THE REMOVAL OF ACLONIFEN FROM WATER BY ADSORPTION USING CARBON NANOTUBES

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ABSTRACT

THE REMOVAL OF ACLONIFEN FROM WATER BY ADSORPTION USING CARBON NANOTUBES

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Aclonifen has adverse human and environmental effect at high concentrations. Conventional treatment may be insufficient for aclonifen treatment and may cause toxic effects on the living organisms. Therefore, removal of Aclonifen from wastewater is important in terms of ensuring surface water quality and preventing harmful effects. Adsorption, which is one of the advanced treatment methods, is generally applied by using activated carbon. However, recently adsorption with carbon nanotubes (CNT) is attracted great interest. In the removal of various inorganic and organic pollutants from water, the superior adsorption ability of carbon nanotubes is remarkable when compared with activated carbon. In this study, the aim was to investigate removal of aclonifen from wastewater by adsorption process with carbon nanotubes. Based on the monitoring results of TÜBİTAK project (115Y013) "Management of Point and Diffuse Pollutants Sources in Yeşilırmak River Basin" aclonifen was observed to exceed to Environmental Quality Standards (EQS) in early sampling seasons. Aclonifen is also in the new priority substance list that was recently revised (2013/39/EU). Thus, aclonifen was selected as model pollutant. To investigate effectiveness of different adsorbent aclonifen removal, laboratory scale batch experiments were carried out. In the equilibrium studies, different aclonifen/adsorbent ratios were used. Throughout this work, isotherm and kinetic model studies were performed, effects of pH, sonication and water matrix were studied. As a result of equilibrium studies, COOH functionalized CNT was chosen as the best adsorbent for the removal of aclonifen. Maximum removal was observed at the 1/100 aclonifen/adsorbent ratio. The removal efficiencies for aclonifen observed as 96%, 96%, 96%, 95% and 92% for COOH CNT, MWCNT, PAC, OH CNT and SWCNT respectively. It was observed that pH and temperature of the solution do not affect the adsorption of aclonifen by CNTs. Moreover, sonication of the CNT suspensions significantly accelerated the COOH CNT.

Keywords: Aclonifen, Adsorption, CNT

ÖZ

AKLONİFENİN, KARBON NANOTÜP KULLANILARAK ADSORPSİYON YÖNTEMİ İLE SULARDAN ARITIMI

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Aklonifen, yüksek konsantrasyonlarda, insan ve çevre açısından olumsuz bir etkiye sahiptir. Geleneksel arıtma yöntemleri aklonifen arıtımı için yetersizdir ve bunun sonucunda canlı organizmalar üzerinde toksik etkilere neden olabilir. Bu nedenle, aklonifenin atık sulardan arıtılması, yüzey suyu kalitesinin sağlanması ve zararlı etkilerin önlenmesi açısından önemlidir. İleri arıtma yöntemlerinden biri olan adsorpsiyon, genellikle aktif karbon kullanılarak uygulanmaktadır. Bununla birlikte, son zamanlarda karbon nanotüplerle (CNT) adsorpsiyon büyük ilgi görmüştür. Çeşitli inorganik ve organik kirleticilerin sudan arıtılmasında, karbon nanotüplerin üstün adsorpsiyon yeteneği, aktif karbon ile karşılaştırıldığında dikkat çekicidir. Bu çalışmada amaç, karbon nanotüpler kullanılarak adsorpsiyon yöntemi ile aklonifenin atıksudan uzaklaştırılmasını araştırmaktır. “Yeşilırmak Havzasındaki Noktasal ve Yayılı Kirletici Kaynakların Yönetimi” isimli TÜBİTAK projesinin (115Y013) izleme sonuçlarına göre, erken örnekleme mevsimlerinde aklonifenin, Çevresel Kalite Standartlarını (ÇKS) aştığı gözlenmiştir. Ayrıca, aklonifen, yakın zamanda revize edilen öncelikli kirletici maddeler listesindedir (2013/39/EU). Bu nedenle, aklonifen model kirletici olarak seçilmiştir. Farklı adsorbanlar ile aklonifenin uzaklaştırılmasının etkinliğini araştırmak için laboratuvar ölçekli deneyler yapılmıştır.

Çalışmalarda farklı aklonifen/adsorban oranları kullanılmıştır. Bu çalışma boyunca izoterm ve kinetik model çalışmaları yapılmış, pH, sonikasyon ve su matrisinin etkileri çalışılmıştır. Çalışmalar sonucunda, COOH-CNT, aklonifenin uzaklaştırılması için en iyi adsorban olarak seçilmiştir. Maksimum arıtım 1/100 aklonifen/adsorban oranında gözlenmiştir. Bu oranda, COOH CNT, MWCNT, PAC, OH CNT ve SWCNT kullanılarak elde edilen aklonifen arıtım verimleri sırasıyla %96, %96, %96, %95 ve %92'dir. Çözeltinin pH'ının ve sıcaklığının, aklonifenin adsorpsiyonunu etkilemediği görülmüştür. Ek olarak, CNT süspansiyonlarının sonikasyonu COOH CNT'nin arıtma hızını önemli ölçüde hızlandırmıştır.

Anahtar Kelimeler: Aklonifen, Adsorpsiyon, KNT

To My Beloved Family

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LIST OF ABBREVIATIONS

ABBREVIATIONS

AC	Active Carbon
AOP	Advanced Oxidation Process
BTEX	Benzene, Toluene, Ethyl Benzene, Xylene
CNT	Carbon Nanotube
DEHP	Bis (2-ethylhexyl) Phthalate
DPE	Diphenyl Ether
EDC	Endocrine Disrupting Chemical
EQS	Environmental Quality Standard
EU	European Union
GAC	Granular Activated Carbon
HPLC	High Performance Liquid Chromatography
LOD	Limit of Detection
MBR	Membrane Bioreactor
MF	Micro Filtration
MWCNT	Multi Walled Carbon Nanotube
NF	Nano Filtration
NOM	Natural Organic Matter
NSAID	Non-Steroid Anti-Inflammatory Drugs
PAC	Powdered Activated Carbon
RO	Reverse Osmosis
SRT	Solid Retention Time
SWCNT	Single Walled Carbon Nanotube
THM	Trihalomethanes
UF	Ultra Filtration
USEPA	United States Environmental Protection Agency
WFD	Water Framework Directive
WWTP	Wastewater Treatment Plant

LIST OF SYMBOLS

SYMBOLS

C_e	Equilibrium concentration of chemical
C_o	Inıtial concentration of chemical
k1	Rate constant of pseudo first-order adsorption
k2	Rate constant of pseudo second-order adsorption
K_d	Partition coefficient
K_f	Freundlich adsorption constant
K_L	Langmuir adsorption constant
K_{ow}	Octanol-water partitioning coefficient
pH_{pzc}	Point of zero charge pH
pK_a	Logarithmic acid dissociation constant
q_e	Equilibrium amount of solute adsorbed per gram of adsorbent
q_m	Theoretical maximum amount of solute adsorbed

CHAPTER 1

INTRODUCTION

1.1. General

In recent decades, the occurrence of micropollutants in the water environment has become a worldwide problem with increasing environmental concern. Micropollutants are composed of a broad and expanding anthropogenic sequence beside natural substances. These include pesticides, pharmaceuticals, steroid hormones, personal care products, industrial chemicals, and so on. Micropollutants are present in waters ranging from a few ng / L to several µg / L at trace concentrations.

Micropollutants in the environment come from different sources. To illustrate, pharmaceuticals, and personal care products originate from hospitals and household whereas natural hormones and pesticides are released into water body through the effluents from treatment plants and leakage from agricultural lands (Kim & Zoh, 2006).

Micropollutants have a potential to accumulate in human bodies and aquatic organisms. In addition, they are not metabolized and cannot be degraded in the environment so that they have diverse impact. Many researchers conducted studies on the occurrence and fate of these substances in water bodies and reported about the harmful effects on humans and animals like abnormalities of the endocrine system, cancer and decreasing in sperm quantity. In addition, micropollutants can act synergistically with other substances and exacerbate adverse effects (Silva et al., 2017).

In this respect, European Union (EU) Water Framework Directive (WFD) (2013/39/EC amending Directives 2000/60/EC and 2008/105/EC) aims to restore degraded surface and ground waters to achieve “good status” in terms of both ecological and chemical conditions. Achieving good status in a water body requires meeting the Environmental Quality Standards (EQS) for 45 priority pollutants classified as hazardous in the Directive. Priority substances are identified as the substances, which pose an important risk for water environment. These substances are regulated in accordance with WFD and listed in Annex X. As well as priority substance list, specific pollutants were designated by Member States on a country basis. Specific pollutants are substances that pose a risk on national or river basin level due to the significant amount of discharge. The control of priority and specific pollutants in surface waters are ensured by EU Member States by the implementation of their environmental quality standards (EQS) and taking regulatory measures in order to protect human health and the environment. In Turkey, being under the EU harmonization process, 250 specific pollutants have been identified (Ministry of Forestry and Water Affairs, 2016).

In the current conventional wastewater treatment plants, the removal of micropollutants have not been well established, so they are not capable to remove micropollutants effectively. Therefore, many of micropollutants release into the aquatic environment via WWTP effluent. In this respect, WWTP has a significant factor for the control of these compounds in the environment. ın order to eliminate them, it is necessary to upgrade WWTPs with advanced treatment processes, such as adsorption by activated carbon, ozonation, advanced oxidation processes, membrane bioreactors, nanofiltration. In recent years, carbon nanotubes (CNT) have attracted great attention thanks to their good adsorption behaviour for the removal of organic and inorganic pollutants from water. In the literature, superior adsorption characteristics of CNTs over activated carbon (AC) for some pollutants are reported.

This thesis study was performed as a part of TÜBİTAK project (115Y013) on “Management of Point and Diffuse Pollutant Sources in Yeşilırmak River Basin” The main purpose of this project is to develop a management strategy that will ensure a holistic management of point and diffuse pollution in order to ensure the water bodies in the Yeşilırmak Basin reach the target of “good status” in accordance with the

SWQR (2012). For this main purpose, one of the tasks to be performed was to investigate the treatability of micropollutants in WWTPs, particularly toward the assessment of advanced treatment processes to remove priority and specific pollutants which were detected as micropollutants in the Yeşilırmak River Basin.

In this respect, there was a need to evaluate the alternative advanced wastewater treatment processes for the removal of micropollutants from the secondary level treated effluents. Among the several others detected in the Basin, a priority was given to the micropollutant of aclonifen since its treatability has not been studied at all in the literature, probably due to the fact that it has recently been added to the list of priority pollutants in the Directive 2013/39/EU (European Commission, 2013). Aclonifen was detected in the Yeşilırmak Basin, though observed to exceed the EQS value in one sampling period, at concentration of 0.97 μg/L. Therefore, it was deemed worth to study its treatability by means of one of the advanced treatments, namely adsorption by CNTs.

1.2. Aim and Scope of the Study

This thesis mainly aimed to study the removal of aclonifen from water by adsorption on CNTs. To this purpose, different CNT adsorbents such as, single walled CNT (SWCNT) and multiwalled CNT (MWCNT), COOH functionalized CNT (COOH MWCNT), OH functionalized CNT (OH MWCNT) were used, and their adsorption behaviours for aclonifen removal were compared with the conventional adsorbent, namely powdered activated carbon (PAC).

To this purpose, adsorption behaviors were followed through adsorption isotherm tests. Effects of pH, sonication and water matrix on the treatment efficiencies were investigated for a selected CNT type outperforming than others during the first set of experiments. Kinetics of adsorption were also sought. The adsorption performances were supported visually by the help of imaging techniques, such as SEM and FTIR analyses.

CHAPTER 2

LITERATURE REVIEW

2.1. Micropollutants

Micropollutants also known as emerging contaminants have become growing concern in recent decades. They refer to various substances such as pesticides, industrial chemicals, pharmaceuticals, personal care products, steroid hormones, plasticizers, insulating foams (Silva et al., 2017) and have been detected in water courses at concentrations ranging from ng/L to μg/L (Clara , et al., 2005).

Presence of micropollutants and their mobility in the natural water is influenced by their physicochemical properties and bioavailability. Logarithmic acid dissociation constant (pK_a) and the octanol-water partitioning coefficient (K_{ow}) are the chemical properties, which determine the movement of the micropollutants from one phase to another (e.g., soil-water movement) (Kim & Zoh, 2006).

2.1.1. Sources and Occurrence in Water

Micropollutants in the environment come from various sources. Most of them originate from mass produced materials. They are mostly detected in aquatic environments. The possible source and pathways for the introduction of micropollutants into the aquatic environment is illustrated in Figure 1 (Ellis, 2006). In addition, source categories of some major micropollutants in aquatic ecosystem are summarized in Table 1.

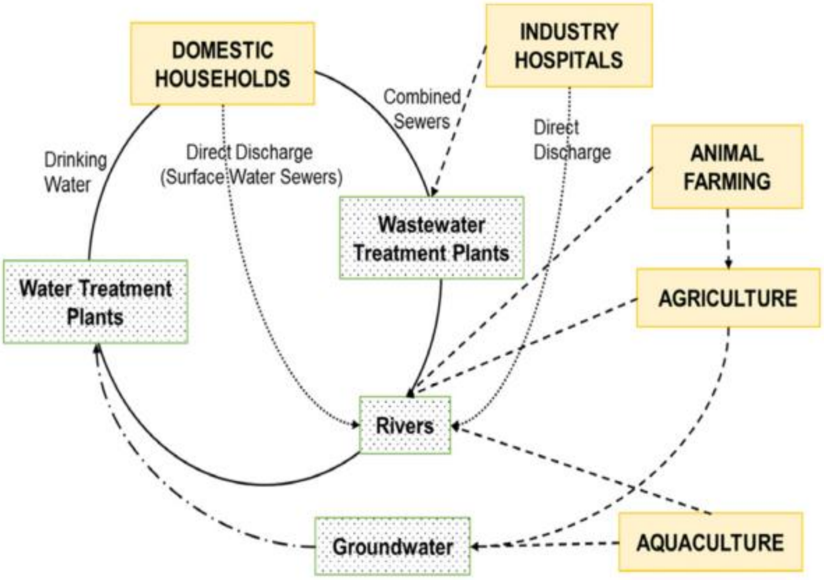


Figure 1. Sources and Pathways of Micropollutants in the Water Cycle (Ellis, 2006)

Table 1. Sources of Micropollutants in the Aquatic Environment

Category	**Micropollutants**	**Major sources**
Pesticides	Organochlorine insecticides, organophosphorus insecticides, herbicides and fungicides	Domestic wastewater (run-off from gardens, roadways), Agricultural runoff
Pharmaceuticals	Antibiotics, lipid regulator, anticonvulsants	Domestic wastewater (from excretion), Hospital effluents, Run-off from aquaculture
Industrial chemicals	Plasticizers, fire retardants	Domestic wastewater (by leaching)
Steroid hormones	Estrogens	Domestic wastewater, Run-off from aquaculture
Surfactants	Non-ionic surfactants	Domestic wastewater, Industrial wastewater
Personal care products	Fragrances, disinfectants, UV filters	Domestic wastewater

2.1.2. Threat for the Environment

Micropollutants in the aquatic environment can cause ecological risk by affecting water quality, drinking water supplies, ecosystem and human health (Rivera, et. al., 2013). The negative effects of micropollutants are caused by the fact that they have a potential to accumulate in aquatic organisms and human bodies, they have a toxic effect and they are not easily degradable in the environment (Antakyali, et al., 2015).

Pharmaceutical organic contaminants and personal care products consist of analgesics, antibiotics, non-steroid anti- inflammatory drugs (NSAIDs), antiseptics, antimicrobials, cosmetics, sunscreen agents, food supplements etc. Environmental bioaccumulation of these contaminants affects hormonal control negatively and leads to reproductive disorders, increasing in incidence of breast and testosterone cancers, and persistent antibiotic resistance (Tijani, et. al., 2013).

Endocrine disruption chemicals (EDCs) are one of the groups attracting great attention among micropollutants. Their effects are not only on environment but also on human beings. The effects caused by the EDCs in the environment are reduction in the breakage of eggs of birds, fishes and turtles, adversities in the reproductive system in birds, fishes, reptiles, and mammals, and feminization of male fish. In addition, decreasing in the amount of sperm of human, increasing in the incidence of breast, testicle and prostate cancers are reported as human related effects of EDCs (Esplugas et al., 2007).

Moreover, pesticides have negative effect on the humoral and cellular immunity of fish and mammals in aquatic environment. In addition, they lead to changes in tissue structure of anterior kidney (Dunier & Siwicki, 1993)

Surfactants are other groups of micropollutants, which are responsible for the endocrine activity by influencing the physical stability of human growth hormone formulations (Katakam et. al., 1995).

2.1.3. Environmental Regulations

The Water Framework Directive 2000/60/EC (CEC, 2000) is a European-wide legislation addressing the hazards and risks resulting from priority substances. It aims to achieve “good ecological status” and “good surface water chemical status” in the surface water bodies and regulates monitoring and measures of the EU Member States to improve surface water quality (Loos, 2012).

In 2008, a list of 33 priority substances was established by the Directive 2008/105/EC (Environmental Quality Standards Directive, EQSD) in the field of water policy. Environmental quality standards (EQS) were identified for these 33 priority substances and for other eight pollutants which were already regulated at EU level under existing legislation with the purpose to protect the aquatic environment from negative effects of these priority substances (Ribeiro et al., 2015).

In 2013, the new Directive 2013/39/EC (CEC, 2013), which amended the Directive 2000/60/EC and 2008/105/EC (CEC, 2008) came into force. Especially, twelve new substances were introduced so that 45 compounds are now classified as priority substances. A significant number of substances listed in the priority substance list, particularly biocides and industrial auxiliary chemicals are considered as micropollutants due to their nature, impact and concentration range (Antakyali, et al., 2015).

In Turkey, surface water quality regulations (SWQR) was published by the Ministry of Forestry and Water Affairs to maintain the water quality. As a EU candidate cauntry, Turkey is also responsible for meeting EQS. These EQS values for 250 specific pollutants and 45 priorty substance are given in SWQR (Appendix 5, table 4 and table 5).

2.2. Micropollutant Subject to the Study: Aclonifen

2.2.1. Structure and Properties of Aclonifen

Aclonifen (CAS: 74070-46-5) is the ISO common name for 2-chloro-6-nitro-3-phenoxyaniline. It belongs to the diphenyl ether (DPE) group. It is most widely used in Europe. It has been used for many years in the control of weeds seen in corn, sunflower, potatoes and legumes. In Turkey, it is used for weed control especially in sunflower, chickpea and lentil farming (Kılınç, 2015). Aclonifen is applied by spraying directly to the soil. As a result of spraying, they mix with water body through leakage from agricultural lands and farm yards (ENTEC, 2011).

The chemical structure of aclonifen is given in Figure 2. Aclonifen is both selective and systemic herbicide. It is not only acting through a phytotoxic protoporphyrin IX accumulation but also through an inhibition of carotenoid biosynthesis in contrast with other herbicides of the same family (bifenox, acifluorfen, oxyfluorfen) (Kılınç, 2015). Nitro diphenyl ether herbicides are strong herbicides. Some metabolites and parent compounds are considered as possible mutagens and endocrine disruptors. Both characteristics constitute serious health and environmental risks (Keum et. al., 2008).

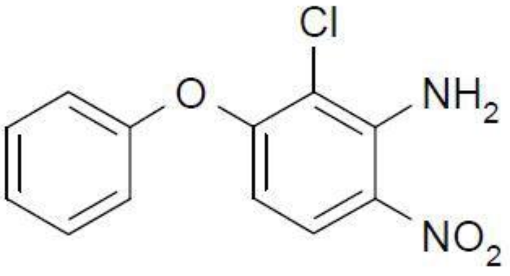


Figure 2. Structural Formula of Aclonifen (European Commission, 2012)

Aclonifen is a hydrophobic pollutant, and its octanol-water partition coefficient (K_{ow}) is 4.37. K_{ow} is generally used in order to predict absorption of micropollutants on solids. In addition, according to Rogers (1996), the micropollutants with logK_{ow} value higher than 4 have high sorption potential. In addition, in a study conducted by Tadkaew et al., (2011), it is suggested that K_d is also relative accurate indicator of organic contaminant sorption behaviour, and it is reported that the micropollutants with log$K_d > 3.2$ have high removal efficiency (above 85%) due to sorption properties. In addition, aclonifen is non-ionic herbicide and it has low solubility in water 1.4 mg L^{-1} (Azzi, et al., 2018).

Physical, chemical, and technical properties of aclonifen are summarized in Table 2.

Table 2. Physical and Chemical Properties of Aclonifen (European Commission , 2012; Hansen, 2004; Hertfordshire, 2017)

Chemical name (IUPAC)	**2-chloro-6-nitro-3-phenoxyaniline**
CAS No	74070-46-5
Molecular formula	$C_{12}H_9ClN_2O_3$
Molecular mass	264.7 g/mol
Melting point (state purity)	81.2 °C
Temperature of decomposition	297 °C
Solubility in water	1.40 mg/L at 20 °C at pH 5, 7 and 9
Vapor pressure	0.016 mPa at 20 °C
Appearance	yellow powder
Octanol- Water Partition coefficient (Log K_{ow})	4.37
Organic Carbon- Water Partition coefficient (Log K_{oc})	3.9
Acid dissociation constant (pka)	-3.15 at 25 °C
Solid-Water Distribution Coefficient (K_d)	892 L/kg

2.2.2. Environmental Fate and Behavior of Aclonifen

Aclonifen is stable to hydrolysis at pH 5, 7 and 9. The aqueous photolysis study shows that aclonifen is slowly degraded as a result of photolysis in water environment. A growing body of literature has investigated the degradation of aclonifen. In one of these studies (EFSA, 2008), two water sediment systems have been carried out under dark aerobic conditions at 20 °C ($pH_{water} = 6.7 – 7.5$; $pH_{sed} = 6.8 – 8.4$, organic carbon 3.8 – 5.7%, clay 10.54 – 28.99%). It was observed that aclonifen stably partitioned to the sediment and degraded in both water/sediment systems. It was also noted that mineralization was negligible in both systems. Overall results show that aclonifen is not readily biodegradable and it has no risk for contamination of ground water above the trigger of 0.1 µg/L (EFSA, 2008).

The route of the degradation of aclonifen in soil was also examined under dark and aerobic conditions. Studies have shown that mineralization of aclonifen is very low and it has moderate to high persistent in soil under aerobic conditions at 20 °C. However, these studies have failed to assess the level of risk associated with aclonifen in soil due to inadequate data (EFSA, 2008).

As well as water and soil, behavior of aclonifen in air is also evaluated and it is considered that transport through air and environmental concentrations in air are negligible due to low potential of volatilization.

2.2.3. Toxicity of Aclonifen

Risk assessment studies on aclonifen revealed that, risk to aquatic organisms such as fish, algae and higher aquatic plants is very high while the risk to terrestrial species is lower (Table 3) (EFSA, 2008).

Table 3. Risk Assessment of Aclonifen (EFSA, 2008)

Media	**Toxicity**
Soil	The toxicity and the risk to soil dwelling organisms is low
Ground water	The toxicity and the risk to ground water is high
Surface water and sediment	The toxicity and the risk to aquatic organisms is assessed as very high
Air	Not toxic

Regarding the mammalian toxicity of aclonifen, what is reported in the literature is that it is greatly metabolized and completely eliminated therefore there is no potential for accumulation of aclonifen in the body (EFSA, 2008).

It is also reported that aclonifen causes decrease in bodyweight, changes in clinical parameters; also, it has some negative effects on liver (EFSA, 2008). Consequently, aclonifen was proposed as harmful (limited evidence of a carcinogenic effect).

2.3. Removal of Micropollutants from Water

There is no specific treatment method to treat all micropollutant groups completely from wastewater due to their various properties. Treatment options to treat micropollutants are coagulation-flocculation, activated carbon adsorption (powdered and granular), and advanced oxidation processes (AOPs), membrane processes and membrane bioreactor (MBR) (Nas et al., 2017).

2.3.1. Coagulation-Flocculation

Coagulation-flocculation is a process used for removal of particulate matter, colloids and some dissolved substances. However, this process is not an effective way to eliminate the most of micropollutants. According to a study done by Matamoros and Salvado (2013), maximum removal efficiency was found 50% in a coagulation/flocculation-lamellar clarifier. Another study shows that treating landfill leachate by coagulation and sedimentation was not able to eliminate bisphenol A. However, higher removal efficiencies were achieved for bis (2-ethylhexyl) phthalate (DEHP) and nonylphenol as 70% and 90% respectively (Asakura & Matsuto, 2009).

Furthermore, Suárez et al., (2009) stated significant reduction of musks such as tonalide and galaxolide that was around 80% during the treatment of hospital wastewater by coagulation-flocculation. The removal efficiencies for diclofenac, naproxen and ibuprofen were found as max. 46% max. 42% and max. 23% respectively.

Considering all of these studies, it can be stated that coagulation-flocculation provides low removal efficiencies for most of micropollutants except for some pharmaceuticals such as diclofenac and nonylphenol. This method also provides poor yields for pesticides. In addition, both coagulant dose and operation temperature cannot influence the removal efficiency of pesticide significantly (Thuy et al., 2008). On the other hand, composition of wastewater highly affects the removal rates. For example, high fat content improve removal efficiencies of hydrophobic compounds (Suarez et al., 2009). Likewise, dissolved humic acid improves the removal rates of pharmaceuticals (Vieno et. al., 2006). On the other hand, dissolved organic matter in wastewater may inhibit the removal of micropollutants (Choi et al., 2008). In addition to these, mixing conditions, alkalinity, pH and temperature also affect the performance of this method (Alexander et al., 2012).

2.3.2. Adsorption

Another method for removal of micropolllutans is adsorption by activated carbon. The major usage area of activated carbon is solving taste and odour problem in wastewater especially in drinking water. This method gives best removal efficiency results in secondary effluent treatment due to blockage problem. It is also more effective than coagulation-flocculation for treatment of micropollutants (Choi et al., 2008). Both powdered activated carbon (PAC) and granular activated carbon (GAC) have been commonly used to treat micropollutants as adsorption applications. Removal efficiencies can change in this method due to properties of both used as adsorbate and adsorbent (Kovalova, et al., 2013).

PAC is an effective adsorbent for organic compounds that are resistant and non-biodegradable. Using PAC provides many advantages such as supplying fresh carbon continuously that can be used when the concentration of pollutant rise in water bodies (Snyder, et al., 2007). For example, in a study done by Kovalova et al. (2013), PAC was used to treat micropollutants in MBR treated hospital wastewater. In this study, retention time was chosen as 2 days and dosage of PAC were selected as 8.23 mg/L and 43 mg/L. Removal efficiency results show that PAC reached significant removal efficiencies especially for pharmaceuticals, industrial chemicals and metabolites. The removal rates were found as 86%. Another study done by Hernandez-Leal et al. (2011) shows that higher removal efficiencies (>94%) can be reached for personal care products, bisphenol A and nonylphenol.

Removal rates of PAC usage depend on PAC dosage, physical properties of pollutants, contact time and composition of wastewater (Boehler, et al., 2012) (Snyder, et al., 2007). A study shows that higher PAC dosages (20 mg/L) improve the removal efficiencies of micropollutants regardless of micropollutant's initial concentration (Westerhoff, Yoon, Snyder, & Wert, 2005).

According to a study, using the dose of 10 mg/L GAC to control the odour and taste possibly caused by micropollutants in drinking water is sufficient treatment method to reach removal rates of 99 % in lake water (Rossner, Snyder, & Knappe, 2009). As mentioned for PAC, contact time is affecting parameter for efficiency of removal rate. Lower contact time decreases adsorption performance of GAC process significantly. In other words, removal rates of pollutants depend upon interaction time between particle and pollutant. However, GAC gives poor results for highly contaminated wastewater due to pore blocking (Bolong, Ismail, Salim, & Matsuura, 2009).

In general, studies show that both GAC and PAC reactors can be considered as effective methods to remove micropollutants. It can be said that higher removal rates can be provided by non-polar characteristics of targeted compounds and higher compliance of pore size with shape of contaminants (Rossner et al., 2009; Verlicchi et al., 2010). However, presence of natural organic matter decreases the active carbon efficiency due to pore blocking.

2.3.3. Advanced Oxidation Processes

Conventional biological treatment methods are not effective to remove most of micropollutants because they have persistent structure. In such cases, AOPs such as UV radiation, UV/Cl_2 and UV/O_3 can be considered as better solution. This method can be applied most of micropollutants to have high removal rate. In addition, these processes make easier to reuse of water due to disinfecting effect of method (Hernandez-Leal et al., 2011).

Ozonation is a promising method to remove micropollutants in a full-scale wastewater treatment plant. Hernández-Leal et al., (2011) studied on removal of many micropollutants from biologically treated grey water, and found that all compounds were removed at the rate of 79% and more with ozone dose of 15 mg/L. In another study carried out by Sui et al., (2010), higher removal efficiencies (>95%) were achieved even though ozone dose were lower for the pollutants carbamazepine, indomethacin, diclofenac, trimethoprim, and sulpiride. On the other hand, removal rate of bezafibrate was about 14% due to stable molecular structure of it. In addition, oxidation processes cannot provide complete mineralization of pollutants. Therefore, by-products and metabolites show up from these reactions. Sand filtration or activated carbon column can be used to remove undesirable compounds (Nas et al., 2017).

2.3.4. Membrane

Another removal mechanism of micropollutants is membrane processes that consist of adsorption onto membrane and charge repulsion. The removal rate of membrane process depends on characteristics of membrane, type of membrane process, operating conditions and properties of selected micropollutants (Schafer et al., 2011).

Microfiltration (MF) with a pore size of around 0.1 µm and ultrafiltration (UF) with a pore size of around 0.01 µm are very effective membrane processes to solve turbidity problem in wastewater. However, these methods cannot remove micropollutants effectively due to smaller size of pollutants. On the other hand, micropollutants can be removed via interaction with natural organic matter (NOM) or adsorption onto membrane polymers (Luo et al., 2014). In a study carried out by Jermann et al., (2009) removal efficiencies of ibuprofen and estradiol were investigated without existing the NOM. Removal rates were negligible for ibuprofen and 8% for estradiol in hydrophilic UF membrane. However, removal efficiencies reached up to 25% for ibuprofen and 80% for estradiol in hydrophobic membrane. In general, MF and UF processes are not used alone to remove micropollutants due to their poor performance. That is why these processes are combined with nanofiltration (NF) and reverse osmosis (RO). Reverse osmosis is one of the great processes used to remove micropollutants. In a study carried out by Garcia et al. (2013), it was found that removal rates rise from 50% to 90% by adding RO to MF processes. In addition, Sui et al., (2010) shows that removal rate of neutral and ionic contaminants in RO system were found as 82% and 97%, respectively.

2.3.5. Membrane Bioreactor (MBR)

Another alternative method for removal of micropollutants is MBR, which can be defined as combination of biological treatment that is activated sludge and membrane filtration (MF or NF). This method provides many advantages such as higher effluent quality, easy control of solid retention time, higher biomass concentration, less space requirement, and minimum rising sludge problem. In addition, this method has great potential to remove most of micropollutants even if they are resistant to activated sludge process. Treatment efficiency depends on concentration, SRT, contents of wastewater, conductivity, pH, and operating temperature (Nas et al., 2017).

In a study conducted by Trinh et al. (2012) for full-scale MBR process, efficiencies more than 90% were obtained for most of micropollutants. However, removal rate of pharmaceuticals such as amitriptyline, carbamazepine, diazepam and diclofenac were about 24 – 68 % (Verlicchi et al., 2010).

2.4. Adsorption

Adsorption is a physicochemical process for the treatment of water and wastewater. In this process, organic and inorganic compounds are removed from water by the mechanism based on mass transfer phenomenon owing to different interactions between molecules and the adsorbent surface. In adsorption, molecules diffuse from a liquid phase to a solid surface that is called adsorbent while the adsorbed component is called as adsorbate.

Adsorption process is carried out in four different steps (Tan & Hameed, 2010; Zhang et al., 2012):

1. Bulk diffusion: the molecules transport from the bulk fluid to the boundary layer surrounding the adsorbent.
2. Film diffusion: the molecules diffuse from boundary layer of the adsorbent to the external surface sites of adsorbent.
3. Pore diffusion: the molecules diffuse to inside the pores of the adsorbent particle.
4. Sorption: Physical attachment of the molecules on the surface of the adsorbent or in the mesopores and micropores.

Adsorption is divided in two types according to adhesion of molecules onto adsorbent surface: physical adsorption and chemical adsorption. In physisorption, there are van der Waals forces between the adsorbate molecules and adsorbent surface. These forces are weak interactions, so process can be reversed easily. This process is exothermic results in decrease of free energy. On the other hand, in chemisorption, molecules usually attach to the surface by covalent bonds. Temperatures should be much higher than the critical temperature in order to make chemisorption be effective. In spite of pyhsisorption, chemisorption process is not easily reversed. In some cases, both physisorption and chemisorption can occur at the same time (Dąbrowski, 2001).

2.4.1. Adsorption Isotherms

Adsorption isotherm is a major tool that is a curve explaining the mobility of a substance from the aqueous media to solid phase at various concentration (Limousin, et al., 2007) constant pH and temperature (Foo & Hameed, 2010). The isotherms are created by the data obtained at equilibrium concentration that is achieved when the amount of adsorbed molecules is equal to the amount being desorbed. Various isotherm models such as Langmuir, Freundlich, Tempkin, Redlich-Peterson are used to evaluate the equilibrium characteristics of the adsorption process. Among these, Langmuir and Freundlich models are the most common used equations applied in solid/liquid systems. The amount of adsorbed components (q_e) at equilibrium time is calculated from the mass balance equation given below where m is the mass of used adsorbent, V is the volume of solution, C_o and C_e are the initial and equilibrium pollution concentration (Gimbert, Crini, Renault, Badot, & Crini, 2008).

$$qe = \frac{V(Co\text{-}Ce)}{m} \tag{1}$$

2.4.1.1. Langmuir Isotherms

The Langmuir isotherm theory refers to homogeneous adsorption and it assumes that adsorption of each adsorbate molecules onto the surface of the adsorbent has equal sorption activation energy and all adsorption sites are identical. Also, it is assumed that adsorption occurs at specific adsorption sites (Allen, et al., 2004).

Due to the monolayer assumption, Langmuir model is more commonly used for low concentration. This model can be represented in non-linear form as given in the Equation 2.

$$q_e = \frac{qm*b*Ce}{1+b*Ce} \tag{2}$$

Where,

q_e = equilibrium amount of solute adsorbed per unit amount of adsorbent (mg/g)

C_e = equilibrium solute concentration in the solution (mg/l)
b = Langmuir adsorption constant (l/mg)
q_m = theoretical maximum amount of solute adsorbed per unit amount of adsorbent (mg/g)

The linear form of Langmuir isotherm is represented as Equation 3 given below (Nethaji et al., 2013).

$$\frac{1}{q_e} = \frac{1}{qm*b*Ce} + \frac{1}{q_m} \tag{3}$$

2.4.1.2. Freundlich Isotherms

Freundlich isotherm model is applicable to heterogeneous adsorption with non-uniform distribution of adsorption heat (Foo & Hameed, 2010). It is assumed that adsorbed adsorbate concentration increases as concentration of adsorbate increases (Hamdaoui & Naffrechoux, 2007).

Because of these assumptions, Freundlich model is generally appropriate for high concentrations. This isotherm can be expressed non-linear form as Equation 4 given below.

$$q_e = \mathrm{K_f C_e}^{\ 1/\mathrm{n}} \tag{4}$$

where,
q_e = equilibrium amount of solute adsorbed per gram of adsorbent (mg/g)
C_e = equilibrium solute concentration in the solution (mg/l)
K_f = Freundlich adsorpstion constant (l/mg)
1/n = Constant for adsorption intensity (dimensionless)

Linear form of Freundlich isotherms is represented as Equation 5 given below.

$$\mathrm{logq_e} = \mathrm{logK_f} + \frac{1}{\mathrm{n}} * \mathrm{logC_e} \tag{5}$$

When plotting log q_e vs log C_e, the slope gives information on surface heterogeneity and adsorption intensity. As the value of slope closes to zero, heterogeneity increases. In addition, the value of 1/n explains the degree of non-linearity between concentration of solution and adsorption. If the value of 1/n is equal to 1, adsorption is linear. While the value of 1/n is above one, adsorption process is physical, the value is below one, adsorption process is chemical (Al-Duri, 1996).

2.4.2. Adsorption Kinetics

Adsorption kinetics is essential for determination of the rate at which adsorption process takes place. It is necessary for determining the adsorbate residence time and system design. To describe the adsorption kinetics of a specific system, many models have been developed such as pseudo- first order model, pseudo- second order model, elovich model (Yakout & Elsherif, 2010). The most common used kinetic models for solid-liquid adsorption processes are pseudo first order and pseudo second order models.

2.4.2.1. Pseudo First Order Kinetics

The non-linear form of Pseudo first order kinetic equation is as follow:

$$q(t) = q_e * (1 - e^{-K_1 * t}) \text{ (Kumar, 2006)} \qquad (6)$$

Where q_e is amount of adsorbate adsorbed per gram of adsorbent at equilibrium (mg/g), q(t) is amount of adsorbate adsorbed per gram of adsorbent at time t (mg/g), K1 (min-1) is the rate constant of pseudo first-order adsorption.

2.4.2.2. Pseudo Second Order Kinetics

Nonlinear forms of pseudo second order kinetic model is as fallow:

$$q(t) = \frac{K_2 * q_e^2 * t}{1 + K_2 * q_e * t} \text{ (Kumar, 2006)} \qquad (7)$$

Where K_2 is the equilibrium rate constant of pseudo second order adsorption (g/(mg*min)), qe is amount of adsorbate adsorbed per gram of adsorbent at equilibrium (mg/g) and q(t) is amount of adsorbate adsorbed per gram of adsorbent at time t (mg/g).

2.5. Adsorbents

Carbonaceous materials are widely used as adsorbent materials in adsorption process for wastewater treatment. Agricultural wastes, polymeric materials such as nonionic polymeric resins, industrial wastes such as fly ash, and fertilizer waste can be used as low cost adsorbent as well as carbonaceous materials (Ali, Asim, & Khan, 2012). General features of commercial adsorbents include large surface area, porous structure, high mechanically strength easy regeneration. As it is known that activated carbon derived from chemical treatment and pyrolysis of sources including coal, nutshells, wood, bamboo and other organic materials (Ando, et al., 2010) is the most popular and common used adsorbent among the all adsorbent type. Owing to its highly porous internal structure, and extended surface area (ranging 600-2000 m^2/g) (Bhatnagar & Minocha, 2006), activated carbon is very efficient for removal of pesticides from wastewater (Ahmad, et al., 2010).

Activated carbon that consists of polycondensated aromatic species, nitrogen, hydrogen, oxygen, sulphur is produced by raw material dehydration, carbonization, and activation. They exist in two forms as powdered activated carbon (particle size <0.1 mm) and granular activated carbon (particle size 0.2 - 5 mm) depending on the average particle size. In addition, according to their pore sizes PAC can be classified as macro (>50 nm), meso (2–50 nm) and micro (<2 nm) pores (Han, et al., 2003).

2.6. A New Alternative to Conventional Adsorbents: Carbon Nanotubes

Although activated carbon is effective and widely used adsorbent, carbon nanotubes (CNTs) have been popular adsorbents for removal of organic materials in recent years due to their unique physicochemical and electrical properties, which differentiate them from conventional materials.

CNTs were first discovered by Iijima as multi-walled form in 1991 (Iijima, 1991) and as single walled CNTs in 1993 (Iijima & Ichihashi, 1993) Since then, they have received a lot of focus due to their unique properties, such as electrical conductivity, optical activity, and mechanical strength (Pan & Xing, 2008). Because CNTs' large surface area and large micropore volume, they have been suggested and examined as superior adsorbents for water treatment applications and environmental remediation (Chen, Duan, & Zhu, 2007).

2.6.1. Structure of CNT

CNTs that are members of the fullerene family are long, thin, concentric hollow cylinders. They consist of one or more rolled graphene sheets. Like graphite, graphene, diamond, fullerene and amorphous carbon, CNT is one of the allotropic forms of carbon (Jeon et al., 2011). In Figure 3 crystal structures of different allotropes of carbon are showed.

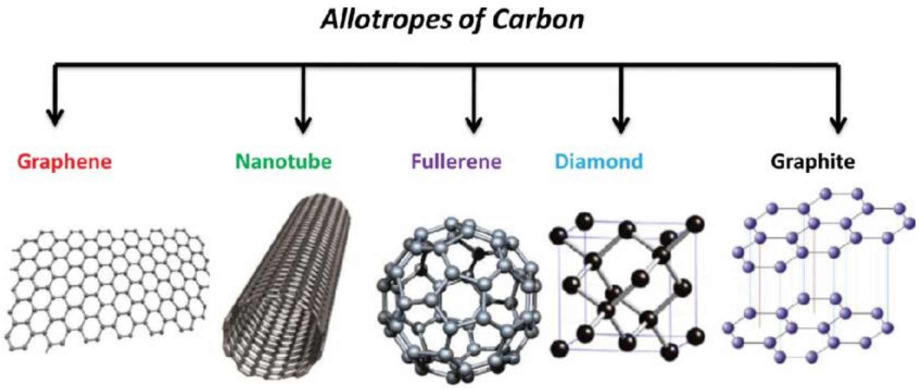


Figure 3. Crystal Structures of Different Carbon Allotropes (Movlaee et al., 2017)

CNTs have a unique tubular structure with nanometer scale diameters and large length/diameter ratios. The bonding in carbon nanotubes is sp^2; each carbon atom is joined to three carbon atoms like in graphite (Jeon et al., 2011).

Carbon nanotubes can be classified as SWCNTs and MWCNTs based on the number of graphite layers.

SWCNTs consist of only one layer of graphene rolled into a cylinder. Diameter of SWCNTs is ranging between 0.7 and 10 nm, although most of them have diameters less than 2 nm (Gangupomu, 2013). MWCNTs are made by two or more graphene cylinders, which are concentric to each other. The interlayer spacing between graphitic shells of MWCNTs is 0.34 nm (Ren, et al., 2011). Diameters of MWCNTs show differences depend on the number of cylinders. The outer diameter of MWCNTs ranges from 2 to 30 nm and the inner diameter ranges from 0.4 nm up to a few nanometers (Gangupomu, 2013)

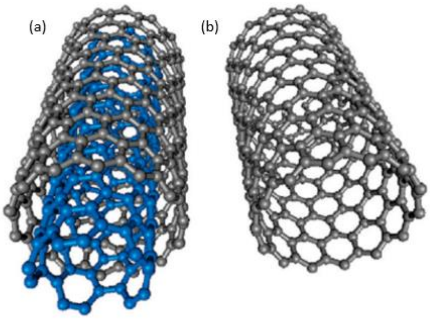


Figure 4. Structural Representations of (a) MWCNT (b) SWNT (Zhao & Stoddart, 2009)

CNTs are extremely hydrophobic and they tend to aggregate in aqueous solution because of high Van der Waals interactions along the length axis. Therefore, they are not easily dispersible in water (Schierz et al., 2009; Girifalco et al., 2000; Shaffer et al., 1998).

The solubility, dispersibility and processibility of CNTs in aqueous solution can be increased by functionalization process such as surface oxidation or by the addition of surfactants (Zhu, et al., 2003; Mickelson, et al., 1999).

In recent years, CNTs are considered to be extremely good adsorbents for the removal of a large number of different organic compounds from water because of their unique physical and chemical properties. CNTs have high surface area, high surface active site to volume ratio and large micropore volume, so they have high sorption capability and efficiency (Ong et al., 2010).

Aggregation creates new adsorption sites on CNTs and contributes to overall adsorption. There are four possible adsorption sites in CNT bundles for the adsorption of different pollutants (see Figure 5). Internal sites that are the interior of individual carbon nanotubes (these sites are accessible only if end of the CNTs are opened). The interstitial channels are between carbon nanotubes in bundles. The grooves present on the circumference of the nanotube bundle, and the external surface that are the curved surface of individual carbon nanotubes on the external of the nanotube bundles. Interstitial channels and grooves are formed as a result of aggregation (Das, 2017).

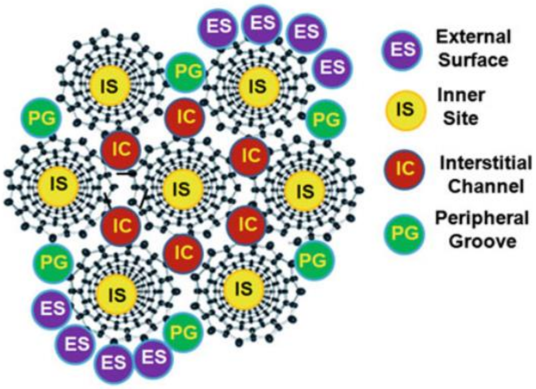


Figure 5. Structural Representation of Four Possible Major Adsorption Sites of CNT Bundle (Das, 2017)

Even groove and external surface areas are more available for adsorption than the interstitial channel and inner pores due to the dimensional restrictions though molecules as big as enzymes were reported to enter the inner pores of CNTs with diameter 3-5 nm in the study conducted by Davis et al., (1998). Also, the inner pores can be blocked by amorphous carbon, functional groups and metal catalysts (Yang et al., 2006; Pan & Xing, 2008).

2.6.2. Properties and Applications of CNTs

CNTs have unique properties like optical activity, mechanical strength, electrical and thermal conductivity Thanks to these properties, CNTs have used in many areas with different application since its discovery.

In terms of mechanical properties, CNTs are considered as the strongest and the stiffest materials in nature. The reason of strength is the covalent sp^2 bonds formed between the individual carbon atoms (Terrones , 2004). The strength of carbon is very high that they have the ability to bend and twist when the external force is applied and return to their original state when the force is removed due to elastic modulus. CNTs are also characterized by their high elasticity.

In addition, CNTs have very good thermal conductivity. Thermal conductivity of MWCNT is about 3,000 W/K at room temperature. This makes CNTs useful in some thermal management applications (Saeed & Khan, 2013).

Besides, CNTs have excellent electrical properties. They can be conducting or semi-conducting. This can be explained by the bonding of carbon atoms in CNTs. Each carbon atom is bonded covalently to three neighbor carbons and sp^2 molecular orbitals are formed. The fourth valence electron remains free, and these free electrons are delocalized over all atoms and enable CNTs to conduct the electricity (Hahm et al., 2011 (Saito et al., 1992). Therefore, they are attractable for the applications in constructing electronic devices.

Carbon nanotubes can be used in many applications such as electronic, medical, space and military applications, biomedicine, and especially in environmental applications thanks to their superior properties. To illustrate, they can be used in tissue engineering, drug delivery, cancer cell identification and artificial implant as medical application (Eatemadi, et al., 2014). Also, they are used for field emission sources, lithium ion batteries, and energy storage and conversion devices.

2.6.2.1. Environmental Applications

Using carbon nanotubes for the environmental applications especially for the water and wastewater treatment have been an attractable issue for researchers. Firstly, CNTs have so high surface active site to volume ratio and controlled pore size distribution that they are used as adsorbent for removal of pollutant. As well as serving as an adsorbent, CNTs are used as a membrane for reducing particle concentrations in wastewater, desalination and disinfection (Ahmad et al., 2016). They exhibit strong antimicrobial activity (Kang et al., 2007), and provide efficient bacterial inactivation and viral retention at low pressure (Brady-Estévez et al., 2010). Moreover, the CNTs membrane has self-cleaning and antifouling abilities with high recrudescence and reusability facilities due to the CNTs cytotoxicity.

Another application of CNTs is that they are excellent catalyst support in photo catalysis of multiple water pollutants and in the process called catalytic wet air oxidation due to their high electrical conductivity and charge transferring ability. In the photo catalysis process, CNTs promote electron transfer from the conducting band of TiO_2 to the CNTs surface as in contact with TiO_2 nanoparticles. They store photo-generated electrons. These electrons can be transferred to another electron acceptor and form reactive oxygen species (O^{-2}, H_2O_2 and $\cdot OH$) that degrade and mineralize organic pollutants (Liu et al., 2013). In the catalytic wet air oxidation process CNTs are used along with other catalysts such as platinum (Pt), palladium (Pd), ruthenium (Ru), and so on (Garcia et al., 2006; Yang et al., 2007) to increase catalytic efficiency and decrease costs. They also can act as catalyst. The carboxylic groups on CNTs and the oxygen atoms dissociation on the graphite layers form $HO_2\cdot$ radicals via hydrogen bonding that leads to organic pollutant degradation. (Liu et al., 2013). Besides wastewater treatment, CNTs can be used in air pollution control as sensing element. Toxic gases released in the environment can be detected and monitored by CNTs. The detection is based on the changes of resistance or conductance in CNTs (Ong et al., 2010).

2.6.3. Adsorption Mechanism of CNT

Water pollutants are adsorbed onto CNT by different mechanisms such as covalent bonding, hydrogen bonding, electrostatic interactions, ion exchange, hydrophobic interactions, π-π electron coupling, and mesopore filling.

Carbon atoms have π electron orbit that is perpendicular to CNTs surface. Thus, π-π bonds can be formed between CNT surface and organic molecules that contain π

electrons such as benzene rings or organic molecules with C=C double bonds. It is suggested that the π-π electron-donor–acceptor mechanism involving the carboxylic oxygen-atom of CNT surface as the electron-donor and the aromatic ring of BTEX as the electron-acceptor is responsible for the uptake of BTEX by CNTs. (Lu, Su, & Hu, 2008)

Electrostatic interaction is one of the interaction forces for ionic chemicals adsorption on CNTs. Ionic compounds can be negatively, neutrally or positively charged because of the difference between their pK_a and the solution pH. When the solution pH is higher than pH_{PZC} (pH_{PZC}:a pH value, called 'point of zero charge', at which the net surface charge is zero), surface of the CNTs are negatively charged and this provides electrostatic interactions which are favorable for adsorbing cation ions. Although electrostatic attraction and repulsion between CNT and ionic compounds have a role on adsorption capacity, this mechanism does not play a dominant role in the adsorption of organic chemicals. (Liu et al., 2013).

Hydrogen bonding that is dipole-dipole attraction between a hydrogen atom and an electro negative atom such as oxygen or nitrogen is another mechanism for the sorption of organic compounds on CNTs. The OH substitution on the adsorbate compounds and the hydroxylic/carboxylic groups on the CNT surface may form hydrogen bonds. According to (Lin & Xing, 2008) adsorption affinities are increased with decreasing hydrophobicities i.e. pyrogallol (3 -OH) > catechol (2 -OH) > phenol (1 –OH), that was related to the presence of hydrogen bonding.

CNTs can supply hydrophobic regions due to their main composition of carbon backbone/nonpolar graphene sheets. As a result, CNTs have a strong affinity to organic chemicals, mostly to nonpolar organic compounds (Liu et al., 2013). Hydrophobic interaction can be described by the octanol–water partition coefficient (K_{ow}) of organic chemicals. There is a strong interaction between chemicals with high hydrophobicity and hydrophobic adsorption sites on adsorbents. Therefore, hydrophobic interaction is expected to play important role on the adsorption of these chemicals (Liu et al., 2013). However, hydrophobic interactions cannot completely explain the interaction between organic chemicals and CNTs. Chen et al. (2007) investigated the adsorption of several polar and nonpolar pollutants onto CNTs and suggested that hydrophobic effect was not the dominant mechanism. To illustrate; cyclohexane has a much higher K_{ow} value than nitrobenzene, 2, 4- dinitrotoluene, 4-nitrotuluene, benzene, toluene. Also, it is less soluble than these chemicals. If hydrophobic partitioning were the predominant mechanism, adsorption of cyclohexane should have been stronger. However, the adsorption affinity of cyclohexane was weaker than that of nitrobenzene. In addition, the adsorption of nitrobenzene was much stronger than that of benzene, toluene, and chlorobenzene, even though it is less hydrophobic. This situation indicates that π–π electron donor-acceptor (EDA) interaction between the nitro aromatics (π acceptors) and the grapheme sheets (π donors) of CNTs is the predominant mechanism (Chen et al., 2007)

2.6.4. Factors Affecting Adsorption of Organics on CNTs

Adsorption of organic chemicals on CNTs can be affected by several factors such as functionalization of CNT surface, pH of the solution and ionic strength.

Functionalization that is a process of adding functional groups to the surface of CNTs affects the adsorption properties of CNTs greatly. Functional groups such as -OH, C=O and -COOH could be intentionally introduced onto CNT surfaces by acid oxidation or air oxidation (Liu et al., 2012). Those functional groups have different effects on polar and nonpolar chemicals. While the adsorption tends to increase with increased CNTs oxygen content for polar organic chemicals due to the enhanced H-bond or EDA interaction, the adsorption may decrease with increased CNTs oxygen content for non-polar chemicals as a result of the depressed hydrophobic interaction (Pan et al., 2008). Functional groups can make CNTs more hydrophilic by changing wettability of CNT surfaces. This promotes the adsorption of polar compounds and relatively low molecular weight compounds. Functional groups may also enhance dispersion of CNTs and increase the size of interstitial channel. This will increase the available adsorption sites on CNTs. On the other hand, functional groups and water clusters formed by means of hydrogen bonds around the functional groups can block the interstitial channels and inner cavities of CNTs. Additionally, water molecules compete with organic chemicals for adsorption sites. Carbonyl sites are blocked by water clusters formed on carbonyl groups. Besides, oxygen groups on CNTs surface localize the π electrons that reduce the π-π interactions between the CNTs graphitic surface and benzene rings of aromatic synthetic organic compounds (SOCs). As a result, adsorption of organic chemicals is decreased (Cho et al., 2008; Apul, 2014). The accessibility and affinity of CNT surfaces for organic chemicals are also reduced due to increased diffusional resistance caused by functional groups (oxygen groups) on CNTs (Pan et al., 2008). Yu et al. (2012) studied the effects of oxygen content on adsorption capacity. They found that increasing in surface oxygen content per specific surface area (SSA) up to ~8% for MWCNTs increases adsorption capacities of ethylbenzene, toluene and m-xylenethanks to the dispersion of CNTs. Nevertheless, if the oxygen content per SSA increases up to 18%, adsorption capacity decreases. The reason of this opposing behavior is that a water cluster formation effect dominates the CNTs dispersion effect on adsorption (Yu, Ma, & Wu, 2012).

Sheng et al. (2003) studied the treatment of aromatic compounds (1-naphthylamine, 1-naphthol and phenol) with and without functional CNTs and compared their performance. They observed that CNTs having functional groups have more surface area but have less adsorption capacity. The reasons for this were explained as such that carboxylic groups make the surface of the CNT negatively charged and so increase the electrostatic repulsion with negatively charged ionizable aromatic compounds. In addition, carboxylic groups reduce the adsorption by interfering with the π-π bonds between aromatic compounds and CNTs. Finally, as a result of functionalization, oxygen compounds present on the CNT surface attract water molecules, blocking the surfaces on which aromatic compounds can adhere, which also reduces adsorption.

In contrast, Lu et al. (2008) reported a positive effect of functional groups on the adsorption capacity of CNTs when BTEX (benzene, toluene, ethyl benzene, p-xylene) molecules were used as adsorbate. CNTs were oxidized with various chemicals and their adsorption performances were compared. It was observed that the CNT oxidized with NaOCl salt contains the greatest amount of carboxylic groups and has the highest capacity followed by the HNO_3-oxidized CNTs, the H_2SO_4-oxidized CNTs and then the HCl oxidized CNT where the carboxylic oxygen atoms on the surface of CNTs acted as electron donors, and aromatic rings of BTEX molecules acted as electron acceptors, in a way, a stronger π-π bond was formed and adsorption increased. Another factor that increases the adsorption capacity was reported as the electrostatic interaction between the BTEX molecules and the CNT surface. This factor was linked to the functionalization process through which the surface of the CNT is negatively charged and in a way attracts the positively charged BTEX molecules.

Functional groups on CNTs could also be affected by the pH of the medium. At higher pH, oxygen groups can be ionized easily and formation of water cluster is enhanced. This hinders access of adsorbate to the CNT surface and reduces H-bond formation between adsorbates and carbonyl sites on the CNTs. Hence, the lower adsorption capacity could be experienced at higher pH (Peng et al., 2003). In addition, an increase in pH makes both ionizable organic compounds and surface of CNTs more negatively charged. This would increase the electrostatic repulsion between adsorbates and CNTs, hence resulting in lower adsorption (Lin & Xing, 2008) (Yang & Xing, 2009). Supportingly, Zhang et al., (2010) investigated the adsorption of nonionic phenanthrene and ionizable 2-phenylphenol by CNTs under varying pH values. It was found that adsorption of nonionic phenanthrene did not change when pH values of background solution varied between 4 and 10. On the other hand, adsorption of ionizable 2-phenylphenol was observed to decrease when the pH of the solution was over the pK_a of 2- phenyl phenol due to the increased ionization and decreased hydrophobicity. Similar results were reported in different studies (Chen et al., 2008; Chen et al., 2007; Li et al., 2011).

In an another study by Peng et al (2003), the removal of 1, 2-dichlorobenzene from water by using as-grown and graphitized CNTs were studied under various pH conditions ranging between 3-10. They reported that when the pH is above 10, the removal of 1,2-dichlorobenzene from water reduced since the water molecules are adsorbed to carboxylic and hydroxylic groups and they inhibit adsorption of 1, 2-dichlorobenzene onto CNT surface. They also studied the effect of temperature and observed that the adsorption increased with the temperature. This shows that the adsorption of 1,2-dichlorobenzene on CNT is an endothermic reaction.

In another study conducted by Peng et al., (2009), removal of endrin and cadmium from water by oxidized CNTs was investigated. It was observed that the adsorption of endrin increases in cases where the pH is less than 6, but decreases when it is higher, and the optimum pH was determined as 6.

Ionic strength is another factor that affects the adsorption of organic compounds on CNTs. The influence of ionic salts on adsorption capacity depends on the configuration, electrostatic nature and hydrophobicity (due to “salting out” effect) of the adsorbates. Positive salt cations can neutralize the negative charge of both adsorbate and CNT surface, leading to decrease the electrostatic repulsion between them (Camara, et al., 2007).

Natural organic matter (NOM) also influences the adsorption of organic compounds by CNTs by changing the surface charge, aggregation behavior and mobility of CNTs in aquatic systems. Effects of NOM on adsorption can be explained by different routes. Firstly, NOM can increase the dispersion of CNTs, leading to change in adsorption sites (Hyung & Kim, 2008; Hyung, et al., 2007). Secondly, NOMs compete with adsorbate molecules for adsorption sites on CNT. Finally, they can increase the solubility of hydrophobic organic compounds and decrease their adsorption on CNTs (Cho, et al., 2008).

2.7. Comparison between PAC and CNT

CNTs have some similarities to PAC as well as some differences. While bonding structure of the carbon backbone and the adsorption mechanisms of both CNTs and PAC are similar, they exhibit different adsorption capacities because of some differences. While the surface areas of carbon nanotubes are typically in the range of 200-900 m^2/g (Xie et al., 2005) and the surface areas of PAC are in the range from 800-1200 m^2/g (Cooper & Alley, 2002). However, CNTs have higher adsorption capacity than traditional PAC resulting from high-energy binding sites and weak interaction with water. This means that surface area is not only factor to determine adsorption capacity (Pan & Xing, 2008).

CNTs have less porous structure comparing to PAC so that adsorbates access to inner surface of CNTs easier than that of PAC. In addition, pi electrons can easily interact with the surface by dispersive forces (Carabineiro et al., 2012). These render that CNTs has shorter equilibrium times than traditional PAC (Peng, et al., 2003).

Due to van der walls forces between CNTs they tend to aggregate so that CNTs has ordered pore structure. Ordered pore structure also enables pollutants to diffuse to adsorption site easily (Lu et al., 2005). The compounds diffuse into porous structure of PAC, which is rich in micropores. However, micropores of PAC is generally not available for the access of large organic molecules. On the other hand, CNTs is not limited by internal diffusion for interaction with compounds. While, for larger compounds, surface of the CNTs is the primary adsorption site, internal meso and micro pores in their aggregated form are appropriate for smaller species (Czech & Oleszczuk, 2016).

Although CNTs are more costly than PAC, it should be emphasized that CNTs can be regenerated and reused through many cycles of water treatment processes without decreasing in adsorption efficiency. Therefore, they last longer than PACs do. As a result, the operational cost for CNTs in water treatment could be lower if they are properly regenerated (Pan & Xing, 2008).

CHAPTER 3

MATERIALS AND METHODS

3.1. Wastewater Sample Used

Synthetic wastewater was used throughout the adsorption experiments, unless otherwise stated. To prepare this synthetic wastewater, aclonifen stock solution was spiked at desired amounts into ultra-pure water produced by the Millipore ultra-pure water system. In order to investigate the effect of wastewater matrix, biologically treated (via lab scale biological treatment system) synthetic wastewater originally spiked with aclonifen was used.

Aclonifen stock solution was prepared with Millipore ultra-pure water at the beginning of the studies. However, the solubility of aclonifen in water was very low (1.4 mg/L) leading to difficulties in preparing the solution. Thus, stock solution of aclonifen was prepared by using acetonitrile in 10 mL vial (200 mg/L). Vials are covered with aluminum foil to eliminate the effect of light and stored in room temperature. Then, this stock solution was injected into the Millipore ultra-pure water while preparing the solutions. The volume percentage of the stock solution was kept below 0.2% (v/v) to minimize the co-solvent effect.

3.2. Aclonifen as Micropollutant Studied

Aclonifen was used as a model micropollutant. The structure and physico-chemical properties of aclonifen was provided in Sec 2.2.1. As stated earlier, Aclonifen is one of the new priority pollutant recently added to the Annex X list of the WFD 2013/39/EU (European Commission, 2013). It is also covered in Turkish regulation of SWQR (2012). In both of the regulations, annual average EQS (AA-EQS) and Maximum EQS (MAC-EQS) are set as 0.12 μg/l for freshwater bodies.

The reason for selecting the aclonifen as a model micropollutant, in this study, lies behind the facts that:

- Aclonifen was observed to exceed the EQS value in the Yeşilırmak River Basin.
- Aclonifen is one of the 45 priority pollutants listed in the recently revised WFD (2013/39/EU).
- Aclonifen treatability has not yet been studied in the literature/

The concentration range to study was determined as 2 mg/L – 0.01 mg/L, considering the solubility of aclonifen in water (1.4 mg/L) and the analytical capability i.e. LOD of the method applied for measuring the concentration of the aclonifen (0.01 mg/L) so that the concentration of aclonifen after treatment could be measurable.

3.3. Adsorbents Tested

Four different CNTs were tested in this study, namely, multiwalled carbon nanotube (MWCNT), -OH functionalized MWCNT, COOH functionalized MWCNT and single walled CNT (SWCNT). The technical properties of the CNTs are summarized in Table 4. PAC (Norit N.V. Amersfoort Netherland) was used a reference adsorbent for the sake of comparison with CNTs.

Table 4. Technical Properties of the CNTs Used

Technical properties	**MWCNT**	**COOH MWCNT**	**OH MWCNT**	**SWCNT**
Purity	>%92	>%92	>%92	>%92
Color	Black	Black	Black	Black
Outer diameter	8-15 nm	8-15 nm	8-15 nm	1-2 nm
Inner diameter	5-8 nm	3-6 nm	4-7 nm	0,8-1,6 nm
Length	1-3 µm	30-50 µm	10-25 µm	5-35 µm
Tap density	0,3 g/cm^3	0,12 g/cm^3	0,3 g/cm^3	0,45 g/cm^3
True density	2,4 g/cm^3	2,2 g/cm^3	2,4 g/cm^3	2,2 g/cm^3
Specific surface area	240 m^2/g	260 m^2/g	65 m^2/g	400 m^2/g
Electrical conductivity	98 S/cm	98 S/cm	98 S/cm	98 S/cm

Table 4. (Continued)

Technical properties	**MWCNT**	**COOH MWCNT**	**OH MWCNT**	**SWCNT**
Manufacturing method	Chemical vapor deposition (CVD)	CVD	CVD	CVD
Supplier	Nanography Nanotechnology, METU Technocity, Ankara			

3.4. Experiments

Experiments performed using four CNT and one PAC as adsorbents to adsorb aclonifen from solutions are presented in Table 5.

Table 5 Experimental Matrix Used

Set No	T (ºC)	pH	Shaking rate (rpm)	Sonication	Aclonifen / Adsorbent (mg/mg)				
					MWCNT	**COOH MWCNT**	**OH MWCNT**	**SWCNT**	**PAC**
1	20	No pH adjustment	140	X	1/5	1/5	1/5	-	-
2	20	No pH adjustment	140	X	1/10	1/10	1/10	-	-
3	20	No pH adjustment	140	X	1/15	1/15	1/15	1/15	1/15
4	20	No pH adjustment	140	X	1/37	1/37	1/37	1/37	1/37
5	20	No pH adjustment	140	X	1/50	1/50	1/50	1/50	1/50
6	20	No pH adjustment	140	X	1/65	1/65	1/65	1/65	1/65
7	20	No pH adjustment	140	X	1/100	1/100	1/100	1/100	1/100
8	20	5.06	140	X	-	1/100	-	-	-
9	20	6.01	140	X	-	1/100	-	-	-
10	20	7.14	140	X	-	1/100	-	-	-
11	20	8.17	140	X	-	1/100	-	-	-
12	20	No pH adjustment	-	√	-	1/100	-	1/100	

During conducting the experiments indicated in Table 5, firstly, for each adsorbent type studied, kinetic tests were performed and time-dependent change of the aclonifen with seven different aclonifen (mg)/adsorbent (mg) ratios, namely, 1/100, 1/65, 1/50, 1/37, 1/15, 1/10, 1/5 mg aclonifen/mg adsorbent, was observed. Batch experiments were carried out in 250 mL glass beaker by adding different amount of adsorbents in 100 mL of aclonifen solutions. The prepared solutions were shaken by incubator shaker (ZHWY 200B, Zhicheng) (Figure 6) at 140 rpm, at 20˚C, unless otherwise stated. During the shaking period, samples were taken with 2 mL syringe at determined time intervals (0.5, 1, 2, 4, 6, 8, 10, 15, 20, 30, 45, 60, 80, 110, 150 minutes). In order to separate the adsorbent from the solution 0.22 μm syringe filter was used. However, it was observed that the PACs cannot be completely separated and a better separation is achieved by plugging cotton into 0.22 μm syringes. To prevent impurities from the cotton, the solvent (acetonitrile) and then distilled water were passed through the filter clogged with cotton. Finally, time-dependent graphs were drawn and pseudo first order and pseudo second order adsorption kinetic models analysis were performed. Moreover, in these time course aclonifen graphs, equilibrium concentrations were recorded and adsorption isotherm profiles were obtained. The isotherm data were then used to test for fitting of the adsorption process to Langmuir and Freundlich isotherm models.

As mentioned before aclonifen concentration is too low and it is difficult to study with high aclonifen concentration near to its solubility. Thus, in batch experiments, in order to achieve different adsorbate/adsorbent ratios, amount of adsorbent was altered while keeping aclonifen concentration constant at the highest possible value. In a way, the aclonifen concentration was tried to be kept at about 1±0.2 mg/L while altering the adsorbent amounts between 0.5 - 12 mg to get 1/5, 1/10, 1/15, 1/37, 1/50, 1/65, 1/100 aclonifen/ adsorbents ratios in 100 mL solution. To illustrate, for 1 mg/L aclonifen solution 10 mg adsorbent were used and this was stated as 1/100 mg/mg.

Before started each adsorption experiment, prepared aclonifen solutions were filtered by vacuum filtration. At the beginning, 0.45 μm filter was used. When the aclonifen concentration of a prepared solution was measured via HPLC, different values were obtained with each injection. Therefore, it was thought that the insoluble aclonifen remained in the solution, and the solutions were filtered through a 0.1 μm filter.

Figure 6. Shaking Incubator Used (ZHWY 200B, Zhicheng)

3.4.1. Effect of pH

Effect of pH on the extent of adsorption process was evaluated by carrying out batch experiments at different pH values, namely 5, 6, 7 and 8. This part of the study was conducted for only one of the CNTs tested, namely, COOH MWCNT as it outperformed among the others during the first phase of the experimentations. To this purpose, experiments were performed at constant adsorbate/adsorbent ratio of 1/100 mg aclonifen/mg COOH MWCNT that had appeared as optimum ratio during the initial phase of experiments with COOH MWCNT, while varying pH. In addition, temperature and rpm were set as 20 ˚C and 140 rpm, respectively.

During the setting for pH values, pH 6, 7 and 8 were adjusted by using 0,1 M buffer prepared by 1 M K_2HPO_4 and 1 M KH_2PO_4 whereas pH 5 was adjusted by using another 0,1 M buffer solution prepared by 1M $Na_2HPO_42H_2O$ and 1 M KH_2PO_4 as given by DeAngelis, 2007; Kimyaevi, n.d Conditions for the pH experiments are given in Table 6.

Table 6. Conditions for the pH Experiments

Set no (as from Table 5)	**pH**	**Aclonifen/CNT (mg/mg)**	**Temperature (˚C)**	**Agitation rate (rpm)**	**Used CNT**
8	5.06	1/100	20	140	COOH MWCNT
9	6.01	1/100	20	140	COOH MWCNT
10	7.14	1/100	20	140	COOH MWCNT
11	8.17	1/100	20	140	COOH MWCNT

3.4.2. Effect of Sonication

In order to investigate effect of sonication on adsorption of aclonifen on CNTs, ultrasonic water bath was coupled to the experimental system. This effect was investigated with COOH MWCNT, as in the case of effect of pH study and with SWCNT. The reason for inclusion of SWCNT in this part of the study lies behind the fact that there would be a potential of aggregation of SWCNT in water solution and it would be possible to eliminate this undesirable condition via sonication. Aclonifen/CNT ratio was kept at 1/100 mg/mg. Temperature of ultrasonic water bath was set as 20 ˚C and water make-up was up to about ¾ of the beaker. However, it was realized that temperature could not be fixed at 20 ˚C due to sonication, although it was set as 20 ˚C. Thus, ice bar was used in order to prevent increasing in temperature, and it was controlled with thermometer. Sonication was commenced as soon as adding the adsorbent into the reaction solution, and samples were taken at regular time intervals for aclonifen analysis.

3.4.3. Effect of Water Matrixes

The above-mentioned experimental studies were conducted with synthetic wastewater produced via spiking aclonifen into the Millipore water. The aim was to observe the adsorption behavior of aclonifen onto CNTs. However, it is of the fact that in real domestic or urban wastewater there will be some other ingredients, primarily an organic matter. So, one should expect some interaction (interference and/or enhancement) between aclonifen and organic matters during adsorption. Therefore, adsorption trial was also performed using a biologically treated (secondary level treatment) wastewater containing aclonifen originally. In another study conducted in our department, also as part of the same TÜBİTAK project, biologically treated effluents were generated from the lab scale sequential batch reactors receiving synthetic domestic wastewater spiked with aclonifen. And, aclonifen adsorption experiment was conducted with this effluent. No additional aclonifen was spiked to this effluent, just the removal of the existing (i.e. remaining) aclonifen was monitored. In this experiment, adsorption isotherms were not dealt with. It was carried out just to see the effect of wastewater matrix on the treatment efficiency by COOH MWCNT under optimum conditions obtained with synthetic wastewater (i.e. aclonifen solution). The conditions for this experiment are given in Table 7.

Table 7. The Conditions for the Experiment Carried out with Biologically Treated Wastewater

Wastewater	**Temperature (˚C)**	**Agitation rate (rpm)**	**Aclonifen/ CNT (mg/mg)**	**Used CNT**	**pH**
Biologically treated wastewater	20	140	1/100*	COOH MWCNT	6.4 – 6.5 (No pH adjustment)

*in the synthetic domestic wastewater fed to the lab scale biological treatment unit.

3.4.4. Verification of Aclonifen Adsorption via SEM, FTIR Analysis

The morphology and surface structure of adsorbents before and after adsorption were been examined with scanning electron microscope (SEM) and Fourier transform infrared (FTIR) analysis were been performed for the analysis of the chemical surface groups of these adsorbents at the Central Laboratory (METU).

3.5. Analytical Methods

3.5.1. Measurement of Aclonifen-HPLC Method

Shimadzu LC10AT high performance liquid chromatography (HPLC) (Figure 7) was used for the analysis of aclonifen.

Figure 7. Shimadzu LC10AT HPLC Device

As there is no USEPA method available for aclonifen analysis, there was a need to develop a suitable measurement method for aclonifen analysis via HPLC. To this purpose, taking the literature studies into consideration, 8 different wavelengths of 296 nm, 299 nm, 290 nm, 270 nm, 238 m, 279 nm, 320 nm and 220 nm were tested and the optimal wavelength was determined as 220 nm. Other conditions determined for aclonifen analysis are provided in Table 8.

Through this method, calibration curve (R^2 = 0.9999) was obtained by using acetonitrile solutions of 2 mg/L, 1 mg/L, 0.5 mg/L, 0.1 mg/L, 0.05 mg/L, 0.02 mg/L, 0.01 mg/L. The calibration curve is given in Figure 8. HPLC operating conditions are also given in Table 8.

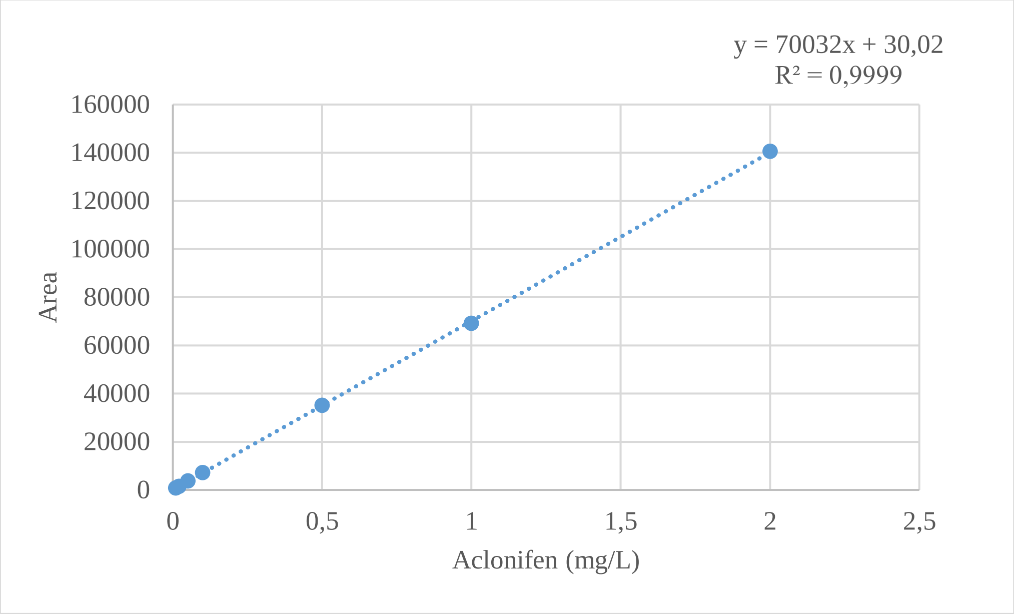


Figure 8. Calibration Curve for Aclonifen

Table 8. Operating Conditions of HPLC for Analysis of Aclonifen

Mobile phase	60% Acetonitrile- 40% water
Flow rate	1,5 mL/min
Column	InertSustain C18 colon (4.6 × 250 mm, 5-µm)
Column furnace temperature	40 ºC
Retention time	8.3-9 min
Detector	SPD-10 Avp UV\VIS
Detection wavelength	220 nm
Injection volume	20 µL

3.5.2. Measurement of Temperature and pH

Temperature and pH were measured with Hach HQ40D portable multimeter (Hach, USA).

3.6. Adsorption Isotherm Analysis

For every adsorption experiment, adsorbates adsorbed on adsorbents were plotted against with the solution equilibrium concentration; then, Langmuir and Freundlich isotherm curves that which describe the equilibrium relationship were figured out.

Langmuir isotherm: the linear form of Langmuir isotherm is represented by Equation 8 (Nethaji et al., 2013).

$$\frac{1}{q_e} = \frac{1}{qm*b*Ce} + \frac{1}{q_m} \qquad (8)$$

Where,

q_e = equilibrium amount of adsorbate adsorbed per gram of adsorbent (mg/g)

C_e = equilibrium adsorbate concentration in the solution (mg/l)

b = Langmuir adsorption constant (l/mg)

q_m = theoretical maximum amount of adsorbate adsorbed per unit amount of adsorbent (mg/g)

Hence, by plotting $1/q_e$ vs $1/c_e$, the value of q_m is obtained from the intercept ($1/q_m$) and the value of b is obtained from the slope ($1/q_m b$).

Freundlich isotherm: the linear form of Freundlich isotherm is represented by Equation 9

$$\log q_e = \log K_f + \frac{1}{n} * \log C_e \qquad (9)$$

Where,

q_e = equilibrium amount of adsorbate adsorbed per gram of adsorbent (mg/g)

C_e = equilibrium adsorbate concentration in the solution (mg/l)

K_F = Freundlich adsorption constant (l/mg)

1/n = Constant for adsorption intensity (dimensionless)

When plotting log qe vs log Ce, n can be obtained from the slope that is 1/n and K_f can be obtained from the intercept ($\log K_f$) (Al-Duri, 1996).

3.7. Adsorption Kinetics Analysis

Pseudo-first-order and pseudo-second--order adsorption kinetic models were tested for the adsorption data obtained.

The linear form of pseudo first order kinetic equation (Equation 10) is given below (Kumar, 2006).

$$log(q_e - q(t)) = log(q_e) - \frac{K_1 * t}{2,303} \tag{10}$$

where:

qe = amount of adsorbate at equilibrium (mg/g)

K1 = equilibrium rate constant of pseudo first-order adsorption (min^{-1})

q(t)= amount of adsorbate adsorbed per gram of adsorbent at time t (mg/g)

t=adsorption time (min)

K1 and qe can be obtained from the intercept and slope of linear plot of log (qe-q) vs t.

$$\mathrm{K}_1 = -2.303 * \mathrm{slope}, \quad \mathrm{qe} = 10^{\mathrm{intercept}}$$

The linear from of pseudo-second-order kinetics equation is given below (Kumar, 2006).

$$\frac{t}{q(t)} = \frac{1}{K_2 * q_e^2} + \frac{t}{q_e} \tag{11}$$

Where:

q(t)= amount of adsorbate adsorbed per gram of adsorbent at time t (mg/g)

K2= equilibrium rate constant of pseudo-second-order adsorption (g/(mg*min))

By plotting t/q (t) vs t graph, K_2 and q_e can be obtained from the intercept and slope of this graph.

$$\mathrm{K}_2 = \mathrm{slope}^2/\mathrm{intercept}, \ \mathrm{qe} = 1/\mathrm{slope} \tag{12}$$

3.8. Chemicals

Aclonifen standard solution (99%) used in the study was purchased from Ehrenstorfer GmbH (Augsburg, Germany). HPLC grade acetonitrile (gradient grade, > 99.9), sodium phosphate dibasic dihydrate (≥ %99.5), dipotassium hydrogen phosphate (≥ %98) were purchased from Merck (Darmstadt, Germany).

3.9. Laboratory Devices and Equipment

All lab wares (beakers, glass pipettes, volumetric flasks, vacuum filtration glasswares etc.) used during the experiments were washed and dried before usage to eliminate any associated contamination interference (i.e. impurities etc.) and ultimately to obtain safe and reliable data sets. The following steps carried out this cleaning. First, the lab wares were washed with a detergent called Alconox in hot water, rinsed with tap water and then ultra-pure water, and final rinsing was done with HPLC grade acetonitrile. Finally, the lab wares were dried at 105°C for 1 h after the cleanup procedure.

Laboratory devices and equipment used during the experiments are listed in Table 9 with the intended use of each.

Table 9. Laboratory Devices and Equipment

Name/Model	**Intended Use of Device**
HPLC- SHIMADZU, LC 10AT	Pesticide analysis
Incubator Shaker/ ZHWY-200B	Provide mixing for homogeneous conditions
Ultra-pure Water Device/ MilliporeMilli- Q Simplicity 188	Ultra-pure water obtainment
Magnetic Stirrer/ Isolab 613.03.001	Solutions preparation
Analytical Balance/ Sartorius GC8035-OCE	Chemical weight measurement

Table 9. (Continued)

Name/Model	**Intended Use of Device**
Ultrasonic Water Bath/ Cole-Parmer	Degassing of Mobile phase used in HPLC and sonication for prevention of CNT aggregation
Refrigerator	Safely storage of the samples and solutions
Furnace Nüve FN/032/055/120 Dry Heat Sterilizer	Drying apparatus
Multi meter/ HQ40d multi	pH and temperature measurement

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, the results obtained from the experimentations carried out toward the treatment of aclonifen via adsorption by CNTs and PAC are given. In addition, the inferences that can be drawn out from the results are discussed.

4.1. Effectiveness of Adsorbent Type on Aclonifen Removal

Batch experiments were performed to investigate effectiveness of adsorbent type on aclonifen removal efficiency. As explained in Section 3, different aclonifen/adsorbent ratios were used to get adsorption isotherms. Therefore, effect of these ratios on removal efficiency was also observed, concurrently. In the following sections, removal of aclonifen by PAC, MWCNT, COOH MWCNT, OH MWCNT and SWCNT were explained by the evaluation of time dependent aclonifen removal graphs.

4.1.1. Powdered Activated Carbon (PAC)

Time dependent aclonifen removal by PAC for different adsorbate to adsorbent ratios and the corresponding removal efficiencies attained when equilibrium is reached are shown in Figure 9. As shown in Figure 9a, for all aclonifen/PAC ratios tested, the removal of aclonifen started immediately with the addition of PAC to the solution. In the first few minutes, there was a rapid decline in aclonifen concentration. In the subsequent period, the removal rate ceased down. In addition, it is seen that time to reach equilibrium increased with the increase in aclonifen/PAC ratio. The equilibrium time for the ratio of 1/100 was 10 min., while it was about 55 min for the ratio of 1/10. However, when they reached equilibrium, no significant differences in final removal percentages were observed as seen in Figure 9b. The removal efficiencies were 96%, 94%, 95%, 91%, and 85% for the ratio of 1/100, 1/65, 1/50, 1/28, 1/10, respectively. Beyond the ratio of 1/50, there was no significant change in the removal efficiency.

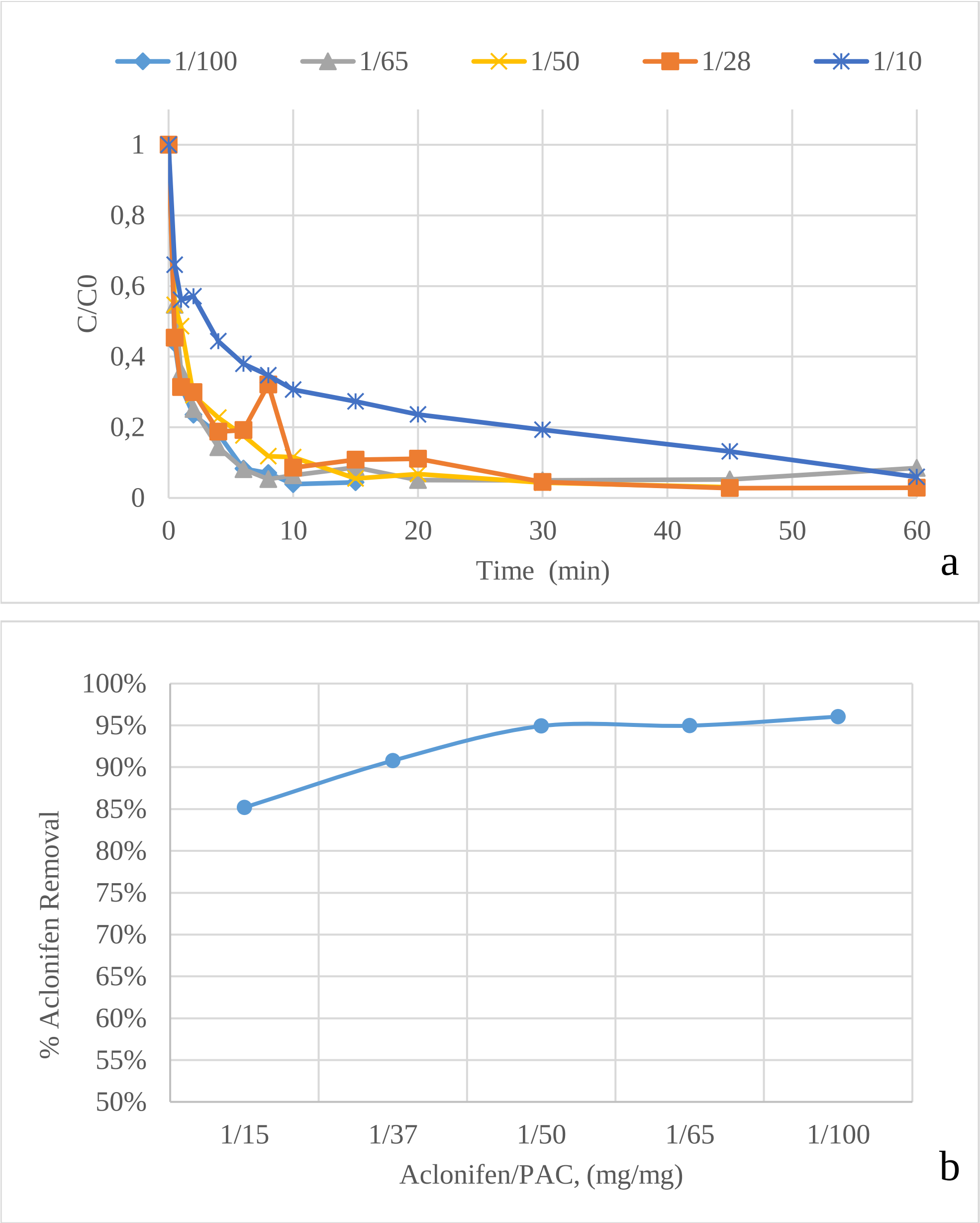


Figure 9. Removal of Aclonifen from Aqueous Solutions by PAC: (a) Time Course Variation of Aclonifen at Different Aclonifen/PAC Ratios; (b) % Aclonifen Removal vs Aclonifen/PAC Ratio

In Figure 10 SEM images of activated carbon both before and after aclonifen adsorption are given. In these figures, it is clear that aclonifen was adsorbed onto surface of activated carbon. In the images belonging to the PAC before adsorption, pores can be seen easily, while they cannot be seen after adsorption. This confirms that pores were filled up by aclonifen.

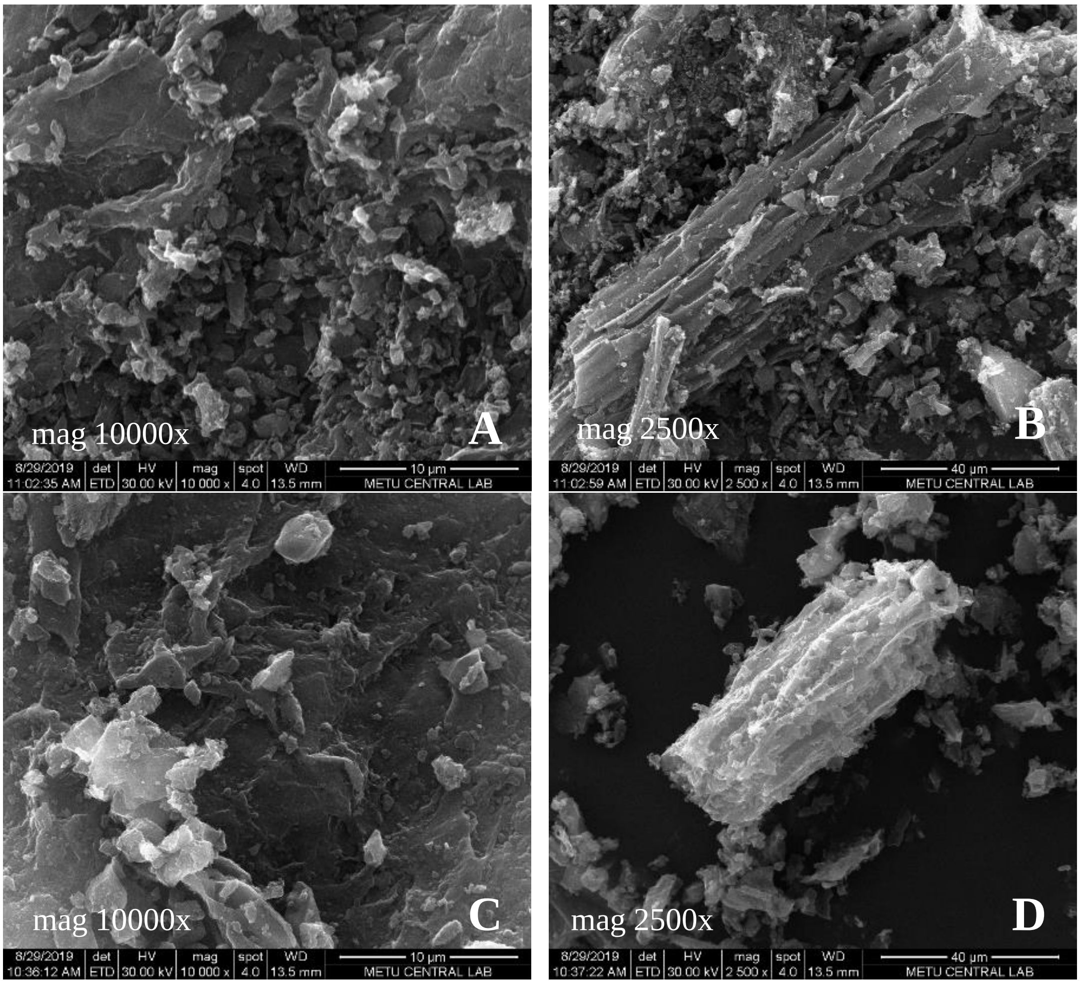


Figure 10. SEM Images of AC. (A-B) Before Adsorption, (C-D) After Adsorption

4.1.2. Carbon Nanotubes

4.1.2.1. Multiwalled Carbon Nanotubes

In Figure 11, Figure 13 and Figure 15, the effect of aclonifen/adsorbent ratio on the removal of aclonifen from aqueous solution are shown for MWCNT, COOH MWCNT and OH MWCNT with the graph of time dependent aclonifen removal. As shown in the graphs, effect of all three type of MWCNT on the removal of aclonifen are similar. Aclonifen removal began immediately with the addition of adsorbent to the solution. In the first few minutes, rapid decrease was observed in aclonifen concentration followed by a slowdown in the removal rate. In addition, it is clear that as the ratio of aclonifen/adsorbent increases (i.e. 1/50 > 1/100), equilibrium time increases and the removal efficiency is reduced considerably. This is due to the fact that the available active adsorption sites increase with the amount of adsorbent at constant adsorbate concentration.

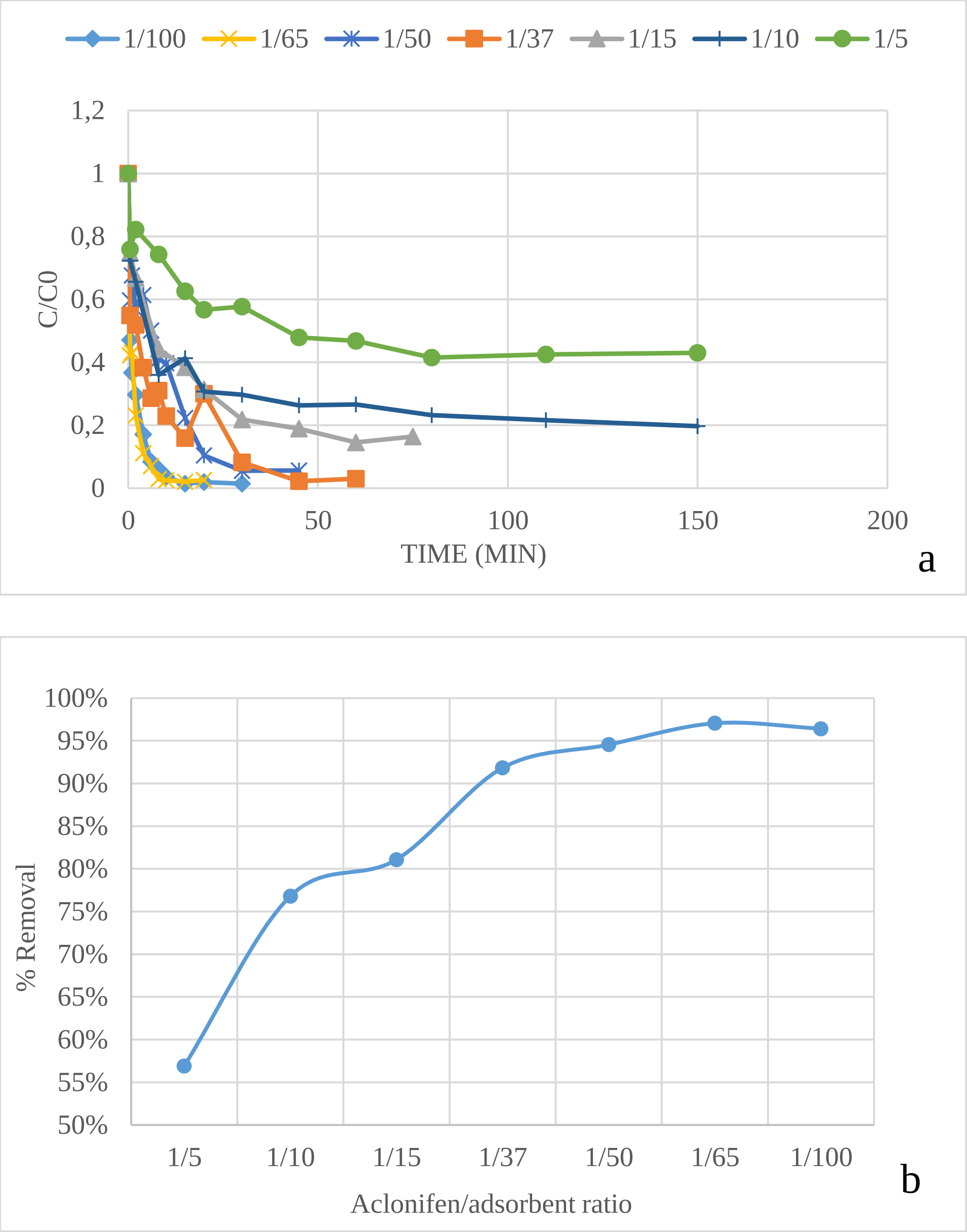


Figure 11. Removal of Aclonifen from Aqueous Solutions by MWCNT: (a) Time Coarse Variation of Aclonifen at Different/MWCNT Ratios; (b) % Aclonifen Removal vs Aclonifen/MWCNT Ratio

When the results for MWCNT were examined, it can be seen that removal efficiencies were 96%, 97%, 95%, 92%, 81%, 77% and 57% for the ratio of 1/100, 1/65, 1/50, 1/37, 1/15, 1/10 and 1/5 respectively. Beyond the ratio of 1/50, there was no significant change in removal efficiency.

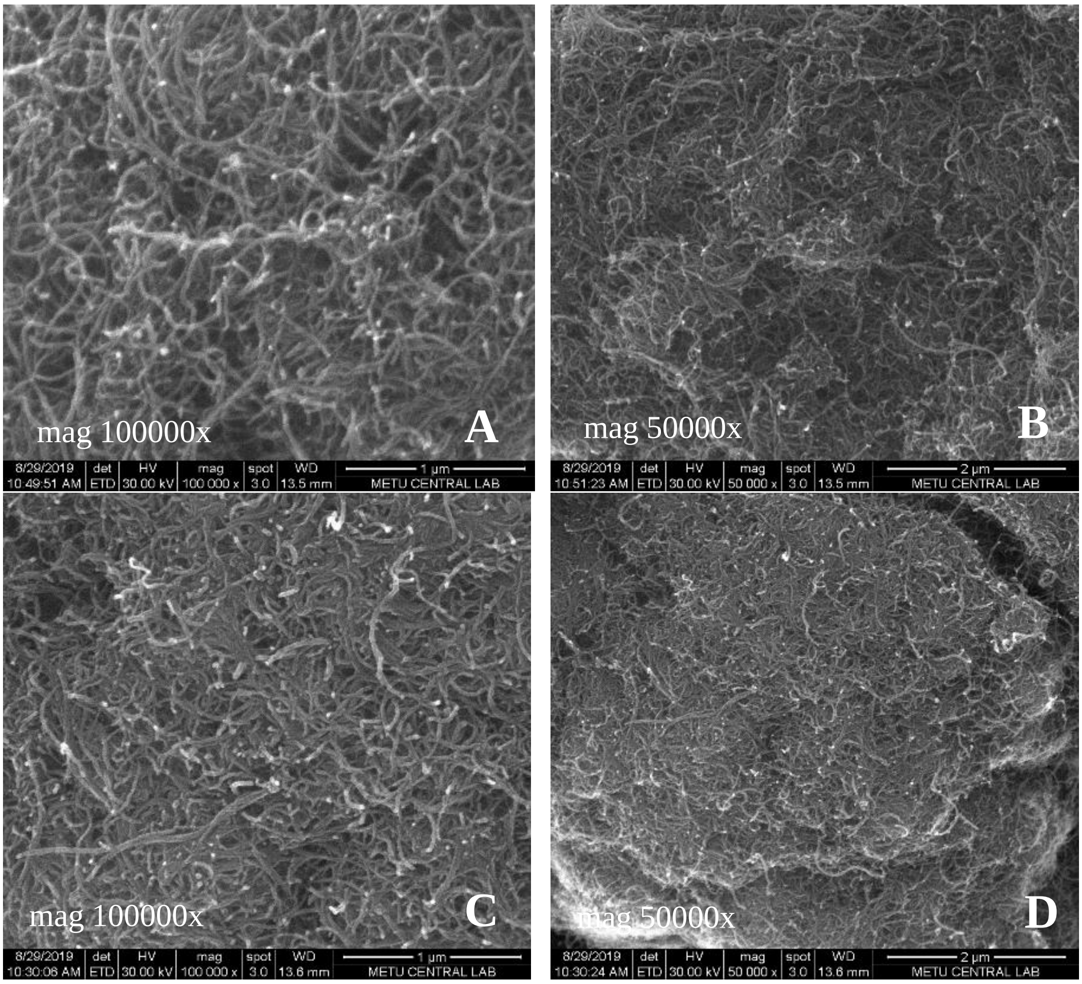
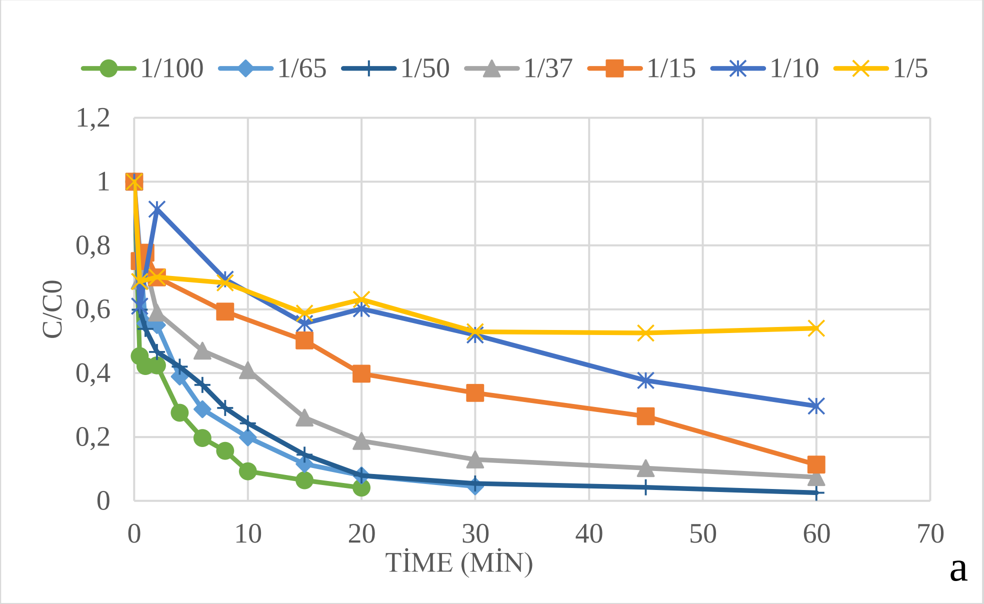


Figure 12. SEM Images of MWCNT. (A-B) Before Adsorption, (C-D) After Adsorption

SEM images of MWCNT before and after aclonifen adsorption are given in Figure 12. The gaps between the tubes of MWCNT were seen filled after adsorption, being more compact after adsorption. This can be taken as a verification of adsorption of aclonifen on external surface, interstitial channels and grooves of MWCNT.



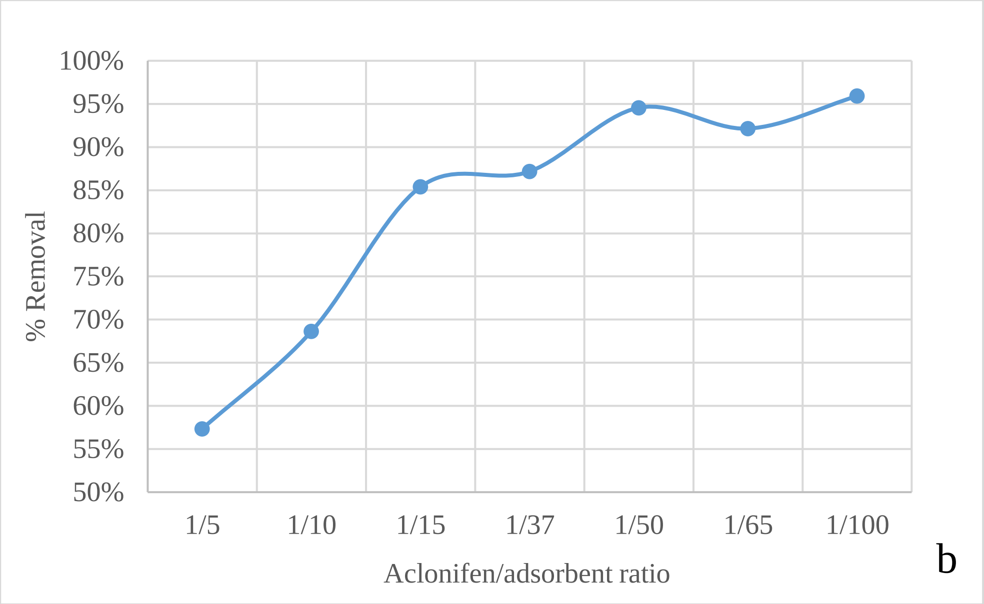


Figure 13. Removal of Aclonifen from Aqueous Solutions by COOH MWCNT: (a) time Coarse Variation of Aclonifen at Different/COOH MWCNT Ratios; (b) % Aclonifen Removal vs Aclonifen/COOH MWCNT Ratio

Additionally, from Figure 13 it is seen from Figure 13 that as the ratio of aclonifen/COOH MWCNT increases there occurred a progressive decrease in the removal efficiencies. This decrease was less pronounceable beyond the ratio of 1/37.

The removal efficiencies attained were 96%, 92%, 95%, 87%, 85%, 69%, 57% when the ratios were 1/100, 1/65, 1/50, 1/37, 1/15, 1/10, 1/5 respectively.

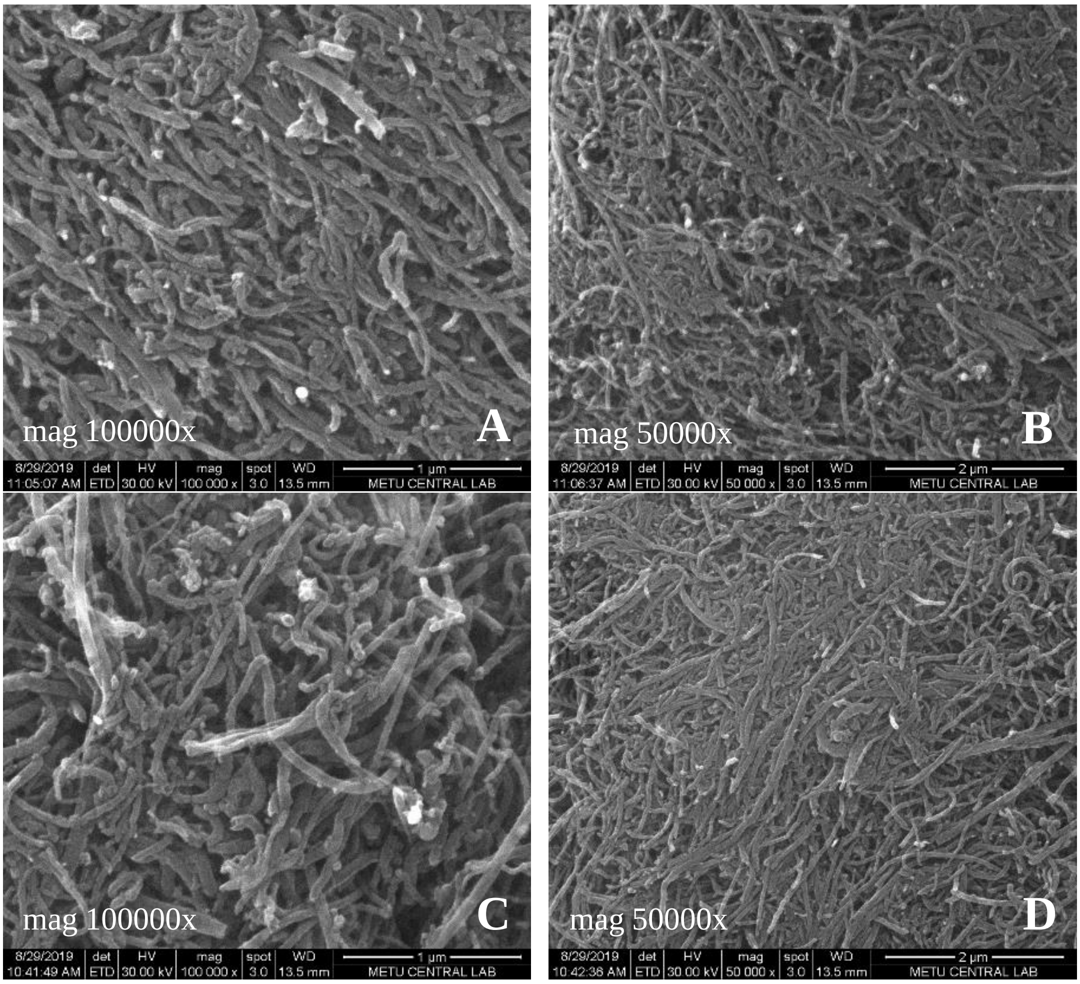


Figure 14. SEM images of COOH MWCNT. (A-B) Before Adsorption, (C-D) After Adsorption

SEM images of COOH MWCNT before and after aclonifen adsorption are provided in Figure 14. It is clear from the figure that diameter of the tubes was increased after adsorption. Thus, it can be said that aclonifen was adsorbed onto the surface of COOH MWCNT. Also, it is seen that the gaps between the tubes were packed after adsorption as for the other CNTs, which can be inferred as a visual indication adsorption of aclonifen into the interstitial channels and grooves.

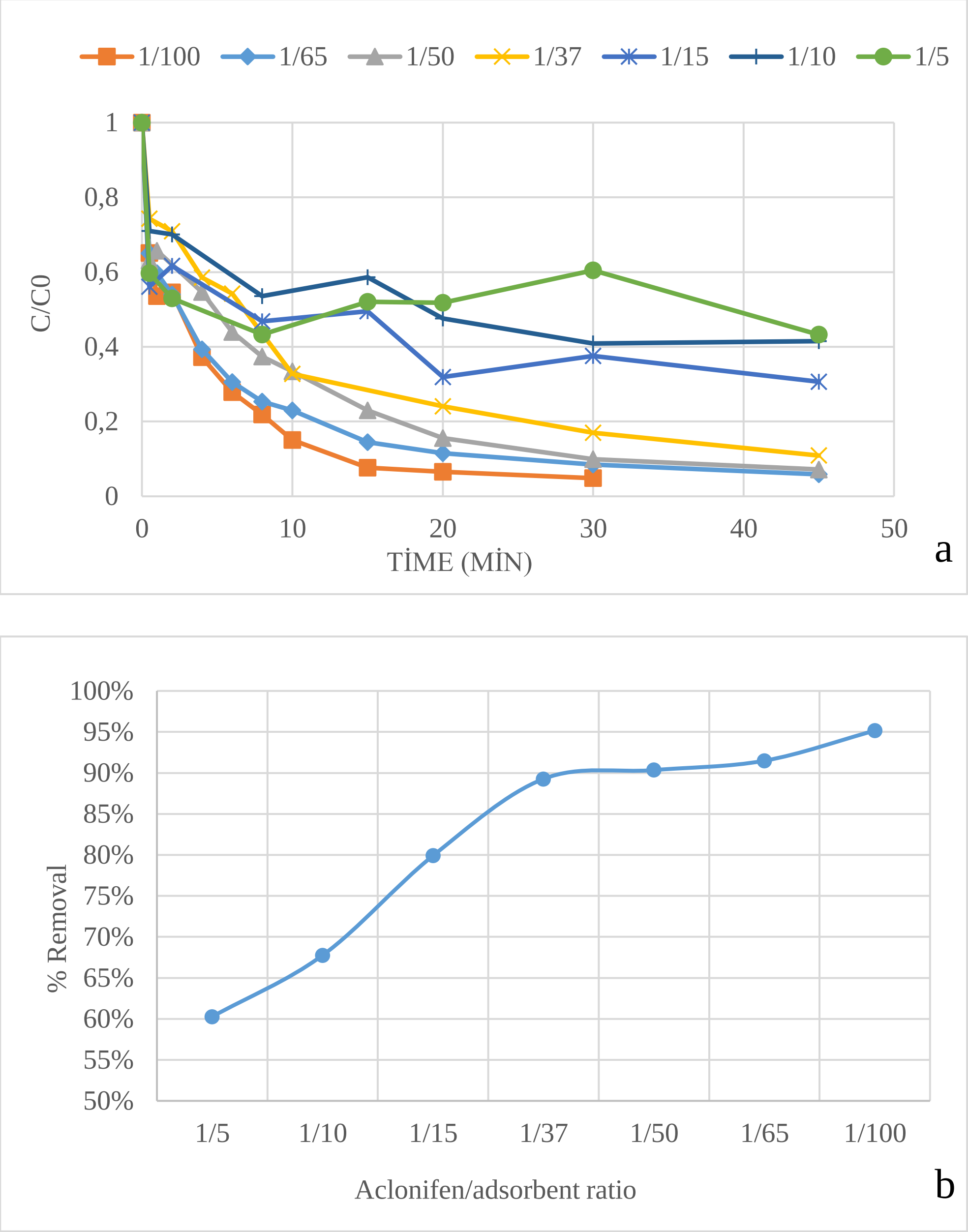


Figure 15. Removal of Aclonifen from Aqueous Solutions by OH MWCNT: (a) Time Coarse Variation of Aclonifen at Different/OH MWCNT Ratios; (b) % Aclonifen Removal vs Aclonifen/OH MWCNT Ratio

Figure 15 presents the removal of aclonifen by OH MWCNT at different aclonifen/OH MWCNT ratios. As seen from this figure, that there was a quite distinct removal trends for the ratios above and below 1/37. The removal efficiencies were 95%, 91%, 90%, 89%, 80%, 68%, and 60% for the ratios 1/100, 1/65, 1/50, 1/37, 1/15, 1/10, 1/5 respectively. There was no significant change in the removal efficiency when the ratio is less than 1/37 (i.e. all above 90%).

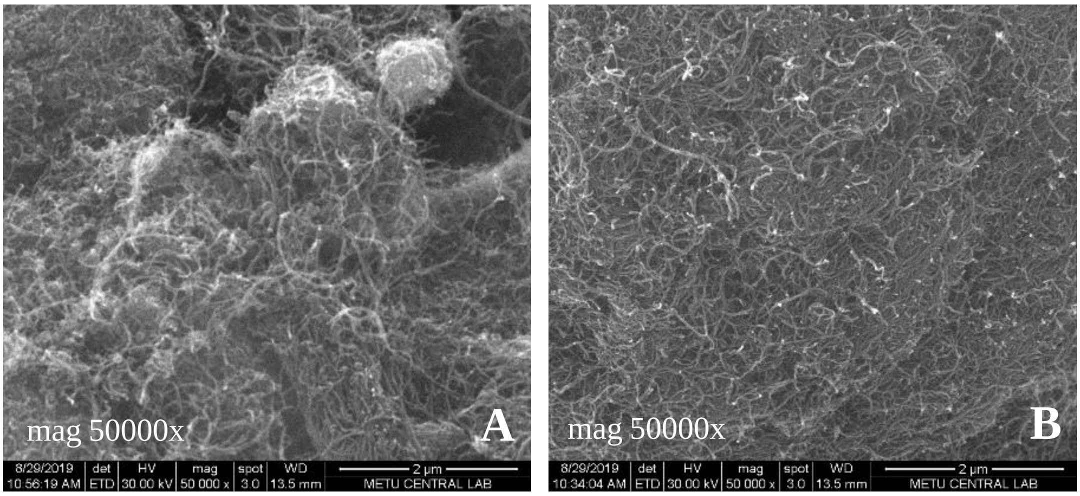


Figure 16. SEM Images of OH MWCNT. (A) Before Adsorption, (B) After Adsorption

Figure 16 presents SEM images of OH MWCNT before and after aclonifen adsorption. Despite the evidence of aclonifen adsorption by OH MWCNT through the experimental measurements (Figure 15), it was clearly observable from the SEM images. Still, the image belonging to the stage after adsorption (Figure 16B) seems more packed when it is scrutinized. This could be attributed to the probable fill of the interstitial channels of OH MWCNT by the aclonifen.

4.1.2.2. Single Walled Carbon Nanotubes

As can be seen from Figure 17, aclonifen removal immediately started with the addition of SWCNT to the solution. In the first minutes, the aclonifen concentration decreased sharply, and the removal rate slowed down in the subsequent process. It can be inferred from Figure 17 that in contrast to other used adsorbent (i.e. MWCNT), the change in the ratio of aclonifen/SWCNT did not have a remarkable effect on the equilibrium time and the removal efficiency. The effect of aclonifen/SWCNT ratio on the removal efficiency is shown in Figure 17. As seen from this figure, there was no clear trend in the removal efficiencies with respect to the aclonifen/SWCNT ratio. Nevertheless, it would not be wrong to state that higher removal efficiencies are attained with lower aclonifen/SWCNT ratios. Lower ratios than 1/65 enabled to reach the removal efficiencies above 90%.

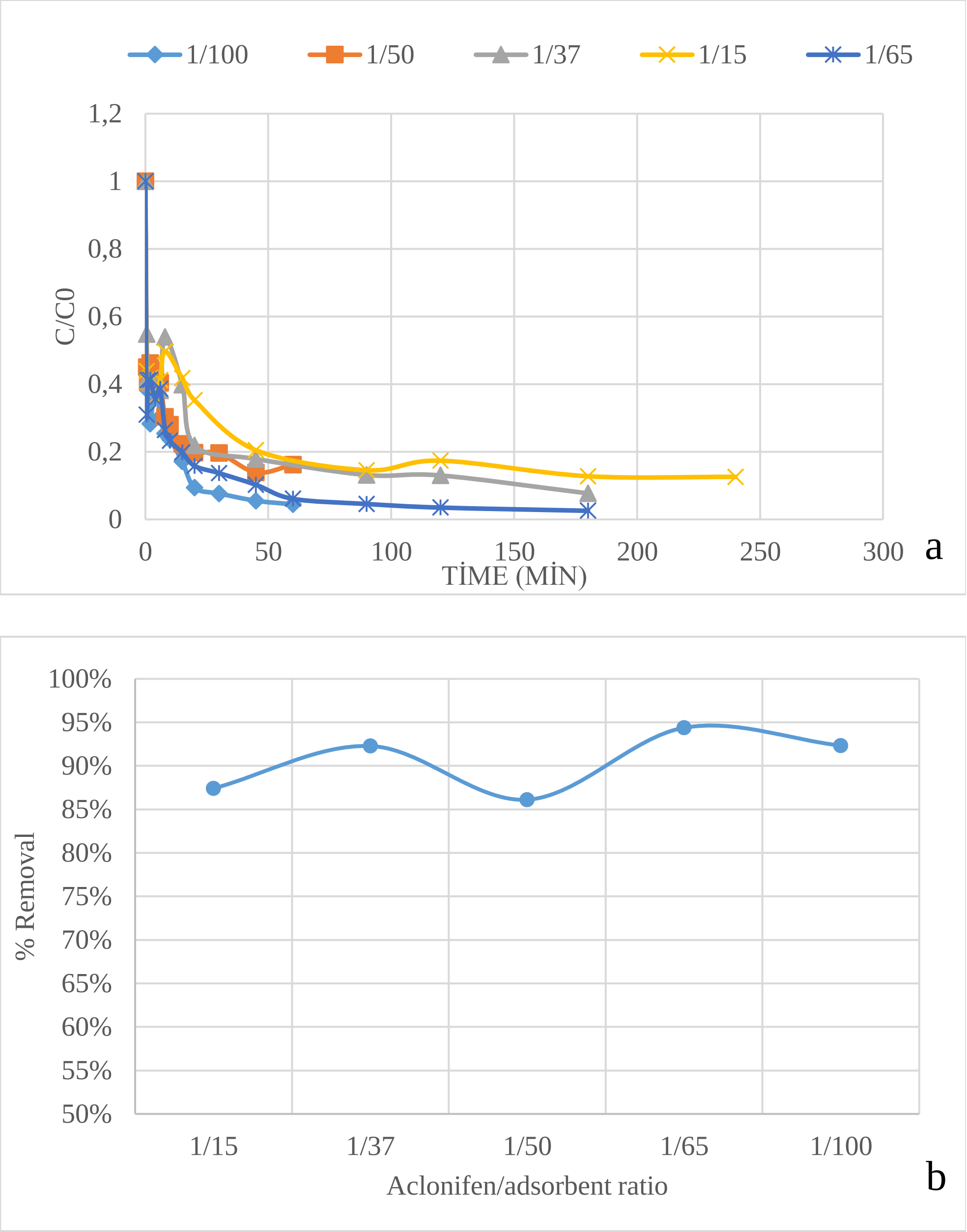


Figure 17. Removal of Aclonifen from Aqueous Solutions by SWCNT: (a) Time Course Variation of Aclonifen at Different/SWCNT Ratios; (b) % Aclonifen Removal vs Aclonifen/SWCNT Ratio

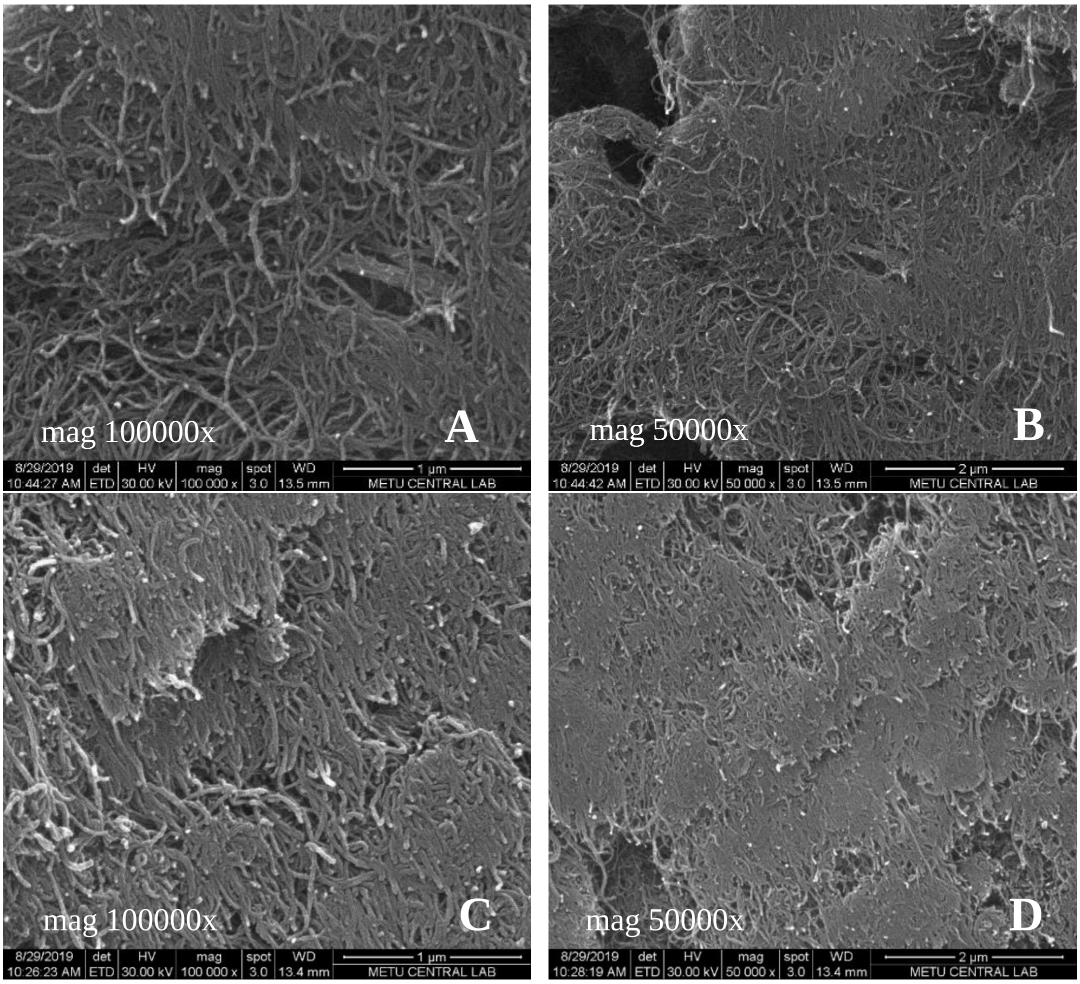


Figure 18. SEM images of SWCNT. (A-B) Before Adsorption, (C-D) After Adsorption

SEM images of SWCNT before and after aclonifen adsorption are shown in Figure 18. It is clearly seen from the images that aclonifen filled the spaces between the tubes of SWCNT that form the interstitial channels and groves.

4.1.3. Adsorption Isotherms

Figure 19 presents the adsorption isotherms for aclonifen with different adsorbents. This graph depicts the relationship between the amount of aclonifen adsorbed per unit mass of a given carbon-based adsorbent and the equilibrium concentration of aclonifen in the solution. As can be seen, although there are no remarkable differences, aclonifen molecules are favorable to be adsorbed onto COOH MWCNT, followed by OH MWCNT, MWCNT, SWCNT and PAC.

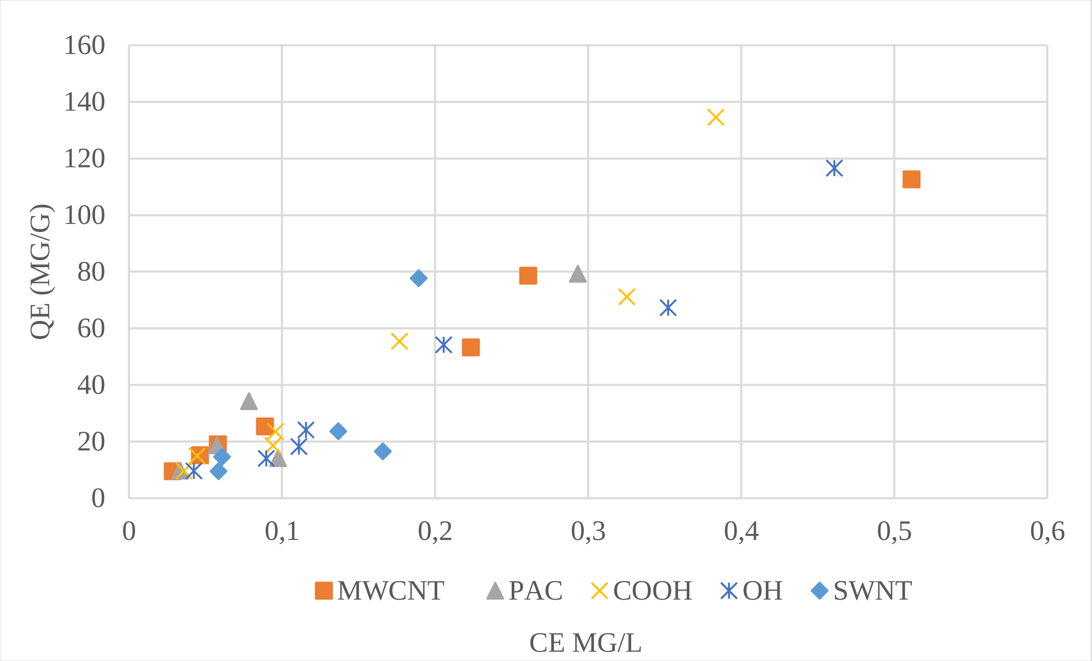


Figure 19. Adsorption Isotherms of Aclonifen for Different Types of Adsorbent

When comparing the MWCNTs and PAC, it is obvious that MWCNTs have higher adsorption capacities than PAC. This may be attributed to the electronic properties and unique structure of CNTs. The CNTs consist of hexagonal arrays of carbon atoms in graphene sheets that surround the tube axis. One should expect strong interactions between the benzene ring of aclonifen and the surface of the CNTs (Long & Yang, 2001). Indeed, CNTs have similar adsorption mechanisms to PAC, via physical adsorption and interaction of specific chemical functionality with the carbon lattice. However, as mentioned in Chapter 3, diffusion into the porous structure is only way for interaction of compounds with PAC, while internal diffusion is not a limiting factor for compounds to interact with CNTs.

Supportingly, Pan and Xing (2008) claimed that the adsorption advantage of MWCNTs over traditional PAC do not result from greater overall surface area, but from high-energy binding sites and weak interaction with water. Lu et al., (2005) also observed that CNTs have shorter adsorption equilibrium time and higher adsorption capacity for trihalomethanes (THMs) than powdered activated carbons. Additionally, in another study conducted by Peng et al., (2003) it was observed that CNTs have high adsorption efficiency and short equilibrium time (40 min) for removal of 1,2-dichlorobenzene by CNTs from water. As well, the sorption of dioxin by both CNT and PAC was studied by Long & Yang, (2001). It was found that adsorption energy of dioxin on CNTs is much higher (approximately 3 times) than that of activated carbon. Therefore, higher dioxin removal efficiency was expected with CNTs than that with PAC due to the strong interaction between dioxin and CNTs. This was attributed to the electronic properties and unique structure of carbon nanotubes. Strong interactions between the two benzene rings of dioxin and the surface of the CNTs are expected. In addition, the dioxin molecule interacts with all surfaces on the walls of CNTs within the small pore (i.e., 2.9 nm), and adsorption potentials occur in the pores are improved by overlapping these interaction potentials.

However, several studies have observed low adsorption capacities for CNT, and it is thought to have resulted from that those CNTs were not open-ended. It means that the ends of tubes were closed by impurities and the access of pollutants to inner space were blocked (Gangupomu, 2013).

When the adsorption capacities of MWCNTs, COOH functionalized CNTs and OH functionalized CNTs are compared, the capacities of COOH MWCNTs and OH MWCNTs are almost the same, but they are a little more than that of MWCNT. This can be attributed to that hydrogen bonding can be formed between oxygen-containing functional groups (OH and COOH) and aclonifen. In addition, it can be explained by the π- π electron-donor–acceptor mechanism. The carboxylic oxygen atom of CNT surface may act as the electron-donor and the aromatic ring of aclonifen may act as the electron acceptor.

Supportively, Lu et al., (2008) studied on adsorption of BTEX molecules (benzene, toluene, ethylbenzene and p-xylene) by CNTs and observed that functional groups increase the adsorption capacity. It was attributed to the electrostatic interaction between the positively charged BTEX molecules and the negatively charged surface of COOH functionalized CNTs. In addition, it was suggested that the increase in adsorption is resulted by the π-π electron-donor–acceptor mechanism. Carboxylic oxygen-atom of CNT surface act as the electron-donor and the aromatic ring of BTEX acts as the electron-acceptor. Yu et al., (2012) reported a drastic increase (~100%) in adsorption capacities of ethylbenzene, toluene and m-xylene with increasing surface oxygen content per specific surface area (SSA) of MWCNTs up to ~8%. It was thought that this increase was due to the increased dispersion of CNTs as well as the increased available adsorption sites. However, when oxygen content per SSA increased up to 18%, adsorption capacity exhibited a decreasing trend.

In contrast, Sheng et al., (2010) found that functional groups of CNTs inhibit the adsorption of ionizable aromatic compounds (IACs) on MWCNTs because of repulsion of negative charges. Also, they expected that carboxylic groups on the surfaces of MWCNTs may act as the electrons withdrawing groups for π system of MWCNTs. So, π-π dispersion forces between the aromatic rings of IAC and the structure of MWCNT could be interfered. Moreover, several studies also demonstrated that an increase in surface oxygen content of CNTs causes the synthetic organic compounds SOC adsorption to decrease. (Shen et al., 2009; Cho et al., 2008; Zhang et al., 2010; Li, et al., 2011).

The experimental data for aclonifen adsorption onto CNTs and PAC were translated into the isotherm models of Langmuir and Freundlich in linearized form as provided in Figure 20. Langmuir constant q^{max} and b, Freundlich constants K_f and n determined are presented in Table 10.

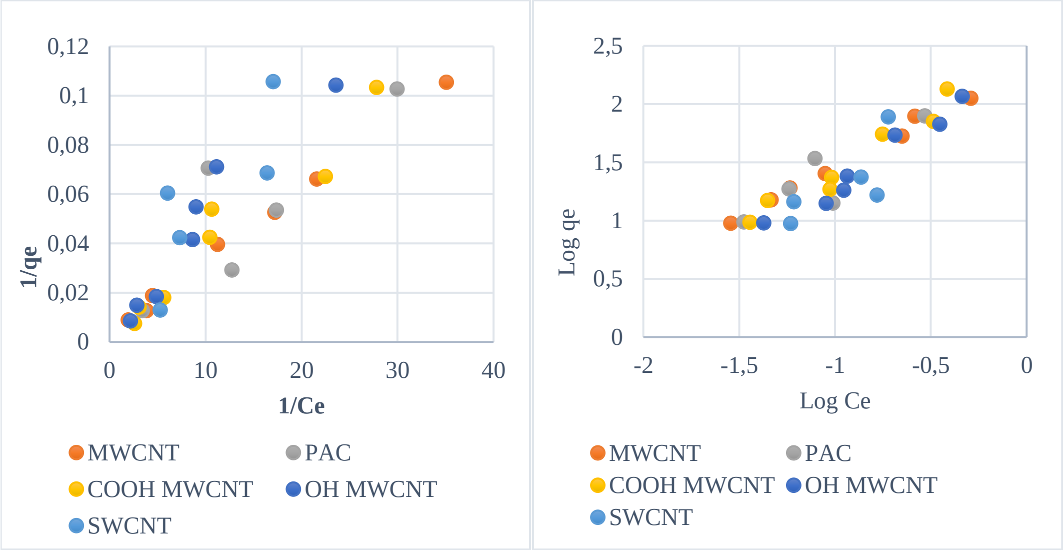


Figure 20. Langmuir and Freundlich Isotherm Plots for the Adsorbents Tested for Aclonifen Adsorption

Table 10. Langmuir and Freundlich Isotherms

Isotherms	Parameters	PAC	MWCNT	COOH MWCNT	OH MWCNT	SWCNT
Langmuir $qe=(q^{max}*b*Ce)/(1+b*Ce)$	q^{max}(mg/g)	110.740	249.582	278.790	254.434	125.576
	b (L/mg)	2.980	1.385	1.054	0.855	1.659
	R^2	0.721	0.997	0.936	0.930	0.668
Freundlich $qe=Kf*Ce^\wedge(1/n)$	K_f (L/mg)	214.852	213.394	274.945	239.493	231.076
	Log K_f	2.332	2.329	2.439	2.379	2.364
	n	1.114	1.155	0.992	0.925	0.926
	R^2	0.770	0.991	0.947	0.957	0.575

The value of R^2 closer to one indicates that the respective equation better fits the experimental data. When the R^2 values in Table 10 are examined, it can be stated that both Langmuir and Freundlich isotherm models match the experimental data very well for MWCNT, with the correlation coefficient values of 0.997 and 0.991 respectively. The parameters obtained from the two models provide significant information on the adsorption mechanism and the affinity of the adsorbent. The values determined using the equations provided in Chapter 3 are given in Table 10. The maximum adsorption capacity of MWCNT calculated from Langmuir model is found as 249.582 mg/g.

Also, K_f value, which is indicative of the relative adsorption capacity, calculated from Freundlich model is 213.94 L/mg.

For COOH MWCNT and OH MWCNT, the higher coefficients of R^2 (0.947 and 0.957) of the Freundlich equation suggest that the Freundlich equation can be used to fit the experimental adsorption data and evaluate the maximum aclonifen adsorption capacities of these two adsorbents. One of the major assumptions of Freundlich equation is heterogeneous surface composed of different classes of active sites. Therefore, better agreement of Freundlich isotherm with aclonifen adsorption may indicate that aclonifen was adsorbed on some classes of active sites, not on all of available active sites of COOH MWCNT and OH MWCNT. K_f and n are Freundlich constants related to adsorption capacity and adsorption intensity of the adsorbents, respectively. The K_f values given in Table 10 show that the adsorption capacities of aclonifen are in accordance with the orders of COOH MWCNT > OH MWCNT > SWCNT > MWCNT > PAC.

When the data for SWCNT and PAC are examined, it is seen that R^2 values of SWCNT and PAC are not very high for both Langmuir and Freundlich isotherm model. Therefore, it can be said that both of these models do not perfectly describe aclonifen adsorption on PAC and SWCNT.

4.1.4. Adsorption Kinetics

Kinetic models show how fast the chemical or physical reaction takes place and what affects this rate. As known, adsorption process depends on the physical and chemical properties of the adsorbents and the conditions of the experimental setup. The most commonly used kinetic models for solid-liquid adsorption processes are pseudo-first order and pseudo second-order (Kumar, 2006). Therefore, these two kinetic models were applied to data obtained.

Pseudo First Order Model

The nonlinear form of the model equation, as also provided in Sec 2.4.2.1. is as follows.

$$q(t) = q_e * (1 - e^{-K_1 * t}) \text{ (Kumar, 2006)} \qquad (13)$$

This equation is converted to the linear form as given below and pseudo first-order model graph is drawn. K_1, namely velocity constant, and theoretical q_e values were calculated with the help of the equation given below. Linear plots of log (q_e–$q_{(t)}$) vs. t for the aclonifen/adsorbent ratio of 1/100 are shown in Figure 21, and all constants calculated are presented in Table 11. Also, variation of K_1 q_e values with $q_{(t)}$ values are shown in Figure 22 and Figure 23 for better comparison.

$$log(q_e - q(t)) = log(q_e) - \frac{K_1 * t}{2{,}303} \qquad (14)$$

$$K_1 = -2{,}303 * slope, \ qe = 10^{intercept} \qquad (15)$$

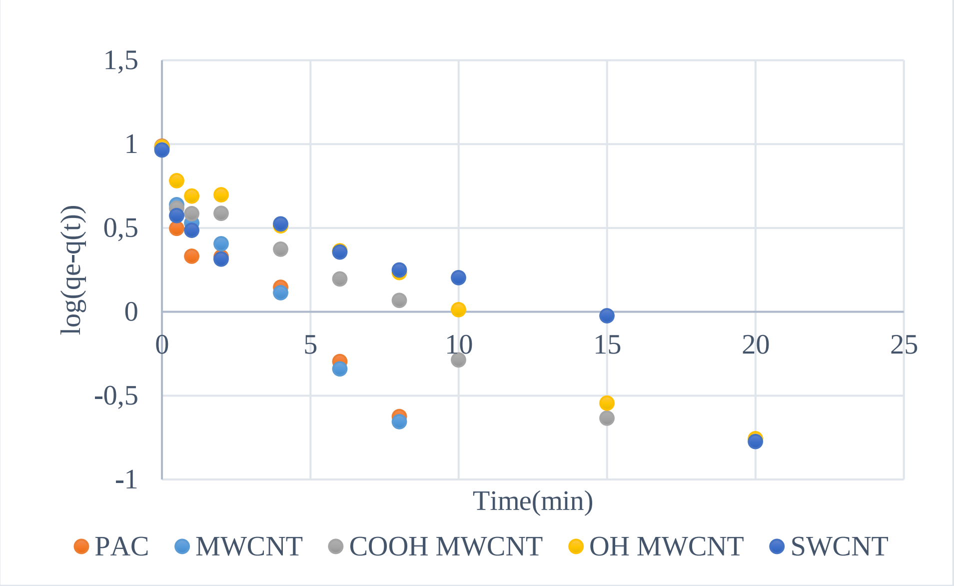


Figure 21. Kinetics of Aclonifen Adsorption onto PAC and CNTs: Pseudo-First-Order Model

Table 11. Pseudo First Order Kinetic Model Constants

C/CNT	MWCNT			PAC			COOH MWCNT			OH MWCNT			SWCNT		
	K1	R^2	qe	K1	R^2	qe	K1	R^2	qe	K1	R2	qe	K1	R^2	qe
1/100	0,4291	0,9757	6,4703	0,382	0,9087	5,0758	0,2233	0,9605	6,003	0,1959	0,9832	7,295	0,144	0,844	5,059
1/65	0,4908	0,955	10,144	0,5343	0,9714	10,267	0,1957	0,9783	11,067	0,1575	0,9825	9,947	0,052	0,899	6,208
1/50	0,1221	0,9125	16,134	0,2585	0,9326	11,375	0,1509	0,956	14,047	0,1187	0,9718	14,36	0,079	0,813	7,503
1/37	0,0792	0,5634	13,042	0,3845*	0,8738*	18,846*	0,1167	0,9624	18,353	0,0843	0,9653	18,73	0,051	0,764	11,27
1/15	0,0972	0,962	43,822				0,0441	0,9705	42,296	0,038	0,8678	30,95	0,024	0,78	32,87
1/10	0,0499	0,8185	38,694	0,0767	0,9035	48,975	0,0381	0,8253	56,283	0,0367	0,8722	39,9			
1/5	0,0424	0,9478	81,912				0,0178	0,8918	95,642	0,0559	0,4166	41,32			

* C/CNT for PAC is 1/27

Table 11 shows that pseudo first order model poorly describes the kinetic behaviour as indicated by the values of R2 smaller than 90%. , The match of model and data are admitted when R^2 values are around 0.99 as mentioned in the study (Li X. , et al., 2011).

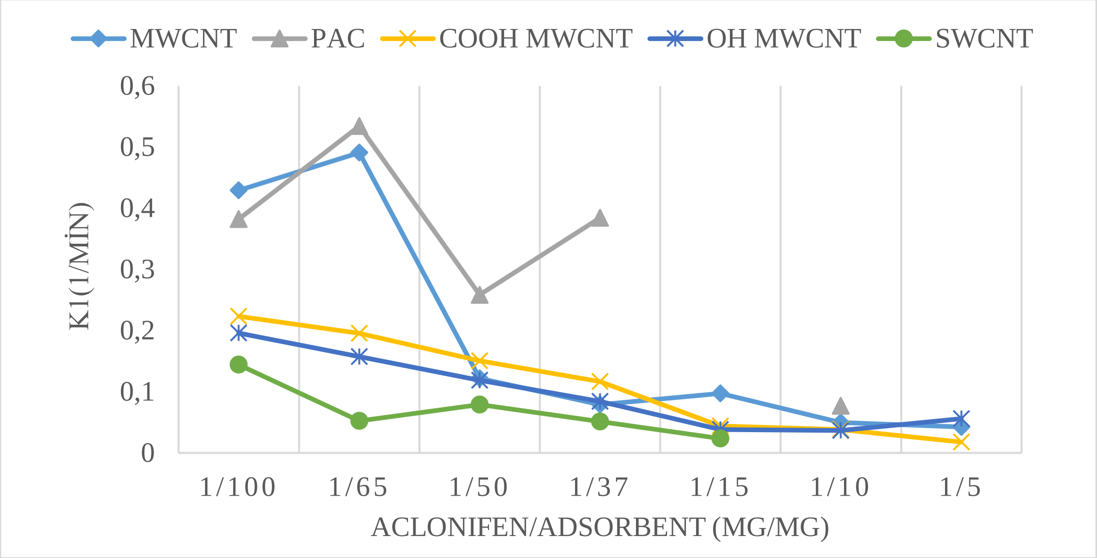


Figure 22. Pseudo-First-Order Model- Velocity Constants

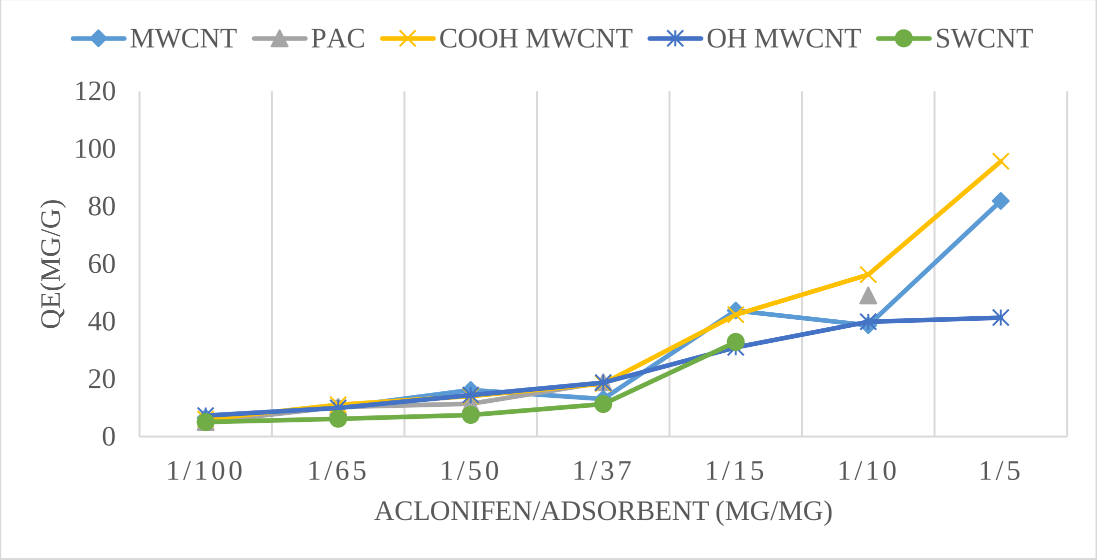


Figure 23. Pseudo-First-Order Model- Theoretical Capacity Values

As shown in Figure 22 and Figure 23, the capacity increases as the amount of pollutants per unit adsorbent increases, and the highest capacity at equilibrium belong to COOH MWCNT. As reported by Kumar (2006), capacity and velocity constants have inverse relationship. Also, as it can be seen from Figure 22, although PAC and MWCNT have the highest speed in higher adsorbate/adsorbent ratio, the other adsorbents have similar velocity constant. On the other hand, when adsorption capacities are examined, lower adsorbate/adsorbent ratio gives similar adsorption capacities. In higher ratios, COOH MWCNT shows differences than others. OH MWCNT follows second place in terms of capacity.

Pseudo Second Order Model

The nonlinear form of the model, as also provided in Sec 2.4.2.2. is as follows.

$$\mathrm{q}(t) = \frac{K_2 * q_e^2 * t}{1 + K_2 * q_e * t}\ (\mathrm{Kumar}, 2006) \qquad (16)$$

This equation is converted to the linear form as given below and pseudo-second-order model graph ($t/q_{(t)}$ vs t) is drawn. K_2, namely velocity constant and theoretical qe values were calculated with the help of the equation given below. Linear plots of $t/q_{(t)}$ vs. t are shown in Figure 24 and all constants calculated are presented in Table 12. In addition, variation of K_2 and qe values as a function of aclonifen/adsorbent ratio are shown in Figure 25 and Figure 26 respectively, for better comparison.

$$\frac{t}{q(t)} = \frac{1}{K_2 * q_e^2} + \frac{t}{q_e} \qquad (17)$$

$$K_2 = slope^2/intercept,\ qe = 1/slope \qquad (18)$$

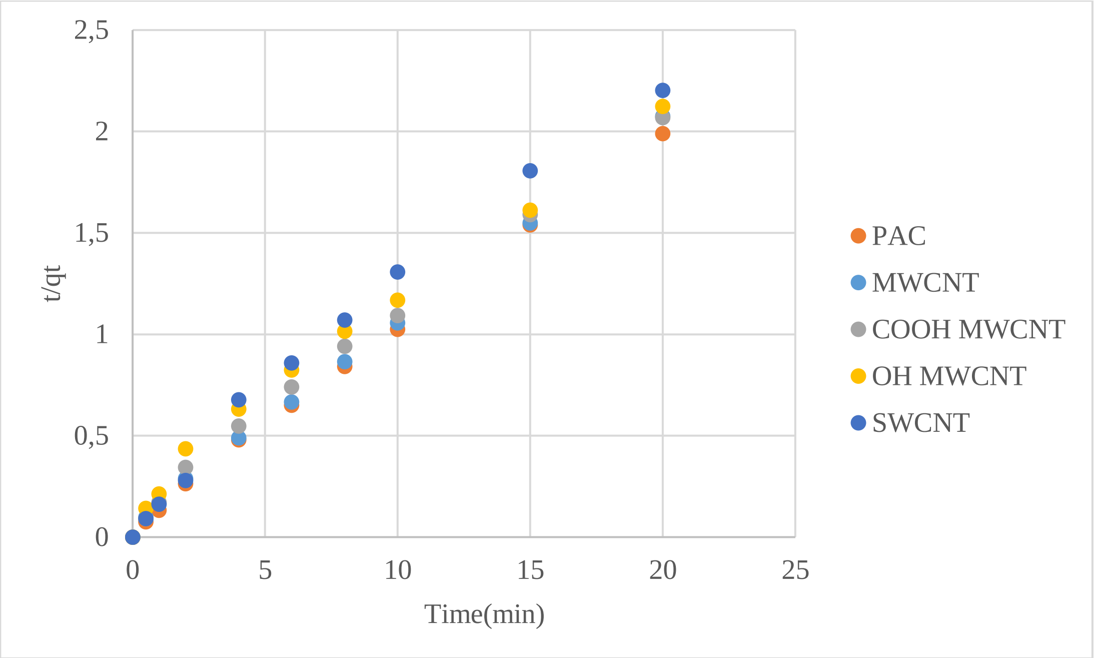


Figure 24. Adsorption Kinetics of Aclonifen Adsorption onto PAC and CNTs: Pseudo Second Order Model

Table 12. Pseudo Second Order Kinetic Model Constants

C/CNT	MWCNT			PAC			COOH MWCNT			OH MWCNT			SWCNT		
	K2	**R2**	**qe**	**K2**	**R2**	**qe**	**K2**	**R2**	**qe**	**K2**	**R2**	**qe**	**K2**	**R2**	**qe**
1/100	0,1868	0,9986	9,9164	0,2571	0,9993	10,035	0,1155	0,9946	9,9151	0,0663	0,994	10,01	0,075	0,995	9,616
1/65	0,1602	0,999	15,579	0,517	0,9993	14,139	0,0374	0,9936	15,511	0,0386	0,997	14,87	0,029	0,999	15,15
1/50	0,0143	0,9757	20,332	0,0658	0,9995	19,54	0,0248	0,997	20,174	0,0177	0,987	19,6	0,045	0,998	16,97
1/37	0,0145	0,9874	27,41	0,0361*	0,9992*	34,775*	0,0134	0,9927	25,055	0,0093	0,9947	26,36	0,012	0,997	24,92
1/15	0,0055	0,9946	57,217				0,003	0,983	59,352	0,0044	0,9916	55,56	0,004	0,999	82,65
1/10	0,004	0,9985	82,406	0,004	0,9909	92,383	0,0014	0,9737	75,399	0,0028	0,993	71,01			
1/5	0,0014	0,9937	117,69				0,0007	0,9652	143,56	0,0052	0,9987	117,6			

* C/CNT for PAC is 1/27

Unlike for the pseudo first order kinetics, pseudo-second-order kinetic model strongly fit the data. As it can be seen from Table 12, R^2 is more than 0.99 for most of the experiment result. Thus, it can be suggested that pseudo-second-order model is more applicable to fit the kinetic experimental data for all of the adsorbents used.

As shown in Table 12, the rate constant (K_2) for aclonifen adsorption on MWCNT and PAC was the largest among all adsorbents, indicating that the sorption of aclonifen on MWCNT and PAC were the fastest process. This may be attributed to the differences in the surface chemistry of CNTs and PAC. Hydrophilic oxygen-containing groups, such as carboxylic, and hydroxyl groups make surface of the MWCNT more negatively charged because of deprotonation of carboxylic groups at the equilibrium sorption pH of 6, since at this pH the adsorption of water is more favorable relative to the sorption of aclonifen molecules. Therefore, the adsorption of aclonifen onto functionalized CNTs is slowdown.

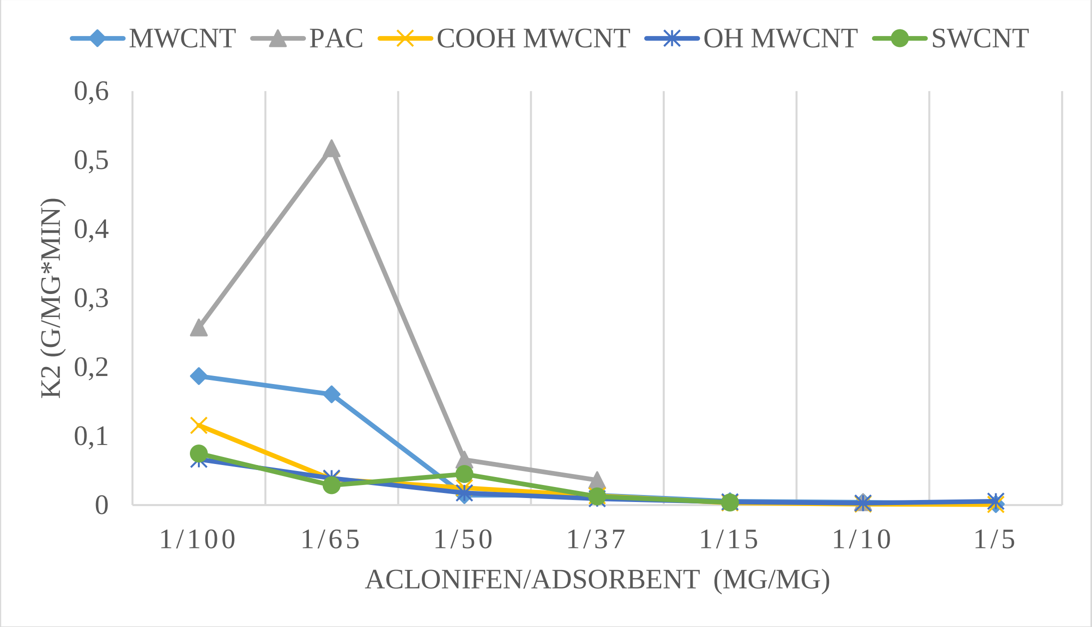


Figure 25. Pseudo Second Order Model - Velocity Constants

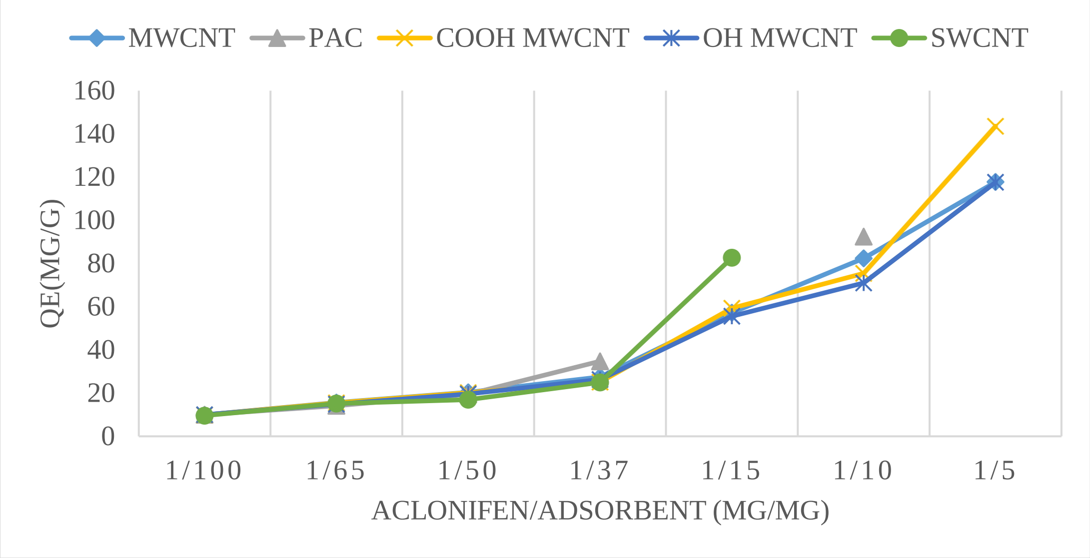


Figure 26. Pseudo Second Order Model - Theoretical Capacity Values

As shown in Figure 25 velocity constants are higher at lower adsorbate/adsorbent ratios. On the other hand, there is no significant difference at higher adsorbate/adsorbent ratios. Furthermore, Figure 25 shows that the capacity increases as the amount of pollutants per unit adsorbent increases and the highest capacity at equilibrium belongs to COOH MWCNT. As mentioned before, capacity and velocity constant have inverse relationship (Kumar, 2006). In addition, when Figure 23 and Figure 26 are compared, it can be seen that theoretical capacity values in pseudo-second-order model are higher than pseudo-first-order model results. Fitness of pseudo-second-order model is higher as mentioned before based on the R^2 values. Therefore, it can be said that pseudo-second-order model gives more reliable results for the experiments of this study.

4.1.5. Fourier Transform-Infrared (FTIR) Investigations

FTIR studies are suitable to determine qualitatively chemical bonds and functional groups, which make the adsorption possible. The FTIR spectra of PAC, MWCNT, COOH MWCNT, OH MWCNT and SWCNT are shown collectively in Figure 27. The broad peak around 3866, 3733 and ~3600 cm^{-1} for CNTs and 3930 and 3663 cm^{-1} for PAC can be assigned to –OH stretching vibration due to the existence of surface hydroxylic groups (Li, et al., 2013; Yan, et al., 2008; Shen, et al., 2009; Hua, et al., 2017). The peak at ~2354cm^{-1} can be related to -OH stretch from strong H-bonded-COOH (Lu, et al., 2008). The peak at 1680 and 1570 cm^{-1} for SWCNT, MWCNT and PAC are associated with the carboxylic acid and carboxylate anion stretch mode (C=O) due to functionalization (Hua et al., 2017; Lu, Liu, & Rao, 2008; Sivaraj & Vijayalakshmi, 2018). In addition, the peaks at 1510 and 1466 cm^{-1} for CNTs and PAC represent C-N and N-CH$_3$ stretching vibrations (Misra, Tyagi, Rai, & Misra, 2007). Furthermore, the band at 1085 cm^{-1} corresponds to aromatic C-H in-plane bending vibration (Ibrahim & Wasfi, 2019). The FTIR spectrum of all the studied CNTs and PAC confirmed the existence of the carboxylic groups (–COOH), carbonyl groups (–CO), and hydroxyl groups (–OH). As a result, it can be suggested that oxygen-containing functional groups are produced abundantly on the surface of sorbents that can provide numerous chemical sorption sites.

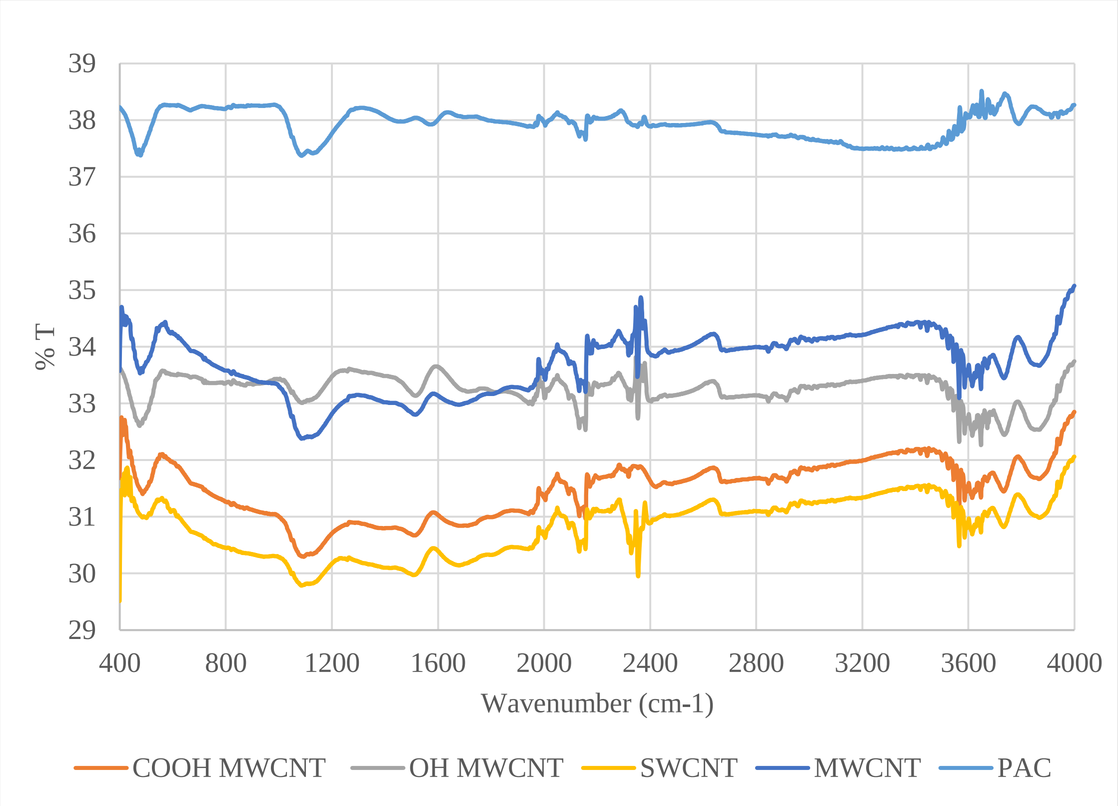


Figure 27. Fourier Transform Infrared Spectra of COOH MWCNT, OH MWCNT, MWCNT, SWCNT and PAC

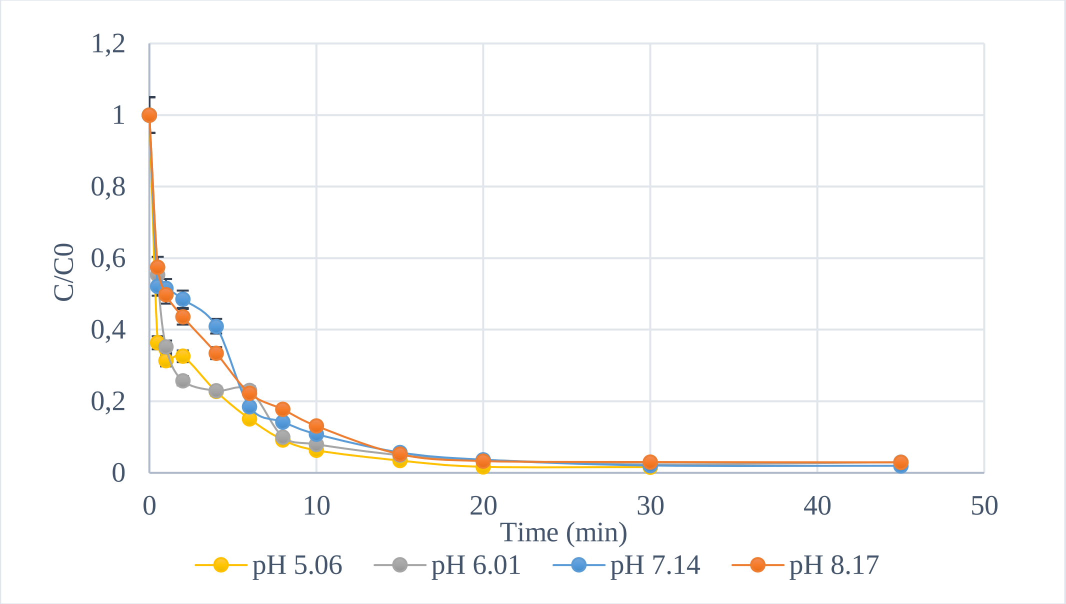
When Figure 27 is investigated, comparing the peaks and their intensity of CNTs and PAC, it can be revealed that there are more oxygen functional groups on the surface of CNTs than those on AC. In addition, the IR spectra of CNTs display almost similar peak distributions, but the FTIR spectra of COOH MWCNT has some differences at the band of 2300-2400 cm^{-1}. There is no peak that can be observed. This may influence the adsorption characteristics of COOH MWCNT from the other sorbents.

4.2. Aclonifen Removal by COOH MWCNT

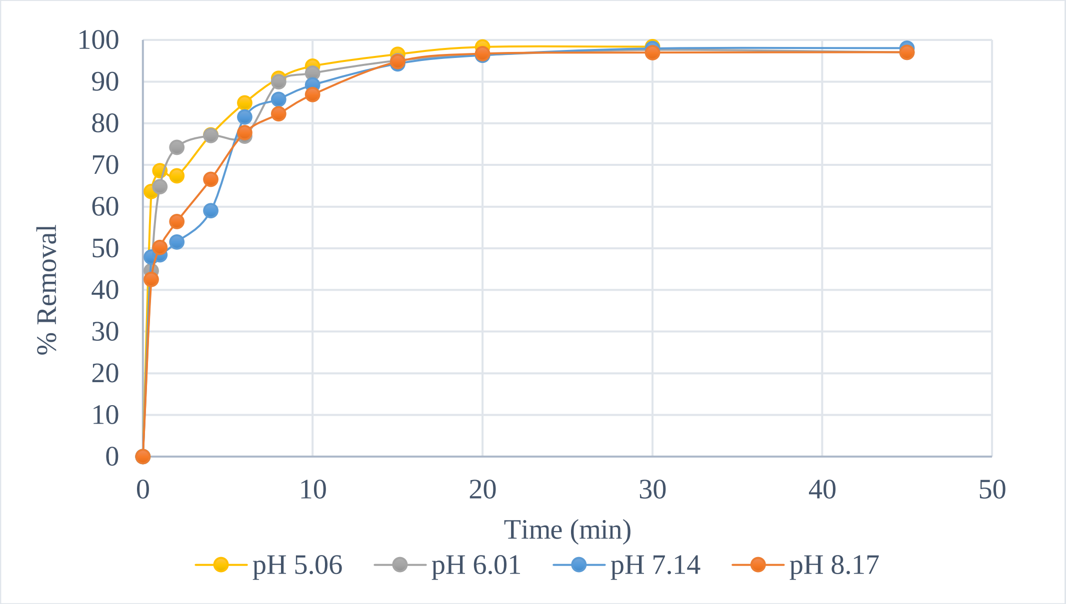
As presented in above subsections, COOH MWCNT was found to exhibit the best performance among the others tested, towards the adsorption of aclonifen. Therefore, parametric study was performed for COOH functionalized MWCNT only. In this respect, effect of pH, sonication and water matrix were sought. The results obtained are provided below.

4.2.1. Effect of pH on Aclonifen Removal by COOH MWCNT

The effect of pH on adsorption of aclonifen by COOH MWCNTs was evaluated and results are shown in (a)Figure 28. It was observed that the adsorption of aclonifen onto COOH MCWNTs is not drastically influenced by the solution pH. This may be due to the fact that aclonifen is non-ionising pesticide. However, it was observed that removal efficiency at pH 8 is slightly less than at the range between 5-7. This can be attributed to competition between OH ions and aclonifen species for active sorption sites. Because; at higher pH values, more oxygen containing groups on the MWCNTs surface are ionized. Therefore, they adsorb more water molecules (Peng, et al., 2003). Then, the access of aclonifen molecules to adsorption sites are blocked due to formation of water cluster on these groups. This can result in less adsorption of aclonifen on CNTs. The results obtained from the experiment are supported by the other studies in the literature. For example, Zhang et al., (2010) compared the adsorption of ionizable 2-phenylphenol and nonionic phenanthrene on CNTs under different pH values. They found that phenanthrene adsorption was not affected from the pH values ranging from 4 – 10. On the other hand, they observed that adsorption of ionizable 2-phenylphenol decreased when the pH of the solution was higher than pKa of 2- phenylphenol. This decrease was due to decreasing hydrophobicity and increasing ionization.



(a)



(b)

Figure 28. Effect of pH on Aclonifen Adsorption a) Variation in Aclonifen Concentration b) Aclonifen Removal Efficiencies

4.2.2. Effect of Sonication on Aclonifen Removal by COOH MWCNT and SWCNT

Effect of sonication of removal of aclonifen from aqueous solutions was investigated for COOH MWCNT and SWCNT in the ultrasonic water bath. Sonication supplies certain vibrational energies to agglomerated CNTs, thus they become dispersed within a solvent. As shown in the Figure 29, ultrasonication of the CNT suspensions significantly accelerated their adsorption kinetics but had no big effect on their equilibrium capacities. Without sonication, the equilibrium adsorption capacity of COOH MWCNT was 9.59 mg/g and it was 9.65mg/g with sonication. For SWCNT, the adsorption capacities were 9.45 and 9.77 for without sonication and with sonication, respectively.

When the graphs provided in Figure 29 are investigated, it can be seen that while sonication decreased the equilibrium time for SWCNT considerably, it has no effect on the equilibrium time for COOH MWCNT. Without sonication the equilibrium time was 20 and 45 min for COOH MWCNT and SWCNT respectively. It was remained same for COOH MWCNT with sonication, although it was decreased to 8 min for SWCNT.

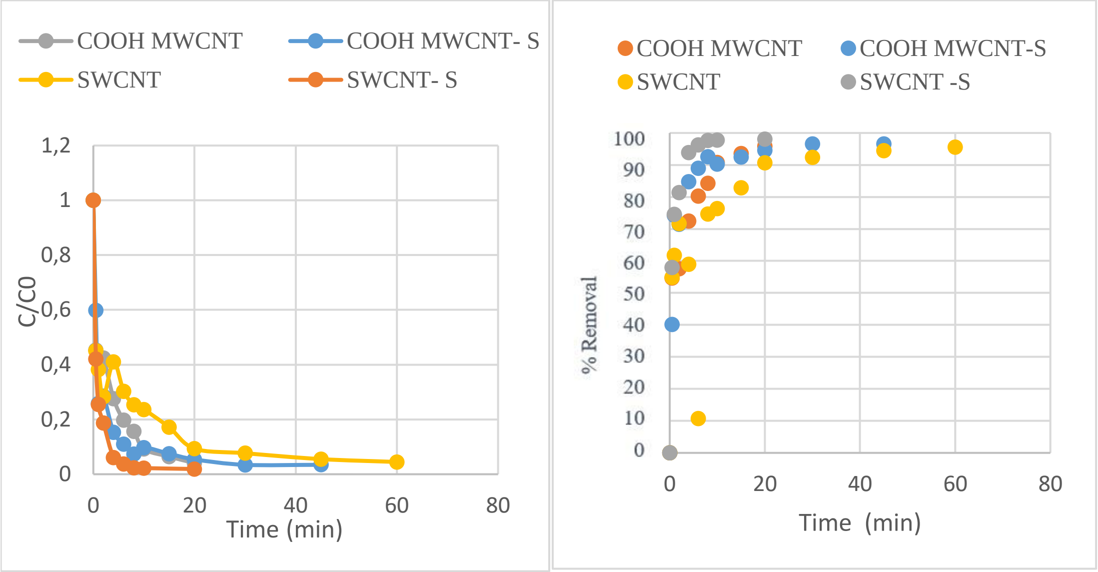


Figure 29. Effect of Sonication on Removal of Aclonifen by COOH MWCNT and SWCNT

In addition, as seen from Figure 30, without sonication, both the SWNT and the COOH MWCNT had agglomerated structures. Sonication dispersed the CNTs in the solution well. Whereas the aggregation changed the structures of CNTs, it did not affect their adsorption capacities for aclonifen. Maybe, it changed the relative contributions of the four different adsorption sites. More outer surface and inner cavities were available, whereas peripheral grooves and interstitial channels were lost after sonication.

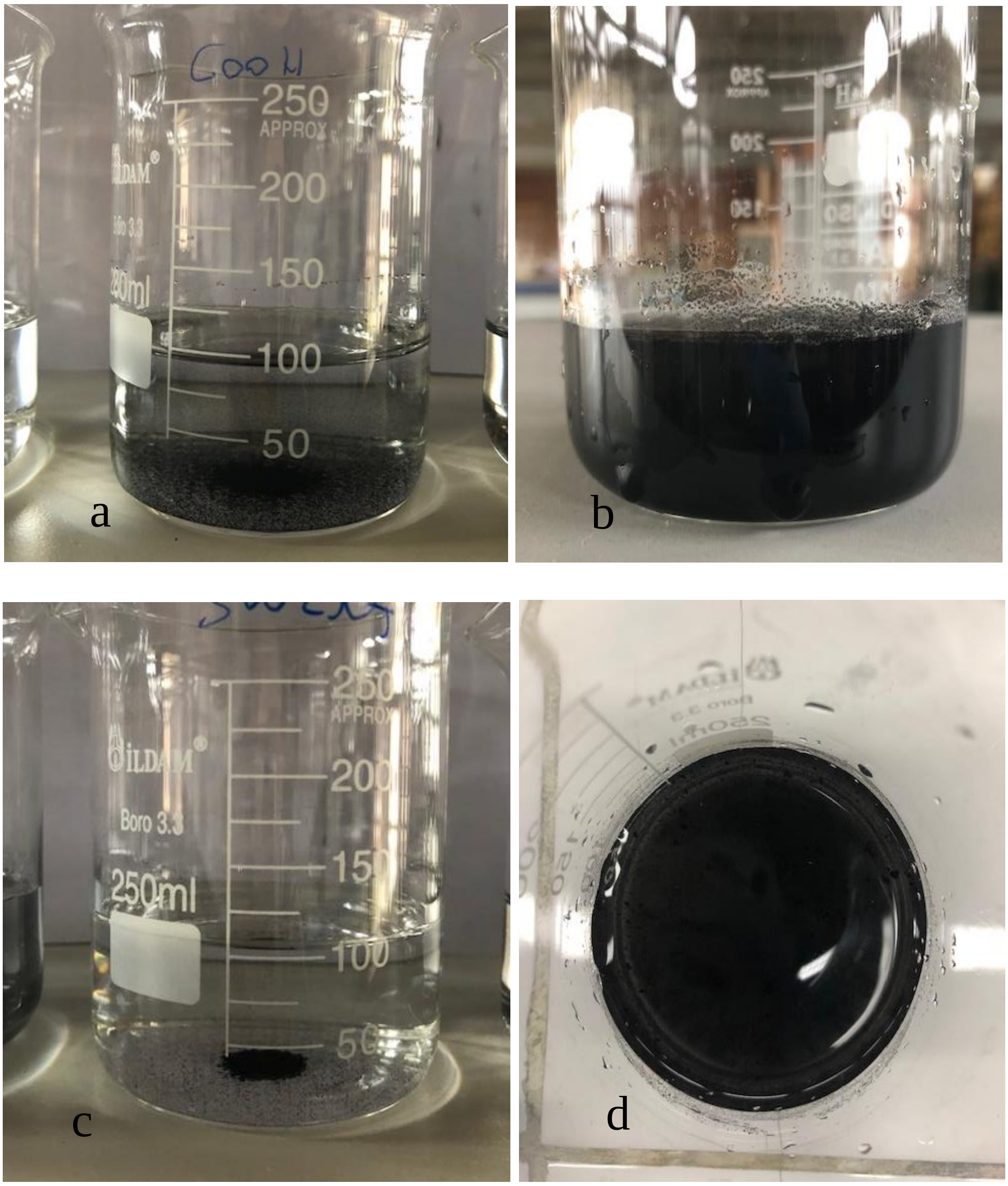


Figure 30. Images of the Solutions After Adsorption with Sonication and without Sonication (a) Adsorption by COOH without Sonication, (b) Adsorption by COOH with Sonication, (c) Adsorption by SWCNT without Sonication, (d) Adsorption by SWCNT with Sonication

In Table 13, the pseudo-second-order constants of COOH MWCNT and SWCNT are provided for the sonication experiments in comparison to no sonication. As summarized in Table 13, the regression coefficients of t/q versus t plots were about

0.99 for the adsorption of aclonifen on both COOH MWCNT and SWCNT. The parameters in Table 13 demonstrate that, ultrasonication of the solution lead to the accelerated adsorption kinetics especially for SWCNT, while it had no effect on their equilibrium capacities.

Table 13. The Pseudo-Second-Order Constants for Aclonifen Adsorption onto COOH MWCNT and SWCNT with and without Sonication

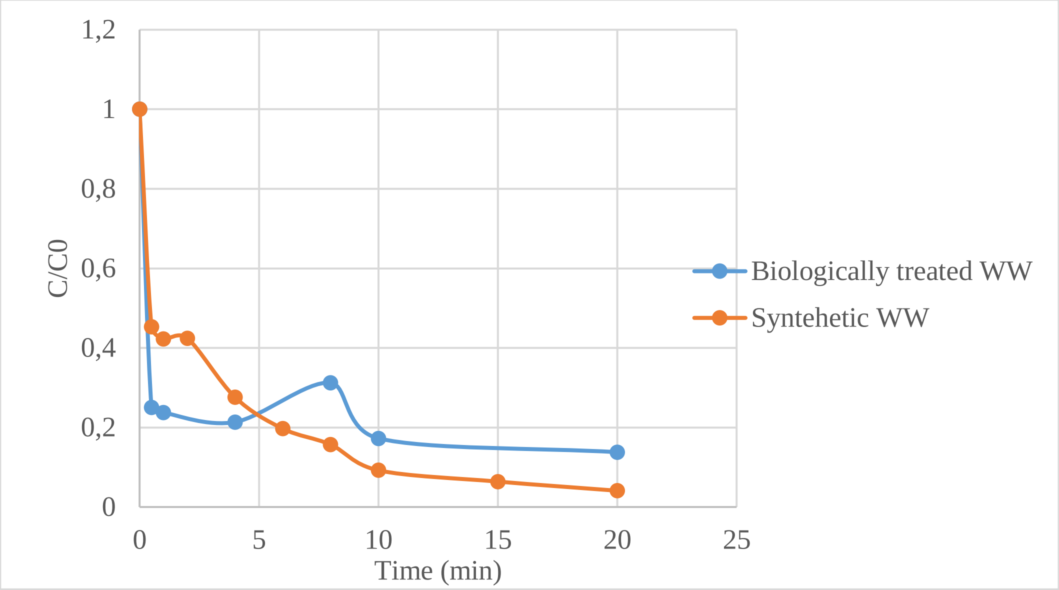
	K_2	R^2	q_e
COOH MWCNT	0.1155	0.9946	9.9151
COOH MWCNT-S	0.1902	0.9997	9.7593
SWCNT	0.074	0.9953	9.616
SWCNT-S	0.4036	0.9995	9.9593

These findings are supported by literature studies, though conducted with other pollutants. For example, Zhang et al., (2012) studied on adsorption of aromatic compounds by CNT and activated carbon. They also investigated effect of sonication on adsorption capacity and kinetics. They used phenanthrene and biphenyl which are different in hydrophobicity and planarity as adsorbate and four different adsorbent; ACF10, HD400, SWCNT and MWCNT. In that study, they found that sonication did not cause any change in the equilibrium capacities, but it resulted in faster sorption kinetics.

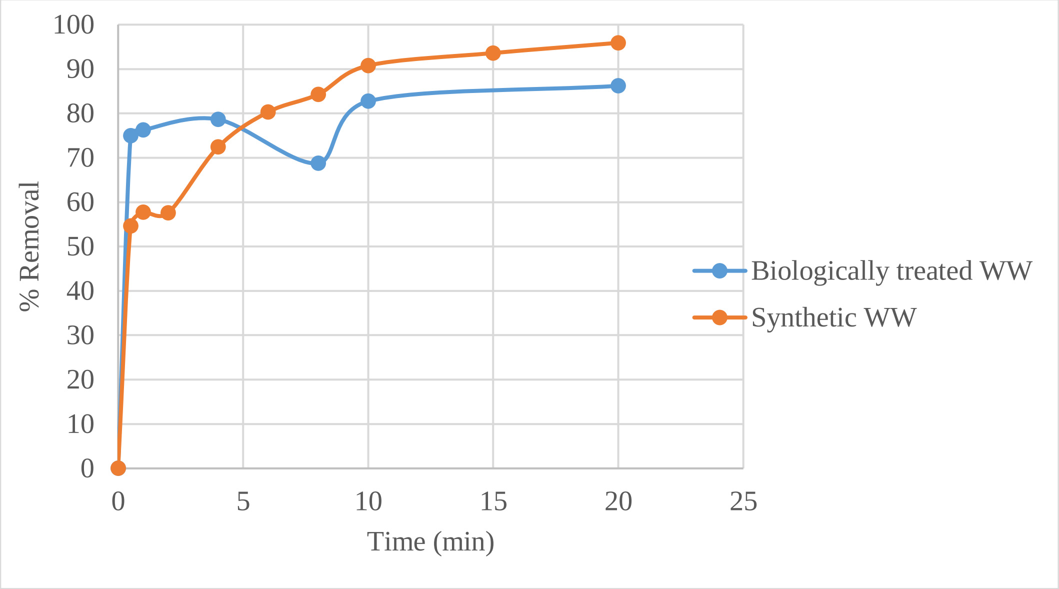
In another study conducted by Ncibi & Sillanpaa (2015), adsorption of two antibiotics, Oxytetracycline (OXY) and Ciprofloxacin (CIP) by different CNT types were investigated. They found that ultrasonication enhanced adsorption capacities of all tested CNTs for the case of OXY; while there was no improvement in overall removal for the case of CIP, which was attributed to the release of some parts of the adsorbed molecules caused by further sonication.

4.2.3. Effect of Water Matrix on Aclonifen Removal by COOH-MWCNT

In order to understand the effect of wastewater matrix on aclonifen removal adsorption using COOH MWCNT, adsorption experiments were performed with the water samples produced by Kocaman (2019) during her thesis study where she investigated the biological treatment of aclonifen bearing synthetic wastewater. So, biologically treated effluents were subjected to the adsorption by COOH MWCNT, as a means of advanced treatment following secondary treatment. Then, the results obtained in experiments conducted with synthetic water (Section 4.1.) were compared with those obtained with biologically treated wastewater of Kocaman (2019). The results obtained are shown in Figure 31. Although the initial concentrations were not same, the ratio of aclonifen/adsorbent were equalized with the amount of adsorbent.



(a)



(b)

Figure 31. Effect of Water Matrix on Aclonifen Removal by Adsorption using COOH MWCNT a) Variation of Aclonifen Concentration b) Removal Efficiency

As shown in Figure 31, in biologically treated wastewater, the percentage of aclonifen removal in the first 4 minutes is higher than in synthetic water. However, the 95% aclonifen removal was achieved with synthetic water at the end of the 20 min, while

88% aclonifen removal was achieved with biologically treated wastewater. This can be explained by the fact that the other remained organic compounds in the biologically treated wastewater may also be adsorbed onto the CNT surface, thereby decreasing the available sites for aclonifen adsorption.

CHAPTER 5

CONCLUSION

The main conclusions that can be obtained from this study are as follows:

- COOH functionalized CNT had the greatest adsorption capacity for aclonifen adsorption followed by the OH CNT, MWCNT, SWCNT, AC. Dominant adsorption mechanism is probably π-π electron-donor–acceptor interaction between the aromatic ring of aclonifen and the surface carboxylic groups of CNTs.
- For COOH MWCNT and OH MWCNT, adsorption isotherms were in better agreement with Freundlich isotherm model. For PAC and SWCNT, both Langmuir and Freundlich isotherm models were not found suitable, whereas for MWCNT, adsorption isotherms were well described by both Langmuir and Freundlich isotherm models.
- The pseudo-second-order model well described the adsorption kinetics for all of the sorbents tested.
- pH did not affect the aclonifen removal efficiencies of COOH MWCNT due to non-ionic properties of aclonifen.
- Sonication decreased the equilibrium time for SWCNT considerably, while it has no effect on the equilibrium time for COOH MWCNT. In addition, sonication enabled both the SWNT and the COOH MWCNT to disperse in the solution well. However, it did not affect their adsorption capacities for aclonifen.
- The overall aclonifen removal was higher in the synthetic wastewater than biologically treated wastewater. So, some fraction of total adsorption capacity

of MWCNT will be consumed by other organics likely to be present in the secondary level treated effluents.

CHAPTER 6

RECOMMENDATIONS

Further studies are needed to assess the full-scale applications of adsorption by CNT for treating wastewater in full scale WWTP. In the literature, most of the studies have been conducted in batch system. There is just a few study conducted recently using the fixed bed column type reactors (Xu et al., 2018; Rahman et al., 2017). Such studies are important considering the very small particle size of CNTs, which would limit their use in column applications. Such studies should be increased towards the practical applicability of CNTs in treatment plants. In fact, CNT applications at full scale are also limited by their higher cost. However, is the things has changed recently; thanks to increased industrial production of CNTs, the unit prices of commercially available CNT materials have decreased from $1500/g in 2000 to $1.48/g in 2017 (Ali et al., 2019).

Use of CNTs during the biological treatment (similar to PAC application) could be worth to investigate, especially considering their size limitation to be applied in columns.

Although activated carbon is more preferred as carbon based adsorbent materials, CNTs offer important advantages over PAC regeneration. There are some literature reports stating that CNTs could be reused through lots of regeneration cycles and then this make them cost effective and feasible practically. Therefore, to support this, desorption cycles for the aclonifen adsorption case could be worth to investigate.

So, as a future study overall, the fixed bed column adsorption studies could be investigated. Also, desorption experiments could be performed.

REFERENCES

Ahmad, A. S., Qureshi, M. I., Anum, S., & Yaqub, D. (2016). Applications of carbon nanotubes (CNTs) for the treatment of drinking and waste water-a brief review. *International Journal of Advanced Research and Development, 1*(12), 11-16.

Ahmad, T., Rfatullah, M., Ghazali, A., Sulaiman, O., Hashim, R., & Ahmad, A. (2010). Removal of Pesticides from Water and Wastewater by Different Adsorbents: A Review. *Journal of Enviromental Science and Health, Part C, 28*, 231-271.

Al-Duri, B. (1996). *Use of adsrobent for the removal of Pollutants from Wastewaters.* (G. McKay, Ed.) CRC Press.

Alexander, J., Hai, F., & Al-aboud, T. (2012). Chemical Coahulation-Based Processes for Trace Organic Contaminant Removal: Current State and Future Potential. *Journal of Environmental Management*, 195-207.

Ali, I., Asim, M., & Khan, T. A. (2012). Low cost adsorbent for the removal of organic pollutants from wastewater. *Journal of Environmental Management, 113,* 170-183.

Ali, S., Rehman, S. A., Luan, H. Y., Farid, M. U., & Huang, H. (2019). Challenges and opportunities in functional carbon nanotubes for membrane-based water treatment and desalination. *Science of the Total Environment, 646*, 1126-1139. doi:10.1016/j.scitotenv.2018.07.348

Allen, S. J., Mckay, G., & Porter, J. F. (2004). Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems. *Journal of Colloid and Interface Science, 280,* 322-333.

Ando, N., Matsui, Y., Kurotobi, R., Nakano, Y., Matsushita, T., & Ohno, K. (2010). Comparison of natural organic matter adsorption capacities of super-powdered activated carbon and powdered activated carbon. *Water Resources, 44*, 4127–4136.

Antakyali, D., Morgenschweis, C., Kort, D., Sasse, R., Schulz, J., & Herbst, H. (2015). Micropollutants in the aquatic enviroment and their removal in wastewater treatment works. *9th European Waste Water Management Conference.* Manchester, UK.

Apul, O. (2014). *Predictive Model Development for Adsorption of Organic Contaminants by Carbon Nanotubes.*

Asakura, H., & Matsuto, T. (2009). Experimental Study of Behavior of Endocrine-Distrupting Chemicals in Leachate Treatment Process and Evaluation of Removal Efficiency. *Waste Management,* 1852-1859.

Azzi, D. E., Laurent, F., Roussiez, V., Chou, L., Guiresse, M., & Probst, J.-L. (2018). Adsorption of Aclonifen, Alachlor, Cd and Cu onto Natural River Suspended Matter in the Context of Multi-Pollutions: Influence of Contaminant Co-Presence and Order of Input into the Aqueous Solution. *water,* 10. doi:10.3390/w10091222

Babaa, M., Pavlovsky, N. D., McRae, E., & Masenelli-Varlot, K. (2004). Physical adsorption of carbon tetrachloride on as-produced and on mechanically opened single walled carbon nanotubes. *Carbon, 42*(8-9), 1549-1554.

Bakkaloglu, S. (2014). Adsorption of synthetis organic chemicals: A comparison of superfine powdered activated carbon with powdered activated carbon. 1-105. doi:10.1007/s13398-014-0173-7.2

Bayer. (2012). *Bayer CropScience SAFETY DATA SHEET.* Retrieved from http://www.gadotagro.com/_Uploads/dbsAttachedFiles/CHALENGE_MSDS_25-7-2012.pdf

Bhatnagar , A., & Minocha, A. K. (2006). Conventional and non-conventional adsorbents for removal of pollutants from water- A review. *Indian Journal of Chemical Technology, 13*, 203-217.

Boehler, M., Zwickenpflug, B., Hollender, J., Ternes, T., Joss, A., & Siegrist, H. (2012). Removal of Micropollutants in Municipal Wastewater Treatment Plants by Powder-Activated Carbon. *Water Science and Technology*, 2115-2121.

Bolong, N., Ismail, A., Salim, M., & Matsuura, T. (2009). A Review of The Effects of Emerging Contaminants in Wastewater and Options for Their Removal. *Desalination*, 229-246.

Brady-Estévez, A. S., Schnoor, M. H., Kang, S., & Elimelech, M. (2010). SWNT-MWNT Hybrid Filter Attains High Viral Removal and Bacterial Inactivation. *Langmuir, 26*(24), 19153-19158. doi:10.1021/la103776y

Camara, M. A., Ramon, M. L., Álvarez-Merino, M. Á., & Moreno-Castilla, C. (2007). Effect of Surface Chemistry, Solution pH, and Ionic Strength on the Removal of Herbicides Diuron and Amitrole from Water by an Activated Carbon Fiber. *Langmuir, 23*(3), 1242-1247. doi:10.1021/la062200f

Carabineiro, S., Thavorn-amornsria, T., Pereira, M., Serp, P., & Figueiredoa, J. (2012). Comparison between activated carbon, carbon xerogel and carbon nanotubes for the adsorption of the antibiotic ciprofloxacin. *Catalysis Today, 186*, 29– 34.

Chen, W., Duan, L., & Zhu, D. (2007, December). Adsorption of Polar and Nonpolar Organic Chemicals to Carbon Nanotubes. *Environmental Science and Technology, 41*(24), 8295–8300. doi:DOI: 10.1021/es071230h

Chen, W., Duan, L., Wang, L., & Zhu, D. (2008). Adsorption of hydroxyl- and amino-substituted aromatics to carbon nanotubes. *Environmental Science and Technology, 42*(18), 6862-6868.

Cho, H. H., Choi, J., Goltz, M. N., & Park, J. W. (2002). Combined Effect of Natural Organic Matter and Surfactants on the Apparent Solubility of Polycyclic Aromatic Hydrocarbons. *Journal of Environmental Quality, 31*(1), 275-280. doi:10.2134/jeq2002.0275

Cho, H. H., Smith, B. A., Wnuk, J. D., Fairbrother, D. H., & Ball, W. P. (2008). Influence of surface oxides on the adsorption of naphthalene onto multiwalled carbon nanotubes. *Environmental Science & Technology, 42*(8), 2899-2905.

Choi, K., Kim, S., & Kim, S. (2008). Removal of Antibiotics by Coagulation and Granular Activated Carbon Filtration. *Journal of Hazardous Materials*, 38-43.

Clara , M., Strenn, B., Gans, O., Martinez, E., Kreuzinger, N., & Kroiss, H. (2005). Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants. *39*, 4797-4807.

Cooper, C. D., & Alley, F. (2002). *Air Pollution Control: A Design Approach* (3 ed.). (Illinois, Ed.) Waveland Press, Inc.

Czech, B., & Oleszczuk, P. (2016). Sorption of diclofenac and naproxen onto MWCNT in model wastewater treated by H2O2 and/or UV. *Chemosphere, 149*, 272–278.

Dąbrowski, A. (2001). Adsorption-from Theory to Practice. *Advances in Colloid and Interface Science, 93*(1-3), 135-224.

Das, R. (2017). Carbon Nanotube in Water Treatment. In *Nanohybrid Catalyst based on Carbon Nanotube* (pp. 23-55). doi:10.1007/978-3-319-58151-4

Davis, J. J., Green, M. L., Hill, H. A., Leung, Y. C., Sadler, P. J., Sloan, J., . . . Tsang, S. C. (1998). The immobilisation of proteins in carbon nanotubes. *Inorganica Chimica Acta, 272*(1-2), 261-266. doi:10.1016/S0020-1693(97)05926-4

DeAngelis, K. M. (2007). *Phosphate buffer*. Retrieved from https://www.unl.edu/cahoonlab/phosphate%20buffer.pdf

Dunier, M., & Siwicki, A. K. (1993). Effects of pesticides and other organic pollutants in the aquatic environment on immunity of fish: a review. *Fish & Shellfish Immunology, 3*(6), 423-438. doi:10.1006/fsim.1993.1042

Eatemadi, A., Daraee, H., Karimkhanloo, H., Kouhi, M., Zarghami, N., Akbarzadeh, A., . . . Joo, S. W. (2014). Carbon nanotubes: properties, synthesis, purification, and medical applications. *Nanoscale Research Letters, 9*, 393.

EFSA. (2008). *Conclusion regarding the peer review of the pesticide risk assessment of the active substance Aclonifen Finalised: 31 July 2008.*

Ellis, J. (2006). Pharmaceutical and personal care products (PPCPs) in urban receiving waters. *Environmental pollution, 144*, 184-189.

ENTEC. (2011). *Technical Support for the Impact Assessment of the Review of Priority Substances under Directive 2000/60/EC.* Retrieved from https://circabc.europa.eu/webdav/CircaBC/env/wfd/Library/framework_directive/thematic_documents/priority_substances/supporting_substances/substance_impacts/Aclonifen.pdf

Esplugas, S., Bila, D. M., Krause, L. G., & Dezotti, M. (2007). Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluent. *Journal of Hazardous Materials, 149*, 631–642.

European Commission . (2012). *Review report for the active substance aclonifen.*

European Commission. (2013). DIRECTIVE 2013/39/EU. *Official Journal of the European Union*. Retrieved from https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2013:226:0001:0017:EN:PDF

Foo, K. Y., & Hameed, B. H. (2010). Insight into the modeling of adsorption isotherm systems. *Chemical Engineering Journal, 156*, 2-10.

Gangupomu, R. H. (2013). *A Comparative Study Of Carbon Nanotubes And Granular Activated Carbon: Physicochemical Properties And Adsorption Capacities.*

Garcia, J. G., Serp, P., Kalck, P., Figueiredo, J., & Faria, J. (2006). Carbon nanotubes supported ruthenium catalysts for the treatment of high strength wastewater with aniline using wet air oxidation. *Carbon, 44*(12), 2384-2391.

Garcia, N. L., Moreno, J., Cartmell, E., & Roda, I. R. (2013). The application of microfiltration-reverse osmosis/nanofiltration to trace organics removal for municipal wastewater reuse. *Environmental Technology, 34*(24), 3183-3189. doi:10.1080/09593330.2013.808244

Gimbert, F., Crini, N. M., Renault, F., Badot, P. M., & Crini, G. (2008). Adsorption isotherm models for dye removal by cationized starch besed material in single component system: Error analysis. *Journal of Hazardous Materials, 157*, 34-46.

Girifalco, L. A., Hodak, M., & Lee, R. S. (2000). Carbon nanotubes, buckyballs, ropes, and a universal graphitic potential. *Physical Review B, 62*(19), 13104-13110. doi:10.1103/PhysRevB.62.13104

Hahm, M. G., Hashim, D., Vajtai, R., & Ajayan, P. M. (2011). A review: controlled synthesis of vertically aligned carbon nanotubes. *Carbon letters, 12*(4), 185-193. doi:10.5714/CL.2011.12.4.185

Hamdaoui, O., & Naffrechoux, E. (2007). Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon Part I . Two-parameter models and equations allowing determination of thermodynamic parameters. *147*, 381-394. doi:10.1016/j.jhazmat.2007.01.021

Han, S., Kim, S., Lim, H., Choi, W., Park, H., Yoon, J., & Hyeon, T. (2003). New nanoporous carbon materials with high adsorption capacity and rapid adsorption kinetics for removing humic acids. *Microporous Mesoporous Mater, 58*, 131–135.

Hansen, O. C. (2004). *Quantitative Structure-Activity Relationships (QSAR) and Pesticides.* Denmark.

Hernandex-Leal, L., Temmink, H., Zeeman, G., & Buisman, C. (2011). Removal of Micropollutants from Aerobically Treated Grey Water via Ozone and Activated Carbon. *Water Research*, 2887-2896.

Hernandez-Leal, L., Temmink, H., Zeeman, G., & Buisman, C. (2011). Removal of Micropollutants from Aerobically Treated Grey Water via Ozone and Activated Carbon. *Water Research*, 2887-2896.

Hertfordshire, U. o. (2017). *PPDB: Pesticide Properties DataBase*. Retrieved 05 2017, from http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/15.htm

Ho, Y. S., & McKay, G. (1999). Pseudo second order model for sorption processes. *Process Biochemistry, 34*, 451-465.

Hollender, J., Zimmermann, S., Koepke, S., Krauss, M., McArdell, C., & Ort, C. (2009). Elimination of Orgnic Micropollutants in a Municipal Wastewater Treatment Plant Upgraded with a Full-scale Post-ozonation Followed by Sand Filtration. *Environmental Science & Technology,* 7862-7869.

Hyung, H., & Kim, J. H. (2008). Natural Organic Matter (NOM) Adsorption to Multi-Walled Carbon Nanotubes: Effect of NOM Characteristics and Water Quality Parameters. *Environmental Science and Technology, 42*(12), 4416-4421. doi:10.1021/es702916h

Hyung, H., Fortner, J. D., Hughes, J. B., & Kim, J. H. (2007). Natural Organic Matter Stabilizes Carbon Nanotubes in the Aqueous Phase. *Environmental Science and Technology, 41*(1), 179-184. doi:10.1021/es061817g

Iijima, S. (1991). Helical microtubules of graphitic carbon. *Nature, 354,* 56-58. doi:https://doi.org/10.1038/354056a0

Iijima, S., & Ichihashi, T. (1993). Single-shell carbon nanotubes of 1-nm diameter. *Nature, 363,* 603-605. doi:https://doi.org/10.1038/363603a0

Jeon, I.-Y., Chang, D. W., Kumar, N. A., & Baek, J.-B. (2011). Functionalization of Carbon Nanotubes. In *Carbon Nanotubes - Polymer Nanocomposites.* doi:DOI: 10.5772/18396

Jermann, D., Pronk, W., Boller, M., & Schäfer, A. (2009). The role of NOM fouling for the retention of estradiol and ibuprofen during ultrafiltration. *Journal of Membrane Science, 329,* 75-84.

Joss, A., Keller, E., Alder, A. C., Gobel, A., McArdell, C. S., Terness, T., & Siegrist, H. (2005). Removal of pharmaceuticals and fragrances in biological wastewater treatment. *Water Research, 39,* 3139-3152.

Kang, S., Pinault, M., Pfefferle, L. D., & Elimelech, M. (2007). Single-Walled Carbon Nanotubes Exhibit Strong Antimicrobial Activity. *Langmuir, 23*(17), 8670-8673. doi:10.1021/la701067r

Katakam, M., Bell, L. N., & Banga, A. (1995). Effect of surfactants on the physical stability of recombinant human growth hormone. *Journal of Pharmaceutical Sciences, 84*(6), 713-716. doi:10.1002/jps.2600840609

Keum, Y., Lee, Y., & Kim, J.-H. (2008). Metabolism of Nitrodiphenyl Ether Herbicides by Dioxin-Degrading Bacterium Sphingomonas wittichii RW1. *International Journal of Agricultural and Food Chemistry, 56,* 9146-9151.

Kılınç, Ö. K. (2015). Aclonifen Uygulama Zamanının Tilki kuyruğu [Alopecurus myosuroides Huds. (Poaceae)] Yapraklarındaki Kritik Konsantrasyon Değerine Etkisi. *Türk Tarım – Gıda Bilim ve Teknoloji Dergisi*, 491-497.

Kim, M. K., & Zoh, K. D. (2006). Occurrence and removals of micropollutants in water environment. *Enviromental Engineering Resource, 21*(4), 319-332.

Kimyaevi. (n.d.). Retrieved from http://www.kimyaevi.org/TR/Genel/BelgeGoster.aspx?F6E10F8892433CFF679A66406202CCB07E03D0C7BDB04C56

Kovalova, L., Siegrist, H., Wittmer, A., McArdell, C., Gunten, U., Eugster, J., . . . Moser, R. (2013). Elimination of Micropollutants During Post-Treatment of Hospital Wastewater with Powdered Activated Carbon, Ozone and UV. *Environmental Science & Technology*, 7899-7908.

Kumar, K. V. (2006). Linear and non-linear regression analysis for the sorption kinetics of methylene blue onto activated carbon. *Journal of Hazardous Materials*, 1538-1544.

Li, X., Zhao, H., Quan, X., Chen, S., Zhang, Y., & Yu, H. (2011). Adsorption of ionizable organic contaminants on multi-walled carbon nanotubes with different oxygen contents. *Journal of Hazardous Materials, 186*(1), 407-415.

Li, X., Zhao, H., Quan, X., Chen, S., Zhang, Y., & Yu, H. (2011). Adsorption of ionizable organic contaminants on multi-walled carbon nanotubes with different oxygen contents. *Journal of Hazardous Materials*, 407-415.

Limousin, G., Gaudet, J. P., Charlet, L., Szenknect, S., Barthes, V., & Krimissa, M. (2007). Sorption isotherms: A review on physical bases, modeling and measurement. *Applied Geochemistry, 22*, 249-275.

Lin, D., & Xing, B. (2008). Adsorption of Phenolic Compounds by Carbon Nanotubes : Role of Aromaticity and Substitution of Hydroxyl Groups Adsorption of Phenolic Compounds by Carbon Nanotubes : Role of Aromaticity and Substitution of Hydroxyl Groups. *Environmental Science & Technology, 42*(2), 7254-7259.

Liu, X., Wang, M., & Zhang, S. (2013). Application potential of carbon nanotubes in water treatment: A review. *Journal of Environmental Sciences 2013,, 25*(7), 1263–1280.

Liu, X., Wang, M., Zhang, S., & Pan, B. (2013). Application potential of carbon nanotubes in water treatment: A review. *Journal of Environmental Sciences 2013,, 25*(7), 1263-1280.

Liu, X., Zhang, S., & Pan, B. (2012). Potential of Carbon Nanotubes in Water Treatment. In *Recent Progress in Carbon Nanotube Research.* doi:http://dx.doi.org/10.5772/51332

Long, R. Q., & Yang, R. T. (2001). Carbon nanotubes as superior sorbent for dioxin removal. *Journal of the American Chemical Society, 9*(123), 2058-2059. doi:10.1021/ja003830l

Loos, R. (2012). *Analytical methods relevant to the European Commission's 2012 proposal on Priority Substances under the Water Framework Directive.* European Commission.

Lu, C., Chung, Y. L., & Chang, K. F. (2005). Adsorption of tri- halomethanes from water with carbon nanotubes. *Water Research, 39*(6), 1183–1189.

Lu, C., Su, F., & Hu, S. (2008). Surface modification of carbon nanotubes for enhancing BTEX adsorption from aqueous solutions. *Applied Surface Science*, 7035-7041.

Mickelson, E. T., Chiang, I. W., Zimmerman, J. L., Boul, P. J., Lozano, J., Liu, J., . . . Margrave, J. L. (1999). Solvation of Fluorinated Single-Wall Carbon Nanotubes in Alcohol Solvents. *Journal of Physical Chemistry B, 103*(21), 4318-4322. doi:10.1021/jp9845524

Ministry of Forestry and Water Affairs. (2016). *YERÜSTÜ SU KALİTESİ YÖNETMELİĞİNDE DEĞİŞİKLİK YAPILMASINA DAİR YÖNETMELİK.*

Movlaee , K., Ganjali, M. R., Norouzi, P., & Neri, G. (2017). Iron-Based Nanomaterials/Graphene Composites for Advanced Electrochemical Sensors. *Nanomaterials*, 1-33. doi:https://doi.org/10.3390/nano7120406

Nas, B., Dolu, T., Ateş, H., Argun, M., & Yel, E. (2017). Treatment Alternatives for Micropollutant Removal in Wastewater. *Selçuk University, Journal of Engineering, Science and Technology*, 133-143.

Ncibi, M. C., & Sillanpaa, M. (2015). Optimized removal of antibiotic drugs from aqueous solutions using single, double and multi-walled carbon nanotubes. *Journal of Hazardous Materials, 298*, 102–110. doi:10.1016/j.jhazmat.2015.05.025

Nethaji, S., Sivasamy, A., & Mandal, A. B. (2013). Adsorption isotherms, kinetics and mechanisms for the adsorption of cationic and anionic dyes obto carbonaceous particles prepared from Juglans regia shell biomass. *International Journal of Enviromental Science and Technology, 10*, 231-242.

Ong, Y. T., Ahmad, A. L., Hussein, S., Zein, S., & Tan, H. (2010). A review on carbon nanotubes in an environmental protection and green engineering perspective. *Brazilian Journal of Chemical Engineering, 27*(02), 227-242. doi:10.1590/S0104-66322010000200002

Pan, B., & Xing, B. (2008). Adsorption Mechanisms of Organic Chemicals on Carbon Nanotubes. *ENVIRONMENTAL SCIENCE & TECHNOLOGY, 42*(24), 9005-9013.

Peng, X., Jia, J., & Luan, Z. (2009). Oxidized carbon nanotubes for simultaneous removal of endrin and CD from water and their separation from water. *Journal of Chemical Technology and Biotechnology*, 275-278.

Peng, X., Li, Y., Luan, Z., Di, Z., Wang, H., Tian, B., & Jia, Z. (2003). Adsorption of 1,2-dichlorobenzene from water to carbon nanotubes. *Chemical Physics Letters*, 154-158.

Rahman, M., Sime, S. A., Hosain, M. A., Shammi, M., Uddin, M., Sikder , M., & Kurasaki, M. (2017). Removal of Pollutants fromWater by Using Single-Walled Carbon Nanotubes (SWCNTs) and Multi-walled Carbon Nanotubes (MWCNTs). *Arabian Journal for Science and Engineering, 42*, 261-269. doi:10.1007/s13369-016-2303-3

Ren, X., Chen, C., Nagatsu, M., & Wang, X. (2011). Carbon nanotubes as adsorbents in environmental pollution management: A review. *Chemical Engineering Journal , 170*, 395–410. doi:10.1016/j.cej.2010.08.045

Ribeiro, A. R., Nunes, O. C., Pereira, M. F., & Silva, A. M. (2015). An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU. *Environment International, 75*, 33-51. doi:10.1016/j.envint.2014.10.027 0160-4120

Rivera-utrilla, J., Sánchez-polo, M., Ferro-garcía, M., & Prados-joya, G. (2013). Pharmaceuticals as emerging contaminants and their removal from water. A review. *Chemosphere, 93*(7), 1268-1287. doi:10.1016/j.chemosphere.2013.07.059

Rogers, H. R. (1996). Sources, behaviour and fate of organic contaminants during sewage treatment and in sewage sludges. *The Science of the Total Environment, 185*, 3-26.

Rossner, A., Snyder, S., & Knappe, D. (2009). Removal of Emerging Contaminants of Concern by Alternative Adsorbents. *Water Research*, 3787-3796.

Saeed, K., & Khan, I. (2013). Carbon nanotubes–properties and applications: a review. *Carbon letters, 14*(3), 131-144. doi:10.5714/CL.2013.14.3.131

Saito, R., Fujita, M., Dresselhaus, G., & Dresselhaus, M. S. (1992). Electronic structure of chiral graphene tubules. *Applied Physics Letters, 60*(18), 2204-2206.

Santhy, K., & Selvapathy, P. (2006). Removal of reactive dyes from wastewater by adsorption on coir pith activated carbon. *Bioresour Technology, 97*.

Schafer, A., Akanyeti, I., & Semiao, A. (2011). Micropollutant Sorption to Membrane Polymers: a Review of Mechanisms for Estrogens. *Advances in Colloid and Interface Science*, 100-117.

Schierz, Schierz, A., & Zanker, H. (2009). Aqueous suspensions of carbon nanotubes: Surface oxidation, colloidal stability and uranium sorption. *Environmental Pollution, 157*(4), 1088-1094. doi:10.1016/j.envpol.2008.09.045

Shaffer, M. S., Fan, X., & Windle, A. H. (1998). Dispersion and packing of carbon nanotubes. *Carbon, 36*(11), 1603–1612.

Shen, X. E., Shan, X. Q., Dong, D. M., Hua, X. Y., & Owens, G. (2009). Kinetics and thermodynamics of sorption of nitroaromatic compounds to as-grown and oxidized multiwalled carbon nanotubes. *Journal of Colloid and Interface Science, 330*(1), 1-8. doi:10.1016/j.jcis.2008.10.023

Sheng, G. D., Shao, D. D., Ren, X. M., Wang, X. Q., Li, J. X., Chen, Y. X., & Wang, X. K. (2010). Kinetics and thermodynamics of adsorption of ionizable aromatic compounds from aqueous solutions by as-prepared and oxidized multiwalled carbon nanotubes. *Journal of Hazardous Materials, 178*(1-3), 505-516. doi:10.1016/j.jhazmat.2010.01.110

Sheng, X., Li, Y., Luan, Z., Di, Z., Wang, H., Tian, B., & Jia, Z. (2003). Adsorption of 1,2-dichlorobenzene from water to carbon nanotubes. *Chemical Physics Letters,* 154-158.

Silva, L. L., Moreira, C. G., Curzio, B. A., & Fonseca, F. V. (2017). Micropollutant Removal from Water by Membrane and Advanced Oxidation Processes—A Review. *Journal of Water Resource and Protection, 9*, 411-431.

Snyder, S., Adham, S., Redding, A., Cannon, F., DeCarolis, J., & Oppenheimer, J. (2007). Role of Membranes and Activated Carbon in the Removal of Endocrine Distruptors and Pharmaceuticals. *Desalination*, 156-181.

Suarez, S., Lema, J., & Omil, F. (2009). Pre-treatment of Hospital Wastewater by Coagulation-Flocculation and Flotation. *Bioresource Technology*, 2138-2146.

Sui, Q., Huang, J., Deng, S., Yu, G., & Fan, Q. (2010). Occurrence and removal of pharmaceuticals, caffeine and DEET in wastewater treatment plants of Beijing, China. *Water Research, 44*(2), 417-426. doi:10.1016/j.watres.2009.07.010

Tadkaew, N., Hai, F., McDonald, J. A., Khan, S., & Nghiem, L. (2011). Removal of trace organics by MBR treatment: the role of molecular properties. *Water Research, 45*(8), 2439-2451.

Tan, I. A., & Hameed, B. H. (2010). Adsorption isotherms, kinetics, thermodynamics and desorption studies of basic dye on activated carbon derived from oil palm empty fruit bunch. *Journal of Applied Science, 10*(21), 2565-2571.

Terrones , M. (2004). Carbon nanotubes: Synthesis and properties, electronic devices and other emerging applications. *International Materials Reviews, 49*(6), 325-77.

Thuy, P., Moons, K., Van Dijk, J., Viet Anh, N., & Van der Bruggen, B. (2008). To What Extent are Pesticides Removed from Surface Water During Coagulation-Flocculation. *Water and Environment Journal*, 217-223.

Tijani, J. O., Fatoba, O., & Petrik, L. F. (2013). A review of pharmaceuticals and endocrine-disrupting compounds: sources, effects, removal, and detections. *Water Air and Soil Pollution, 224*, 1-29. doi:10.1007/s11270-013-1770-3

Trinh, T., Akker, B., Stuetz, R. M., Coleman, H. M., Clech, P. L., & Khan, S. J. (2012). Removal of trace organic chemical contaminants by a membrane bioreactor. *Water Science & TechnologY*, 1856-1863.

Verlicchi, P., Galletti, A., Petrovic, M., & Barcelo, D. (2010). Hospital Effluents as a Source of Emerging Pollutants: an Overview of Micropollutants and Sustainable Treatment Options. *Journal of Hydrology* , 416-428.

Vieno, N., Tuhkanen, T., & Kronberg, L. (2006). Removal of Pharmaceuticals in Drinking Water Treatment: Effect of Chemical Coagulation. *Environmental Technology*, 183-192.

Vorkamp, K., Bossi, R., Bester, K., Bollmann, U. E., & Susanne, B. (2014). New priority substances of the EuropeanWater Framework Directive: Biocides, pesticides and brominated flame retardants in the aquatic environment of Denmark. *Science of the Total Environment, 470-471*, 459–468. doi:10.1016/j.scitotenv.2013.09.096

Wang, X., Tao, S., & Xing, B. S. (2009). Sorption and competition of aromatic compounds and humic acid on multiwalled carbon nanotubes. *Environmental Science and Technology, 43*(16), 6214-6219.

Westerhoff, P., Yoon, Y., Snyder, S., & Wert, E. (2005). Fate of Endoctrine-distruptor, Pharmaceutical and Personal Care Product Chemicals During Simulated Drinking Water Treatment Processes. *Environmental Science & Technology,* 6649-6663.

Xie, X. L., Mai, Y. W., & Zhou, X. P. (2005). *Dispersion and alignment of carbon nanotubes in polymer matrix: A review.* Materials Science and Engineering R.

Xu, L., Wang, S., Zhou, J., Deng, H., & Frost, R. L. (2018). Column adsorption of 2-naphthol from aqueous solution using carbon nanotube-based composite adsorbent. *Chemical Engineering Journal, 335,* 450-457. doi:10.1016/j.cej.2017.10.176

Yakout, S. M., & Elsherif, E. (2010). Batch kinetics, isotherm and thermodynamic studies of adsorption of strontium from aqueous solutions onto low cost rice-straw based carbons. *Carbon- Science and Technology, 3,* 144-153. Retrieved from https://circabc.europa.eu/webdav/CircaBC/env/wfd/Library/working_groups/priority_substances/priority_substances_1/substance_dossiers/final_draft_dossiers/Aclonifen_dossier_20100326%20clean.doc

Yang, K., & Xing, B. (2009). Adsorption of fulvic acid by carbon nanotubes from water. *Environmental Pollution, 157*(4), 1095-1100.

Yang, K., Zhu, L. Z., & Xing, B. S. (2006). Adsorption of polycyclic aromatic hydrocarbons by carbon nanomaterials. *Environmental Science and Technology, 40*, 1855–1861.

Yang, S., Zhu, W., Li, X., Wang, J., & Zhou, Y. (2007). Multiwalled carbon nanotubes as an efficient catalyst for catalytic wet air oxidation of phenol. *Catalysis Communicaitions, 8*(12), 2059-2063.

Yu, F., Ma, J., & Wu, Y. (2012). Adsorption of toluene, ethylbenzene and xylene isomers on multi-walled carbon nanotubes oxidized by different concentration of NaOCl. *Frontiers of Environmental Science and Engineering, 6*(3), 320-329.

Zhang, S., Shao, T., Bekaroglu, S., & Karanfil, T. (2010). Adsorption of synthetic organic chemicals by carbon nanotubes:Effects of background solution chemistry. *Water Research, 44*(6), 2067-2074.

Zhang, S., Shao, T., Kose, H. S., & Karanfil, T. (2012). Adsorption kinetics of aromatic compounds on carbon nanotubes and activated carbons. *Environmental Toxicology and Chemistry*, 79-85.

Zhao, Y., & Stoddart, J. (2009). Noncovalent Functionalization of Single-Walled Carbon Nanotubes. *Accounts of chemical research, 42*(8), 1161-1171.

Zhu, J., Kim, J., Peng, H., Margrave, J. L., Khabashesku, V. N., & Barrera, E. V. (2003). Improving the Dispersion and Integration of Single-Walled Carbon

Nanotubes in Epoxy Composites through Functionalization. *Nano Letters, 3*(8), 1107-1113. doi:10.1021/nl034248

APPENDICES

A. Experiment Results

Table 14. Experiment Results of AC

AC (mg) :	8,50	AC (mg) :	10,00	AC (mg) :	5,15	AC (mg) :	5,00	AC (mg) :	1,50
Adsorbant/ Adsorbate	1/100	Adsorbant/ Adsorbate	1/65	Adsorbant/ Adsorbate	1/50	Adsorbant/ Adsorbate	1/28	Adsorbant/ Adsorbate	1/10
Time (min)	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**
0	0,8613	0	1,5150	0	1,0186	0	1,7900	0	1,4815
1	0,3005	1	0,8281	1	0,5291	1	1,0500	1	0,9948
1	0,2155	1	0,5408	1	0,4853	1	0,8900	1	0,8422
2	0,2145	2	0,3818	2	0,2896	2	0,6800	2	0,8539
4	0,1528	4	0,2171	4	0,2356	4	0,4200	4	0,6704
6	0,0764	6	0,1230	6	0,1741	6	0,4000	6	0,5780
8	0,0536	8	0,0805	8	0,1183	8	0,2400	8	0,5267
10	0,0319	10	0,0974	10	0,1051	10	0,2250	10	0,4630
15	0,0334	15	0,1304	15	0,0507	15	0,1650	15	0,4080
20	0,0065	20	0,0763	20	0,0575	20	0,1747	20	0,3625
30	0,0240	30	0,0757	30	0,0370	30	0,1300	30	0,2933
		45	0,0794	45	0,0259	45	0,0785	45	0,2000
		60	0,1294			60	0,0520	60	0,0820

Table 15. Experiment Results of SWCNT

SWCNT (mg) :	10,60	SWCNT (mg) :	7,02	SWCNT (mg) :	5,20	SWCNT (mg) :	3,87	SWCNT (mg) :	1,16
Adsorbant/ Adsorbate	1/100	Adsorbant/ Adsorbate	1/65	Adsorbant/ Adsorbate	1/50	Adsorbant/ Adsorbate	1/37	Adsorbant/ Adsorbate	1/15
Time (min)	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**
0	1,0619	0	1,0839	0	1,0264	0	1,0506	0	1,0898
0,5	0,4790	0,5	0,3362	0,5	0,4624	0,5	0,5756	0,5	0,4790
1	0,4062	1	0,4452	1	0,4164	1	0,4412	1	0,4440
2	0,3005	2	0,4479	2	0,4745	2	0,4245	2	0,4548
4	0,4354	4	0,3864	4	0,4518	4	0,4165	4	0,3935
6	0,3219	6	0,4180	6	0,4148	6	0,4006	6	0,4489
8	0,2695	8	0,2866	8	0,3109	8	0,5672	8	0,5419
10	0,2510	10	0,2518	10	0,2869	15	0,4179	15	0,4551
15	0,1820	15	0,2147	15	0,2292	20	0,2297	20	0,3843
20	0,0993	20	0,1716	20	0,2024	45	0,1878	45	0,2230
30	0,0814	30	0,1484	30	0,2010	90	0,1380	90	0,1586
45	0,0586	45	0,1109	45	0,1425	120	0,1367	120	0,1894
		60	0,0660	60	0,1658	180	0,0811	180	0,1392
		90	0,0495					240	0,1373
		120	0,0379						
		180	0,0277						

Table 16. Experiment Results of MWCNT

MWCNT (mg) :	8,10	MWCNT (mg) :	10,10	MWCNT (mg) :	5,30	MWCNT (mg) :	3,95	MWCNT (mg) :	1,80	MWCNT (mg) :	1,10	MWCNT (mg) :	0,60
Adsorbant/ Adsorbate	1/100	Adsorbant/ Adsorbate	1/65	Adsorbant/ Adsorbate	1/50	Adsorbant/ Adsorbate	1/36	Adsorbant/ Adsorbate	1/15	Adsorbant/ Adsorbate	1/10	Adsorbant/ Adsorbate	1/5
Time (min)	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**
0	0,7968	0	1,5741	0	1,0664	0	1,0875	0	1,1816	0	1,1249	0	1,1869
0,5	0,3811	0,5	0,6640	0,5	0,6327	0,5	0,5971	0,5	0,8830	0,5	0,8129	0,5	0,9011
1	0,3031	1	0,6787	1	0,7151	2	0,5644	2	0,7886	2	0,7376	2	0,9761
2	0,2349	2	0,3631	2	0,6061	4	0,4162	8	0,5226	8	0,4046	8	0,8827
4	0,1341	4	0,1743	4	0,6498	6	0,3135	15	0,4540	15	0,4650	15	0,7442
6	0,0657	6	0,1098	6	0,5196	8	0,3371	20	0,3716	20	0,3449	20	0,6749
8	0,0465	8	0,0464	8	0,4245	10	0,2495	30	0,2573	30	0,3338	30	0,6862
10	0,0285	10	0,0403	10	0,4106	15	0,1734	45	0,2235	45	0,2962	45	0,5696
15	0,0116	15	0,0325	15	0,2298	20	0,3281	60	0,1719	60	0,2999	60	0,5564
20	0,0151	20	0,0415	20	0,1074	30	0,0888	75	0,1943	80	0,2609	80	0,4931
				30	0,0581	45	0,0242			110	0,2436	110	0,5073
				45	0,0567	60	0,0326			150	0,2218	150	0,5114

Table 17. Experiment Results of OH MWCNT

OH-MWCNT (mg) :	8,70	OH-MWCNT (mg) :	6,85	OH-MWCNT (mg) :	5,70	OH-MWCNT (mg) :	4,00	OH-MWCNT (mg) :	1,50	OH-MWCNT (mg) :	1,10	OH-MWCNT (mg) :	0,60
Adsorbant/ Adsorbate	1/100	Adsorbant/ Adsorbate	1/65	Adsorbant/ Adsorbate	1/50	Adsorbant/ Adsorbate	1/37	Adsorbant/ Adsorbate	1/15	Adsorbant/ Adsorbate	1/10	Adsorbant/ Adsorbate	1/5
Time (min)	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**
0	0,8768	0	1,0536	0	1,1505	0	1,0774	0	1,0232	0	1,0931	0	1,1602
0,5	0,5689	0,5	0,6854	0,5	0,7318	0,5	0,7990	0,5	0,5954	0,5	0,7764	0,5	0,6930
1	0,4687	1	0,6320	1	0,7588	2	0,7628	2	0,6567	2	0,7658	2	0,6143
2	0,4771	2	0,5713	4	0,6279	4	0,6357	8	0,4971	8	0,5859	8	0,5025
4	0,3257	4	0,4147	6	0,5070	6	0,5866	15	0,5216	15	0,6411	15	0,6043
6	0,2435	6	0,3231	8	0,4286	10	0,3420	20	0,3477	20	0,5197	20	0,6010
8	0,1914	8	0,2668	10	0,3864	20	0,2572	30	0,3317	30	0,4470	30	0,5019
10	0,1320	10	0,2422	15	0,2655	30	0,1818	45	0,2744	45	0,4535	45	0,4610
15	0,0673	15	0,1525	20	0,1784	45	0,1156	60	0,2744	60	0,4100	60	0,4610
20	0,0577	20	0,1214	30	0,1111	60	0,0757	80	0,1918	80	0,3524	80	0,4851
30	0,0424	30	0,0897	45	0,0804	80	0,0666	100	0,2056	110	0,2969	110	0,4611
		45	0,0619							150	0,3440	150	0,4596

Table 18. Experiment Results of COOH MWCNT

COOH-MWCNT (mg) :	8,70	COOH-MWCNT (mg) :	6,45	COOH-MWCNT (mg) :	5,85	COOH-MWCNT (mg) :	3,55	COOH-MWCNT (mg) :	1,58	COOH-MWCNT (mg) :	1,00	COOH-MWCNT (mg) :	0,50
Adsorbant/ Adsorbate	1/100	Adsorbant/ Adsorbate	1/65	Adsorbant/ Adsorbate	1/50	Adsorbant/ Adsorbate	1/37	Adsorbant/ Adsorbate	1/15	Adsorbant/ Adsorbate	1/10	Adsorbant/ Adsorbate	1/5
Time (min)	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**	**Time (min)**	**Conc. (mg/L)**
0	0,8773	0	1,0047	0	1,1801	0	0,9312	0	1,0491833	0	1,0368	0	1,0564
0,5	0,3978	1	0,5528	0,5	0,7066	0,5	0,6373	0,5	0,7894	0,5	0,6325	0,5	0,7249
1	0,3706	2	0,5455	1	0,6363	1	0,6906	1	0,8155	2	0,9474	2	0,7425
2	0,3725	4	0,3883	2	0,5502	2	0,5466	2	0,7358	8	0,7196	8	0,7219
4	0,2420	6	0,2843	4	0,4956	6	0,4355	8	0,6182	15	0,5766	15	0,6216
6	0,1728	10	0,1970	6	0,4283	10	0,3814	15	0,5233	20	0,6239	20	0,6672
8	0,1378	15	0,1153	8	0,3429	15	0,2419	20	0,4137	30	0,5383	30	0,5594
10	0,0810	20	0,0789	10	0,2870	20	0,1734	30	0,3532	45	0,3907	45	0,5557
15	0,0562	30	0,0445	15	0,1710	30	0,1195	45	0,2760	60	0,3077	60	0,5714
20	0,0360			20	0,0941	45	0,0958	60	0,1233	80	0,4730	80	0,4506
				30	0,0642	60	0,0691	75	0,1768	110	0,3253	110	0,3836
				45	0,0496			90	0,1534	150	0,3019	150	0,3279
				60	0,0300								

B. Linear Isotherm Graphs

AC	
Ce	**Qe**
0,2195	84,1352
0,1650	32,5000
0,0517	18,7739
0,0763	14,3874
0,0340	9,7324

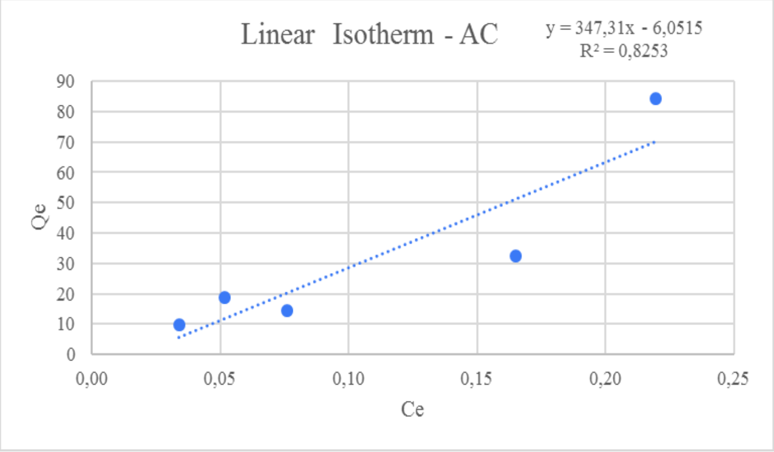


Figure 32. Linear Isotherm Graph of PAC

SWCNT	
Ce	**Qe**
0,0586	9,4648
0,0609	14,572
0,1425	16,999
0,1367	23,615
0,1894	77,623

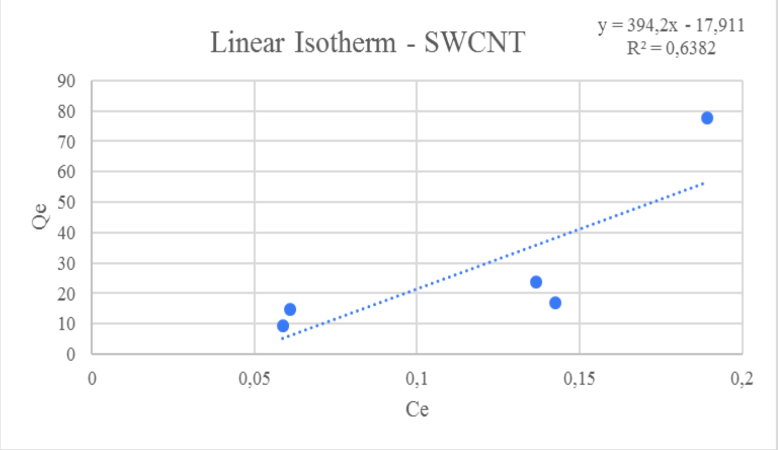


Figure 33. Linear Isotherm Graph of SWCNT

MWCNT	
Ce	**Qe**
0,5114	112,5778
0,2609	78,5477
0,2235	53,2319
0,0888	25,2835
0,0581	19,0239
0,0463	15,1203
0,0285	9,4846

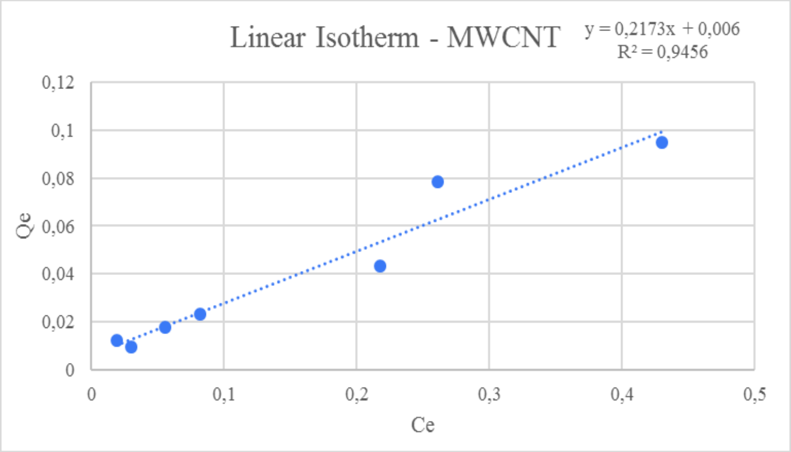


Figure 34. Linear Isotherm Graph of MWCNT

OH-MWCNT	
Ce	**Qe**
0,3972	0,1005
0,3524	0,0673
0,1951	0,0533
0,1091	0,0223
0,0989	0,0158
0,0852	0,0134
0,0485	0,0109

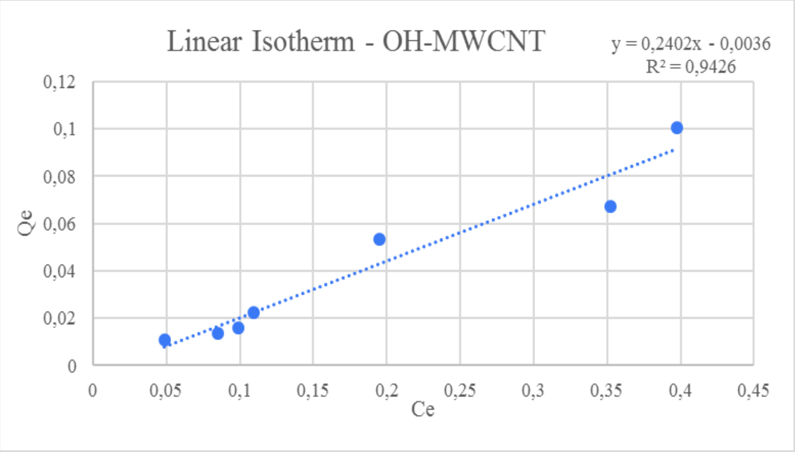


Figure 35. Linear Isotherm Graph of OH MWCNT

COOH-MWCNT	
Ce	**Qe**
0,4506	121,1632
0,3253	71,1583
0,1534	56,8780
0,1195	22,8648
0,0642	19,0745
0,0789	14,3531
0,0360	9,6701

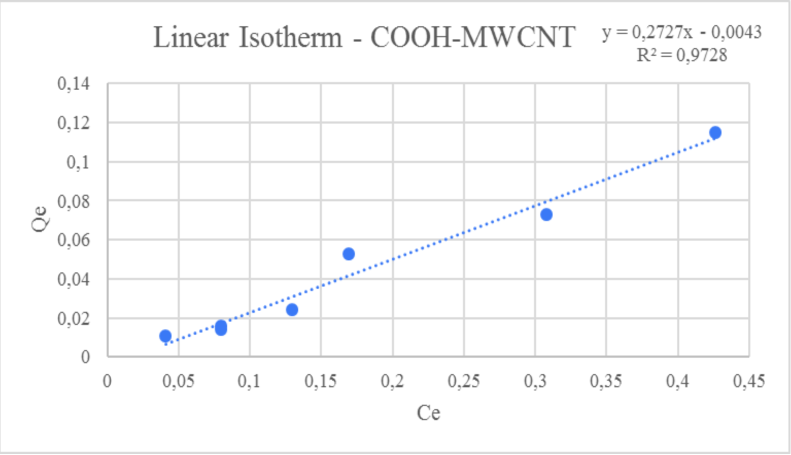


Figure 36. Linear Isotherm Graph of COOH MWCNT

C. Freundlich Isotherm Graphs

AC	
log Ce	**log qe**
-0,6587	1,9250
-0,7825	1,5119
-1,2861	1,2736
-1,1178	1,1580
-1,4685	0,9882

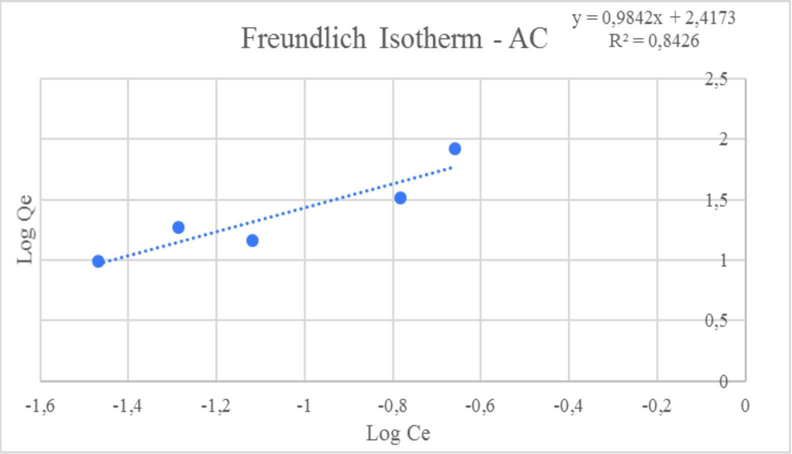


Figure 37. Freundlich Isotherm Graph of PAC

SWCNT	
log Ce	**log qe**
-1,2321	0,9761
-1,2154	1,1635
-0,8462	1,2304
-0,8642	1,3732
-0,7226	1,8900

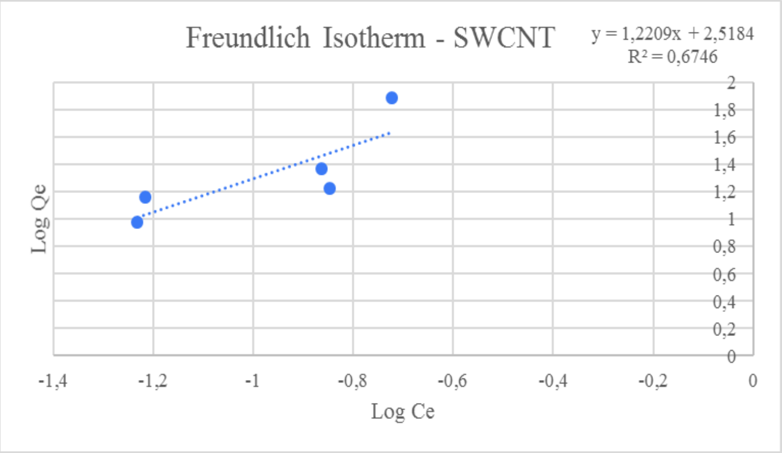


Figure 38. Freundlich Isotherm Graph of SWCNT

MWCNT	
log Ce	**log Qe**
-0,2912	2,0515
-0,5836	1,8951
-0,6508	1,7262
-1,0516	1,4028
-1,2358	1,2793
-1,3344	1,1796
-1,5450	0,9770

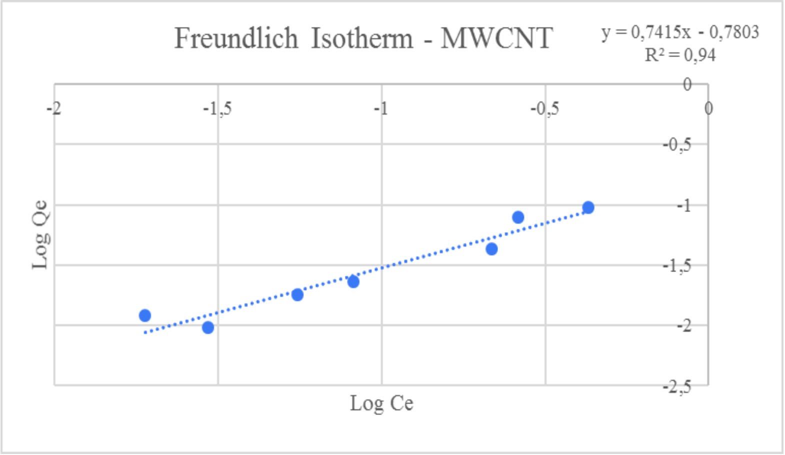


Figure 39. Freundlich Isotherm Graph of MWCNT

OH-MWCNT	
log Ce	**log Qe**
-0,4010	-0,9980
-0,4530	-1,1718
-0,7098	-1,2732
-0,9622	-1,6522
-1,0046	-1,8011
-1,0694	-1,8744
-1,3145	-1,9611

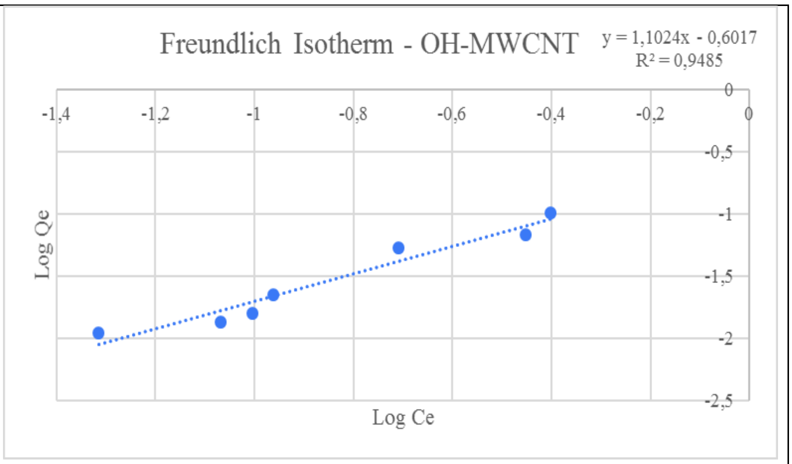


Figure 40. Freundlich Isotherm Graph of OH MWCNT

COOH-MWCNT	
log Ce	**log Qe**
-0,3462	2,0834
-0,4878	1,8522
-0,8143	1,7549
-0,9228	1,3592
-1,1923	1,2805
-1,1027	1,1569
-1,4443	0,9854

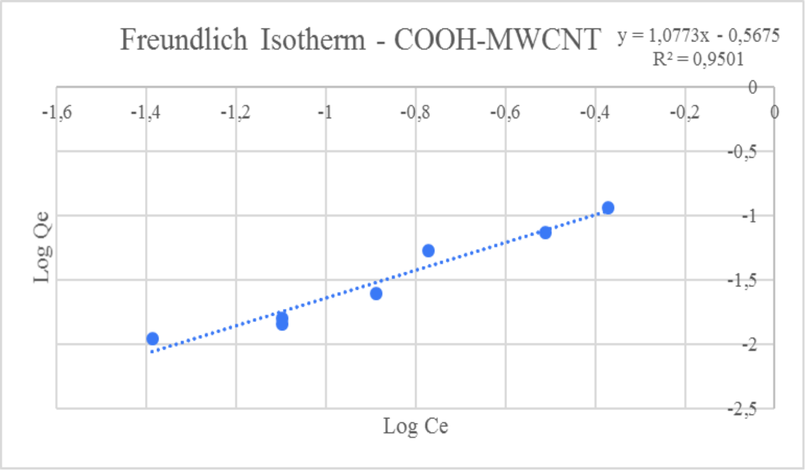


Figure 41. Freundlich Isotherm Graph of COOH MWCNT