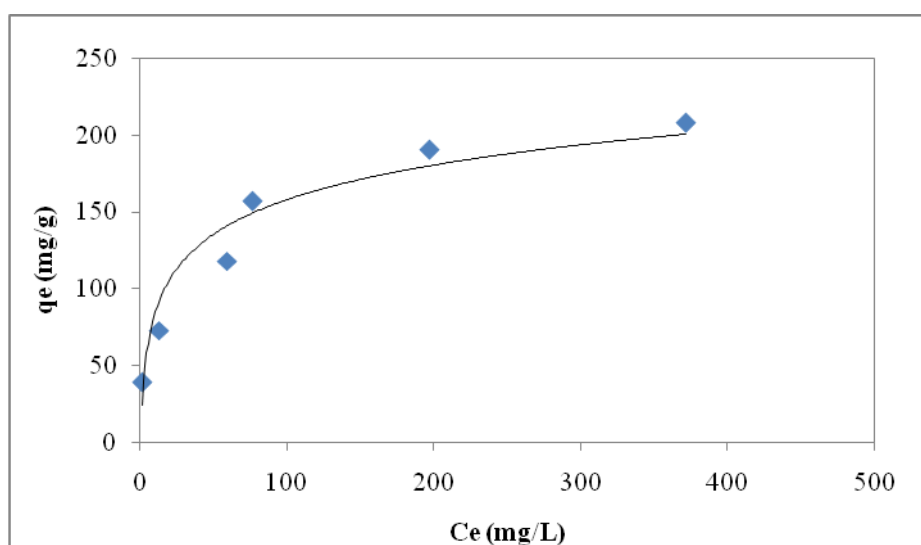


Figure 3.32: Adsorption isotherms of DMP for SP207 adsorbent

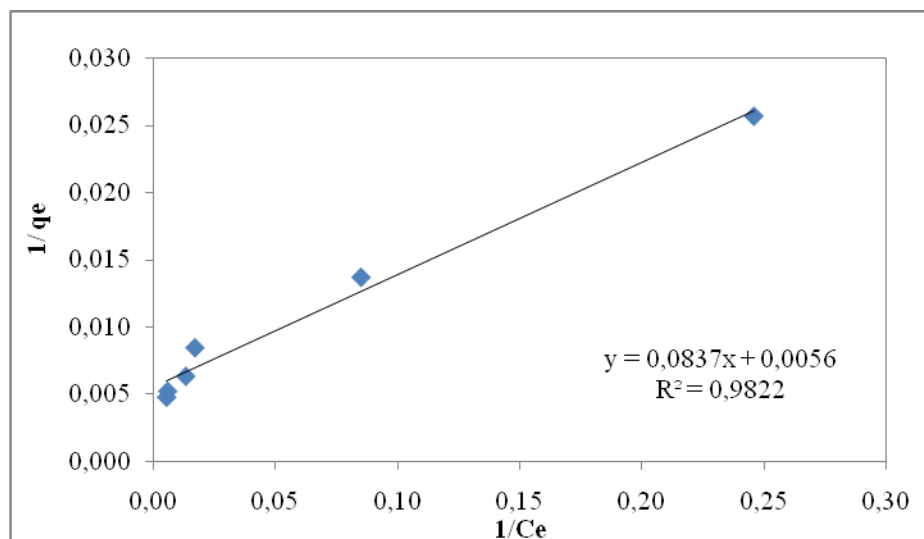


Figure 3.33: Linear form of Langmuir isotherm of DMP for SP207 adsorbent

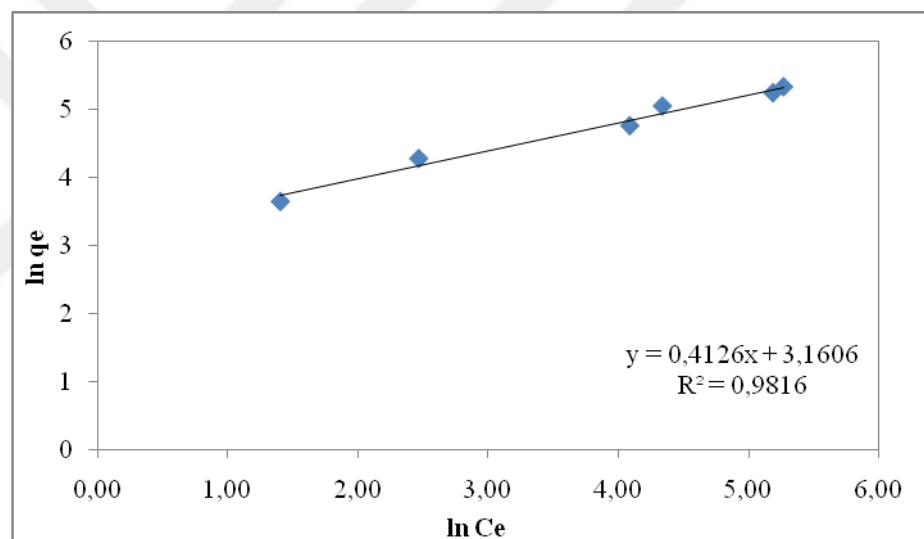


Figure 3.34: Linear form of Freundlich isotherm of DMP for SP207 adsorbent

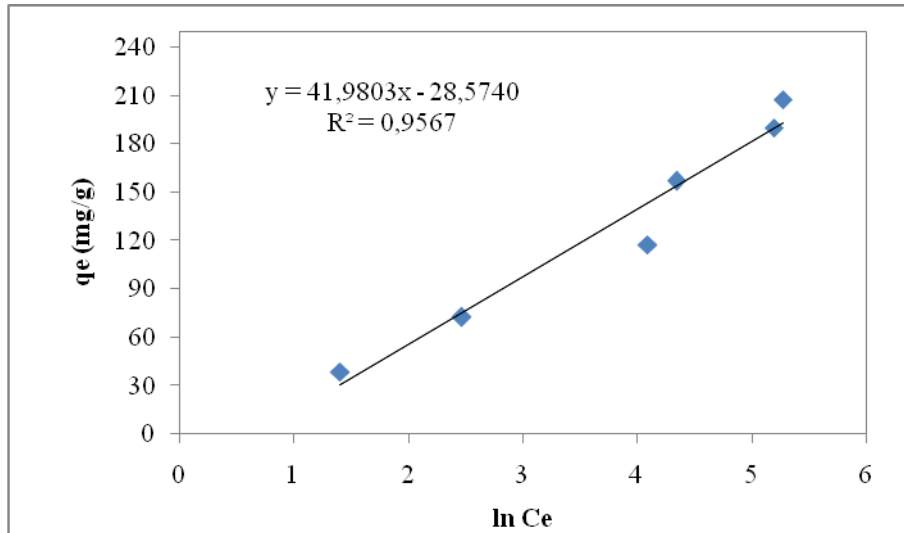


Figure 3.35: Temkin isotherm of DMP for SP207 adsorbent

Calculated Langmuir equilibrium constant, K_L , L/mg and the theoretical monolayer saturation capacity, q_m , mg/g, Freundlich constant K_F , mg/g, N g/L, Temkin constant, b_T , J/mol, equilibrium binding constant, a_T , (L/g) and correlation coefficients of isotherms, R^2 values are given in Table 3.10. The correlation coefficient of Langmuir isotherm equation ($R^2 = 0.9822$) is higher than that obtained for the Freundlich isotherm ($R^2 = 0.9816$) and Temkin isotherm ($R^2=0.9567$) for DMP adsorption onto SP207 adsorbent. As it can be seen from Table 3.10, Langmuir isotherm can be said more fitted to DMP adsorption onto SP207 adsorbent.

Table 3.10: Correlation coefficients and constants of isotherms for adsorption of DMP onto Diaion SP207

Adsorbent		Diaion SP207
Isotherm		
Langmuir	R ²	0.9822
	q _m (mg/g)	200
	K _L (L/mg)	0.060
Freundlich	R ²	0.9816
	K _F (mg/g)	23.58
	N (g/L)	2.42
Temkin	R ²	0.9567
	b _T (J/mol)	41.98
	a _T (L/g)	0.51

Figures 3.36-3.39 were obtained using Diaion SP825 adsorbent for Langmuir, Freundlich and Temkin isotherms.

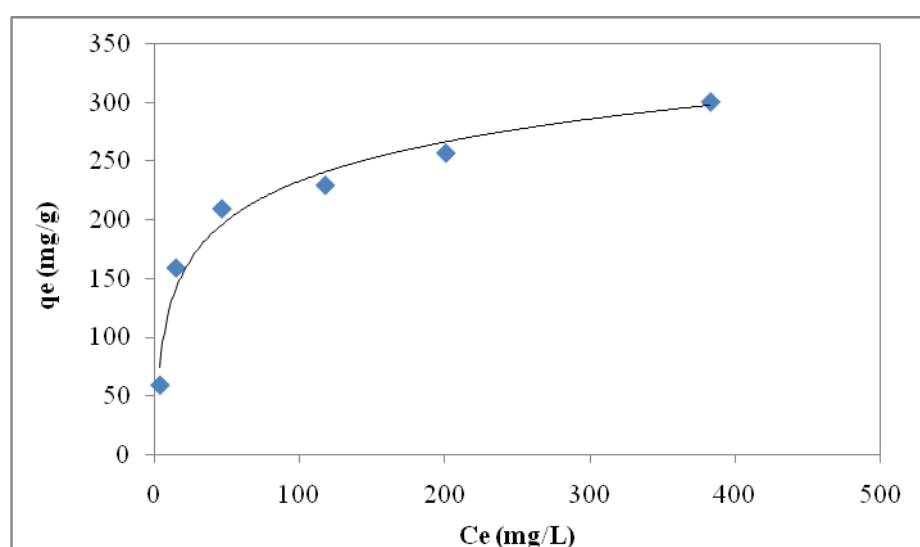


Figure 3.36: Adsorption isotherm for SP825 adsorbent

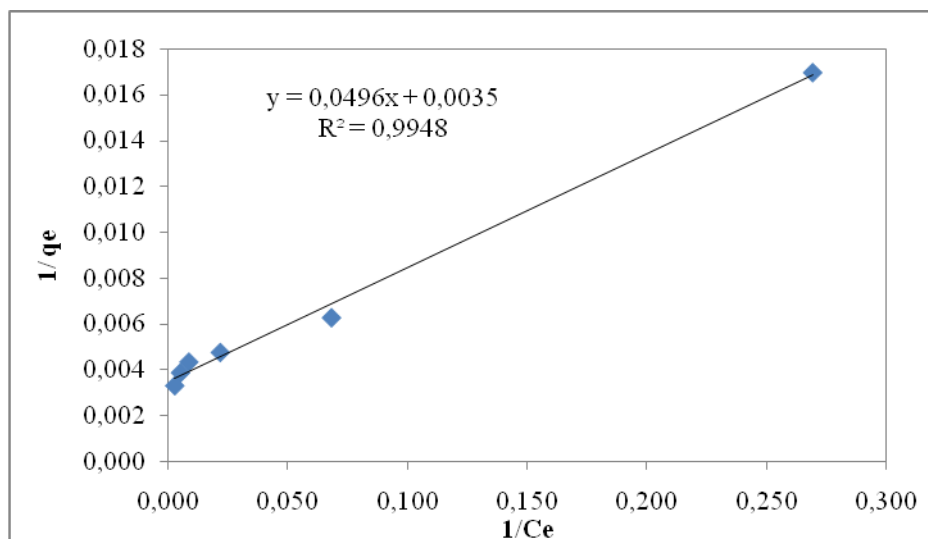


Figure 3.37: Linear form of Langmuir isotherm of DMP for SP825 adsorbent

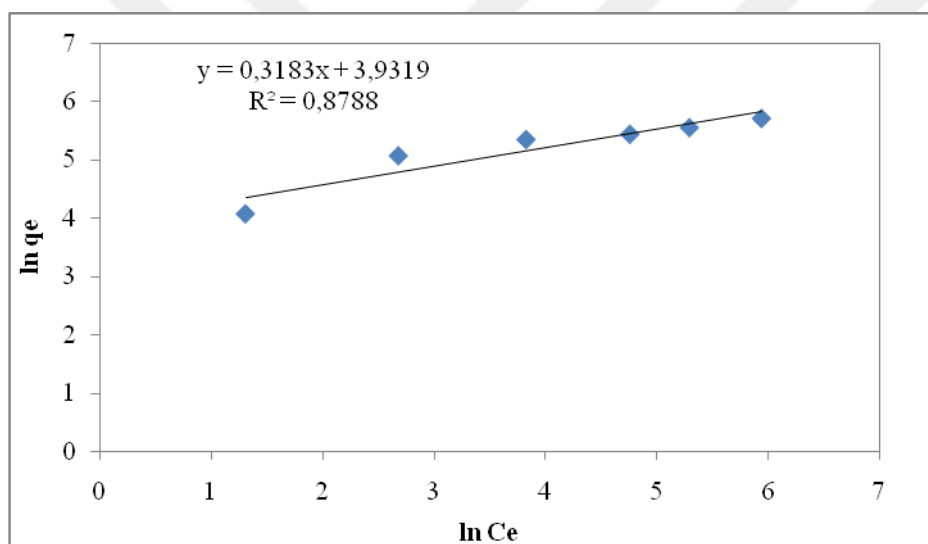


Figure 3.38: Linear form of Freundlich isotherm of DMP for SP825 adsorbent

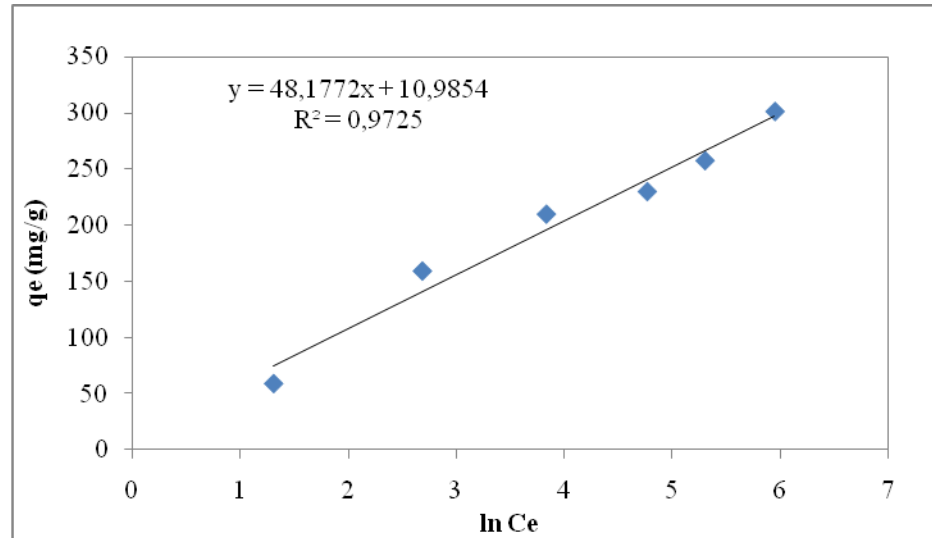


Figure 3.39: Temkin isotherm of DMP for SP825 adsorbent

Calculated Langmuir equilibrium constant, K_L , L/mg and the theoretical monolayer saturation capacity, q_m , mg/g, Freundlich constant K_F , mg/g, N g/L, Temkin constant, b_T , J/mol, equilibrium binding constant, a_T , (L/g) and correlation coefficients of isotherms, R^2 values are given in Table 3.11. The correlation coefficient of Langmuir isotherm equation ($R^2 = 0.9948$) is higher than those obtained for the Freundlich isotherm ($R^2 = 0.8788$) and Temkin isotherm ($R^2=0.9725$) for DMP adsorption by SP825 adsorbent. From that results, it can be considered that the adsorption data fit well to Langmuir isotherm for DMP adsorption onto SP825 adsorbent.

Table 3.11: Correlation coefficients and constants of isotherms for adsorption of DMP onto Diaion SP825

Isotherm \ Adsorbent		Diaion SP825
Langmuir	R^2	0.9948
	Q_m (mg/g)	333
	K_L (L/mg)	0.061
Freundlich	R^2	0.8788
	K_F (mg/g)	50.95
	N (g/L)	3.14
Temkin	R^2	0.9725
	b_T (J/mol)	48.17
	a_T (L/g)	1.26

Figures 3.40-3.43 were plotted using Dowex L493 adsorbent for Langmuir, Freundlich and Temkin isotherms.

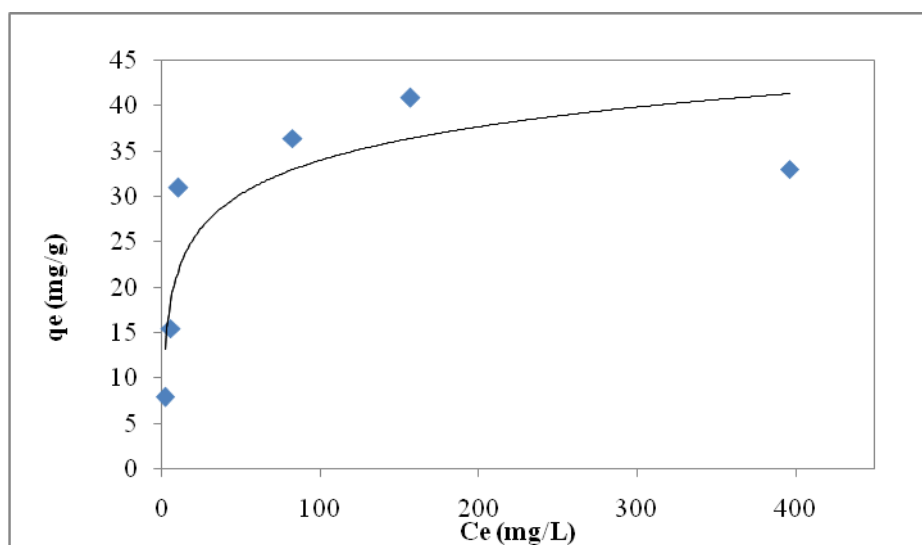


Figure 3.40: Adsorption isotherm for DMP

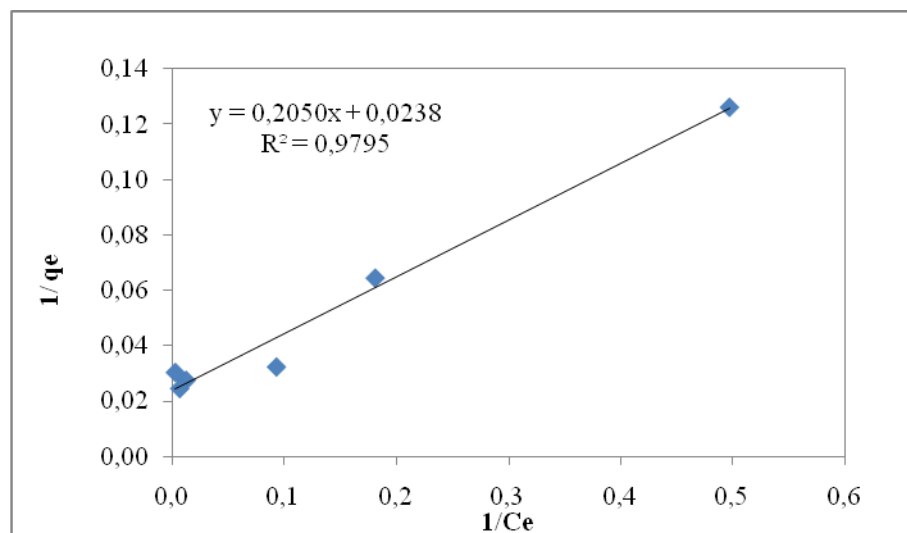


Figure 3.41: Linear form of Langmuir isotherm of DMP for DowexL493 adsorbent

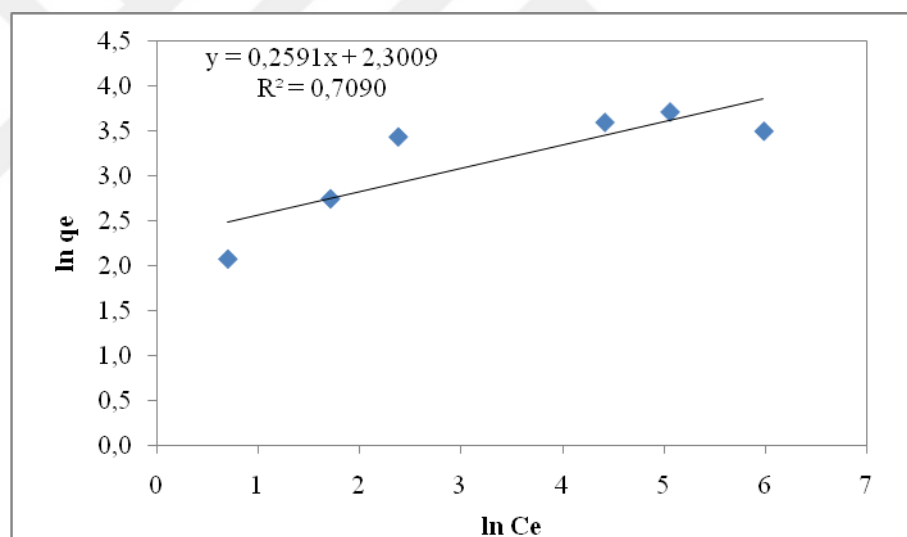


Figure 3.42: Linear form of Freundlich isotherm of DMP for Dowex L493 adsorbent

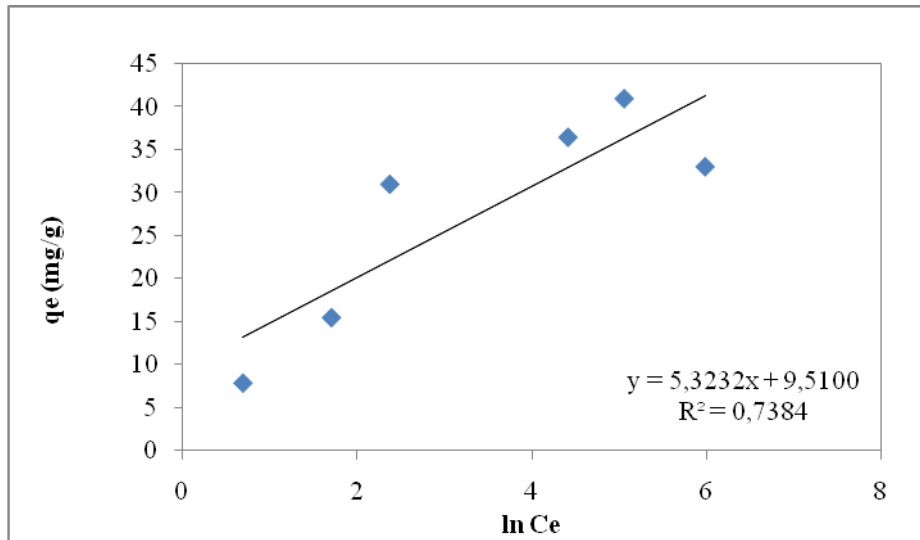


Figure 3.43: Temkin isotherm of DMP for Dowex L493 adsorbent

Calculated Langmuir equilibrium constant, K_L , L/mg and the theoretical monolayer saturation capacity, q_m , mg/g, Freundlich constant K_F , mg/g, N g/L, Temkin constant, b_T , J/mol, equilibrium binding constant, a_T , (L/g) and correlation coefficients of isotherms, R^2 values are given in Table 3.12. The correlation coefficient of the Langmuir isotherm ($R^2 = 0.9795$) is higher than that obtained for Freundlich isotherm ($R^2 = 0.7090$) and Temkin isotherm ($R^2 = 0.7384$) for DMP adsorption by DowexL493 adsorbent. Results revealed that the adsorption data fit well to Langmuir adsorption isotherm was determined for DMP adsorption for DowexL493 adsorbent.

Table 3.12: Correlation coefficients and constants of isotherms for adsorption of DMP onto
Dowex L493

Adsorbent Isotherm		Dowex L493
Langmuir	R^2	0.9795
	q_m (mg/g)	42.02
	K_L (L/mg)	0.116
Freundlich	R^2	0.7090
	K_F (mg/g)	9.98
	N (g/L)	3.86
Temkin	R^2	0.7384
	b_T (J/mol)	5.32
	a_T (L/g)	5.97

3.5.3 Kinetic studies

3.5.3.1 Conventional kinetic models

Pseudo-first order kinetic model

A simple adsorption kinetic model is the pseudo first-order kinetic; Its equation is given below (Ozcaar and Sengil, 2004):

$$\frac{dq_t}{dt} = k_1(q_s - q_t)$$

$q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, gives:

$$\log(q_s - q_t) = \log q_s - \frac{k_1}{2.303} t$$

Where q_e and q_t gives species amounts the sorbed at equilibrium and at time t (mg/g), respectively, and k_1 is the rate constant (min^{-1}).

Pseudo second-order kinetic model

A pseudo second-order kinetic model can be explained by using equation below (Ozcaar and Sengil, 2004):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

After define integration by applying initial conditions, equation becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t$$

Equation can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

Where k_2 is the rate constant of pseudo second-order sorption (g/mg min).

3.5.3.2 Diffusional and Reaction Models

The models of process contain the diffusion steps (bulk solution, a film layer occurs at the surface area of particle) and the exchange reaction occurs on the efficient part. Since the resistance in bulk solution is easily checked and negligible, film diffusion, particle diffusion, and chemical reaction, usually determine the rate of the ion-exchange process. Kinetic study data were considered by using two approaches. The first is relied on Fick's first law of integration of material balance for infinite solution volume (ISV). The unreacted core model (UCM) is the second approach, in which ion exchange is treated as a heterogeneous reaction. According to UCM reaction, first, unreacted particulate in a zone moving through the core particles of the outer skin is formed. The rate-determining steps for kinetic models were given in Table 3.13 (Badruk et al., 1999):

Table 3.13: Diffusional and reaction models

Model	Rate-determining step	Equation
ISV	Particle diffusion	$F(X) = -\ln(1-X^2) = kt$ where $k = D_r \pi^2 / r_0^2$
ISV	Film diffusion	$F(X) = -\ln(1-X) = K_{lf}t$ where $K_{lf} = 3DC/r_0\delta C_f$
UCM	Liquid film	$F(X) = X = (3C_{A0}K_{mA}/a_{r0}C_{s0})t$
UCM	Chemical reaction	$F(X) = 1 - (1-X)^{1/3} = (k_s C_{A0}/a_{r0}C_{s0})t$
UCM	Reacted layer	$F(X) = 3 - 3(1-X)^{2/3} - 2X$ $= (6D_{eR}C_{A0}/a_{r0}^2C_{s0})t$

3.5.3.3 Results for Kinetic Studies

The study of adsorption kinetics is important as it provides valuable insights into the reaction pathways and into the mechanism of adsorption reactions. Additionally, the kinetics define the solute uptake rate which in turn controls the residence time of sorbate uptake at the adsorbent interface (Ho and McKay, 1999). Therefore, it is critical to determine the kinetic performance of adsorbents.

The kinetic behaviors of Purolite PAD400 (0.355-0.500 mm), Diaion SP207 (0.500-0.710 mm), Diaion SP825 (0.500-0.710 mm) and DOWEX L493 (0.500-0.710 mm) adsorbents were studied and checked to see the kinetic performances of adsorbents.

Figures 3.44-3.48 show the kinetic behavior of the Purolite PAD400 adsorbent at a particle size range of 0,355-0,500 mm for DMP removal. The graphs of the ratio of DMP concentration at any time to initial DMP concentration versus time was given in Figures 3.44.

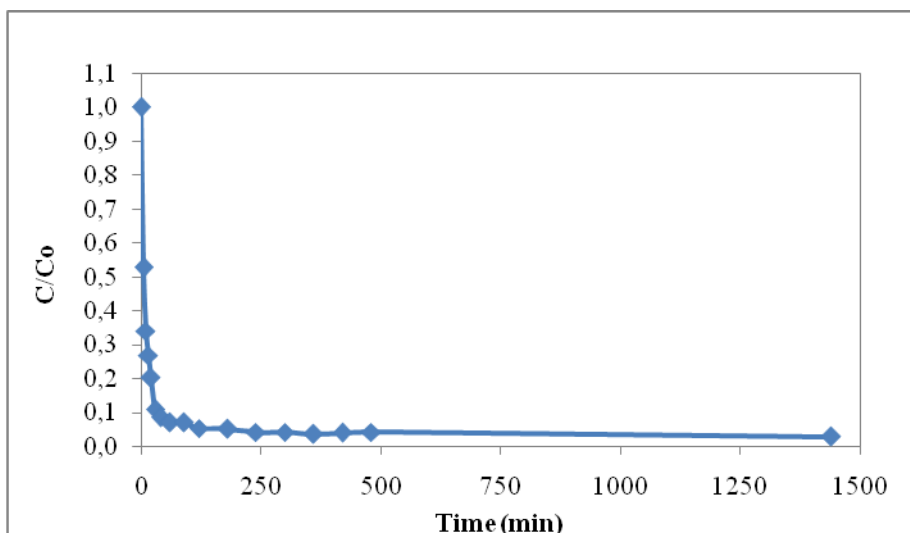


Figure 3.44: Ratio of concentration at any time to initial DMP concentration vs time for Purolite PAD400

Figures 3.45 and 3.46 show the evaluation of kinetic data using conventional kinetic models. The graphs of $\log(q_e - q_t)$ versus t and t/q_t versus t were drawn for both kinetic models (first-order and second-order), respectively, PAD 400 for DMP removal.

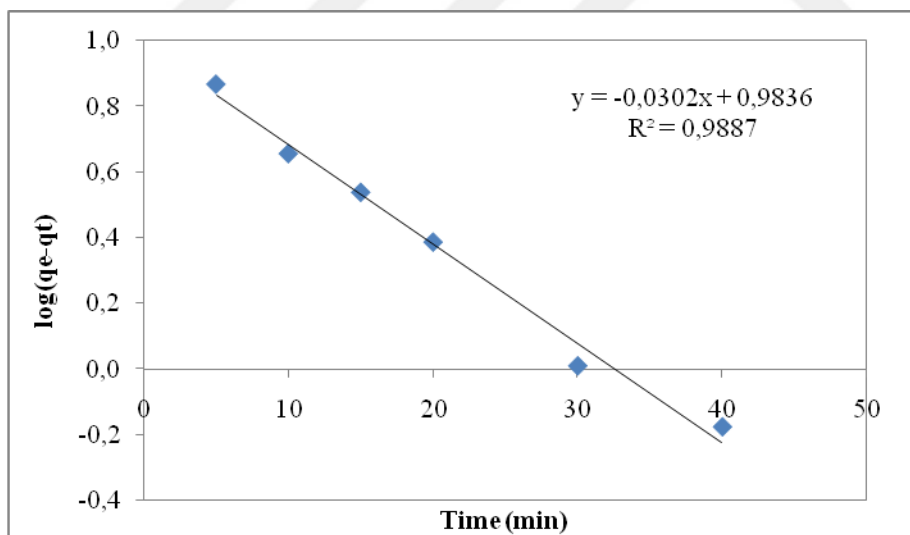


Figure 3.45: Evaluation of kinetic results using pseudo-first-order kinetic model for Purolite PAD400

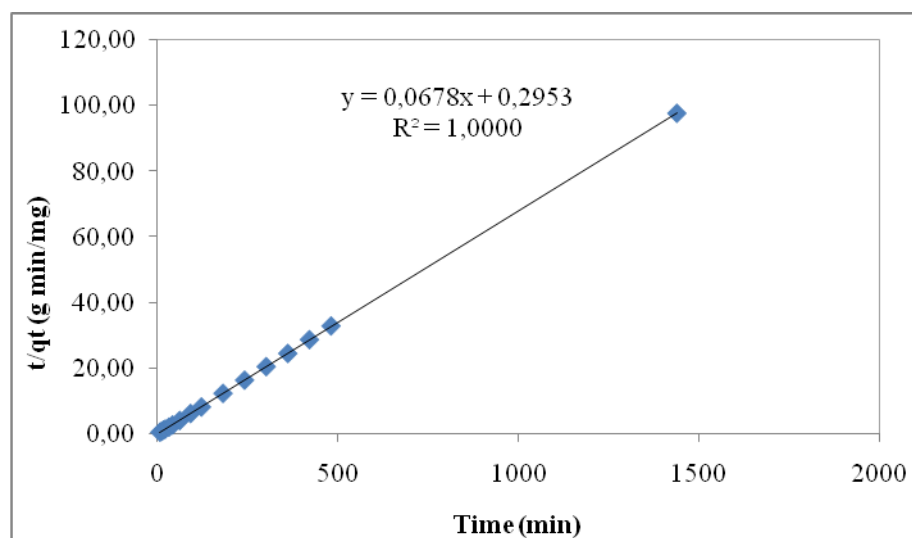


Figure 3.46: Evaluation of kinetic results using pseudo-second-order kinetic model for Purolite PAD400

Plots are linear and it means that conventional kinetic equations can be applied for DMP adsorption on the adsorbent. According to Table 3.14, it can be said that the adsorption of DMP by PAD400 adsorbent obeys the pseudo-second-order kinetic model. K_1 , rate constant of pseudo-first-order kinetic and K_2 , rate of constant pseudo-second-order kinetic model, q_e , DMP amount at the equilibrium are calculated and given in Table 3.14. As seen from rate constant of kinetics, pseudo-second-order kinetic model can be said it is fit well.

Table 3.14: Consideration of kinetic results obtained using conventional kinetic modeling for PAD400

Adsorbent amount (g/L)	First Order Kinetics			Second Order Kinetics		
	R^2	q_e	K_1	R^2	q_e	K_2
3	0.9887	9.63	0.0695	1.0000	14.75	0.0156

The kinetic data were also evaluated for diffusional and reaction models. Figures 3.47 and 3.48 show the evaluation of kinetic data using unreacted core model (UCM) and using infinite solution volume model (ISV) for Purolite PAD400 adsorbent.

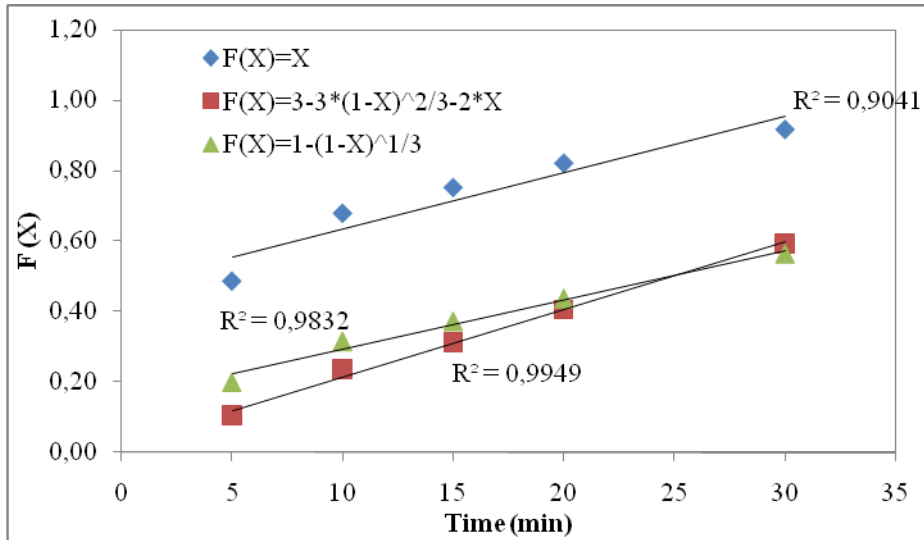


Figure 3.47: Evaluation of kinetic results using unreacted core model (UCM)

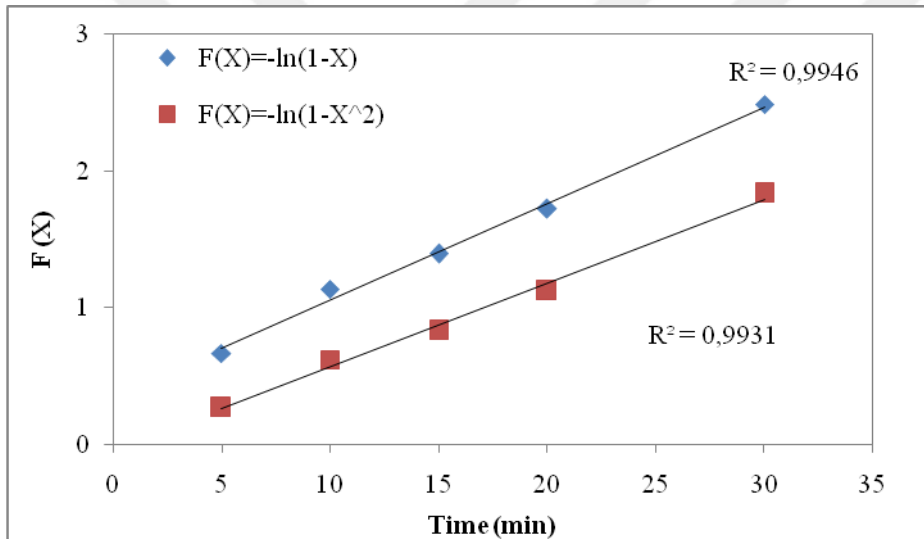


Figure 3.48: Evaluation of kinetic results using infinite solution volume model (ISV)

Table 3.15 gives correlation coefficients. The maximum correlation coefficients designate that film diffusion is rate determining step for ISV model and particle diffusion according to UCM models for PAD400 adsorbent.

Table 3.15: Consideration of kinetic results obtained using diffusional and reaction models for PAD400

R^2				
ISV		UCM		
$-\ln(1-X)$	$-\ln(1-X^2)$	X	$3-3(1-X)^{2/3}-2X$	$1-(1-X)^{1/3}$
0.9946	0.9931	0.9041	0.9949	0.9832

The ratio of DMP concentration at any time to initial DMP concentration versus time for Diaion SP207 were given in Figures 3.49.

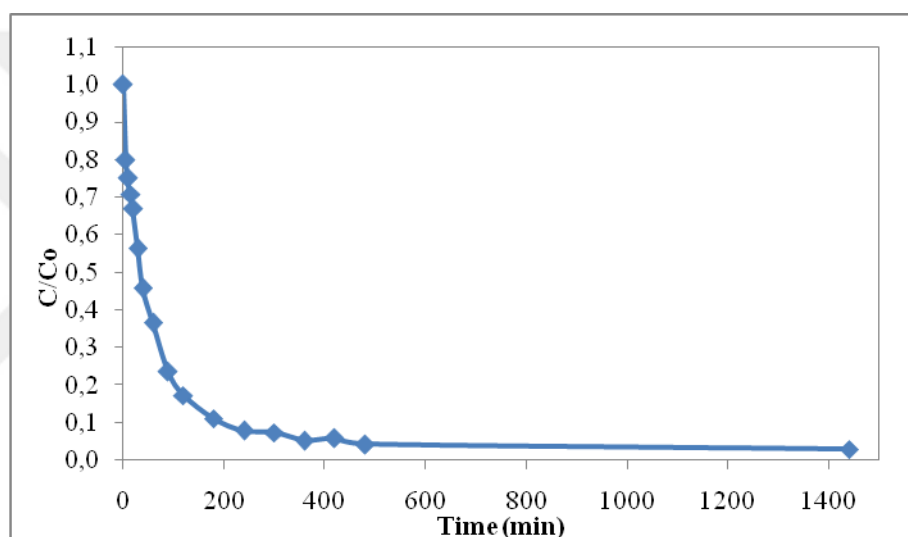


Figure 3.49: Ratio of concentration at any time to initial DMP concentration vs time for Diaion SP207

Figures 3.50 and 3.51 show the evaluation of kinetic data for pseudo-first- and second-order kinetic models. The graphs of $\log(q_e - q_t)$ versus t and t/q_t versus t were drawn for both kinetic models for DMP removal by Diaion SP207.

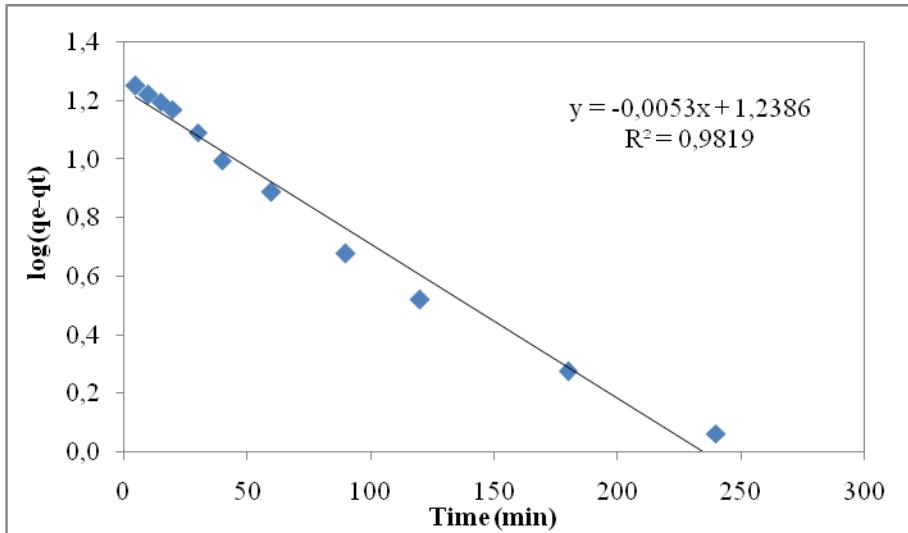


Figure 3.50: Evaluation of kinetic results using pseudo-first-order kinetic model for DMP using Diaion SP207

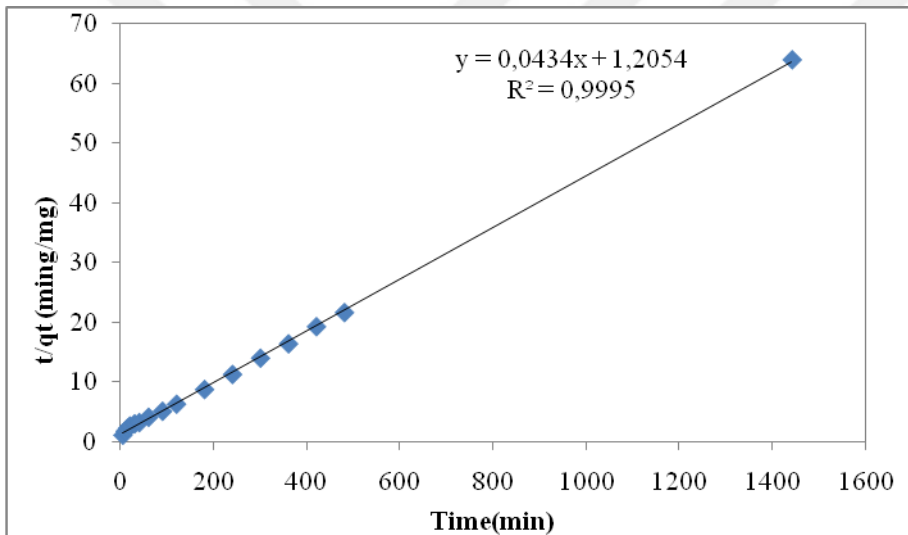


Figure 3.51: Evaluation of kinetic results using pseudo-second-order kinetic model for DMP using Diaion SP207

Plots are linear and it means that the pseudo first order or pseudo second order kinetic equations can be applied for DMP adsorption by SP207 adsorbent. According to Table 3.16, adsorption data (R^2 and q_e) of SP207 adsorbent agreed well with the pseudo-second-order model.

Table 3.16: Evaluation of kinetic results obtained using conventional kinetic modelling for Diaion SP207

T	Adsorbent	First Order Kinetics			Second Order Kinetics		
	Amount (g/L)	R^2	q_e (mg/g)	K_1 (g/mg.min)	R^2	q_e (mg/g)	K_2 (g/mg.min)
	2	0.9819	17.32	0.0122	0.9995	23.04	0.0016

The kinetic results were also evaluated with diffusional and reaction models. Figures 3.52 and 3.53 show the evaluation of kinetic data using unreacted core model (UCM) and infinite solution volume model (ISV) for Diaion SP207 adsorbent.

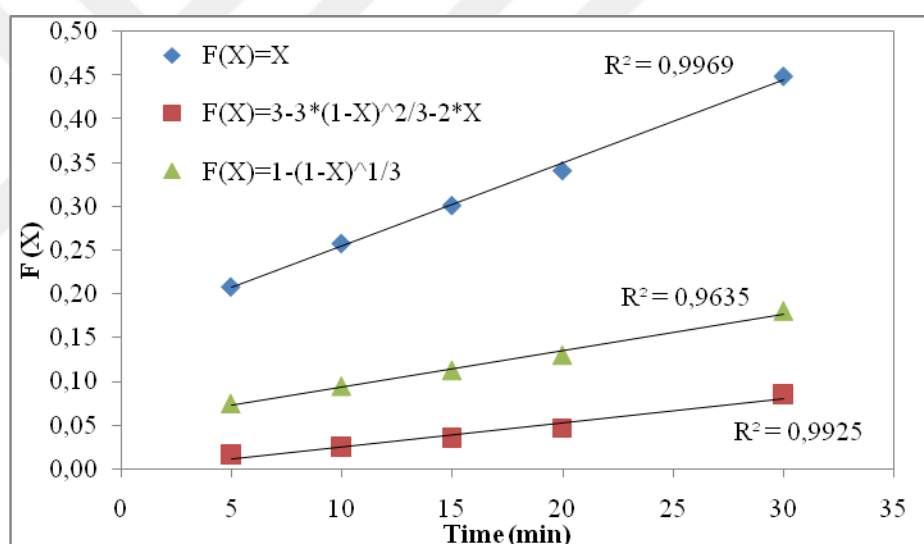


Figure 3.52: Evaluation of kinetic results using unreacted core model (UCM)

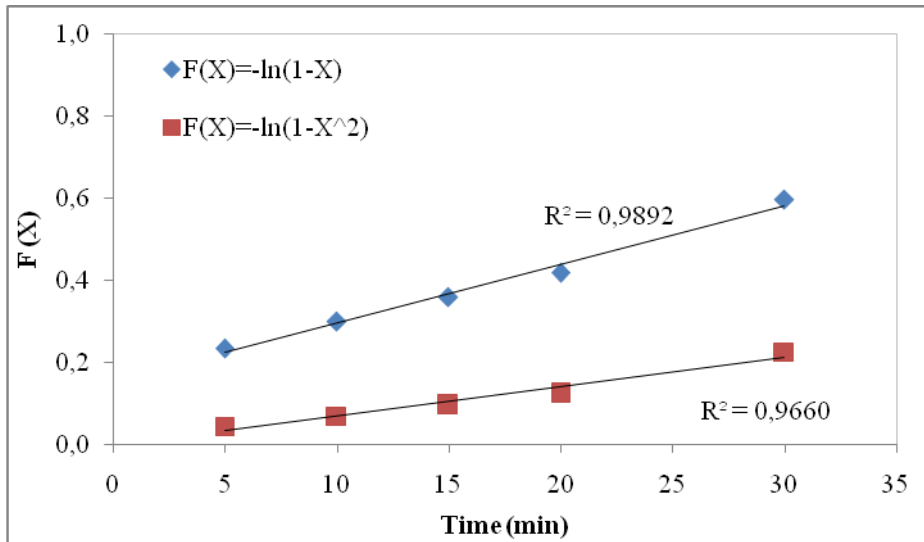


Figure 3.53: Evaluation of kinetic results using infinite solution volume model (ISV)

Table 3.17 gives correlation coefficients obtained. The maximum correlation coefficients can be explained that rate controlling step is film diffusion for both ISV and UCM models for SP207 adsorbent.

Table 3.17: Evaluation of kinetic results obtained using diffusional and reaction models for SP207

R^2				
ISV		UCM		
$-\ln(1-X)$	$-\ln(1-X^2)$	X	$3-3(1-X)^{2/3}-2X$	$1-(1-X)^{1/3}$
0.9892	0.9660	0.9969	0.9635	0.9925

Figures 3.54-3.58 show the kinetic behavior of the SP825 adsorbent at a particle size range of 0,500-0,710 mm for DMP removal. The graphs of ratio of DMP concentration at any time to initial DMP concentration versus time was given in Figures 3.54.

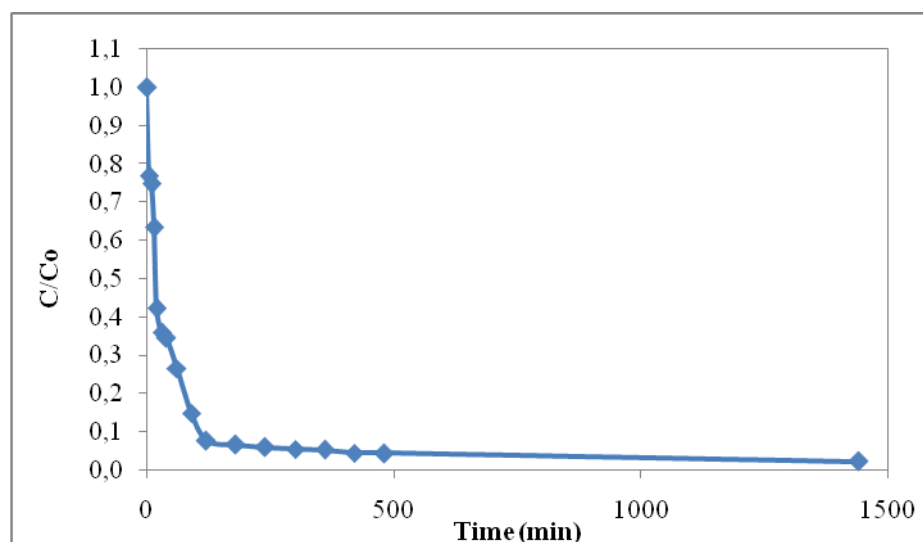


Figure 3.54: Ratio of concentration at any time to initial DMP concentration vs time for Diaion SP825

The graphs of 3.55 and 3.56 show the plots drawn according to first and second-order kinetic models, respectively.

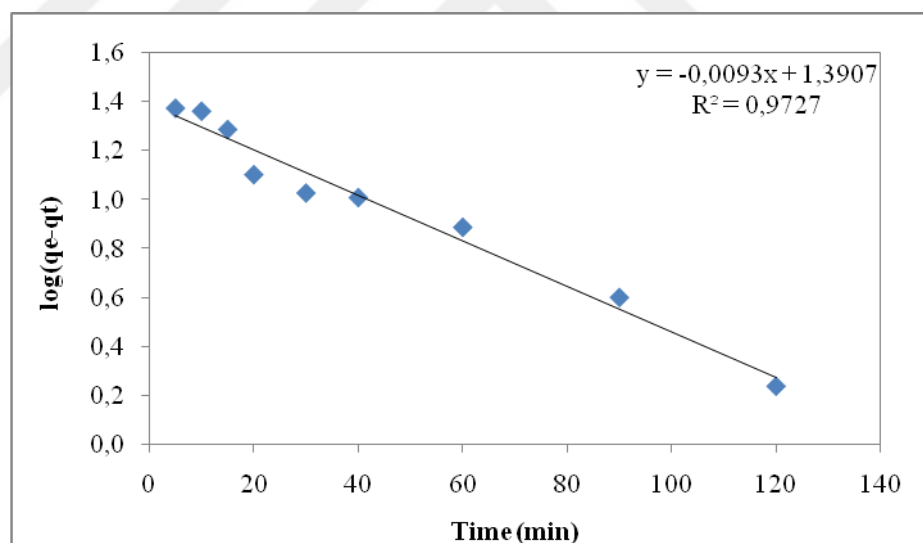


Figure 3.55: Evaluation of kinetic results using pseudo-first-order kinetic model for DMP using Diaion SP825

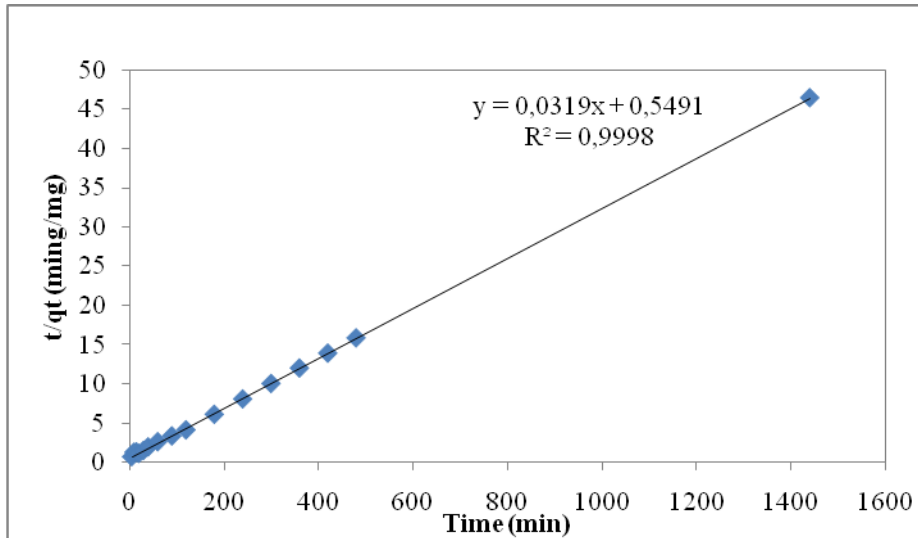


Figure 3.56: Evaluation of kinetic results using pseudo-second-order kinetic model for DMP using Diaion SP825

According to obtained results, figures show the linear lines that these kinetic models can be applied for DMP adsorption on the adsorbent. As seen in Table 3.18, the pseudo-second-order kinetic model is in accord with SP825 adsorbent for the adsorption of DMP.

Table 3.18: Evaluation of sorption kinetic data obtained using conventional kinetic modelling for Diaion SP825

Adsorbent amount (g/L)	First Order Kinetics			Second Order Kinetics		
	R^2	q_e (mg/g)	K_1 (g/mg.min)	R^2	q_e (mg/g)	K_2 (g/mg.min)
Diaion	0.9727	24.59	0.0214	0.9998	31.35	0.0018

Evaluation of kinetic data was also investigated for diffusional and reaction models. Figures 3.57 and 3.58 show the evaluation of kinetic data using unreacted core model (UCM) and using infinite solution volume model (ISV) for Diaion SP825 adsorbent.

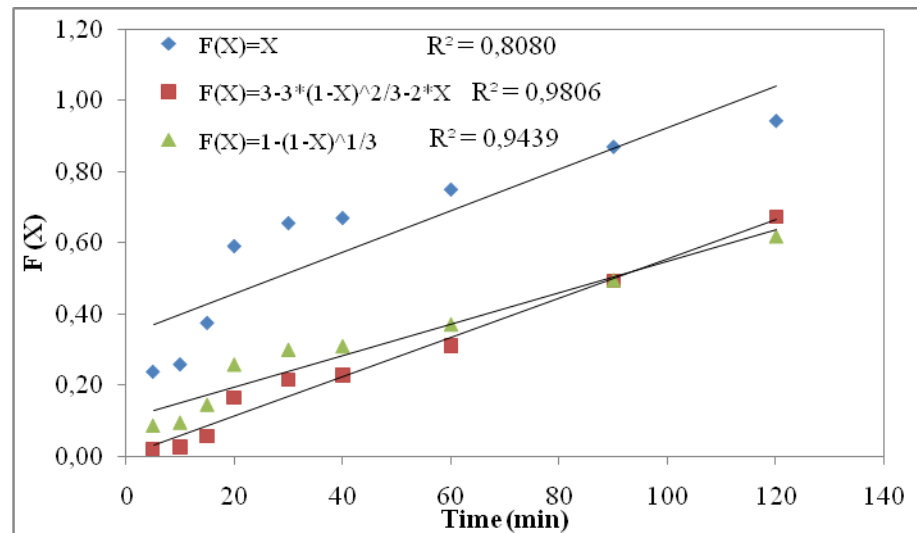


Figure 3.57: Evaluation of kinetic results using unreacted core model (UCM)

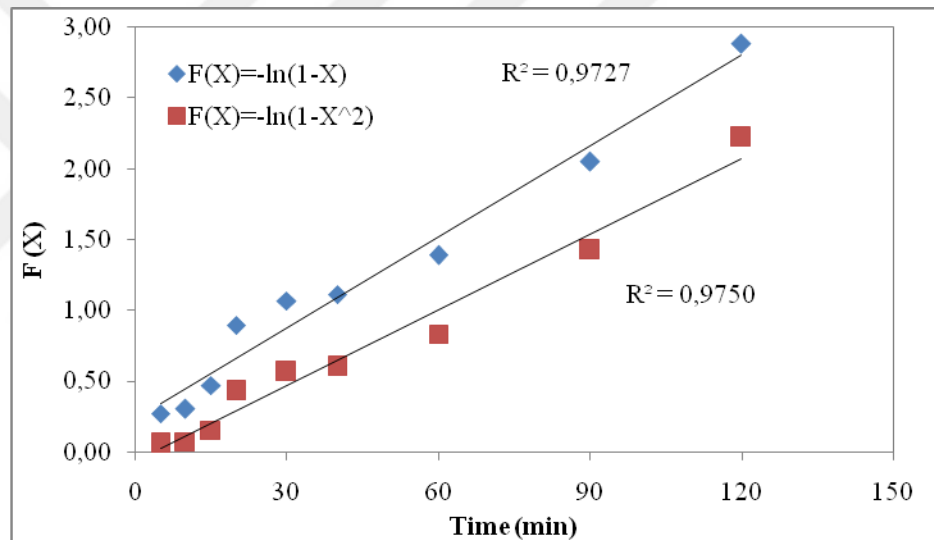


Figure 3.58: Evaluation of kinetic results using infinite solution volume model (ISV)

The linear correlation coefficients of kinetic data obtained were given in Table 3.19. According to results, the rate determining step is particle diffusion for ISV model and particle diffusion for UCM models for Diaion SP825 adsorbent.

Table 3.19: Evaluation of kinetic results obtained using diffusional and reaction models for Diaion SP825

R^2				
ISV		UCM		
$-\ln(1-X)$	$-\ln(1-X^2)$	X	$3-3(1-X)^{2/3}-2X$	$1-(1-X)^{1/3}$
0.9727	0.9750	0.8080	0.9806	0.9439

Figures 3.59-3.63 show the kinetic behavior of the Dowex L493 adsorbent for DMP removal. The graph of C/C_0 versus time was given in Figures 3.59.

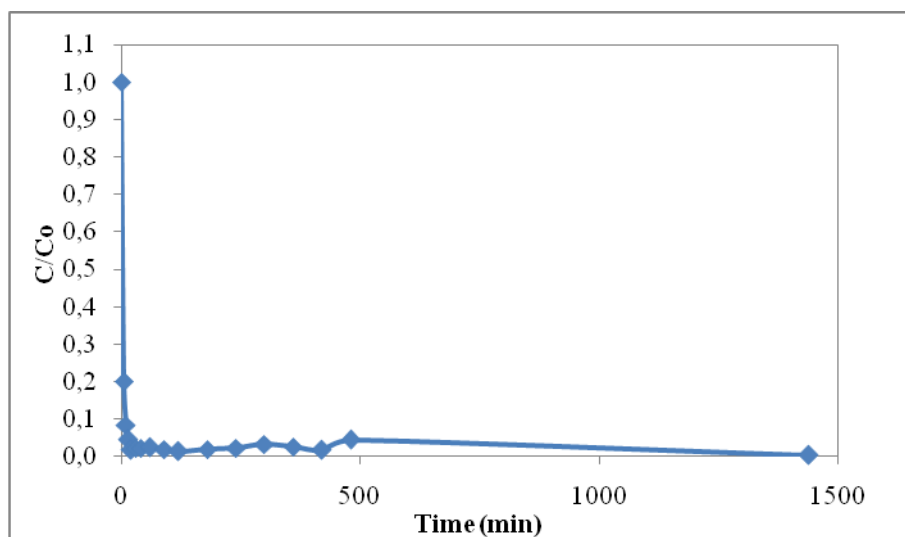


Figure 3.59: Ratio of concentration at any time to initial DMP concentration vs time for Dowex L493

Figures 3.60 and 3.61 were plotted using kinetic results for pseudo-first-order and pseudo-second-order kinetics models. The graphs of $\log(q_e - q_t)$ versus t and t/q_t versus t were drawn for both of kinetic models for DMP removal by Dowex L493.

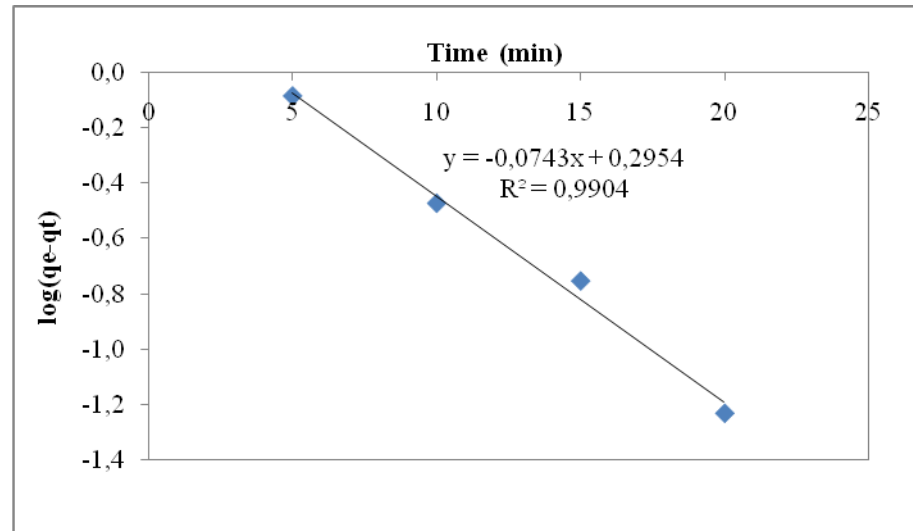


Figure 3.60: Evaluation of kinetic results of Dowex L493 using pseudo-first-order kinetic model

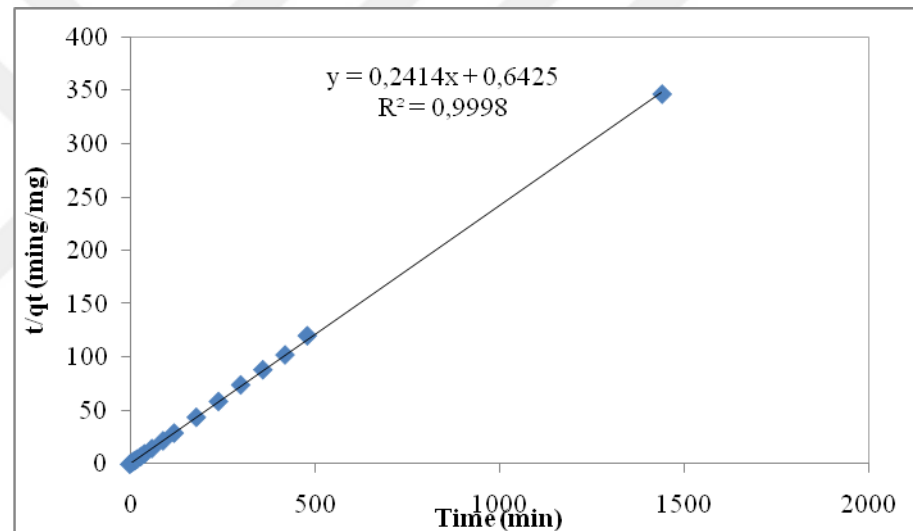


Figure 3.61: Evaluation of kinetic results of Dowex L493 using pseudo-second-order kinetic model

Since the correlation coefficient of pseudo-second-order kinetics (R^2) (Table 3.20) is better than pseudo-first-order kinetics, the adsorption of DMP by Dowex L493 adsorbent obeys the pseudo-second-order kinetic model. At the same time, q_e value of pseudo-second-order kinetic model is bigger than pseudo-first-order kinetics.

Table 3.20: Evaluation of sorption kinetic data obtained using conventional kinetic modeling for DowexL493

Adsorbent Amount (g/L)	First Order Kinetics			Second Order Kinetics		
	R^2	q_e (mg/g)	K_1 (g/mg.min)	R^2	q_e (mg/g)	K_2 (g/mg.min)
12	0.9904	1.97	0.1711	0.9998	4.14	0.0907

The kinetic results were also investigated for diffusional and reaction models. Figures 3.62 and 3.63 show the evaluation of kinetic data using unreacted core model (UCM) and using infinite solution volume model (ISV) for Dowex L493 adsorbent.

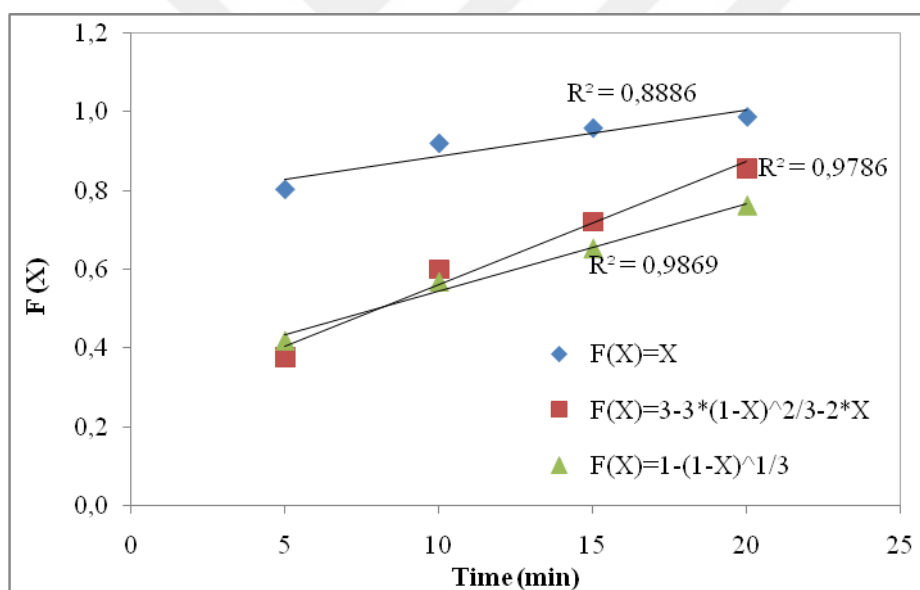


Figure 3.62: Evaluation of kinetic data using unreacted core model (UCM)

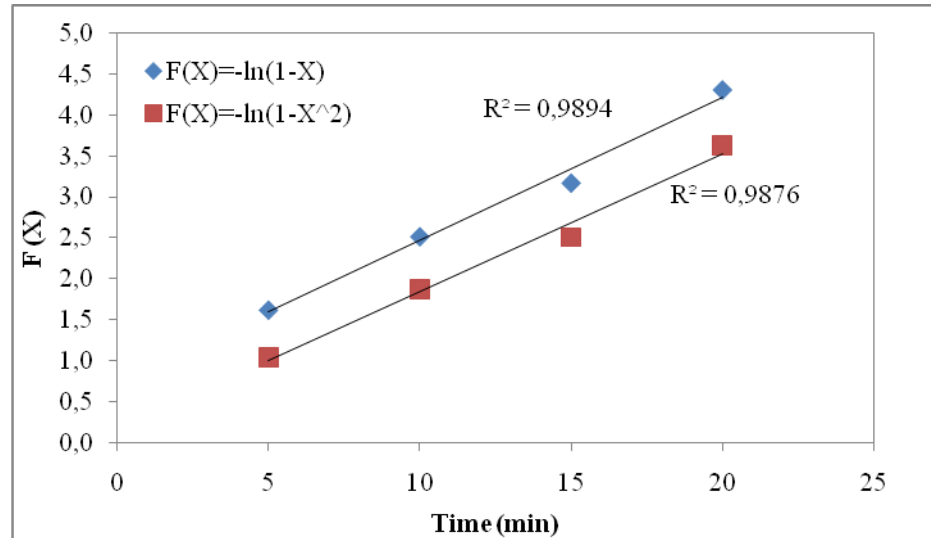


Figure 3.63: Evaluation of kinetic results using infinite solution volume model (ISV)

Table 3.21 gives the plots of $F(X)$ function versus time. According to Figures 3.62 and 3.63, the maximum correlation coefficients show that the rate is controlled with film diffusion and chemical reaction for Dowex L493 adsorbent, as they have greater linear correlation coefficients.

Table 3.21: Evaluation of kinetic results obtained using diffusional and reaction models for DowexL493

R^2				
ISV		UCM		
$-\ln(1-X)$	$-\ln(1-X^2)$	X	$3-3(1-X)^{2/3}-2X$	$1-(1-X)^{1/3}$
0.9894	0.9876	0.8886	0.9786	0.9869

3.6 Removal of DEP from Water

3.6.1. Batch tests

Figure 3.64 shows that for complete removal of DEP using Purolite PAD400 adsorbent, optimum adsorbent dosage is 0.04 g/50 mL.

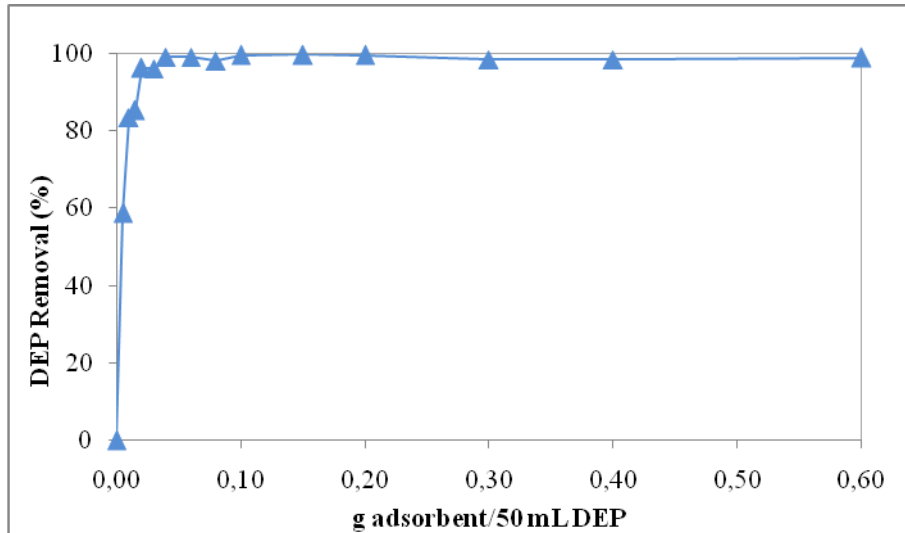


Figure 3.64: Batch study for DEP removal by PAD400 adsorbent

As seen in Figure 3.65, the removal of DEP by SP207, increased with the increase in the concentration of adsorbent in the solution until dosage of 0.04 g SP207 adsorbent /50 mL.

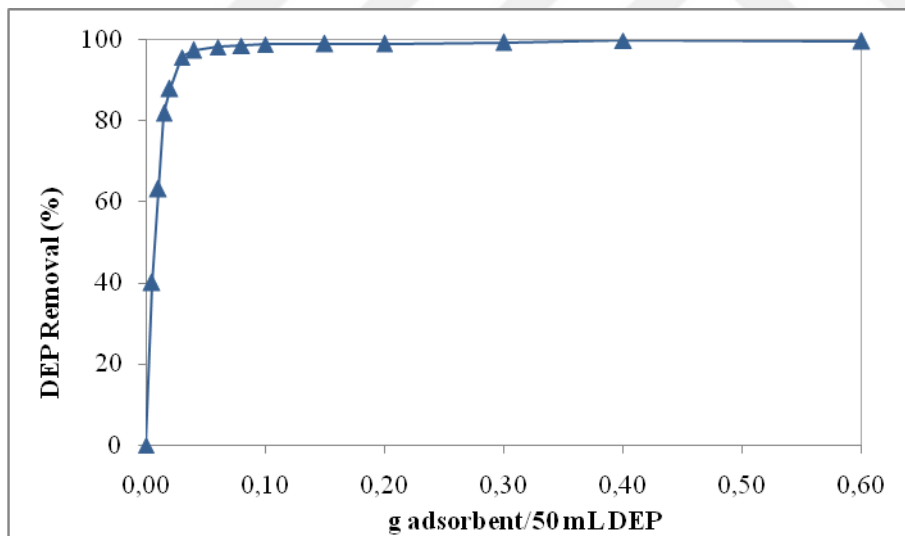


Figure 3.65: Batch study for DEP removal from water by SP207 (500-710 µm)

Removal of DEP using SP825 is shown in Figure 3.66. For DEP, 0.6 g/L was optimum amount of removal.

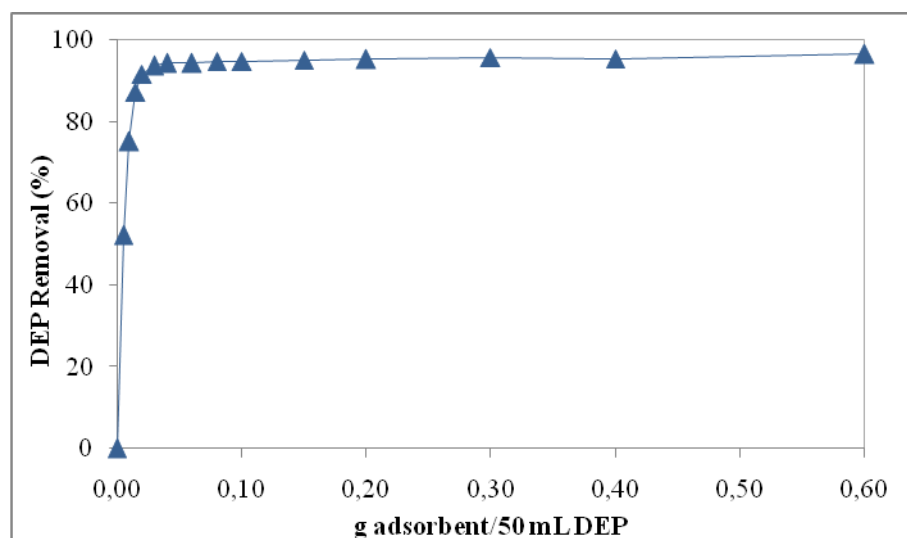


Figure 3.66: Batch study for DEP removal from water by SP825 (500-710 μm)

As seen in Figure 3.67, the best removal of DEP by Dowex L493 was found at an adsorbent concentration of 0.6 g/50 mL.

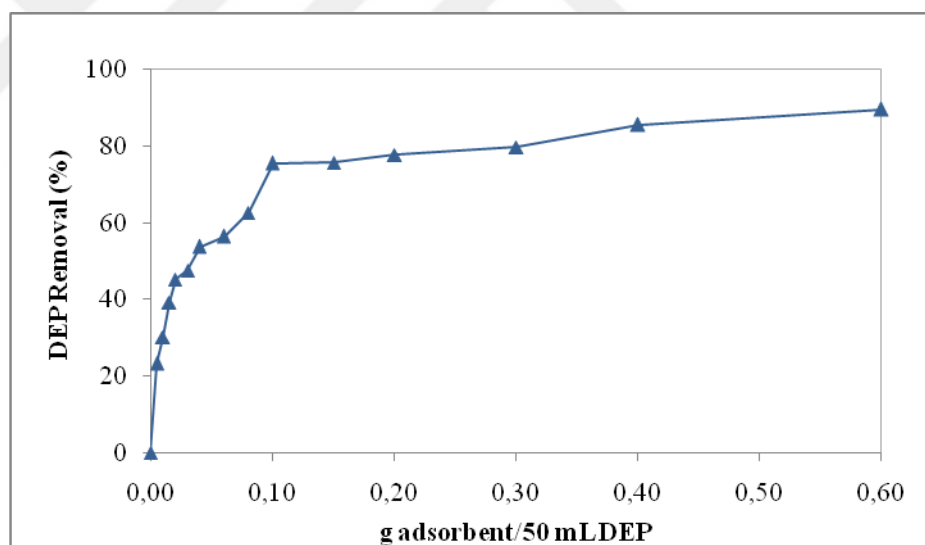


Figure 3.67: Batch study for DEP removal from water by Dowex L493

3.6.2. Isotherm tests for DEP

Adsorption of DEP was investigated using different kinds of adsorbent (Diaion SP207, Mitsubishi Chem, Diaion SP825, Mitsubishi Chem, Dowex L493, Dow Chem and PAD400, Purolite). The Langmuir, Freundlich and Temkin isotherms have been used to describe the adsorption of DEP onto the adsorbents.

Figures 3.68-3.71 were plotted using Purolite PAD400 adsorbent for Langmuir, Freundlich and Temkin isotherms.

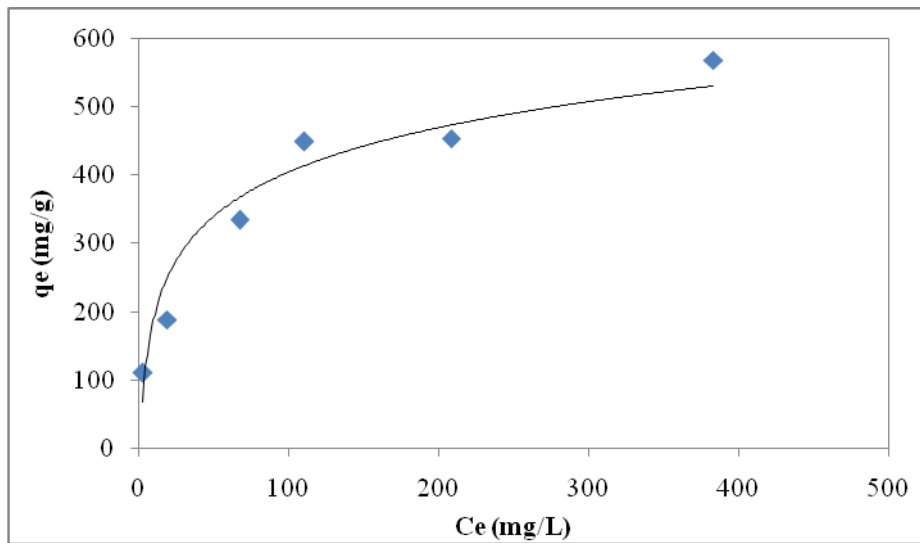


Figure 3.68: Adsorption isotherm of DEP by Purolite PAD400

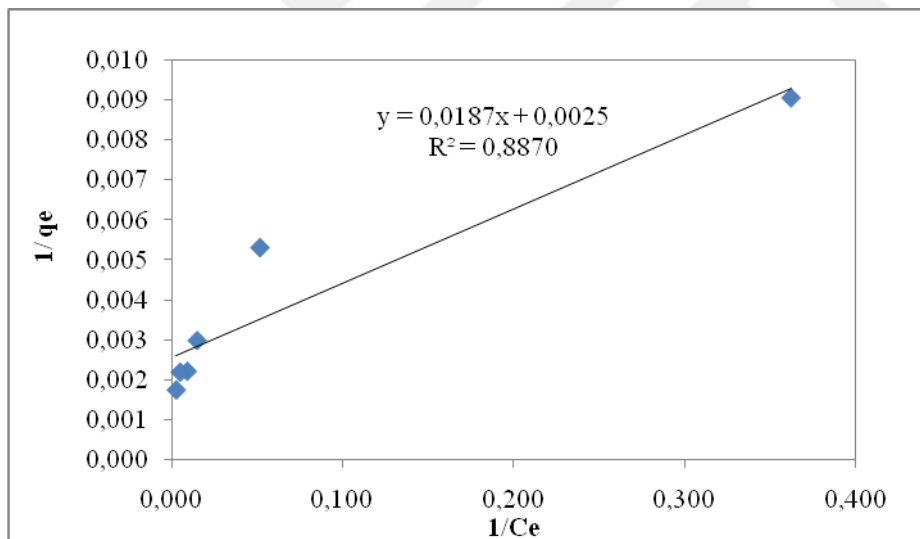


Figure 3.69: Linear form of Langmuir isotherm of DEP by Purolite PAD400

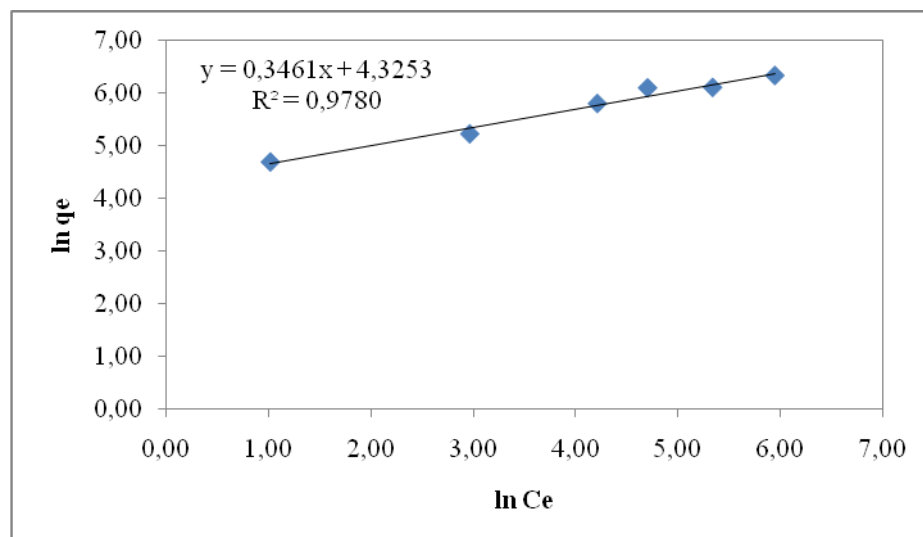


Figure 3.70: Linear form of Freundlich isotherm of DEP by Purolite PAD400

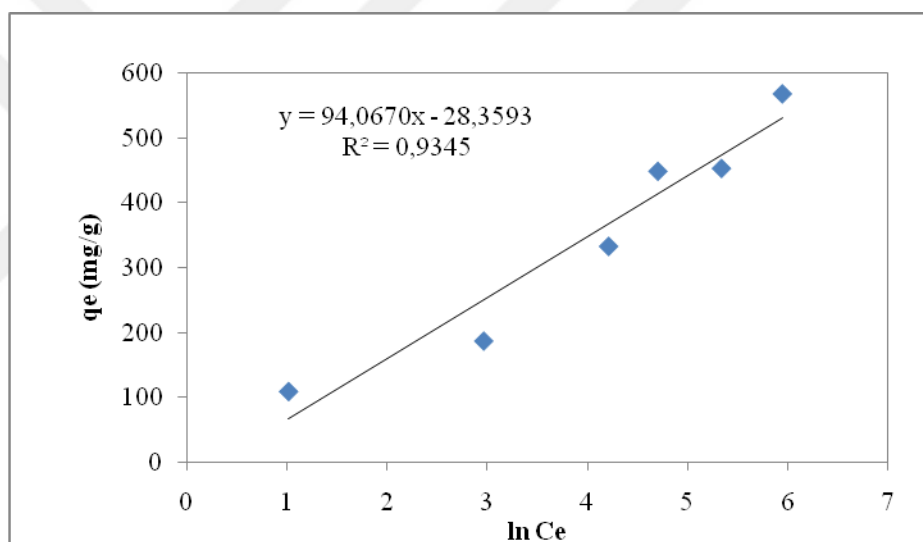


Figure 3.71: Temkin isotherm of DEP by PAD400 adsorbent

Table 3.22: Correlation coefficients and constants of isotherms for adsorption of DEP onto
Purolite PAD400

Adsorbent Isotherm		Purolite PAD400
Langmuir	R^2	0.8870
	q_m (mg/g)	400
	K_L (L/mg)	0.133
Freundlich	R^2	0.9780
	K_F (mg/g)	75.59
	N (g/L)	2.89
Temkin	R^2	0.9345
	b_T (J/mol)	94.06
	a_T (L/g)	0.74

Calculated Langmuir equilibrium constant, K_L , L/mg and the theoretical monolayer saturation capacity, q_m , mg/g, Freundlich constant K_F , mg/g, N g/L, Temkin constant, b_T , J/mol, equilibrium binding constant, a_T , (L/g) and correlation coefficients of isotherms, R^2 values are given in Table 3.22. The correlation coefficient of the Freundlich isotherm ($R^2 = 0.9780$) is higher than that obtained for Langmuir isotherm equation ($R^2 = 0.8870$) and Temkin isotherm ($R^2=0.345$) for DEP adsorption by PAD400 adsorbent. From those results, it was considered that adsorption data fit better to Freundlich isotherm to DEP adsorption by PAD400 adsorbent.

Figures 3.72-3.75 were plotted using Diaion SP207 adsorbent for Langmuir, Freundlich and Temkin isotherms.

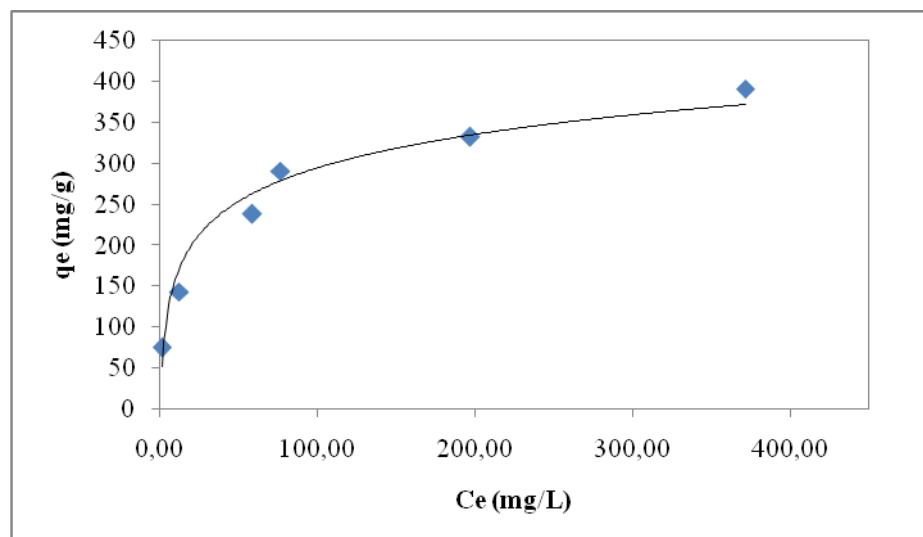


Figure 3.72: Adsorption isotherm of DEP by Diaion SP207

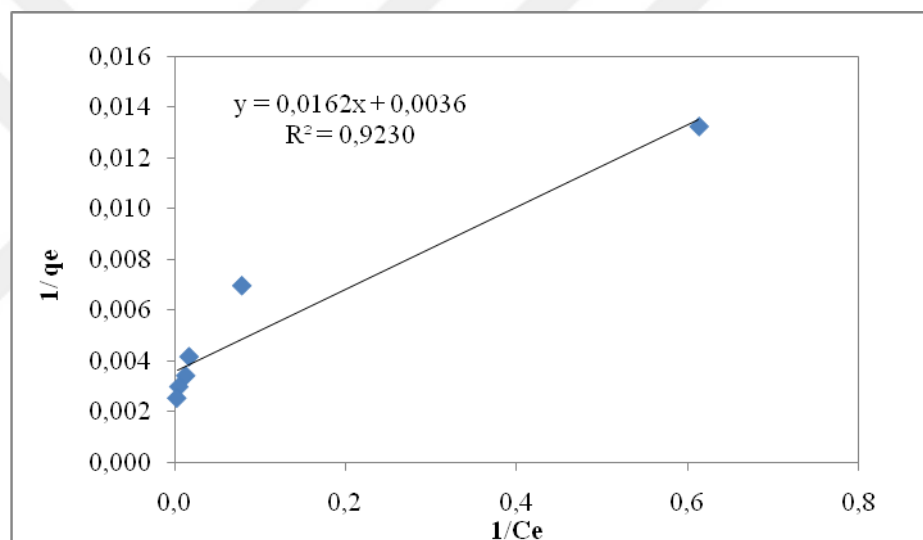


Figure 3.73: Linear form of Langmuir isotherm of DEP of Diaion SP207

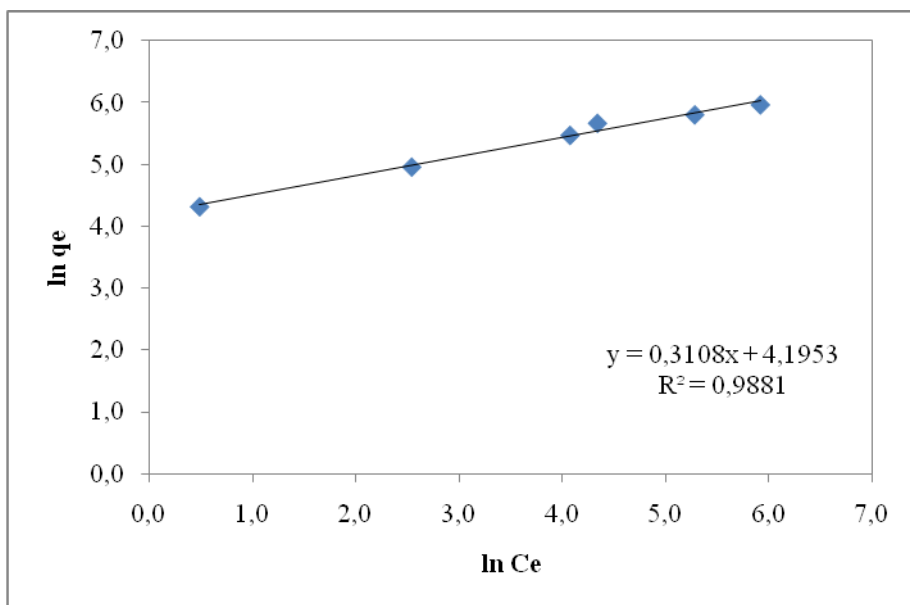


Figure 3.74: Linear form of Freundlich isotherm of DEP for Diaion SP207

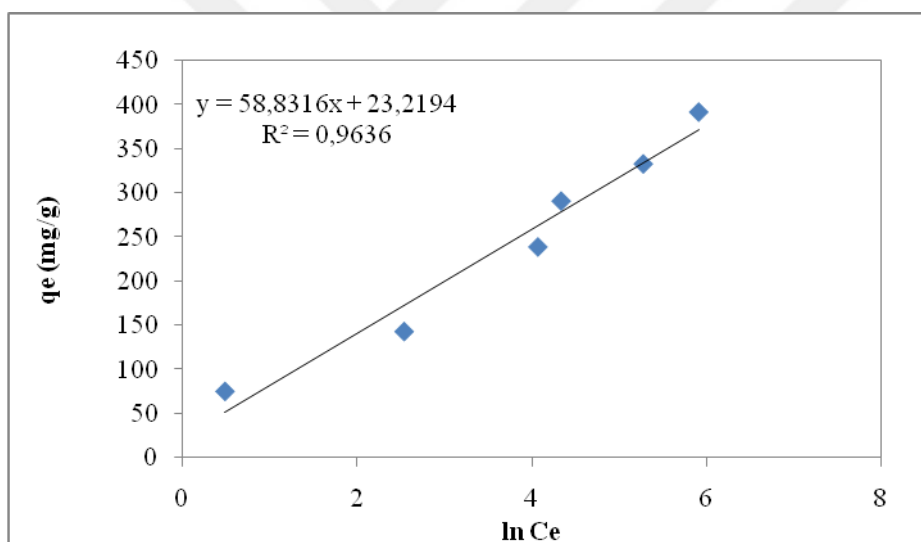


Figure 3.75: Temkin isotherm of DEP for Diaion SP207

Table 3.23: Correlation coefficients and constants of isotherms for adsorption of DEP onto Diaion SP207

Adsorbent Isotherm		Diaion SP207
Langmuir	R^2	0.9230
	$q_{\max}$ (mg/g)	278
	K_L (L/mg)	0.222
Freundlich	R^2	0.9881
	K_F (mg/g)	66.37
	N (g/L)	3.22
Temkin	R^2	0.9636
	B (J/mol)	58.83
	A_T (L/g)	1.48

The correlation coefficient of Freundlich isotherm ($R^2 = 0.9881$) is higher than those obtained for the Langmuir isotherm equation ($R^2 = 0.9230$) and Temkin isotherm ($R^2=0.9636$) for DEP adsorption by SP207 adsorbent. From that result, the adsorption data fit well to Freundlich isotherm for SP207 adsorbent.

Figures 3.76-3.79 were plotted using Diaion SP825 adsorbent for Langmuir, Freundlich and Temkin isotherms.

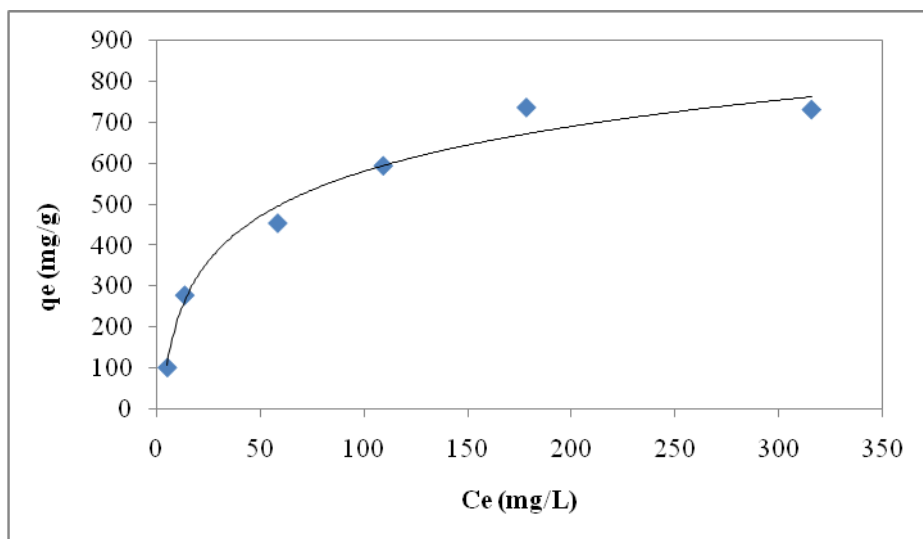


Figure 3.76: Adsorption isotherm of DEP for Diaion SP825

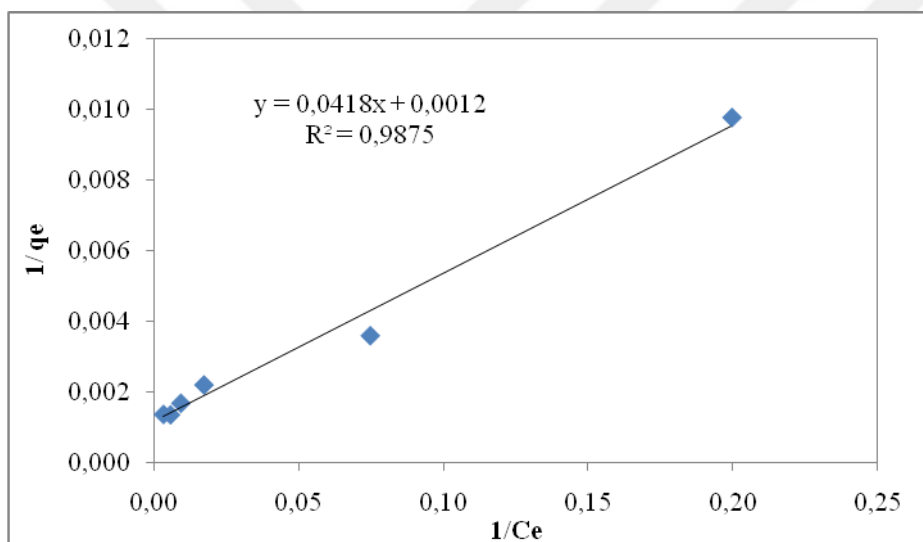


Figure 3.77: Linear form of Langmuir isotherm of DEP for Diaion SP825

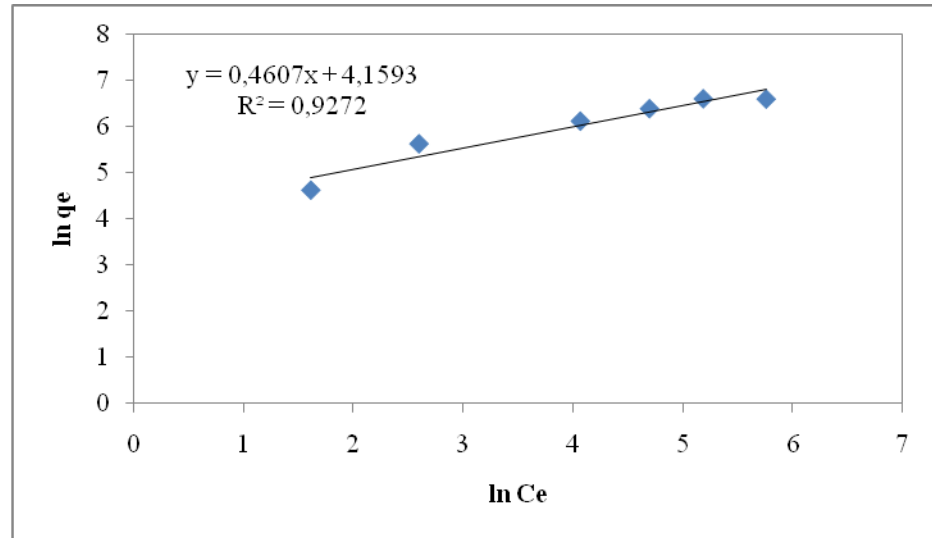


Figure 3.78: Linear form of Freundlich isotherm of DEP for Diaion SP825

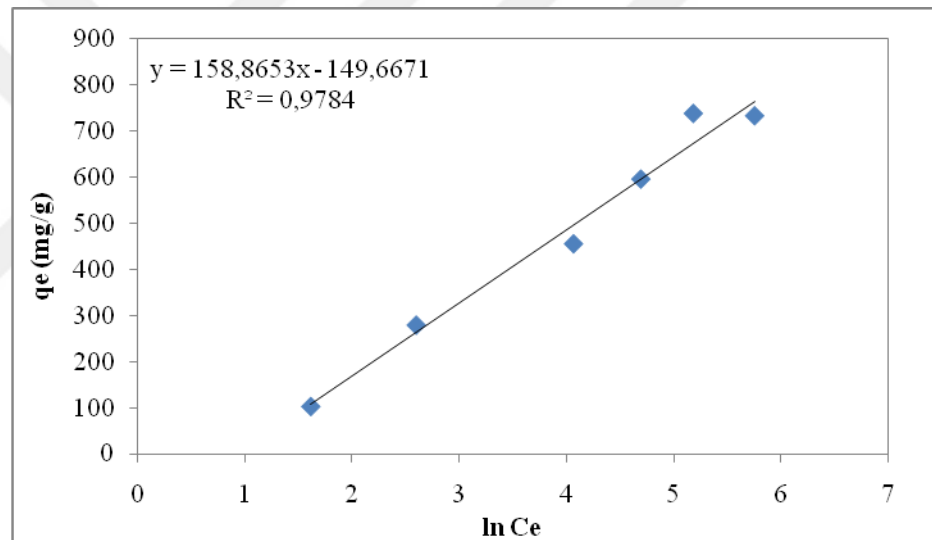


Figure 3.79: Temkin isotherm of DEP for Diaion SP825

The correlation coefficient of Langmuir isotherm equation ($R^2 = 0.9875$) is higher than that obtained for the Freundlich isotherm ($R^2 = 0.9272$) and Temkin isotherm ($R^2 = 0.9784$) for DEP adsorption onto SP825 adsorbent. From the adsorption data Langmuir isotherm can be considered to be better isotherm to explained adsorption data for DEP adsorption onto SP825 adsorbent.

Table 3.24: Correlation coefficients and constants of isotherms for adsorption of DEP onto Diaion SP825

Adsorbent		Diaion SP825
Isotherm		
Langmuir	R ²	0.9875
	q _m (mg/g)	833
	K _L (L/mg)	0.029
Freundlich	R ²	0.9272
	K _F (mg/g)	64.02
	N (g/L)	2.17
Temkin	R ²	0.9784
	b _T (J/mol)	158.86
	a _T (L/g)	0.39

Figures 3.80-3.83 were plotted using Dowex L493 adsorbent for Langmuir, Freundlich and Temkin isotherms.

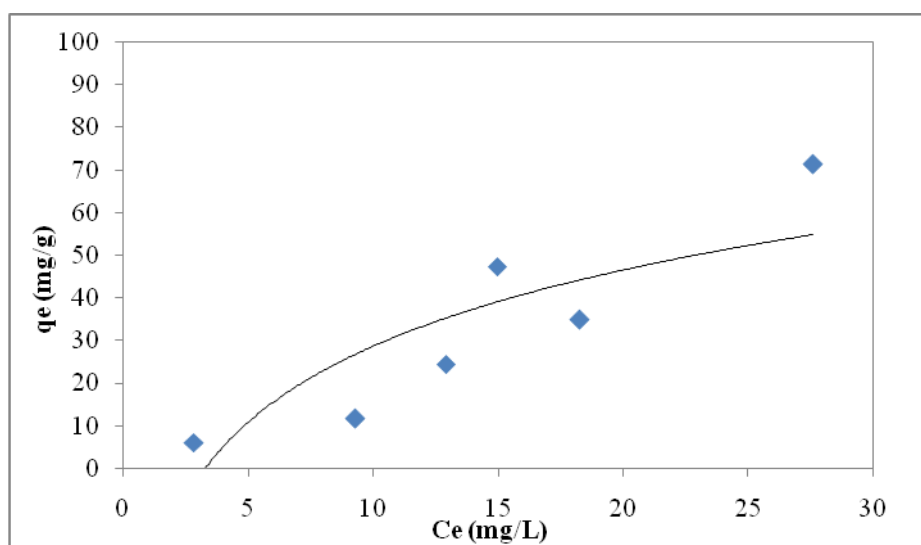


Figure 3.80: Adsorption isotherm of DEP for DowexL493

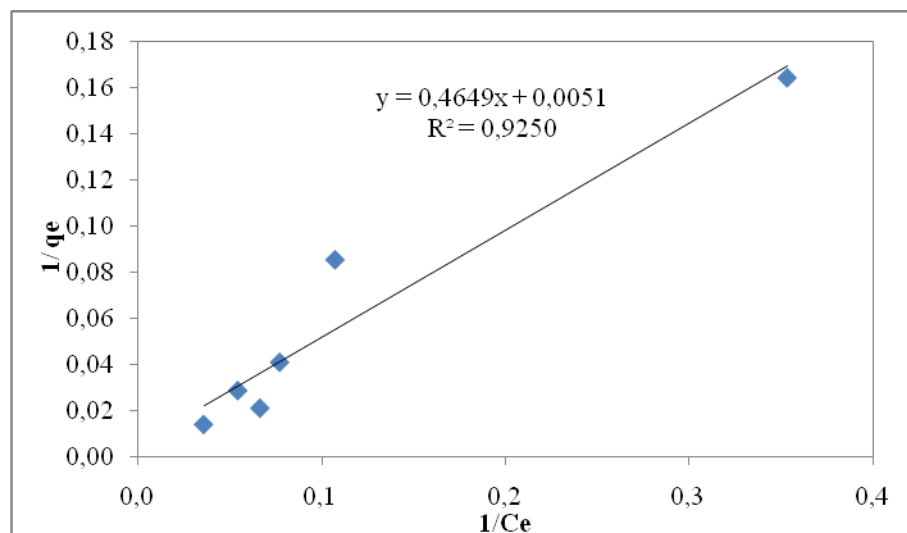


Figure 3.81: Linear form of Langmuir isotherm of DEP for Dowex L493

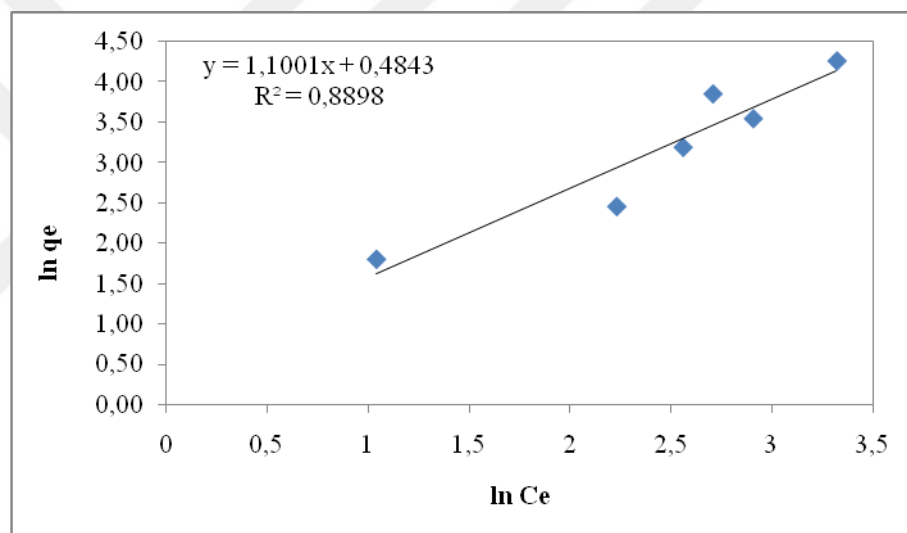


Figure 3.82: Linear form of Freundlich isotherm of DEP for Dowex L493

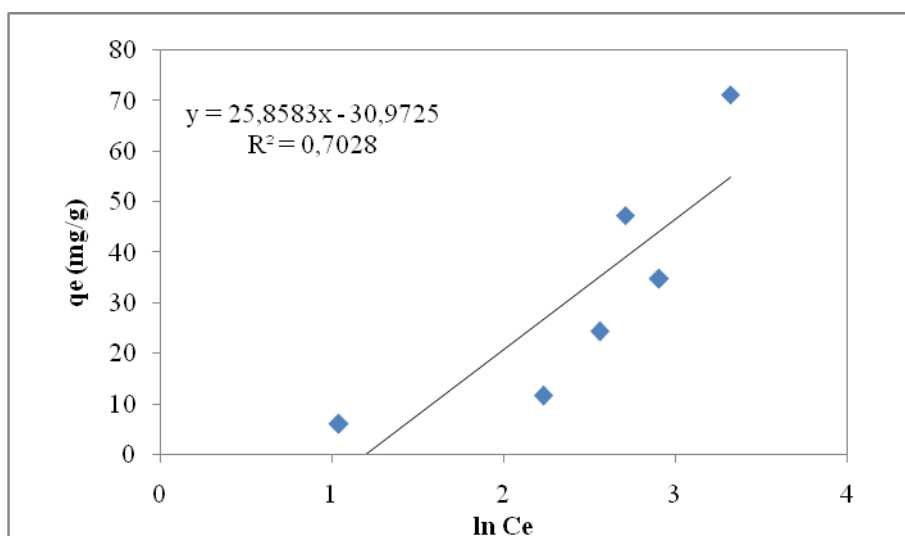


Figure 3.83: Temkin isotherm of DEP for Dowex L493

Table 3.25: Correlation coefficients and constants of isotherms for adsorption of DEP onto Dowex L493

Adsorbent		Dowex L493
Isotherm		
	Langmuir	R^2
		0.9250
		q_m (mg/g)
		196
		K_L (L/mg)
		0.011
	Freundlich	R^2
		0.8898
		K_F (mg/g)
		1.62
		N (g/L)
		0.91
Temkin	R^2	0.7028
		b_T (J/mol)
		25.86
	a_T (L/g)	0.30

Calculated Langmuir equilibrium constant, K_L , L/mg and the theoretical monolayer saturation capacity, q_m , mg/g, Freundlich constant K_F , mg/g, N g/L, Temkin constant, b_T , J/mol, equilibrium binding constant, a_T , (L/g) and correlation

coefficients of isotherms, R^2 values are given in Table 3.25. The correlation coefficient of Langmuir isotherm ($R^2 = 0.9250$) is higher than that obtained for Freundlich isotherm ($R^2 = 0.8898$) and Temkin isotherm ($R^2 = 0.7028$) for DEP adsorption onto Dowex L493 adsorbent. From the obtained results, Langmuir adsorption model is considered to be more suitable model for DEP adsorption by Dowex L493 adsorbent.

3.6.3. Kinetic tests for DEP

Figures 3.84-3.88 show the kinetic behavior of the PAD400 adsorbent at a particle size range of 0,355-0,500 mm for DEP removal. The graphs of the ratio of DEP concentration at any time to initial DEP concentration versus time was given in Figures 3.84.

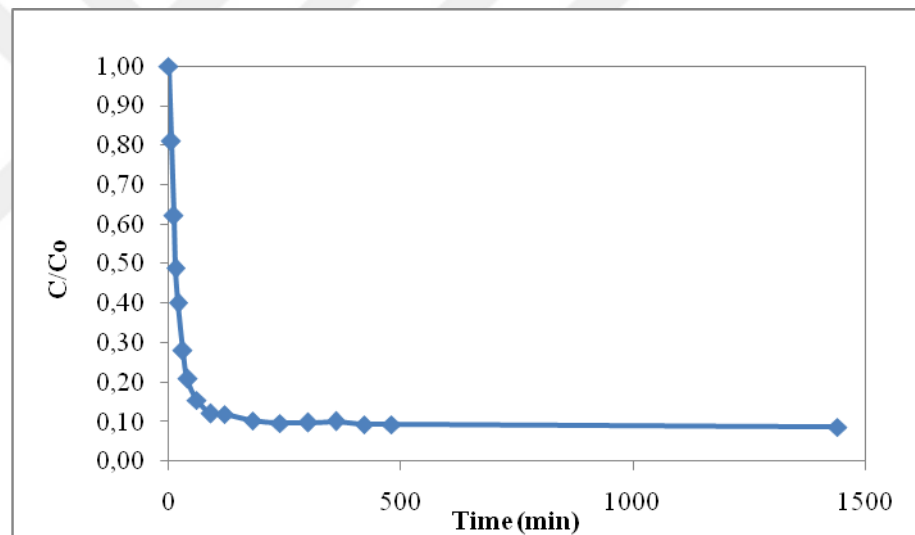


Figure 3.84: Ratio of DEP concentration at any time to initial DEP concentration vs time for Purolite PAD400

The kinetic data were evaluated with pseudo-first-order and pseudo-second-order kinetics models (Figures 3.85 and 3.86). The graphs of first-order and second-order kinetic models, respectively, are given for PAD 400 to determine the correlation coefficients. Since the correlation coefficient and q_e value of pseudo-second-order kinetics (Table 3.26) is higher according to pseudo-first-order kinetics, it can be said that the adsorption of DEP by PAD400 adsorbent obeys the pseudo-second-order kinetic model.

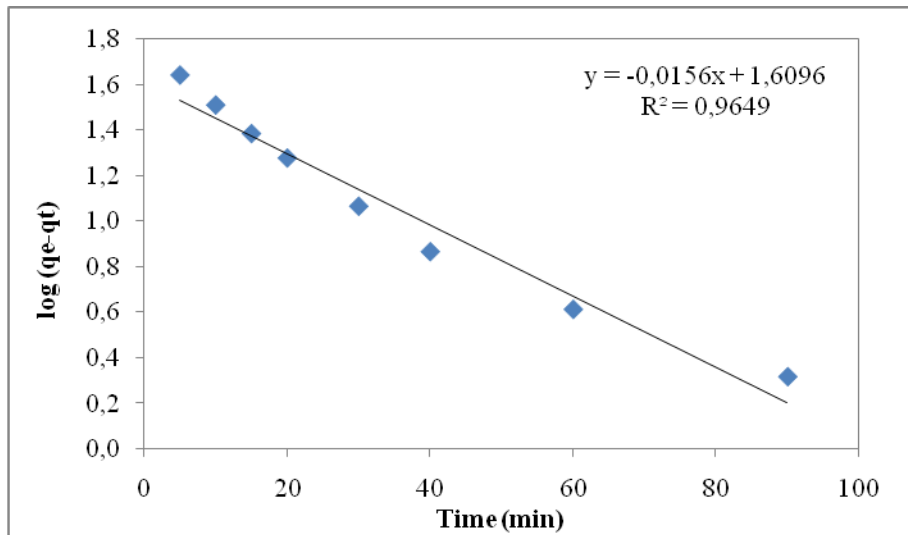


Figure 3.85: Evaluation of kinetic results using pseudo-first-order kinetic model using Purolite PAD400

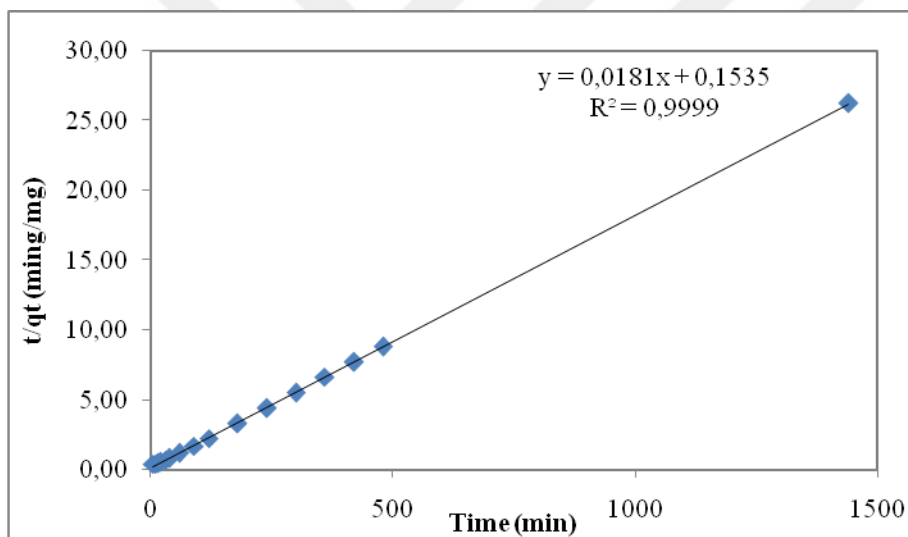


Figure 3.86: Evaluation of kinetic results using pseudo-second-order kinetic model using Purolite PAD400

Table 3.26: Evaluation of kinetic results obtained using conventional kinetic modelling for Purolite PAD400

Adsorbent amount (g/L)	First Order Kinetics			Second Order Kinetics		
	R ²	q _e	K ₁	R ²	q _e	K ₂
		(mg/g)	(g/mg.min)		(mg/g)	(g/mg.min)
0.80	0.9649	40.70	0.0359	0.9999	55.25	0.0021

Figures 3.87 and 3.88 show the evaluation of kinetic data using unreacted core model (UCM) and using infinite solution volume model (ISV) for Purolite PAD400 adsorbent.

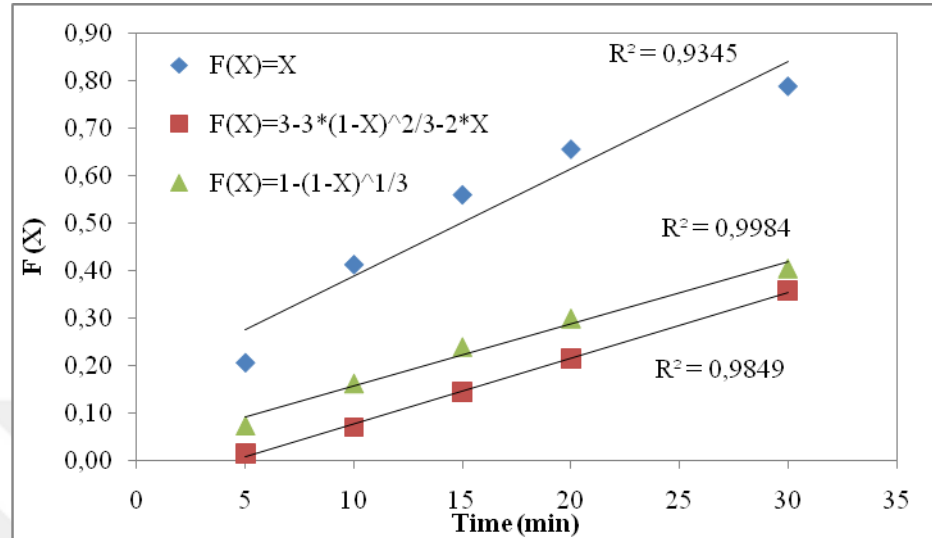


Figure 3.87: Evaluation of kinetic results using unreacted core model (UCM)

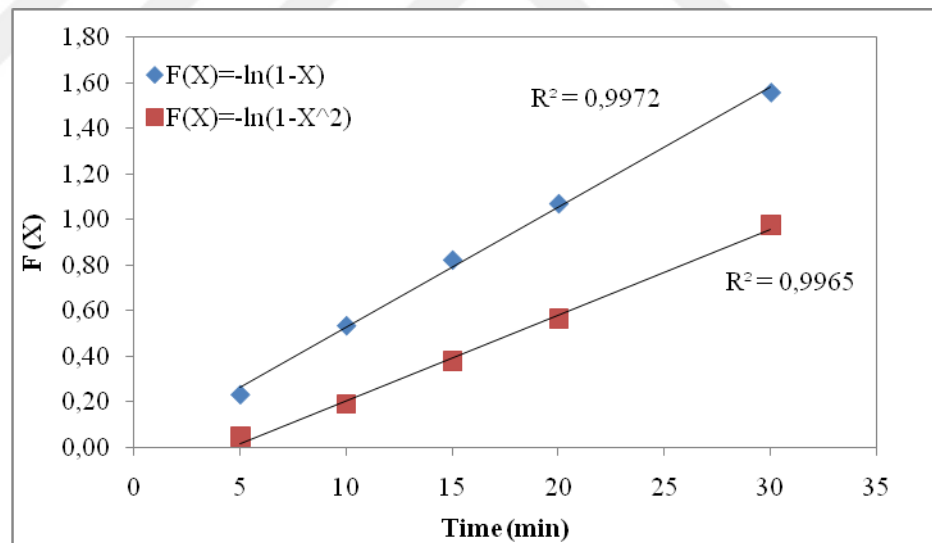


Figure 3.88: Evaluation of kinetic results using infinite solution volume model (ISV)

Table 3.27 shows the plot of $F(X)$ function versus time. Figures 3.87 and 3.88 give linear correlation coefficients. These values show that the rate controlling step is film diffusion according to ISV models and particle diffusion according to UCM models for PAD400 adsorbent, as they have greater linear correlation coefficients.

Table 3.27: Evaluation of kinetic results obtained using diffusional and reaction models for Purolite PAD400

R^2				
ISV		UCM		
$-\ln(1-X)$	$-\ln(1-X^2)$	X	$3-3(1-X)^{2/3}-2X$	$1-(1-X)^{1/3}$
0.9972	0.9965	0.9345	0.9984	0.9849

Figures 3.89-3.93 show the kinetic behavior of the Diaion SP207 adsorbent for DEP removal. The ratio of DEP concentration at any time to initial DEP concentration versus time was given in Figures 3.89.

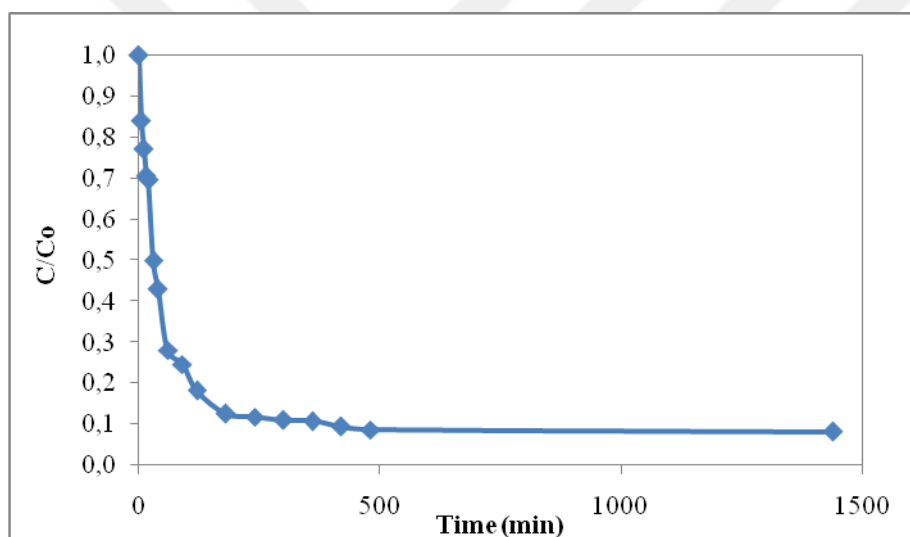


Figure 3.89: Ratio of concentration at any time to initial DEP concentration vs time for Diaion SP207

The kinetic results were investigated for pseudo-first-order and pseudo-second-order kinetics models for SP207 adsorbent (Figures 3.90 and 3.91). The graphs of $\log(q_e - q_t)$ versus t and t/q_t versus t were plotted for first-order and second-order kinetic models, respectively, for both of the experiments done using SP207 adsorbent for DEP removal to determine the correlation coefficients.

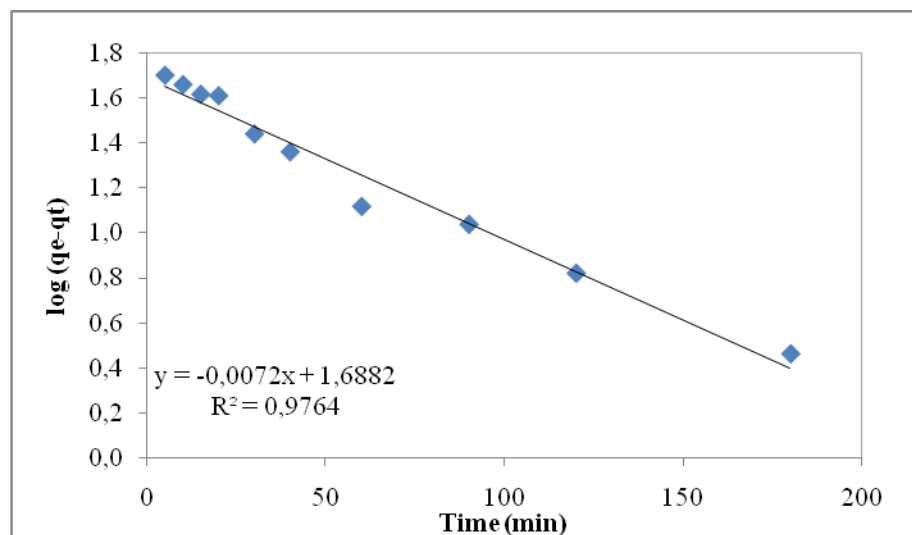


Figure 3.90: Evaluation of kinetic results using pseudo-first-order kinetic model using for Diaion SP207

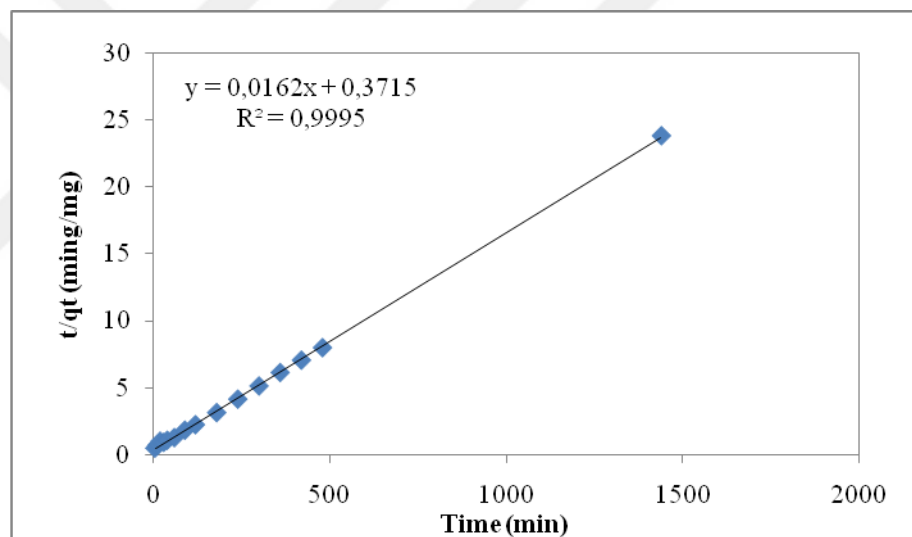


Figure 3.91: Evaluation of kinetic results using pseudo-second-order kinetic model for DEP using for Diaion SP207

Pseudo-first-order or pseudo-second-order kinetic equations are suitable for DEP adsorption on the adsorbent. Since the correlation coefficient of pseudo-second-order kinetics (R^2) (Table 3.28) is greater than pseudo-first-order kinetics, it can be concluded that the adsorption of DEP obeys the pseudo-second-order kinetic model.

Table 3.28: Evaluation of kinetic results obtained using conventional kinetic modeling for SP207

Adsorbent amount (g/L)	First Order Kinetics			Second Order Kinetics		
	R^2	q_e (mg/g)	K_1 (g/mg.min)	R^2	q_e (mg/g)	K_2 (g/mg.min)
0.80	0.9764	48.77	0.0166	0.9995	61.73	0.0007

The kinetic data were plotted for diffusional and reaction models. Figures 3.92 and 3.93 show the evaluation of kinetic data using unreacted core model (UCM) and using infinite solution volume model (ISV) for SP207 adsorbent.

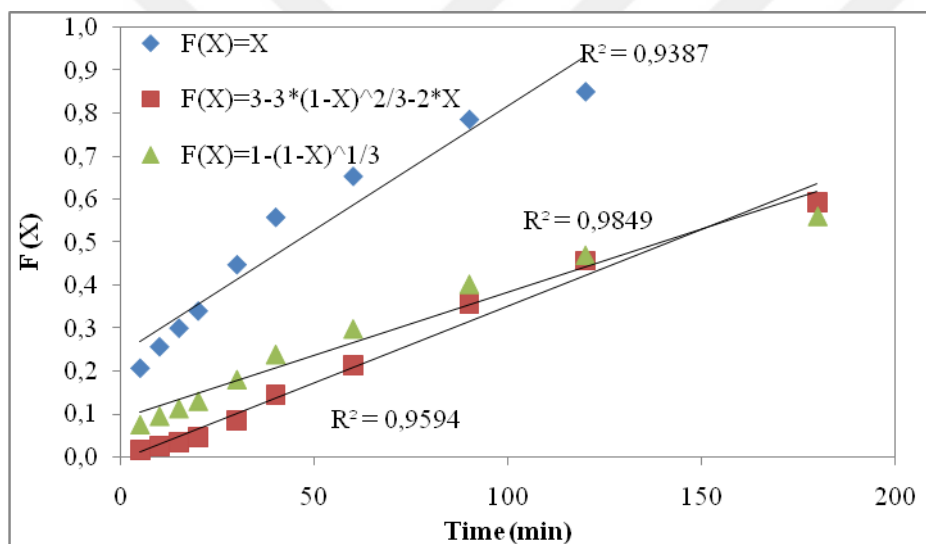


Figure 3.92: Evaluation of kinetic results using unreacted core model (UCM)

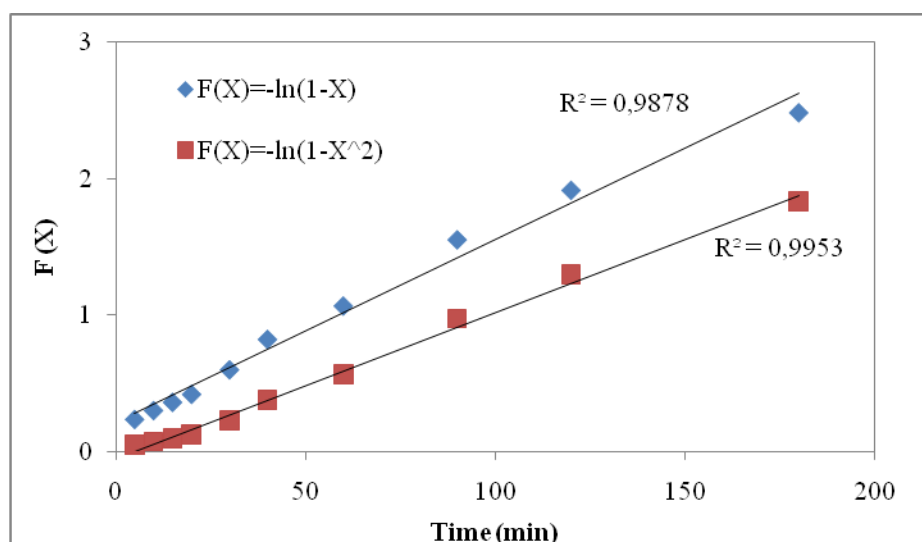


Figure 3.93: Evaluation of kinetic results using infinite solution volume model (ISV)

As seen in Figures 3.92 and 3.93, for linear models rate control step of kinetic is particle diffusion with regard to ISV models and particle diffusion according to UCM models for 0.8 g/L SP207 adsorbent concentration, as they have greater linear correlation coefficients (Table 3.29).

Table 3.29: Evaluation of kinetic results obtained using diffusional and reaction models for Diaion SP207

R^2				
ISV		UCM		
$-\ln(1-X)$	$-\ln(1-X^2)$	X	$3-3(1-X)^{2/3}-2X$	$1-(1-X)^{1/3}$
0.9878	0.9953	0.9387	0.9849	0.9594

Figures 3.94-3.98 show the kinetic behavior of the SP 825 for DEP removal. The ratio of DEP concentration at any time to initial DEP concentration versus time were given in Figures 3.94.

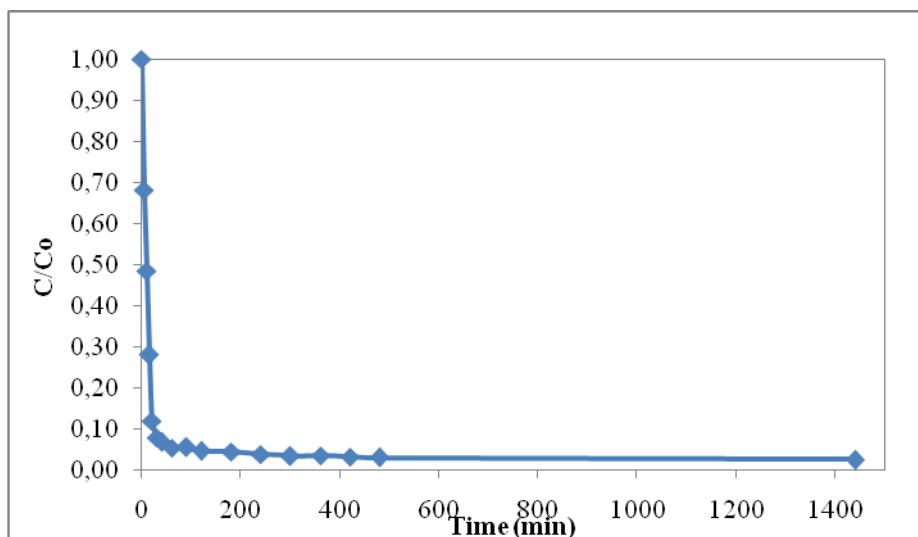


Figure 3.94: Ratio of concentration at any time to initial DEP concentration for Diaion SP825

Results were plotted with first and second-order kinetics (Figures 3.95 and 3.96). The graphs of first and second-order kinetic were drawn, for both of experiments done using SP825 for DEP removal to determine the correlation coefficients.

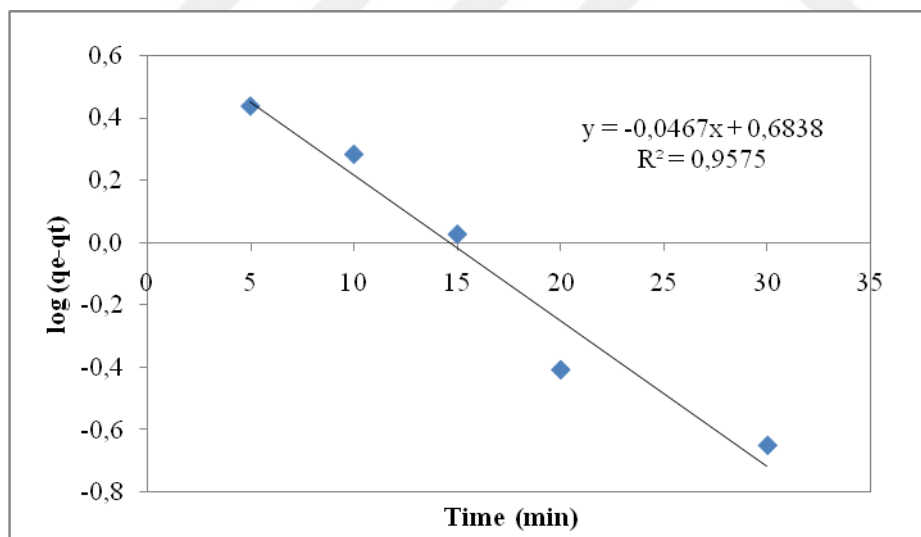


Figure 3.95: Evaluation of kinetic results using pseudo-first-order kinetic model of DEP for Diaion SP825

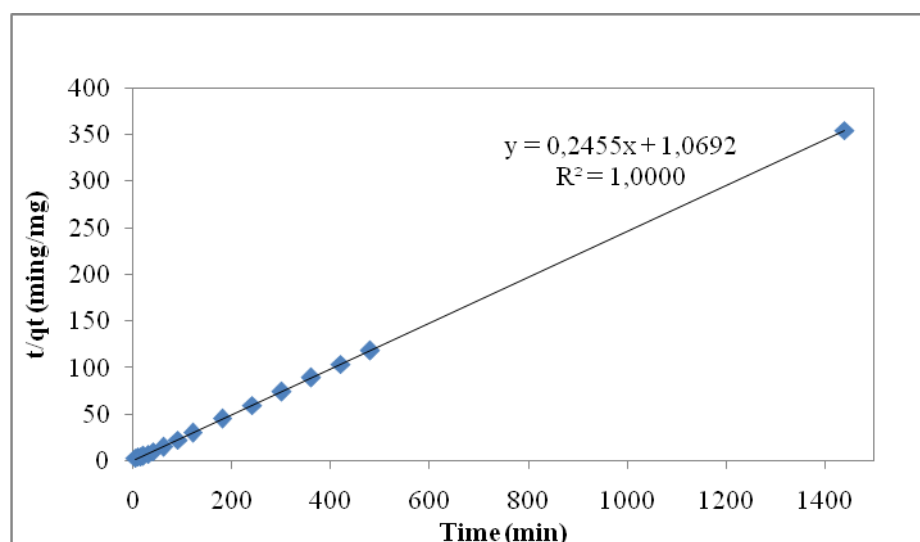


Figure 3.96: Evaluation of kinetic results using pseudo-second-order kinetic model for DEP using Diaion SP825

The correlation coefficient and q_e value of pseudo-second-order kinetics (R^2) (Table 3.30) is greater than pseudo-first-order kinetics. It was concluded that the adsorption of DEP by Diaion SP825 adsorbent obeys second order kinetic model.

Table 3.30: Evaluation of kinetic results obtained using conventional kinetic modelling for SP825

Adsorbent amount (g/L)	First Order Kinetics			Second Order Kinetics		
	R^2	q_e (mg/g)	K_1 (g/mg.min)	R^2	q_e (mg/g)	K_2 (g/mg.min)
12	0.9575	4.83	0.1075	1.0000	4.07	0.0564

The kinetic results were utilized with diffusional and reaction models. Figures 3.97 and 3.98 show the evaluation of kinetic data using unreacted core model (UCM) and using infinite solution volume model (ISV) for Diaion SP825 adsorbent.

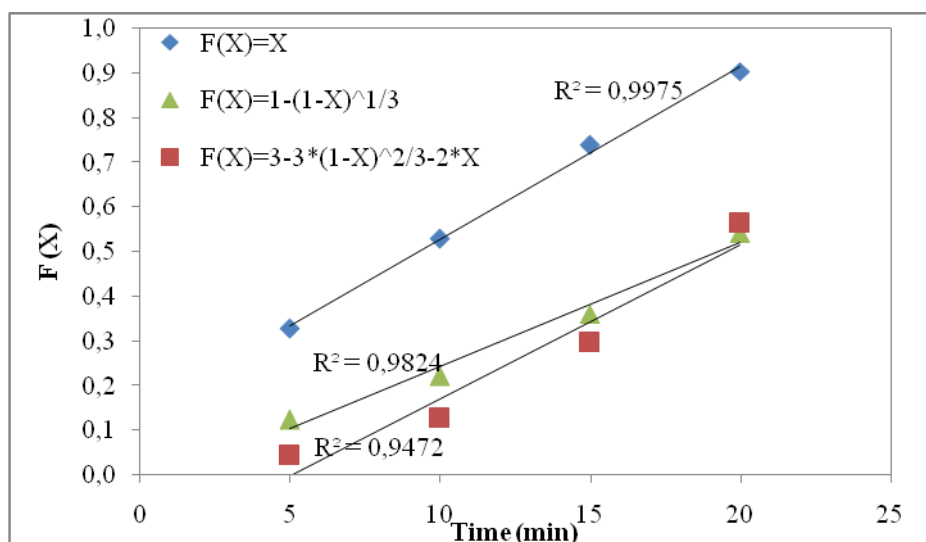


Figure 3.97: Evaluation of kinetic results using unreacted core model (UCM)

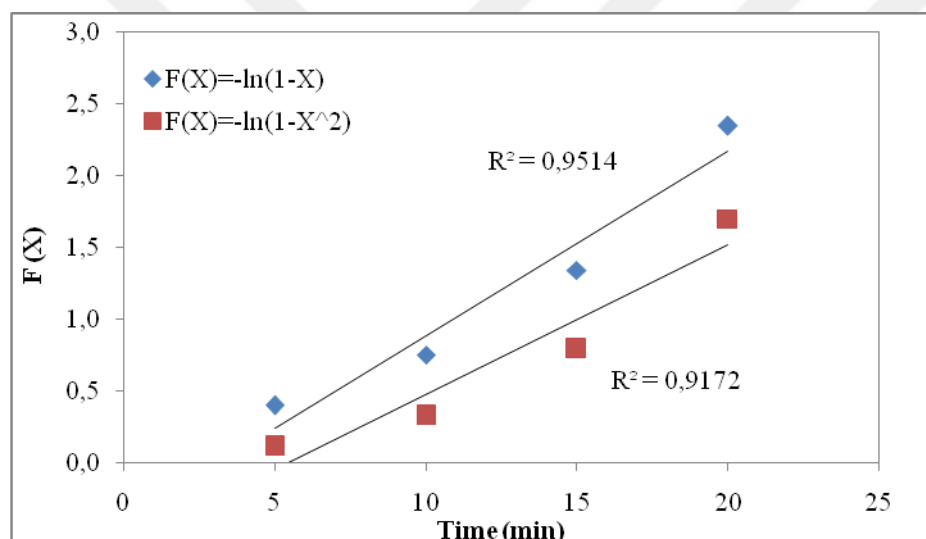


Figure 3.98: Evaluation of kinetic results using infinite solution volume model (ISV)

Table 3.31 gives the linear correlation coefficients obtained from the plots of $F(X)$ function versus time. Film diffusion model in ISV model is determined as a rate step and liquid film is for UCM models for 12 g/L Diaion SP825 adsorbent concentration, as they have greater linear correlation coefficients.

Table 3.31: Evaluation of kinetic results obtained using diffusional and reaction models for Diaion SP825

R^2				
ISV		UCM		
$-\ln(1-X)$	$-\ln(1-X^2)$	X	$3-3(1-X)^{2/3}-2X$	$1-(1-X)^{1/3}$
0.9514	0.9172	0.9975	0.9472	0.9824

Figures 3.99-3.103 show the kinetic behavior of the Dowex L493 adsorbent for DEP removal. The graph of the ratio of DEP concentration at any time to initial DEP concentration versus time was given in Figures 3.99.

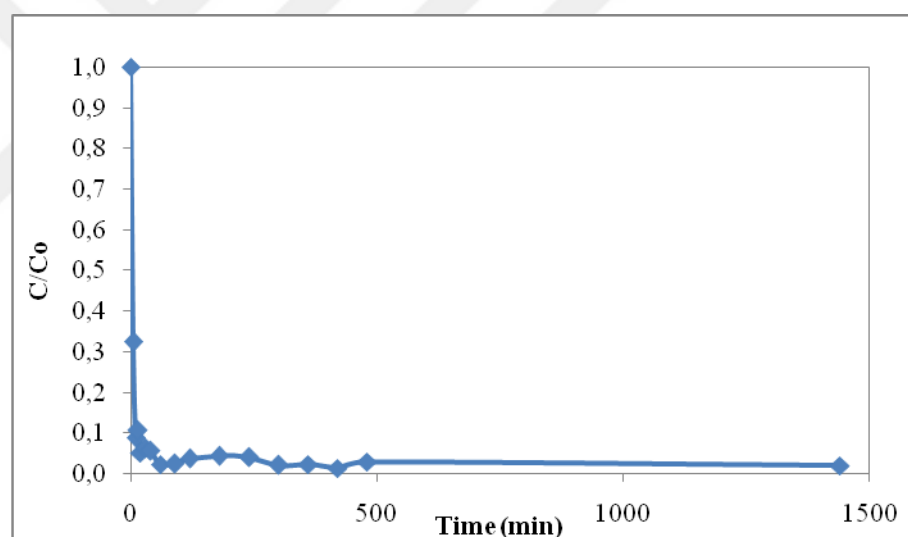


Figure 3.99: Ratio of concentration at any time to initial DEP concentration vs time for Dowex L493

The kinetic results were considered for pseudo-first-order and pseudo-second-order kinetics models (Figures 3.100 and 3.101). The graphs of $\log(q_e - q_t)$ versus t and t/q_t versus t were plotted for first-order and second-order kinetic models, respectively, for both of the experiments done using Dowex L493 adsorbent for DMP removal to determine the correlation coefficients.

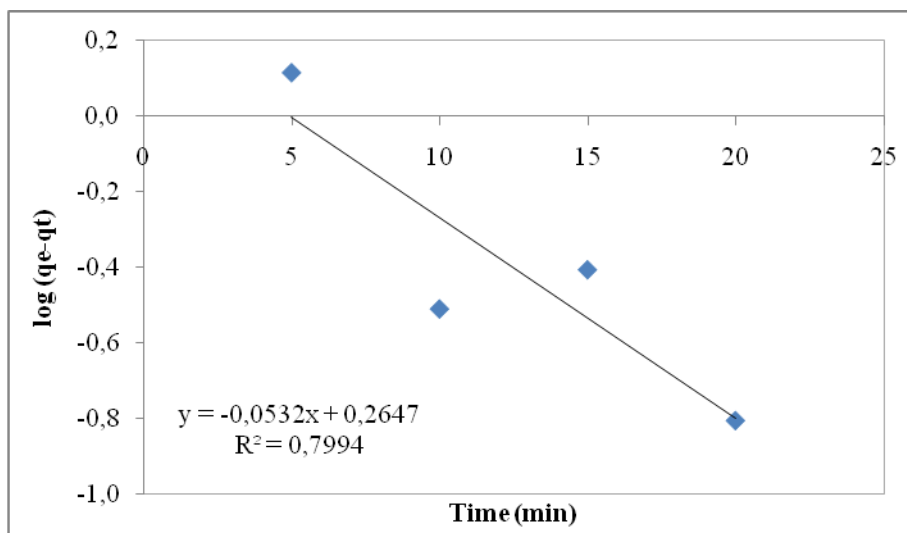


Figure 3.100: Evaluation of kinetic results using pseudo-first-order kinetic model using DowexL493

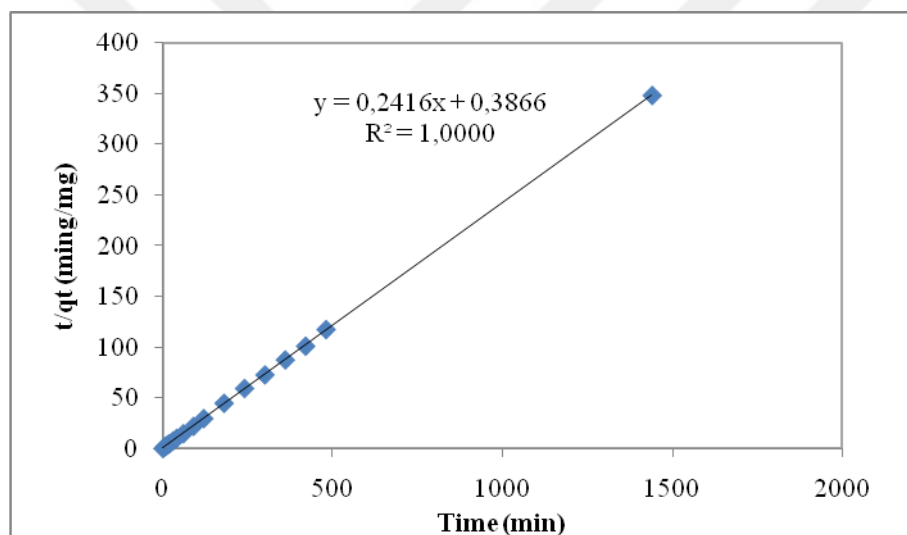


Figure 3.101: Evaluation of kinetic results using pseudo-second-order kinetic model using DowexL493

The correlation coefficient of pseudo-second-order kinetics (R^2) (Table 3.32) is greater than pseudo-first-order kinetics, the adsorption of DMP by Dowex L493 adsorbent obeys the pseudo-second-order kinetic model can be said.

Table 3.32: Evaluation of kinetic results obtained using conventional kinetic modelling for DowexL493

Adsorbent amount (g/L)	First Order Kinetics			Second Order Kinetics		
	R^2	q_e (mg/g)	K_1 (g/mg.min)	R^2	q_e (mg/g)	K_2 (g/mg.min)
12	0.7994	1.84	0.1225	1.0000	4.14	0.1598

The kinetic studies were also considered for diffusional and reaction models. Figures 3.102 and 3.103 show the evaluation of kinetic data using unreacted core model (UCM) and using infinite solution volume model (ISV) for DowexL493 adsorbent.

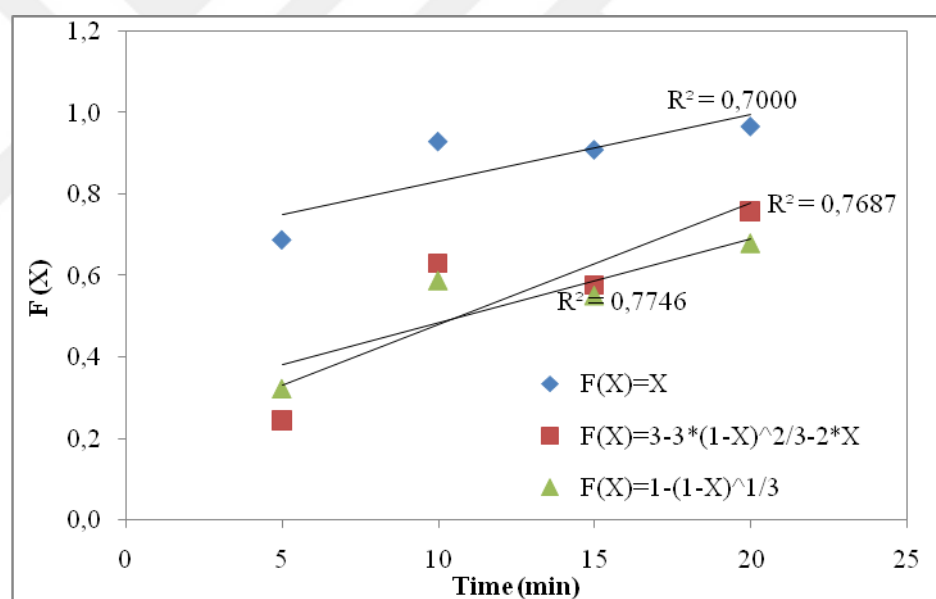


Figure 3.102: Evaluation of kinetic results using unreacted core model (UCM)

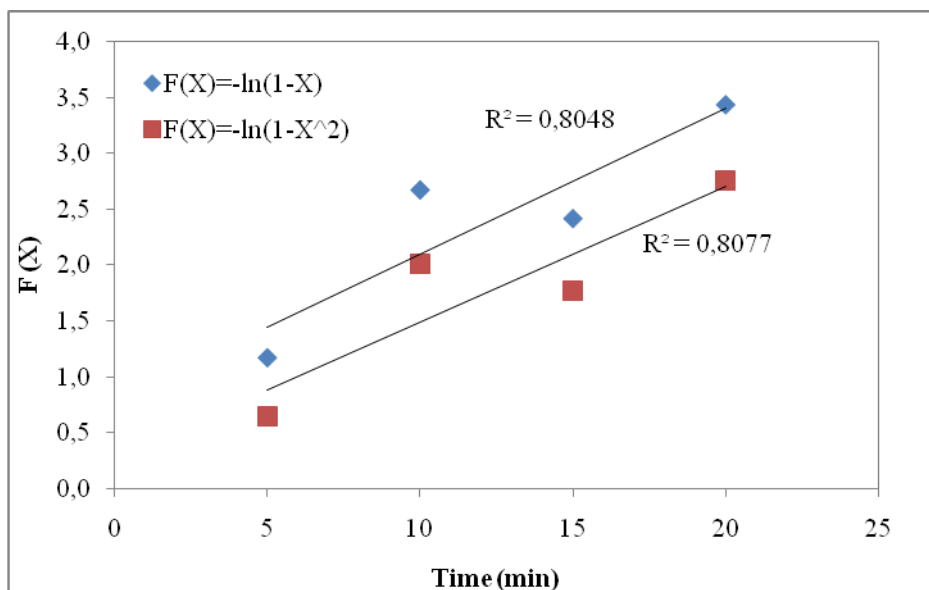


Figure 3.103: Evaluation of kinetic results using infinite solution volume model (ISV)

Table 3.33 shows the linear correlation coefficients obtained from the plots of $F(X)$ function versus time. Particle diffusion controls the rate according to ISV models and chemical reaction controls the rate according to UCM models for Dowex L493 adsorbent concentration, as they have greater linear correlation coefficients.

Table 3.33: Evaluation of kinetic results obtained using diffusional and reaction models for DowexL493

R^2				
ISV		UCM		
$-\ln(1-X)$	$-\ln(1-X^2)$	X	$3-3(1-X)^{2/3}-2X$	$1-(1-X)^{1/3}$
0.8048	0.8077	0.7000	0.7678	0.7746

3.7 Submerged Sorption-Membrane Filtration Hybrid Tests

This study, a new separation system so-called 'hybrid system', which comprises two separation processes is investigated. One of them is adsorption and the other is membrane filtration system. This integrated system has advantages. One of them is high removal efficiency with separation to a large extent. (Koltuniewicz et al., 2004).

3.7.1 Membrane –Alone Test

Membrane (ZeeWeed[®]-1 (ZW-1)) module was operated alone to see if it removes any of DEP and DMP or not. Polymer adsorbent was not used in this experiment. Membrane was submerged into the main tank having DMP/DEP solutions and permeate was withdrawn from UF module at a certain flow rate while solution was fed into the main tank at the same flow rate. Operational parameters were given in Table 3.34.

Table 3.34: Operational parameters for membrane-alone tests

Solution	DMP/DEP (50 mg/L)
Adsorbent	-
Adsorbent Amount (g/L)	-
Particle size of Adsorbent (mm)	-
Solution volume (mL)	1200
$Q_{\text{permeate}}=Q_{\text{feed}}$ (mL/min)	5
$Q_{\text{sat}}=Q_{\text{fresh}}$ (mL/min)	-
Q_{air} (L/min)	4

Permeates were collected with some time intervals during 3 h of operation time. As seen in Figures 3.105 and 3.106, for DMP and DEP respectively, at the beginning of the experiments, hollow fiber ultrafiltration membrane module (ZW-1) removed some of DMP/DEP from water. In the first 5 min of the experiment, the DMP/DEP concentration decreased sharply, but then started to increase and finally reached a plateau. This trend was observed because membrane reached the sorption equilibrium of DMP/DEP and did not remove them further. In this study, the decrease in apparent retention of DMP/DEP by membrane during filtration time can be explained by the adsorption of DMP/DEP onto the membrane surface at the beginning of each run.

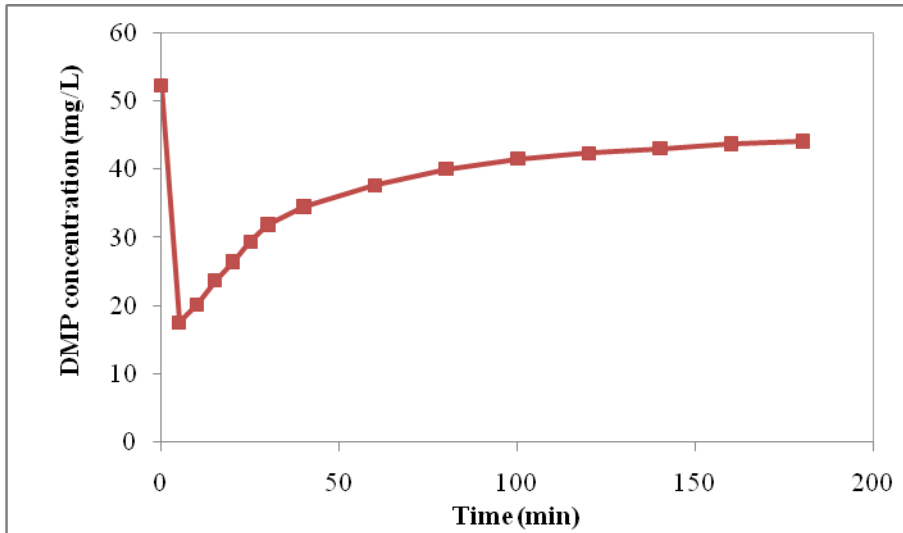


Figure 3.105: Membrane-alone test for DMP removal

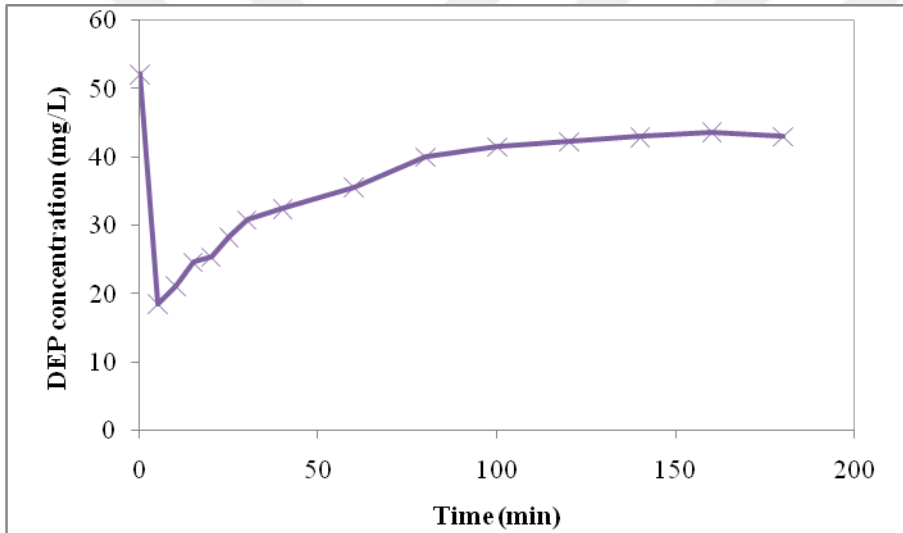


Figure 3.106: Membrane-alone test on DEP removal

3.7.2 Blank tests

Blank tests were also performed to see the dilution effect of water coming from the fresh adsorbent tank along with fresh adsorbent. For this, the tests were performed without using adsorbent, by feeding only deionized water instead of adsorbent-water mixture along with feed DMP/DEP solution into the main tank where ZW-1 module was submerged in. The concentration changes due to water dilution are shown in Figures 3.107 and 3.108 for DMP and DEP, respectively. As expected, DMP and DEP concentration in permeate decreased to the minimum

value at the beginning of the process. This phenomenon was not only governed by the addition of fresh water, but also adsorption of DMP and DEP on the membrane. The difference between the membrane alone tests and the blank tests give the dilution effect of water which comes from the fresh adsorbent suspension. Operational parameters are given in Table 3.28.

Table 3.35: Operational parameters for blank test

Solution	DMP/DEP (50 mg/L)
Adsorbent	-
Adsorbent Amount (g/L)	-
Particle size of Adsorbent (mm)	-
Solution volume (mL)	1200
$Q_{\text{permeate}}=Q_{\text{feed}}$ (mL/min)	5
$Q_{\text{sat}}=Q_{\text{fresh}}$ (mL/min)	6
Q_{air} (L/min)	4

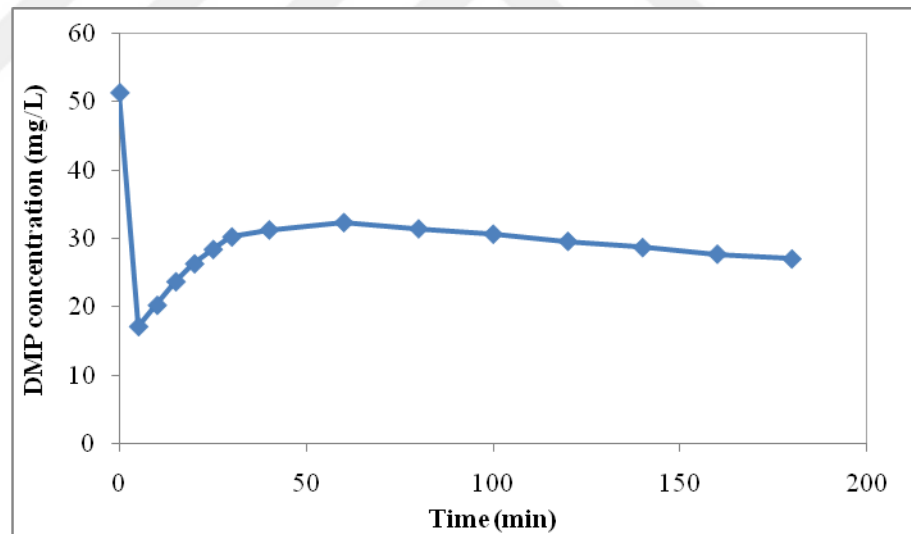


Figure 3.107: Blank test for DMP removal

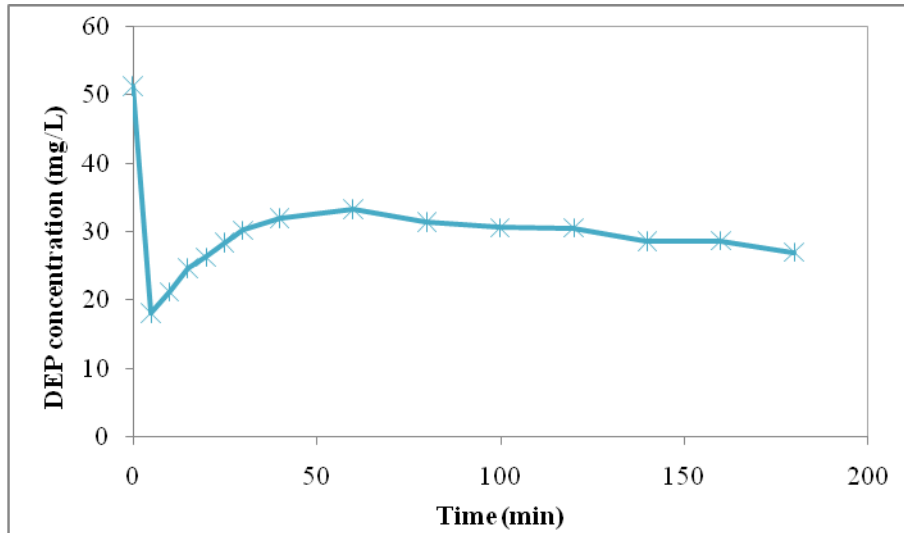


Figure 3.108: Blank test for DEP removal

3.7.3 Hybrid Test Results for DMP and DEP removal

3.7.3.1 Effect of adsorbent concentration for DMP and DEP removal

In order to determine the effect of adsorbent concentration on DMP and DEP removal from water, adsorption-membrane filtration tests were performed using Dowex L493 adsorbent in the particle size ranges of 25-50, 50-100, 100-250 μ m.

The changes in the concentration of DMP and DEP by different fresh adsorbent concentrations were shown in Figures 3.109 and 3.110. In the first 5 min of the experiment, the DMP and DEP concentration decreased sharply due to the membrane sorption, dilution effect and adsorbent sorption.

As seen in Figure 3.109, removal of DMP increased by increasing fresh adsorbent concentration. For adsorbent concentrations of 4 g/L and 6 g/L, there are no significant differences between their removal performances.

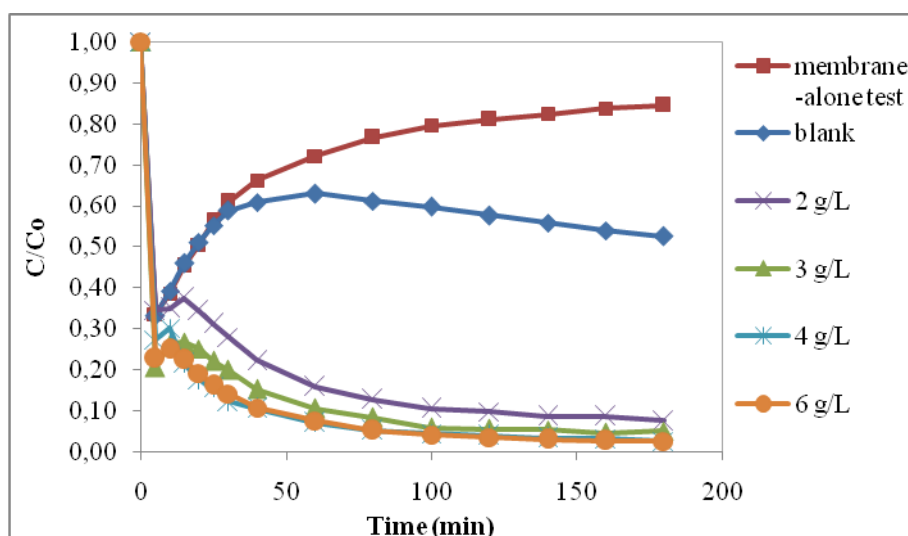


Figure 3.109: Effect of fresh adsorbent concentration on DMP removal

As seen in Figure 3.110, removal of DEP increased by increasing fresh adsorbent concentration. For 2, 3, 4 g/L and 6 g/L adsorbent concentrations, DEP removal was not changed significantly.

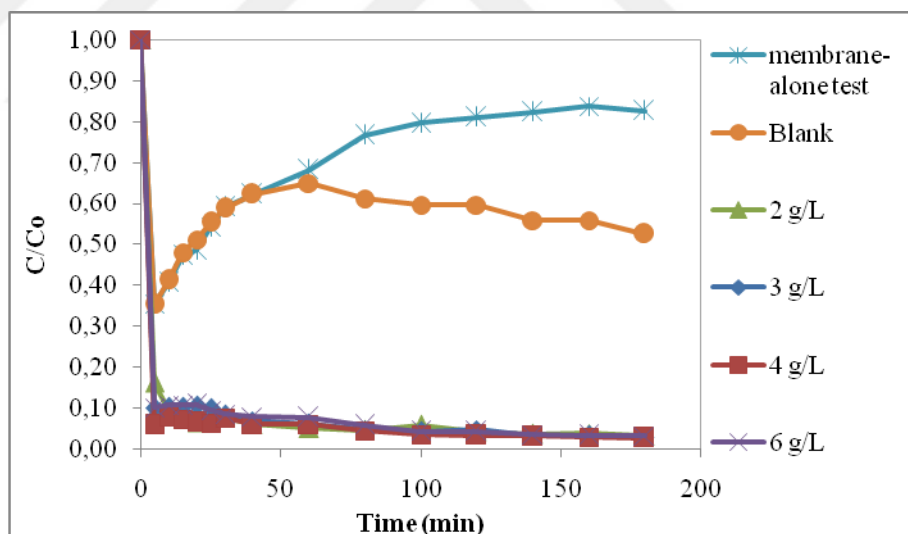


Figure 3.110: Effect of fresh adsorbent concentration on DEP removal

3.7.3.2 Effect of particle size for DMP and DEP removal

Different adsorbent particle sizes such as 100-250, 100-50 μm and 25.50 μm were tested. As shown in Figures 3.111 and 3.112, a decrease in adsorbent particle size did not change DMP and DEP removal significantly.

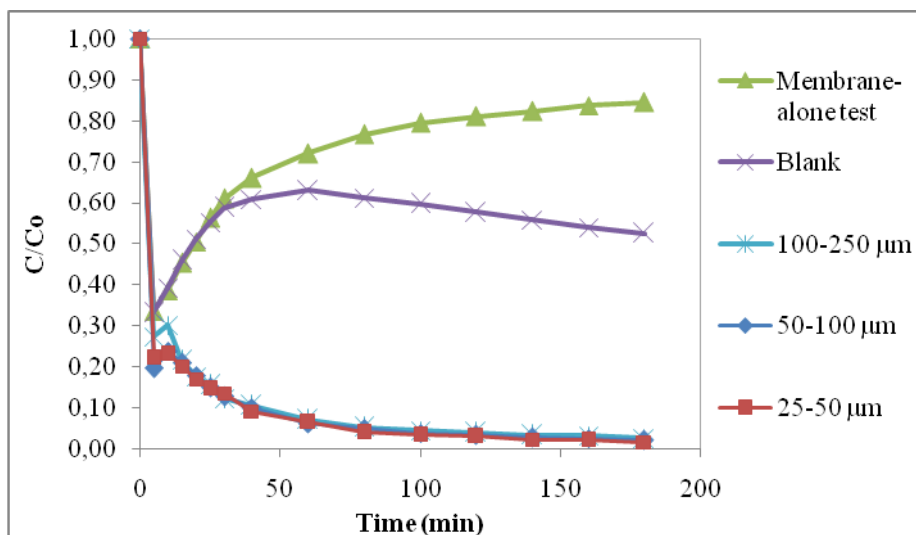


Figure 3.111: Effect of particle size on DMP removal

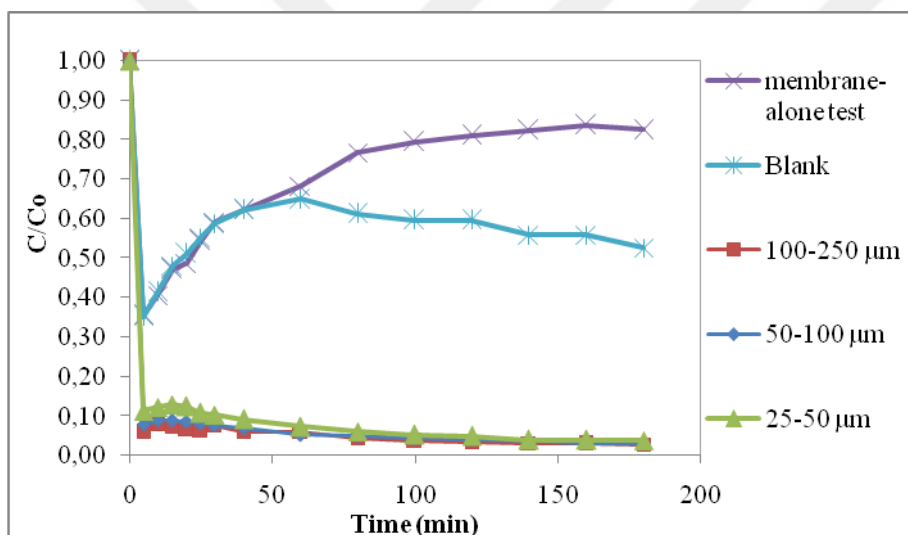


Figure 3.112: Effect of particle size on DEP removal

3.7.3.3 Effect of replacement rate of saturated and fresh adsorbents on DMP and DEP removal

In order to investigate the effect of flow rate of fresh and saturated adsorbent on DMP and DEP removals, 6 and 9 mL/min of flow rates were tested. As it is seen in Figures 3.113 and 3.114, there is almost a same trend for both flow rates for DMP removal. There is a very little decrease in DMP and DEP removals only at the beginning of the experiment for 9 mL/min of flow rate.

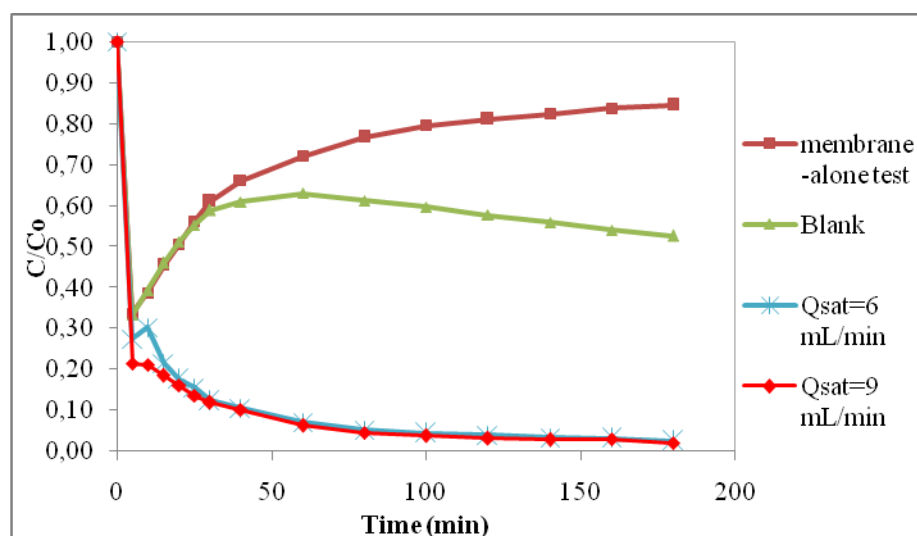


Figure 3.113: Effect of flow rate of saturated and fresh adsorbents on DMP removal

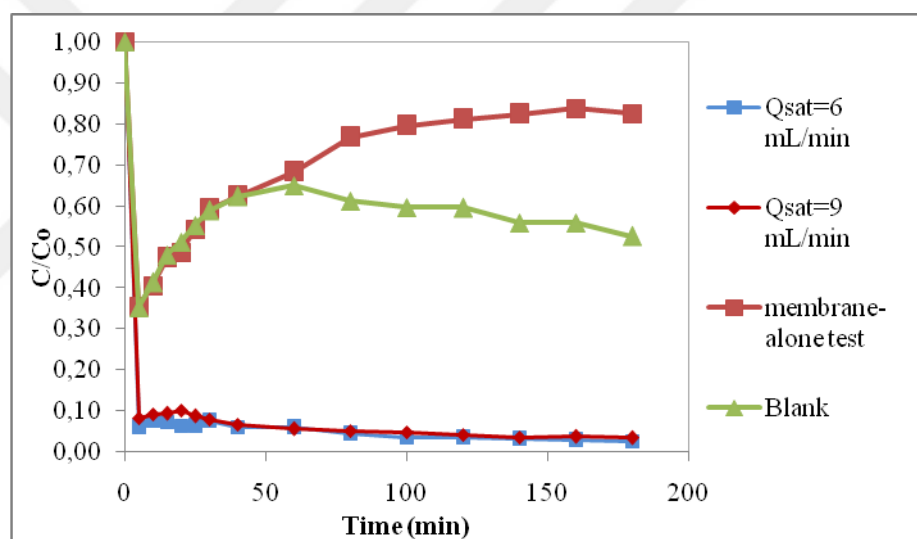


Figure 3.114: Effect of flow rate of saturated and fresh adsorbents on DEP removal

3.7.4 Effect of permeate and feed flow rates on DMP and DEP removal

Hybrid tests were also performed at different feed/permeate flow rates. Feed/permeate flow rates employed were 5 and 3 mL/min.

As seen in Figure 3.115, the decrease in feed/permeate flow rates did not affect the DMP removal significantly. There is a very little decrease in DMP removal only at the beginning of the experiment for 3 mL/min of flow rate. As

seen in Figure 3.116, the decrease in permeate flow rate did not change the DEP removal significantly.

From the economical viewpoint, 5 mL/min of feed/permeate flow rate was decided as suitable to complete the process in a short period.

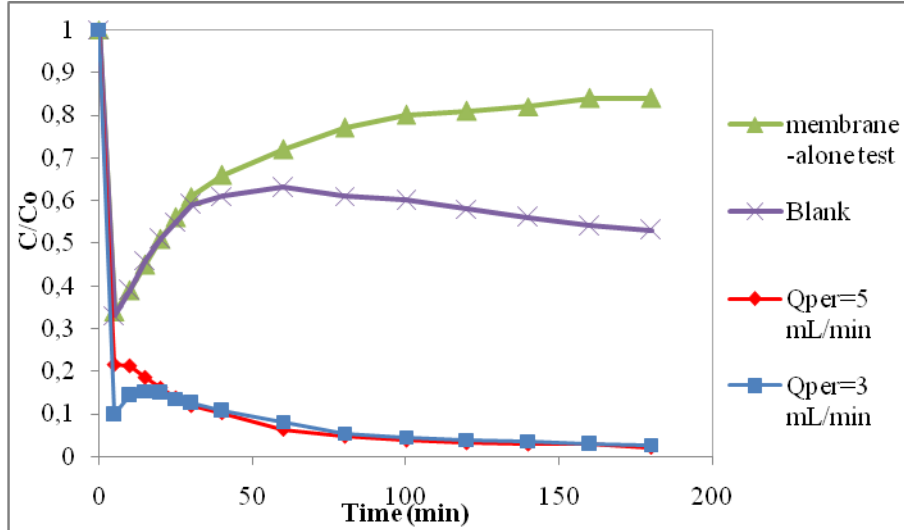


Figure 3.115: Studies for effect of permeate and feed flow rate on DMP removal

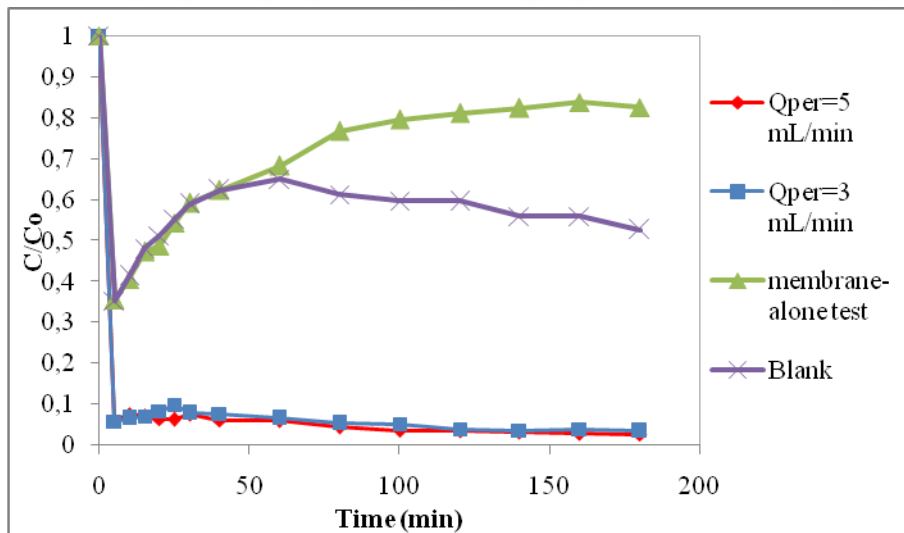


Figure 3.116: Studies for effect of permeate and feed flow rate on DEP removal

The submerged sorption-membrane filtration hybrid system used has the advantage of using fine particles of the adsorbents which increases the surface area and accelerates the separation process significantly. High removal of

DEP/DMP concentration was obtained using fine particles of adsorbent (25-50, 50-100, 100-250 μm). To decrease of DMP and DEP concentration 4 g/L of adsorbent concentration is designated as optimum amount. From the results it was established that DMP and DEP removal was higher by using higher amount of adsorbent.



4. CONCLUSIONS

In this PhD thesis, the analyses of some EDCs (Triclosan, 2,4-dichloro phenol and 2,3,4-trichloro phenol), estrogens (estrone, 17- β -estradiol and 17- α -ethinylestradiol), phthalates (DEP and DMP) and some pharmaceuticals (clofibric acid, clofibrate, clofibrate methyl ester, carbamazepine)) were investigated using GC-MS method. The results related to EDCs removal by highly cross-linked polymer adsorbents and submerged sorption-membrane filtration hybrid system and their determination by using SPE and SPME coupled GC/MS method were presented.

Phthalates (DMP and DEP) were analysed by spectrophotometric method and GC-MS. Calibration curves were plotted. Solid phase extraction (SPE) method was used for pre-concentration of DMP and DEP. Their concentration was measured by Gas chromatography/mass spectrometer (GC-MS). Recovery %, Relative Standard Deviation (RSD) values and LOD values were calculated for this method to determine DEP/DMP concentration.

Triclosan including its metabolites (2,4-dichloro phenol and 2,3,4-trichloro phenol), estrogens (estrone, 17- β -estradiol and 17- α -ethinylestradiol) and some pharmaceuticals (clofibric acid, clofibrate, clofibrate methyl ester, carbamazepine) were analyzed by SPE coupled by GC/MS and plotted calibration curves. 3 polymeric adsorbents (Diaion SP207, Diaion SP825 and Dowex L493) were tested for removing of EDCs. According to the batch tests, optimum adsorbent amount was determined as in the range of 0.5-1.2 g-polymer adsorbent/L for EDCs using polymeric adsorbents, Diaion SP207 and Diaion SP825. Optimum amount was 0.5-0.8 g-polymer adsorbent/L for Dowex L493.

Batch adsorption tests were performed for removal of phthalates (DEP and DMP) from water using highly cross-linked polymer adsorbents (PAD400 (Purolite International Limited), SP207 (MITSUBISHI Chemical), SP825 (MITSUBISHI Chemical) and Dowex L493 (DOW Optipore L493)). For DEP removal, optimum adsorbent amounts of Purolite PAD400 and Diaion SP207

were found to be 0.04 g adsorbent/50 mL and optimum amount Diaion SP825 and Dowex L493 were determined as 0.6 g adsorbent/50 mL model solution. For DMP removal, adsorbent amounts of Purolite PAD400, Diaion SP207, Diaion SP825 and Dowex L493 were found to be 0.15, 0.10, 0.08 and 0.60 g/50 mL, respectively.

The adsorption equilibrium data were evaluated for DMP using Freundlich, Langmuir and Temkin isotherm models. Freundlich model represented adsorption isotherms much more reasonably than the other models for Purolite PAD400 adsorbent. On the other hand, adsorption isotherms data of Diaion SP207, Diaion SP825 and DowexL493 adsorbents agreed well with Langmuir model. It could be concluded that the adsorption isotherms could well be fitted by the Langmuir model. Also, DEP results were evaluated for isotherms according to Freundlich, Langmuir, Sips and Temkin models. Freundlich model represent adsorption isotherms for Purolite PAD400 and Diaion SP207 adsorbents very well. The adsorption isotherms for Diaion SP825 and DowexL493 fit well to Langmuir model.

The kinetic data obtained was also evaluated by using conventional kinetic modeling and diffusional and reaction models (infinite solution volume model (ISV) and unreacted core model (UCM)). It was found that the adsorption of phthlates (DMP and DEP) by high cross linked adsorbents Purolite PAD400 Diaion SP207, Diaion SP825 and DowexL493 obeys the pseudo-second-order kinetic model. Diffusional and reaction models showed differences for each adsorbents.

DEP and DMP removal studies were also performed with the submerged adsorption-membrane filtration system by using DOWEX L493. Compared to a conventional system, the most important advantage of this system is the possibility of using adsorbents as very fine particles, which provides an increase in the surface area, with higher DEP and DMP uptake and faster kinetics. Some parameters such as effect of adsorbent amount, effect of rate of replacement of saturated and fresh adsorbent, effect of flow rate of permeate and feed and effect

of adsorbent particle size in submerged sorption-membrane filtration were investigated for removal of DEP and DMP.

To decrease of DMP and DEP concentration 4 g/L adsorbent is designated as an optimum amount. From the results it can be said that DMP and DEP removal was higher by using higher amount of adsorbent. However, it showed that when the rate of saturated and fresh adsorbent replacement was increased or when the flow rate of permeate and feed was decreased, DMP and DEP concentration was decreased. Because;

- Increasing the rate of replacement of saturated and fresh adsorbent, increases fresh adsorbent amount fed to the suspension tank which realizes a higher DEP/DMP uptake.
- By decreasing the flow rate of permeate and feed, the contact time of the adsorbent with the water increases.

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