



Technische Universität Hamburg-Harburg

Master Thesis

by

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**“Influence of Salinity on Heterogeneous Photocatalytic
Oxidation of Wastewaters”**

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October, 2008

Declaration

I hereby declare that I am the sole author of this thesis and it contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where a reference is made in the text of the thesis.

Darmstadt, 10.10.2011

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.



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Hamburg, 14.10.2008



Altan Özkan

Acknowledgments

I would like to thank Professor Ralf Otterpohl for introducing me the topic ecological sanitation and giving me the opportunity to involve in its research.

I am deeply grateful to Dr. Holger Gulyas for his understanding, encouragement and endless patience when it was most required. Under his guidance, preparation of this master thesis was not only instructive but also fun and exciting.

I would like to acknowledge Susanne Eggers for her assistance in the laboratory.

Finally, I would also like to thank my friends and my family for their support.

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Summary

Solar photocatalytic oxidation of biologically pretreated greywater can be looked as a sustainable process for increasing water security. However, it has been recently observed, that the nanosized photocatalyst TiO_2 is subdued to severe flocculation in the relatively saline matrix of biologically treated greywater. Photocatalyst agglomeration results in reduced efficiency of the process and thus enhances area requirement for solar applications. In this investigation, biologically treated greywater was simulated by solutions of humic acid sodium salt (NaHA) in concentrations of 10 to 50 mg/l and NaCl in concentrations of 1 mg/l to 1000 mg/l in deionized water.

The aim of this study was to determine whether there is a direct relation between the particle size characteristics (due to double layer compression) obtained for TiO_2 in suspensions with varying salt (NaCl) concentrations and the photodegradation rates determined in the same wastewaters.

For the determination of the flocculation effect of NaCl, gravimetric sedimentation analyses (“pipette method”) were conducted. In general, these analyses showed a decreasing TiO_2 concentration in supernatants after 1 hour sedimentation with increasing NaCl concentration reflecting the formation of bigger TiO_2 flocks with higher settling velocity due to double layer compression. From these analyses the point of zero charge (PZC) of suspensions with NaHA concentration of 10 mg/l was determined to be around 5.8. Additionally, it was found that the effect of NaHA on TiO_2 settling was more dramatic especially in lower concentrations when compared with the influence of NaCl (due to pH alteration). The importance of pH on photocatalyst flocculation was corroborated by comparing the NaCl influence with the influence of NaHCO_3 evaluated in another master thesis.

In order to relate the TiO_2 particle size (measured as the surrogate TiO_2 concentration in supernatant after sedimentation measured by gravimetric analysis) to the photodegradation rate, irradiation experiments were made with the identical suspensions

the gravimetric analyses were conducted with. From these photodegradation experiments a direct correlation between the concentrations of TiO_2 in supernatant and their degradation rates could not be found. However, this does not necessarily indicate an ultimate absence of relation between photocatalyst flocculation and efficiency of photocatalysis due to following problems faced during these experiments that might have led to incorrect conclusions: a lag phase observed in suspensions with NaHA concentration of 50 mg/l that affects the calculated initial degradation rate and the low TOC values of suspensions with 10 and 20 mg/l of NaHA that results in high coefficient of variation.

From the analysis between the NaCl content added to the suspensions and their photodegradation rate a distinct pattern could not be found. However, for two of the suspensions (10 and 20 mg/l) for NaCl concentrations above 200 mg/l the rates of degradation found were 0. The reason behind might be the radical scavenging and TiO_2 particle agglomeration effects of the salt addition.

Adsorption of NaHA on TiO_2 was also investigated. The amount of TOC removed from suspensions (TiO_2 particles were separated by centrifugation) without irradiation was assumed to be adsorbed on TiO_2 . From these calculations it was found that the mass of TOC adsorbed per TiO_2 mass decreases with increasing NaCl addition in a low NaCl concentration range, but increases with increasing NaCl concentrations at higher concentration range. The reason behind the decrease of TOC adsorption might be the competitive adsorption of Cl^- ions on TiO_2 and the increase might be due to decreased repulsion between different HA segments with increasing ionic strength resulting in higher adsorbability of HA.

In addition to the model wastewaters mimicking biologically treated greywater, experiments were made with real biologically pre-treated greywater. When compared to the model solutions, the results gathered from experiments with real biologically pre-treated greywater were very different. The gravimetric analysis showed much lower concentrations of TiO_2 in supernatant for real wastewater when compared with models. This can be explained by the higher ionic strength present in real biologically pre-treated

greywater resulting in larger TiO_2 particle sizes with higher settling velocities. In addition to this difference, the degradation rate of biologically pre-treated greywater was much lower when compared to degradation rates obtained with the model solutions. Additional to large TiO_2 particle size formed in real biologically pre-treated greywater and to its different organics, the reasons for far lower mineralization rates in the real wastewater might be the scavenging and competitive adsorption effects of the anion mixture present. The lag phase found in some of the models mimicking biologically pre-treated greywater was not observed for the real greywater. This might be due to organics other than humic acid present in real biologically pre-treated greywater such as fulvic acid and polysaccharides. Thus, when all these differences are considered, it can be concluded that the goal of modeling biologically pretreated greywater with NaHA was not successful. Moreover, the complexity of effects of salts and of the pH buffering property of the selected organic model compound on flocculation of suspended TiO_2 nano-particles show the necessity of selecting model organics not affecting the pH for investigating the influence of TiO_2 flocculation by inorganic salts on photocatalytic oxidation efficiency.

1. Introduction

Water is not only a limited, but also a strategic resource which is a necessity for human need for urban, industrial and agricultural use [1,2]. Thus, in 21st century, life of billions of people will depend on its appropriate management. In addition to its current scarcity, it is estimated that in the year 2025 nearly one-third of people living in developing countries (which is equivalent to 2.7 billion people) will dwell in places that suffer from severe water scarcity [2,3]. Furthermore, in addition to industrialization by that year mainly due to population growth, water supply will need to be increased by 41% [2,4].

In order to meet this demand, development of additional resources is required. However, when it is achieved by means of exploitation of more distant (surface water) and deeper (groundwater) sources or construction of new dams and long conveyance systems, it is likely to result in high direct costs, e.g., construction, operation, maintenance, and indirect costs, e.g., higher pressure on environment. Thus, decreasing the urban water demand became an essential issue for both the water utilities and regulatory bodies. One of the ways to decrease urban water demand is to reuse the water [5]. By doing so an alternative source to meet current and future water demand can be acquired, necessity for fresh water can be decreased, present water supplies can be secured from pollution, the need for the construction of water control structures can be decreased and better compliance with environmental regulations can be achieved [6].

At this point, with attributes such as being polluted with easily and cheaply treatable organics, absence of hazardous chemicals when compared with their possible presence in secondary municipal effluents and having a high volume flow relative to other streams of domestic wastewater, separately collected greywater, being water from kitchen, bathroom and laundries, is an excellent resource for high quality reuse [7, 8, 9].

However, organics still present subsequent to biologically treatment of greywater should be removed with an additional stage due to their possible harms to human health [7]. For this purpose heterogeneous photocatalytic oxidation processes are suitable and titanium

dioxide is the most widely utilized photocatalyst [10,11]. A great advantage of this technology is that it can be operated with solar radiation. The efficiency of this system strongly affects the area needed for solar operation and depends on a number of factors including salt content of the medium [12]. This master thesis is focused on determination of salt effects on photocatalytic oxidation of model wastewater mimicking biologically pre-treated greywater.



2. Fundamentals

2.1 Greywater

2.1.1 Separate Collection of Greywater in Ecological Sanitation

Ecological sanitation is a sustainable closed loop system whose approach is resource minded (Figure 1). The underlying basic purpose is to close the nutrient and water cycles with a minimum expenditure on material and energy in order to contribute to sustainable development. In this system, human excreta are considered as resource and usually treated on site and if necessary processed further off-site for the sake of their recyclability [13].

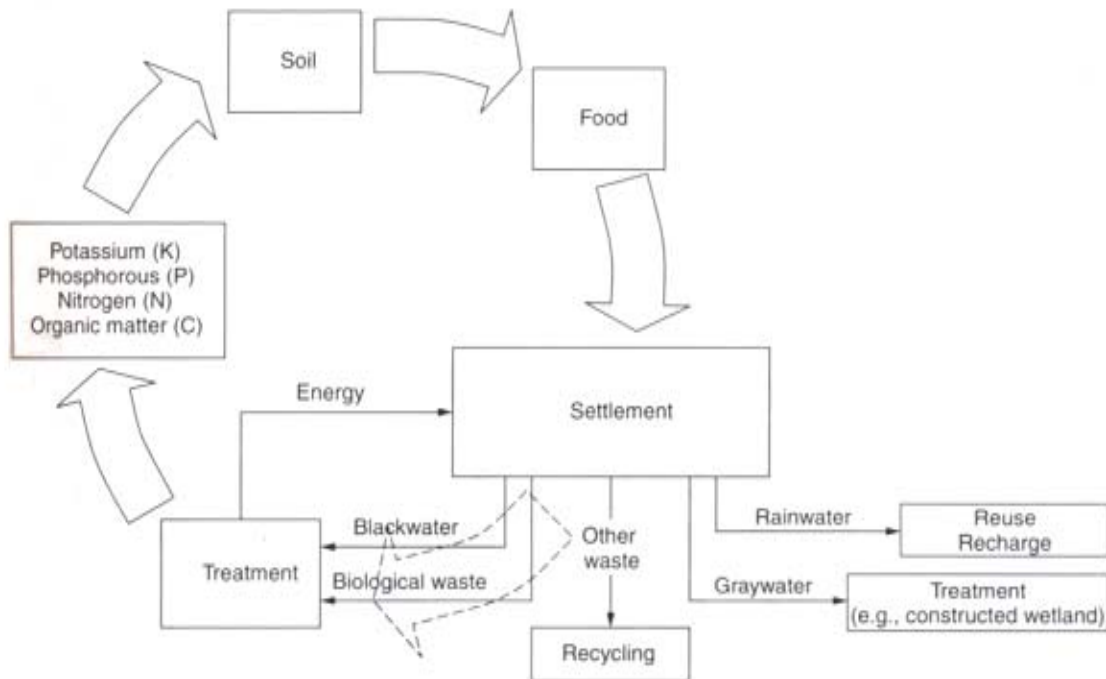


Figure 1. System of ecological sanitation [13].

Ecological sanitation is based on source control in household and the source control itself is based on different characteristics of grey, yellow (urine with or without flush water) and brown water (faeces, toilet paper and flush water) whose characteristics can be found in Table 1.

As it can be inferred from Table 1, greywater with its high specific flow of up to $100 \text{ m}^3/(\text{P}\cdot\text{a})$, represents lower specific mass flows of nutrients than urine and faeces. Simple and low cost options are available for the treatment of greywater and by doing so it can be reused. Faeces exhibit a 10 times less volume than urine and contain both the highest organic load and the largest part of pathogens. However, if they are separated and kept in small volumes with non-flush or low-flush toilets, this provides conditions that are favorable for sanitization (dehydration, composting or vermi-compositing). After proper hygienisation faecal matter can be utilized as soil conditioner. Urine contains most of the soluble nutrients and it may contain pathogens that can be easily eliminated for its reuse in agriculture by simple storage for 6 months due to pH elevation by ureolysis. By separate collection and treatment of different household wastewater streams reuse of resources can be maximized and hygienic standards can be increased [8].

Table 1. Typical characteristic of household wastewater components [8]

	Grey water	Urine	Faeces
Yearly Loads (kg/P·Year)	25,000-100.000 (L/(P·year))	~ 500 (L/(P·year))	~ 50 (L/(P·year))
N ~ 4-5	~ 3 %	~87 %	~ 10 %
P ~ 0.75	~ 10 %	~ 50 %	~ 40 %
K ~ 1.8	~ 34 %	~ 54 %	~ 12 %
COD ~ 30	~ 41 %	~ 12 %	~ 47 %

2.1.2 Composition of Grey Water

Composition of greywater depends on lifestyle of the people producing it. Typically it contains high concentrations of easily biodegradable organics and salts (including salts causing alkalinity like hydrogen carbonates) [14, 15]. Moreover, despite its high volume compared to other wastewater streams arising from households it represents low nutrient mass flows (except for potassium (Table 1)) which can even be lowered by utilization of

phosphorus free detergents. If it is not mixed with other household wastewater fractions, it does not need nitrification and denitrification processes [8]. But even if it is kept separated from faecal matter it is not free of pathogens but it is normally considered to be of no major health concern. However, its high organic content can provide a ground for the regrowth of pathogens [9]. BOD₇ concentrations reported for greywater range is from 350 to 500 mg/l and COD from 495 to 682 mg/l [15]. In addition to these, metals can be found in greywater and sources of these metals can be the water itself, corrosion of pipes, cutlery and shampoos used in household [14]. For instance, cadmium can originate from phosphorus containing detergents and copper and zinc from zinc or copper plated pipes [8]. With the utilization of environmentally friendly chemicals and polyethylene pipes and not using the sink for paint and solvent disposal, the metal and organic content of greywater can be minimized [8, 14].

2.1.3 Treatment Systems for Grey Water

In utilization of biological treatment systems the aim is to decrease the organic content of greywater [8]. Constructed wetlands, sequencing batch reactors (SBR), membrane bioreactors, rotating disc contactors and aerated filters are frequently investigated examples [8, 15]. Constructed wetlands are cheap to operate and build and with an area demand of 2 m² per inhabitant good results have been achieved. When the area is limited, SBR, membrane bioreactors and biologically aerated filters can be possible options. Moreover, if there is an intention to use the effluent for high quality demand reuse purposes like toilet flushing or laundry, biological treatment must be followed by a physical process in order to retain active biomass and minimize the passage of solids into the effluent. In this respect, a membrane bioreactor system, which is a combination of suspended growth reactor and membrane filtration device, has the potential to be the choice of the future particularly for high quality reuse purposes. In this system in addition to intensified biological treatment, there is a capability to provide effluent with non-detectable levels of coliforms [8].

Sand filter, ultrafiltration, micro-filtration, reverse osmosis are the physical methods that can be used for greywater treatment. In previous studies it was found that greywater treated with combinations of SBR and sand filters or microfiltration has the potential to be reused. Furthermore, an effluent that fulfills the European quality target for bathing waters can be gathered when a combination of constructed wetland and TiO_2 based photocatalytic oxidation is utilized for greywater [8].

2.1.4 Greywater Reuse

In literature and internet publications reuse purposes for greywater are mentioned as follows: Garden irrigation, toilet flushing, animal husbandry, industrial use, golf course or cemetery irrigation, groundwater recharge, hand washing, potable water uses, vehicle washing, helicopter washing, firefighting, laundry, bathing/showering, crop irrigation, ornamental lakes and streams, industrial construction, dust control, street washing/snow melting. Different reuse purposes necessitate different quality standards and standards regarding particular reuse purposes are subjected to different jurisdictions in different countries [15]. In previous grey water reuse projects conducted in Germany, four criteria were determined and expected to be fulfilled for reclaimed water [16].

1. Hygienic safety

a) Installation aspects

It should be ensured that there is no cross-connection between drinking water and reclaimed water. Appropriate designation and labeling of pipes, tubes and recycling taps should be made. Registration of the recycling plant should be made to the local health authorities [16].

b) Water Quality Aspects

Water to be reused for high quality demand purposes (toilet flushing, laundry etc.) has to satisfy the criteria listed in Table 2 [16].

Table 2. Water quality parameters of water to be reused for toilet flushing suggested by Berlin University of Technology and Senat of Berlin [16]

Biological Parameters	Physical and Chemical Parameters
Total Coliform Bacteria < 10,000/100mL	BOD ₇ < 5 mg/L
E.coli < 1,000/100 mL	O ₂ saturation > 50%
<i>Pseudomonas aeruginosa</i> < 100/100 mL	UV transmission at 254 nm (1 cm cuvette) > 60 %

2. Aesthetic Aspects

Treated grey water should be nearly free from suspended solids and color and it should not cause inconsistencies like odor [16].

3. Environmental Tolerance

Due to current satisfaction with existing water supply systems, chemical disinfection or energy intensive recycling systems are not suggested as options to be considered [16]. On the other hand, when the reuse purpose requires a high hygienic standard, chlorination of reclaimed greywater is inevitable [18]. However, if the reclaimed water exhibits TOC concentrations above 2 mg/l, the formation of trihalomethanes in concentrations of more than 10 µg/l (Guideline of the German Drinking Water Ordinance) is very likely subsequent to chlorination [17]. Therefore, TOC concentrations of reclaimed greywater should be below 2 mg/l if chlorination is an option [18].

4. Economical Aspects

When compared with drinking water supply and wastewater treatment systems the maintenance and the operation costs of a greywater recycling system should be cheaper [16].

2.2 Photocatalytic Oxidation

2.2.1 Introduction

Advanced oxidation processes (AOP) involve production of highly reactive hydroxyl radicals ($\text{HO}^\bullet$) and they are utilized to degrade or even mineralize a wide range of organic pollutants. Photocatalytic oxidation, which is a particular AOP, utilizes the principle of free radical production through the interaction of a photocatalyst material with photons of proper energy level. Due to the advantageous attributes they possess such as electrical structure (energetic levels of valance and conduction bands), light absorption, charge transport and excited state lifetimes, semiconductors are utilized as photocatalyst material [19].

The main principles behind a semiconductor photocatalytic reaction are represented in Figure 2. When a photon with energy equal to or greater than the bandgap energy (ΔE_{bg}) of the semiconductor hits a photocatalytic surface, a positive hole (p^+ in the valence band) and an electron (e^- in the conduction band) are formed (Eq. (1)) by the excitation of the electrons from the valence band to the conduction band. It has to be noted that the electrons in the conduction band and the holes in the valence band are highly mobile and can migrate across the semi-conductor material, by chance even to the semiconductor particle surface where they can initialize a couple of reactions [19].

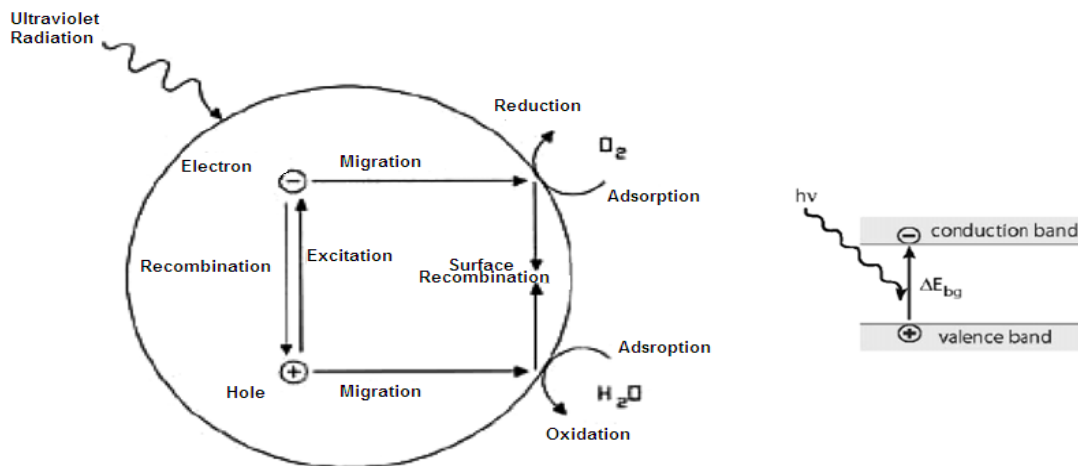


Figure 2. Schematic representations of photochemical activation and electron-hole formation [19].

The pollutants are either directly oxidized by the positive holes (Eq. 2) or they are indirectly oxidized by hydroxyl ions (Eq. 4) formed by the oxidation of water with positive holes. As the holes as well as the hydroxyl radicals are very short-lived, organics are not oxidized by them unless they are adsorbed to the photocatalyst surface, i.e. they are near to that location where the oxidants are generated.



The electron in the conduction band reduces oxygen that is adsorbed at the photocatalyst (TiO₂) surface (Eq. (5)). The O₂^{•-} radical is assumed to generate hydrogen peroxide (H₂O₂) (Eq. 6). H₂O₂ generated at the photocatalyst surface can be reduced by an electron formed by UV absorption of the photocatalyst (Eq. 7). By this reaction, another hydroxyl radical is produced [11].



The reduction process of oxygen and the oxidation process of organics have to take place simultaneously for the efficient photocatalytic oxidation of pollutants. Otherwise, electrons accumulate in the conduction band and enhancement of recombination of electrons and positive holes will be the consequence. Hence, for the efficiency of the system consumption of electrons is a necessity [19].

2.2.2 TiO₂ as a Catalyst

Regarding the selection of semiconductor catalysts there is consensus on TiO₂ due to its attributes such as its high activity, large stability to light illumination, low price and nontoxicity [19].

Three different forms of TiO₂ exist based on their crystal forms: anatase, rutile and brookite. Previous studies assert that a mixture of anatase and rutile gives the best combination. Thus, Degussa P25 grade TiO₂ (mixture of 70% anatase and 30% rutile) gives the best degradation efficiency [19]. It is a powder consisting mainly of particles in the range of 25 nm diameter. The nano-size of the P25 is a prerequisite of its photocatalytic efficiency, as these small particles are highly absorbing UV photons but not visible light, while larger TiO₂ particles are less efficiently absorbing UV light.

2.2.3 The Light Source for Photocatalytic Oxidation

As mentioned above, TiO₂ absorbs radiation that is below the visible range of the light spectrum. Thus, for the photoactivation of TiO₂, radiation with wavelengths of less than or equal to 384 nm is required and the absorbance maximum is at about 340 nm. Light with these wavelengths can be supplied by artificial lamps, but is also part of solar irradiation [19]. About 5 % of terrestrial insolation is represented by UV photons. Even at cloudy conditions, reasonable UV quantities can be detected during the day on the ground.

2.2.4 Reactor Types for Photocatalytic Oxidation

One of the major design criteria for the photocatalytic oxidation is utilization of concentrated or non-concentrated sunlight. In light concentrating systems the concentration of solar light is achieved by utilization of a reflecting surface. By that way, when compared with non-concentrated systems, they require a smaller reactor volume for

the same light-harvest area. Moreover, owing to their wavelengths UV lamps can also be used for photoactivation of TiO_2 particles [19]. However, as the quantum yield of photocatalytic oxidation decreases with increasing light intensity, non-concentrating reactors offer some advantage with respect to efficiency. Concentrating systems are not able to function when the sky is cloudy as the diffuse irradiation can not be concentrated, while non-concentrating systems can also be operated under cloudy conditions.

The second major design criterion for the selection of photocatalytic oxidation reactors is the mode of TiO_2 addition. Two different modes of TiO_2 application are adopted: (1) TiO_2 immobilized on support materials and (2) TiO_2 suspended in aquatic medium. From a technical application point of view, when compared with suspended TiO_2 application, immobilized TiO_2 is advantageous because it does not require an additional step for the recovery of catalyst particles after oxidation. However, in previous works problems such as scouring or detachment of the deposited catalyst were encountered. In addition to these drawbacks, during fixation the porous structure of the photocatalyst is lost due to sintering process which results in a reduced area to volume ratio. Hence, the efficiencies of immobilized systems are generally lower than the dispersed ones [19]. Different reactor types for photocatalytic oxidation are listed in Table 3.

Table 3. Different reactor types for photocatalytic oxidation

	Non-concentrated Sunlight	Concentrated Sunlight	UV Lamps
Suspended Photocatalyst	• Lagoon [20] • Double Skin Sheet Reactor [21]	• Paraboloidal Reflector or Parabolic Trough Reactors [22]	• Immersion Well Photoreactor [19] • Annular Photoreactor [19] • Elliptical Photoreactor [19] • Multi-lamp Photoreactor [19]
Immobilized Photocatalyst	• TiO₂ on Sloped Glass Panes; Coated Mat Reactor [23]	• Fluidized Bed Reactor with TiO₂ Immobilized on Glass Beads in the Focus of Paraboloidal Reflector [24]	• Film type photoreactor [19] • Fluidized bed photoreactor [19]

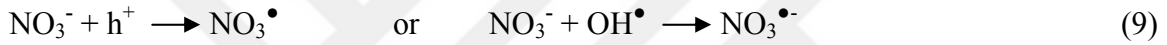
2.2.5 Effects of Inorganic Wastewater Matrix on Photocatalytic Oxidation

The effects of inorganic ions can be divided into three major areas: radical scavenging effects, effects through competitive adsorption to the photocatalyst surface and the effects on electrical properties of TiO₂ which will affect the photocatalyst particle size.

1. Radical Scavenging

The anions rising from inorganic matrix of wastewater can inhibit photo oxidation due to their scavenging effects for hydroxyl radical (OH[•]) or positive hole (h⁺) (Eq. 8-13). Although the radicals that are formed from scavenging reactions are also reactive, their

reactivities with organics are lower when compared to hydroxyl radical or positive hole. Thus, these anions decrease the degradation rate of pollutants [25]. On the other hand, some researchers assert that by the presence of these ions instead of electron and positive hole recombination, radical yield can be increased. In other words, by these researchers it is assumed that although they are not as reactive as the positive hole or hydroxyl radical instead of concurrent reaction of electron and positive hole recombination, production of inorganic radical anions can be beneficial for the degradation rate thanks to the presence of anions [26].



When the pH of the medium is larger than the so-called point of zero charge (PZC) of TiO_2 (see part 3 of this chapter), anions such as Cl^- are repelled due to negative charge of TiO_2 particles. However, in this case cations such as Na^+ can be adsorbed on negatively charged TiO_2 surfaces and they can act as electron acceptors (Eq. 14) [33]. As it is already stated in part 2.2.1 the efficiency of the system depends on the consumption of electrons that is produced by UV adsorption of the photocatalytic particle (in order to hinder recombination of positives hole and electrons). Hence, the reaction between sodium ion and the electron may increase the degradation rate of pollutants [33].



2. Competitive Adsorption of Inorganic Ions and Organics

For any surface mediated chemical process the adsorption of molecules onto surface is a prerequisite [27]. Ions that are introduced into solution can inhibit photocatalytic oxidation through adsorption competitive with reactants on the catalyst surface [28]. The scale of the competitive adsorption depends on a number of factors. First of all, the pH of the solution is critical. When the pH is lower than the PZC, the surface of TiO_2 particles are positively charged (Eq. 15). In this case, anions such as Cl^- can adsorb onto the surface of TiO_2 to form complex species such as $\text{TiOH}_2^+-\text{Cl}^-$. When the pH is higher than PZC, the surface of TiO_2 is negatively charged (Eq. 16). In this case production of complex species such as TiO^-Na^+ can be the result of binding of the cations from the solution by coulomb interactions. Formation of these complex species can decrease the attraction between the surface and the organic to be degraded due to the competition with the salt ions to adsorb on the catalyst surface [29]. From this discussion it can be easily concluded that the electric nature of the organics also plays a role in this context. When organic molecules are dissociating in aqueous solution, the electric charge of the formed organic ion strongly influences its adsorbability. Humic and fulvic acids, e.g., form anions at elevated pH. Thus their adsorbability will be poor under alkaline conditions [30, 31]. This is also the case with phenols. Consequently, Davis and Huang [31] have shown the decrease of photocatalytic oxidation of phenols at pH levels above 9. On the other hand, amines form positively charged organic ammonium cations which will be hardly adsorbed at acidic pH. Solubility of a salt is also essential for the scale of inhibition it can bring about. When compared with a highly soluble one, a salt with a low solubility adsorbs more on TiO_2 particles and the adsorption of organics to be eliminated decreases more [12].

Finally, it is worth to note that reports can be found in literature regarding light reduction (colored ferric ions, e.g. cause an inner filter effect due to their light adsorption) and short circuiting of e^- and h^+ recombination effects of Fe^{3+} . According to previous studies, iodide and bromide trap the positive holes (which inhibits photodegradation) and Ag^+ , Fe^{3+} and Cu^{2+} trap the photogenerated electrons (which enhances photodegradation) at the surface of TiO_2 [28].

3. Effects on Electrical Properties of TiO₂ Particles

Surface charge is the main electrical property of fine particulate matter suspended in water. It hinders the agglomeration of particles and causes them to remain in suspension for long periods of time [32] (“stable suspensions”).

For TiO₂ the surface charge may rise from amphoteric sites which can be charged positively or negatively depending on pH of the solution [33]. The pH which corresponds to a surface charge of zero is defined as point of zero charge (PZC). The PZC for TiO₂ is 6.3 [34]. For TiO₂, above this pH the surface charge is negative (Eq.15) and consequently at pH below the surface charge is positive (Eq.16) [32].



In most natural waters and wastewaters, particles are negatively charged. For the sake of electroneutrality positively charged counterions accumulate near and on the negatively charged particles. As shown in Figure 3, a fixed adsorption layer is formed due to cations that are bound tightly to the particle. The layer of cations that are adsorbed on the particle surface by electrostatic and adsorption forces is called the Stern layer. A net negative charge is present beyond the Stern layer and that attracts an excess of cations and repels anions. These cations and anions move about under the influence of diffusion. Unless all the surface charge and thus electric potential is eliminated, the excess concentration of cations extends into the solution and the layer between the Stern layer and point where the electric potential is eliminated is called the diffuse layer. Taken together, Stern layer and diffuse layer form the electric double layer [32].

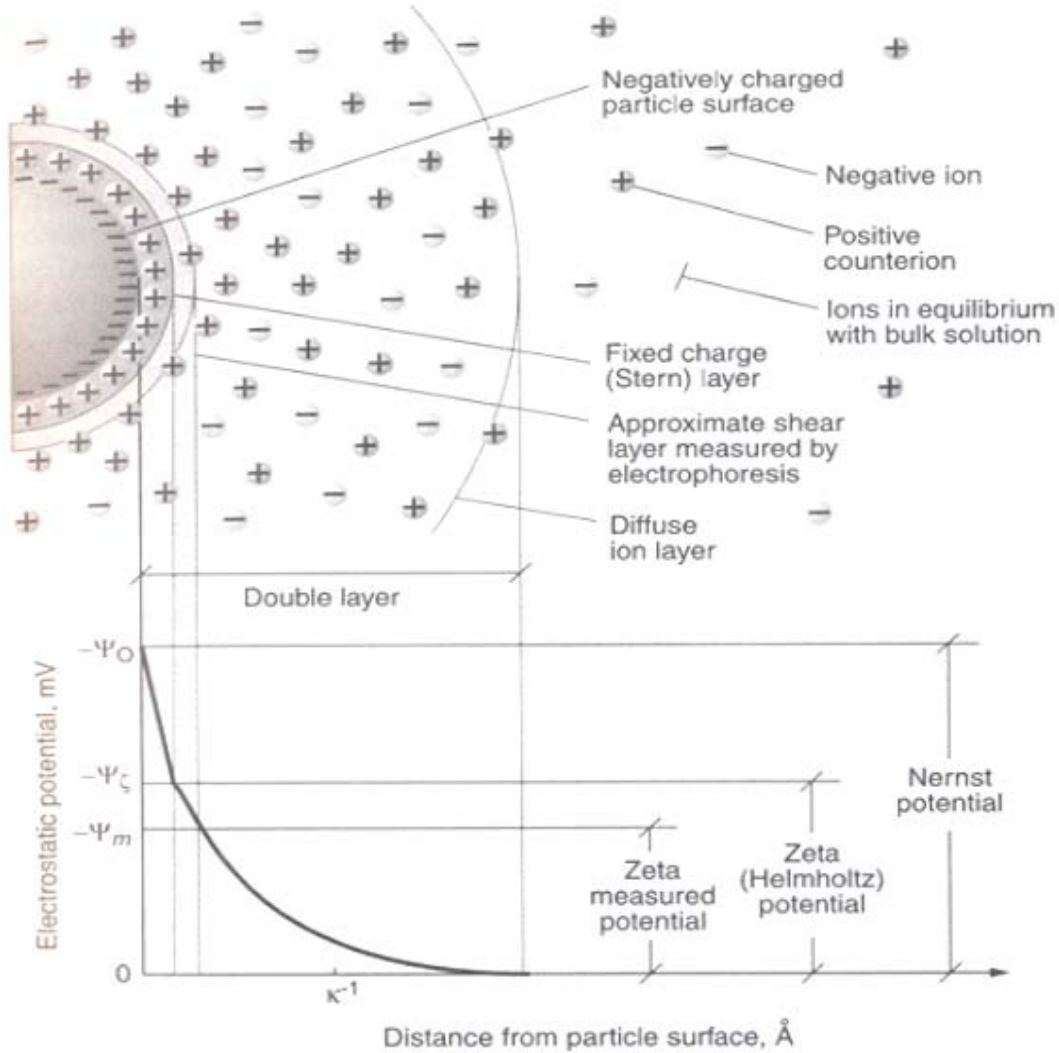


Figure 3. Structure of electrical double layer. The reciprocal double layer thickness is symbolized by κ (Eq. 17) [32].

When a negatively charged particle moves in an electrical field (towards positive electrode) some portion of the water near the particle surface moves with it and this creates the shear plane. The electrical potential between the shear plane and the bulk solution is called zeta potential. Empirically when the absolute value of the zeta potential goes below approximately 20 mV, rapid flocculation occurs due to attraction forces which also act between two particles, but with a much lower range than the repulsive electrostatic forces [32].

The stability of the particles in water is a function of the balance between the repulsive electrostatic force and the attractive forces. As it is already stated, the electrostatic repulsion is the result of a net surface charge which depends on the charge of the particle and the solution characteristics. The source of Van der Waals attractive forces is the electron share of atoms and/or molecules on the particle surface. When these electrons orient themselves in a way that induces synergistic electric and magnetic fields (induced dipoles) the attractive force is created. Also permanent dipole molecules will be oriented in the electric fields of each other leading to attraction (dipole-dipole interaction). Van der Waals as well as dipole-dipole forces of attraction are sufficiently strong to overcome the electrostatic repulsive forces when the induced or the permanent dipole molecules come sufficiently close together. As stated above the range of these forces is much lower than the range of the electrostatic coulomb forces. So, two particles are unable to attract each other at high distances between two particles, since electrostatic repulsive forces and electrical double layer extend further into solution. When case 1 in Figure 4 (high repulsive forces) is considered it can be deduced that the forces of attraction will dominate at very short distances. The net energy curve for case 1 contains a repulsive maximum that must be overcome if the particles shall stick together. The higher the repulsive maximum, (like in “Net Energy 1”) the lower the probability that two particles come so closely together that they enduringly stick together. Due to the short-range attractive forces by reducing the extent of electrical double layer as a consequence of the addition of salts, case 2 will result and in this case there is no energy barrier to be overcome, i.e. more particles will attach to each other after collision [32].

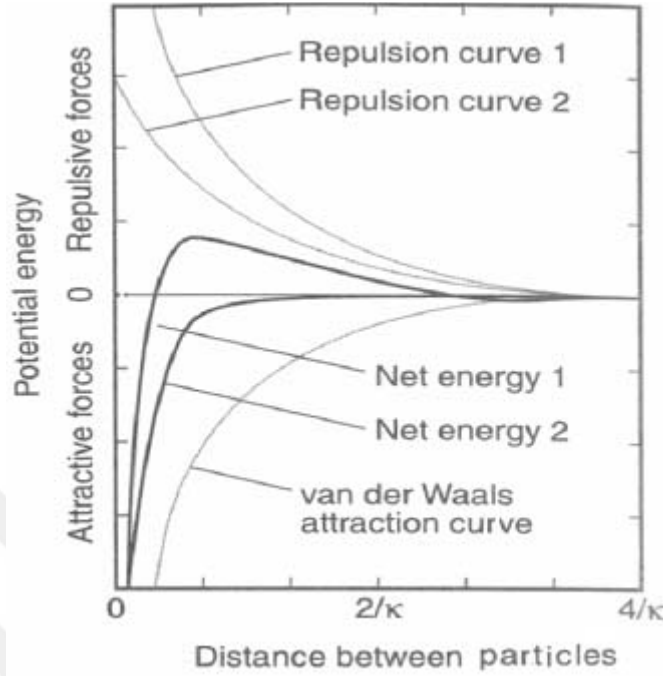


Figure 4. Attractive and repulsive potential energy that results when two particles are brought together. The reciprocal double layer thickness is symbolized by κ (see Eq. 17) [32].

As the ionic strength of a solution is increased, the zeta potential is decreased through the compression of double layer. The thickness of the double layer and its compression depending on ionic strength and electrolyte addition can be described as follows:

$$\kappa^{-1} = 10^{10} \left[\frac{(2)(1000) e^2 N_A I}{\epsilon \epsilon_0 k T} \right]^{-1/2} \quad (17)$$

κ^{-1} = thickness of double layer, Å

10^{10} = length conversion, Å/m

1000 = volume conversion, l/m³

e = electron charge, 1.60210×10^{-19} C

N_A = Avagadro's number, 6.02205×10^{23} /mole

I = ionic strength, mole/l

ϵ = permittivity relative to vacuum (for water 79.54)

ϵ_0 = permittivity in a vacuum, $8.854188 \times 10^{-12} \text{ C}^2/\text{J} \cdot \text{m}$

k = Boltzmann constant, $1.38066 \times 10^{-23} \text{ J/K}$

T = absolute temperature, K

It has to be stated that Eq. 8 is not the actual double layer thickness but is related to how far into the solution the repulsive force will reach. The double layer thickness is approximately equal to the distance where the electrical potential is 37 percent of the value at the particle surface.

The effect of ionic strength is the most important factor for double layer thickness. As it can be seen in Figure 5 and Figure 6 the electrical double layer can be compressed dramatically with increasing ionic strength and valence of the cation (in case of negative particle surface charge) added with the electrolyte. Van der Waals forces extend out into solution for about $10 \text{ \AA}$. Thus, if the electrical double layer can be shrunk more than this, rapid flocculation of suspensions will be the result [32].

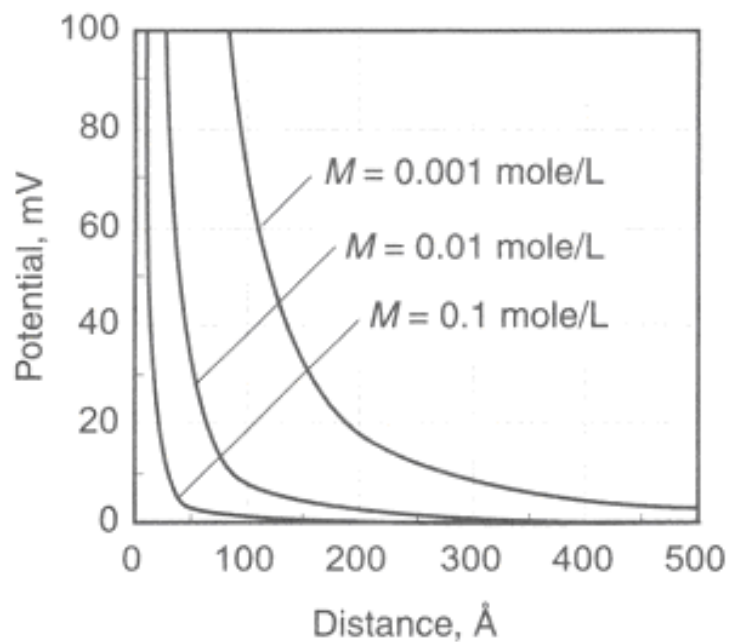


Figure 5. Effect of ion concentration on the extent of the electrical double layer [32].

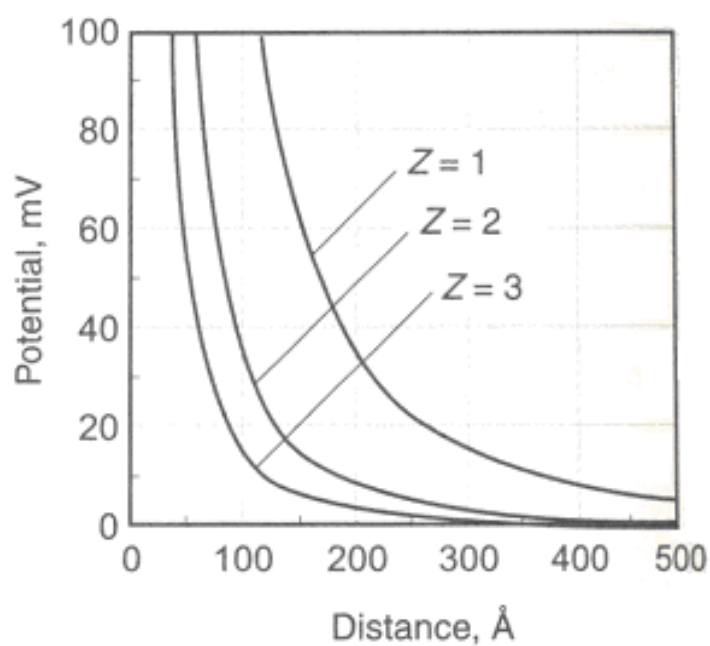


Figure 6. Effect of charge of ions on extent of the electrical double layer [32].

The phenomenon of double layer compression can explain why suspensions are stable in deionized water and flocculate in saline water [32, 35]. Owing to the fact that degradation of pollutants takes place on or near the surface of TiO_2 and that UV photons are efficiently adsorbed by nano-sized TiO_2 particles but only poorly by larger ones, pH and salt content of the wastewater is crucial for photocatalytic oxidation [35]. It is suspected from photocatalytic oxidation experiments with biologically pretreated greywater that flocculation of the photocatalyst in this matrix is the reason for poor efficiency of the process for greywater reclamation [36].



3. Aim of the Study

The aim of this study was to investigate whether flocculation of TiO_2 “P25” photocatalyst particles due to compression of electrical double layer by addition of sodium chloride (NaCl) impairs the photocatalytic oxidation efficiency of a model wastewater containing humic acid sodium salt (NaHA). For this purpose, the study was divided into two main parts. The aim of the first part was the determination of salt concentration effects on aggregation characteristics of TiO_2 in aqueous solutions modeling biologically pre-treated greywater. This was studied by sedimentation analyses of the photocatalyst in the presence of different NaCl concentrations by the so-called pipette method. In the second part investigations were made to determine whether there is a relationship between the aggregation characteristics found for TiO_2 particles at different NaCl concentrations and the photocatalytic degradation rate or not.

4. Materials and Methods

4.1 Gravimetric Analysis of Photocatalyst Flocculation

Gravimetric analyses were conducted for forty four different model wastewaters mimicking biologically pre-treated model greywater. For each analysis one liter of an aqueous solution with different concentration of NaCl and NaHA was added to one gram of TiO₂ (P25 Degussa-Hüls, Hanau/Germany). The NaHA (Roth, derived from lignite) concentrations were 0, 10, 20 or 50 mg/l and NaCl (Merck) concentrations were 0, 1, 2, 5, 10, 20, 50, 100, 200, 500 or 1000 mg/l. The suspensions prepared were mixed for 5 minutes in a graduated cylinder of 1 liter volume by vigorous magnetic stirring. Then stirring was stopped and the suspension was allowed to stand quietly without agitation for a period of one hour. After this time from each graduated cylinder a sample was taken with a 50 ml pipette from 10 centimeters below the suspension surface. The pipette has been adjusted and fixed to this position prior to the sedimentation phase in order to prevent settled TiO₂ from resuspension. Samples were filtered by vacuum filtration using nylon membrane filters (pore size 0.45 µm) with a previously determined dry weight. In order to determine the dry mass retained on each filter utilized, filters were dried in an oven at 105 °C for one day before cooling in a desiccator to room temperature and subsequent weighing.

In addition to the model wastewaters, real biologically pre-treated greywater was also subdued to sedimentation as described above. Therefore, the effluent of constructed wetland for treatment of separately collected greywater was sampled at the EXPO settlement Flintenbreite at the city of Luebeck/Germany.

4.2 Irradiation Experiments

Irradiation experiments were conducted with all suspensions prepared for gravimetric analysis (model wastewaters containing different NaCl and NaHA concentrations as well as real biologically treated greywater, all spiked with 1 g/l TiO₂ P25). Each suspension

(with a volume of 1 liter) was irradiated in a stirred vessel reactor with an inner diameter of 10.8 centimeters with a UV-A radiator leading to a UV-A intensity of about 32 W/m² at the liquid surface which was determined by a pyrometer. Duration of the experiments was 6 to 24 hours. Samples were taken with a 50 ml pipette, after one, two, four, six and twenty four hours of irradiation or at slightly different time intervals as indicated in the respective graphs. Duration of the experiments with greywater was 4 days. Samples of 50 ml from this experiment were taken after one, two and four hours of irradiation for the first day, and during the last three days two samples were taken once per day. Before each sampling, sufficient amount of distilled water was added to the reactor to compensate the evaporation. The amount to be added was determined by the weight loss in the reactor during the period between two consecutive samplings. Each sample taken was centrifuged for 20 minutes at about 7500 g. The supernatant of each sample was utilized for TOC analysis.

Irradiation experiments with the biologically pre-treated greywater were conducted in duplicate in stirred vessel reactors as described above. Two vessels were placed below one UV-A radiator (face tanner Phillips HD 172; emission maximum: 352 nm).

The velocity gradient in each photocatalytic oxidation reactor was determined as follows: By using the difference between wattmeter readings of the magnetic stirrer adjusted to 250 rpm during stirring the reactor in the empty and in the filled state, ΔP (power input of the magnetic stirrer) was determined by means of a wattmeter connected to the power supply while the magnetic stirrer was connected to the socket of the wattmeter. For wattmeter readings with empty reactors stirring bars were wetted by few droplets of deionized water in order to decrease friction. By using the measured power input, ΔP , the suspension volume in the reactor, V_L , the viscosity of the medium (which can be assumed as that of pure water at 30°C), η , and equation 18 the velocity gradient, G , can be calculated [7].

$$G = (\Delta P / V_L \cdot \eta)^{1/2} \quad (18)$$

It was tried to tune the adjustment of the stirrer rates of all utilized magnetic stirrers in a way to yield similar velocity gradients. However, due to very coarse wattmeter readings, this equalization was only done very approximately.

4.3 Chemical Analyses

Conductivity and pH meters (WTW) were utilized for the determination of pH and conductivity of all the prepared suspensions.

Nitrite and nitrate concentrations in biologically pretreated greywater were determined by means of a reflectometer using Reflectoquant test strips (Merck). Alkalinity of biologically treated greywater was measured by titration with 0.01n HCl using methylorange as indicator.

TOC of all samples was determined as “non-purgeable TOC” (npTOC) by acidifying them with concentrated H_3PO_4 to pH ~ 1 -2, purging of formed CO_2 with CO_2 -free air and subsequent TOC analysis by incinerating the sample at 850 °C in the presence of CeO_2 catalyst in a TOC analyzer “multi N/C 3000” (Analytik Jena AG).

For evaluating an eventual influence of NaCl on TOC analysis, npTOC of aqueous 50 mg/l NaHA solution in denionized water was analyzed which had been spiked with NaCl in different concentrations (0, 5, 10, 50, 100, 200, 500, 1000 mg/l). Also “Total Inorganic Carbon” (TIC) concentration in biologically treated greywater was determined with this method. Na^+ , K^+ , Mg^{2+} , Ca^{2+} concentrations of biologically pre-treated greywater were analyzed by inductively coupled plasma optical emission spectrometry (Perkin-Elmer Optima 200 DV) and Cl^- , NO_3^- and PO_4^{3-} by ion chromatography (Dionex). Ortho-phosphate was additionally determined by photometer using a cuvette test (Hach Lange).

5. Results and Discussion

5.1 Factors Limiting the Accuracy of the Results

5.1.1 Gravimetric Analysis

The solutions prepared to mimic biologically pre-treated greywater lack a buffering system due to utilization of distilled water as the aqueous medium. Hence, the pH of the suspensions especially those containing no humic acid sodium salt (which by itself causes some pH buffering capacity) was not stable through the measurements due to the interaction with CO₂ from the air. This might have affected TiO₂ flocculation

The accuracy of gravimetric analyses is of course affected by precision of weight determination: 1st the balances can be read with a precision of 0.1 mg. However, this digit is not stable. It would be more realistic to assume a balance readability of 1 mg. As the filter weights are determined for a sample volume of 50 ml, for the entire suspension volume of 1 liter, the variation due to this limitation would be 20 mg. Related to the total mass of suspended particles of 1000 mg, a contribution of 2 % to the coefficient of variation can be assumed. In flocculated suspensions, where the suspended particle mass is lower, coefficients of variation higher than 2 % due to these discussed limitations can be expected. 2nd the filters usually contain less particles after membrane filtration than have been transferred with the suspension sample, because some particles may have stuck to the glass wall of the filtration device and were lost for quantification.

5.1.2 Irradiation Experiments

1. Lack of Precision of Adjusted Mechanical Energy Input

As stated in Section 4.2, a wattmeter was utilized (to measure power input) in order to standardize the velocity gradients of the stirred vessel reactors in which photocatalytic degradation experiments were made. This standardization is important with respect to two aspects. First of all, through increase in mechanical agitation diffusional length of

reactants from bulk solution to catalyst surface is decreased and secondly the gas/liquid mass transfer of oxygen is increased which is essential for the attainment of oxygen saturation in the suspension and the dissolved oxygen concentration affects the rate of photocatalysis (Section 2.2.1). Mechanical energy introduction has been shown to be of large influence on photocatalytic oxidation efficiency [7]. Thus, coarseness of the wattmeter that was utilized for the experiments might have led to varying mechanical energy inputs into different stirring vessel reactors with the consequence of eventual hiding or falsification of influences of photocatalyst flocculation.

2. TOC Analyses

The results obtained from TOC analyses especially for the samples with NaHA concentrations of 10 and 20 mg/l exhibit standard deviations that are substantial. In other words, the TOC analyzer utilized was not sufficiently sensitive to analyze the samples with low TOC ranges accurately.

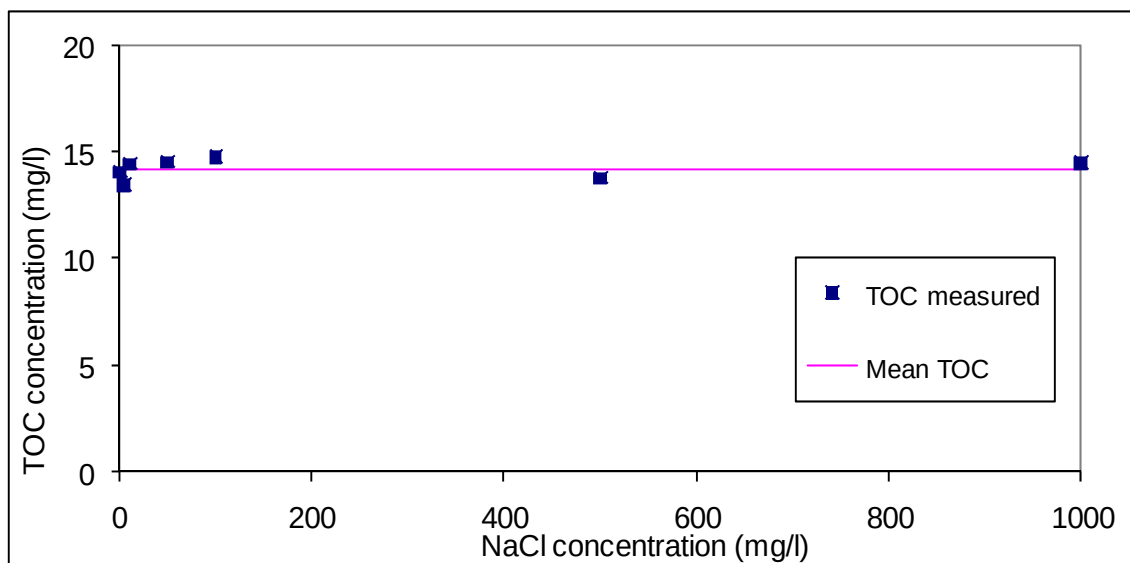


Figure 7. TOC analyses of aqueous solutions containing 50 mg/l NaHA in the presence of different NaCl concentrations

It was demonstrated that NaCl within the investigated range had no influence on the results of TOC analyses. The standard deviation for the TOC data presented in Figure 7 is ± 0.41 mg/l. Thus the coefficient of variation is 2.9 %. This standard deviation is especially essential for the low TOC concentrations (some below 1 mg/l) gathered for the samples with 10 and 20 mg/l NaHA which were thus determined with a high uncertainty.

5.2 Experiments with Model Wastewaters

For the experiments conducted in this section NaHA was utilized in order to mimic TOC content of biologically pre-treated greywater, as humic materials are formed as by-products during biodegradation of organics. Humic substances may explain the yellowish color of the effluent of the constructed wetlands treating separately collected greywater which also had been investigated in this study. On the other hand, using exclusively humic acid as a model wastewater constituent is quite far from reality, as additionally fulvic acid and non-acidic humic substances may be contained in biologically treated wastewaters. Other relevant microbial by-products are polysaccharides which have also been shown to be constituents of biologically treated greywater beside humic substances and low-molecular weight organic acids [7].

5.2.1 Photocatalyst Flocculation

From the gravimetric analyses (pipette method) of aqueous solutions modeling pre-treated greywater containing varying salt and humic acid concentrations, the following results were obtained. Tabled data of these graphs as well as conductivities measured for each suspension can be found in appendix I.

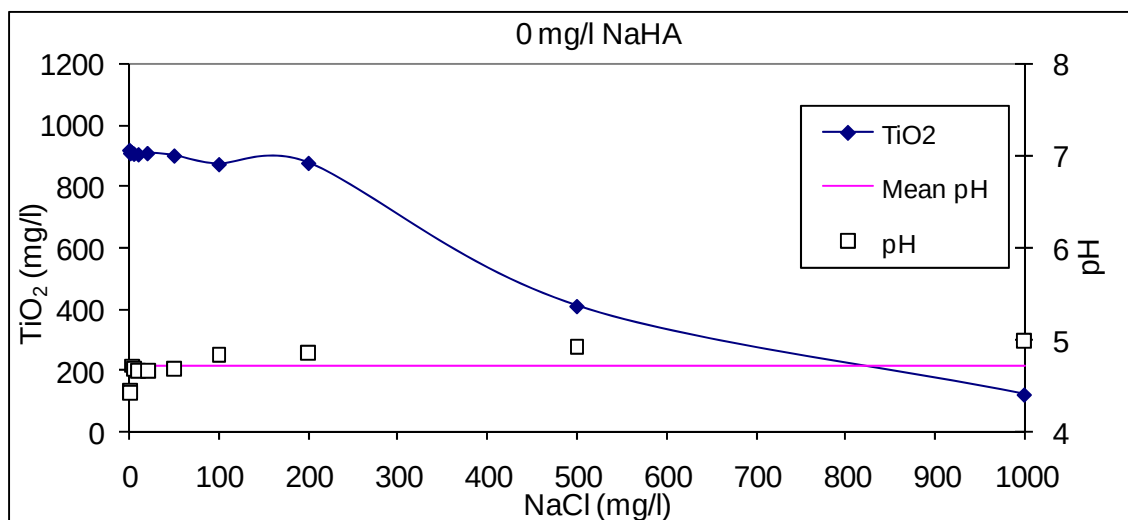


Figure 8. Effect of NaCl concentration on supernatant concentration of TiO₂ 10 cm below suspension surface after 1 hour sedimentation at a NaHA concentration of 0 mg/l as well as pH determined in suspensions

The effect of double layer compression is evident by decreasing TiO₂ concentration in the sedimentation supernatants with increasing salt concentration. This is leading to increased TiO₂ sizes (flocculation) showing increased sedimentation velocities at higher NaCl concentrations due to double layer compression when NaHA concentrations were 0, 20 and 50 mg/l (Figure 8, Figure 10, Figure 11). At the beginning part of the curve for 20 mg/l NaHA (Figure 10) there is an abrupt decrease in TiO₂ concentration. This might be due to experimental errors conducted during the experiments as discussed in chapter 5.1.1. However, the deviation in TiO₂ concentration in the supernatant for 5 mg/l NaCl is much higher (about 40 %) then predicted from discussion of errors. The determined pH in all tested suspensions in the absence of NaHA was well below the PZC of 6.3 reported in literature for TiO₂ [34]. This explains low extent of flocculation at low NaCl concentrations.

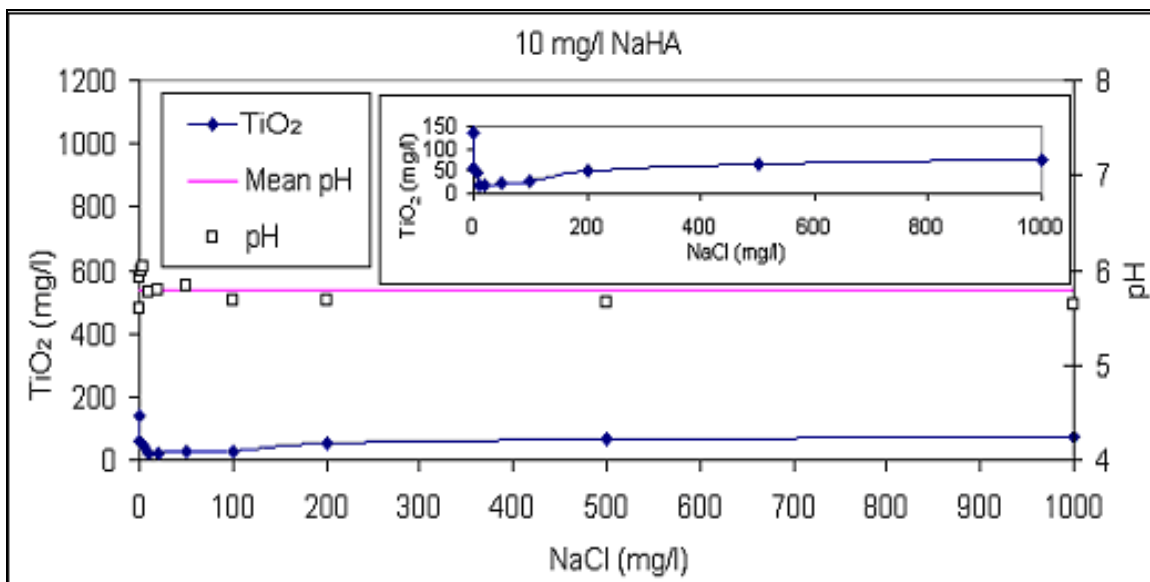


Figure 9. Effect of NaCl concentration on supernatant concentration of TiO_2 10 cm below suspension surface after 1 hour sedimentation at a NaHA concentration of 10 mg/l as well as pH determined in suspensions

For an NaHA concentration of 10 mg/l (Figure 9), extremely low TiO_2 concentrations were observed in the supernatants after 1 hour sedimentation due to strong flocculation. It can be seen that the curve does not fit to the patterns presented by the graphs for other NaHA concentrations (Figure 8, Figure 10, Figure 11) on behind this phenomenon can be the masses of TiO_2 retained on membranes after gravimetric analyses which were only between 1 and 7 mg per 50 ml of TiO_2 supernatant sample. The very low mass of TiO_2 left on membranes after filtration limits the accuracy of the results as discussed in chapter 5.1.1.

The reason behind the very low TiO_2 concentration values gathered for the suspension with 10 mg/l NaHA is considered to be the attainment of a pH around PZC caused by this NaHA concentration. At around PZC the surface of TiO_2 particles are nearly neutral and due to decrease of surface charge they tend to flocculate and settle faster [37]. Normally, PZC for TiO_2 in deionized water is reported to be 6.3 as already stated. However PZC also depends on wastewater matrix (pH and electrolyte concentration) and for the combinations of NaHA and salt concentrations prepared for these experiments, it is

considered to be around 5.8 [38]. Thus the NaHA concentration affects the photocatalyst flocculation behavior much more due to its pH influence than NaCl concentrations of up to 1000 mg/l due to their effects on electrical double layer compression.

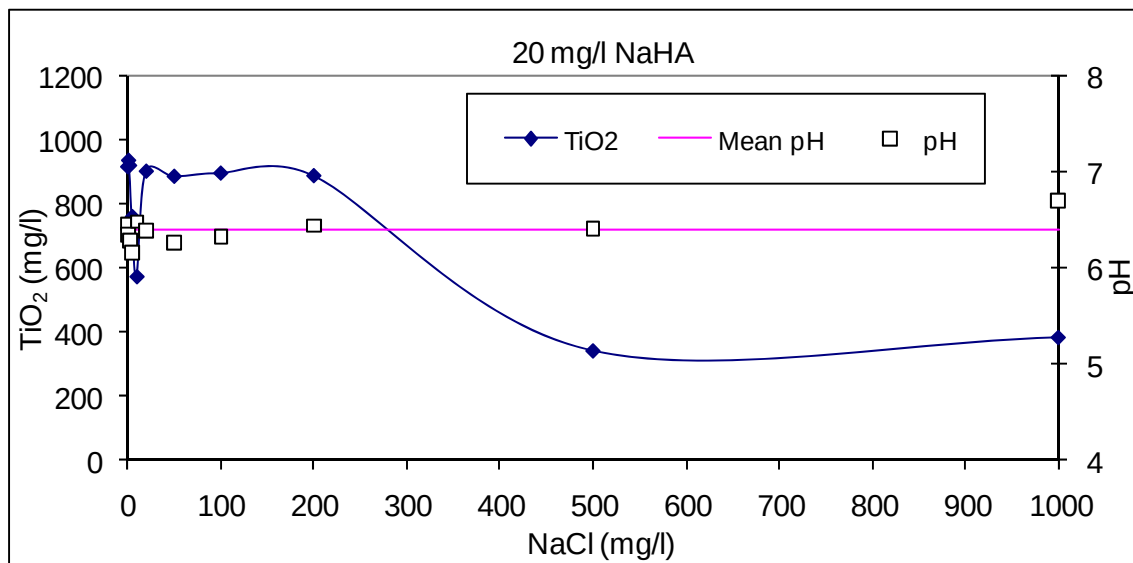


Figure 10. Effect of NaCl concentration on supernatant concentration of TiO₂ 10 cm below suspension surface after 1 hour sedimentation at a NaHA concentration of 20 mg/l as well as pH determined in suspensions

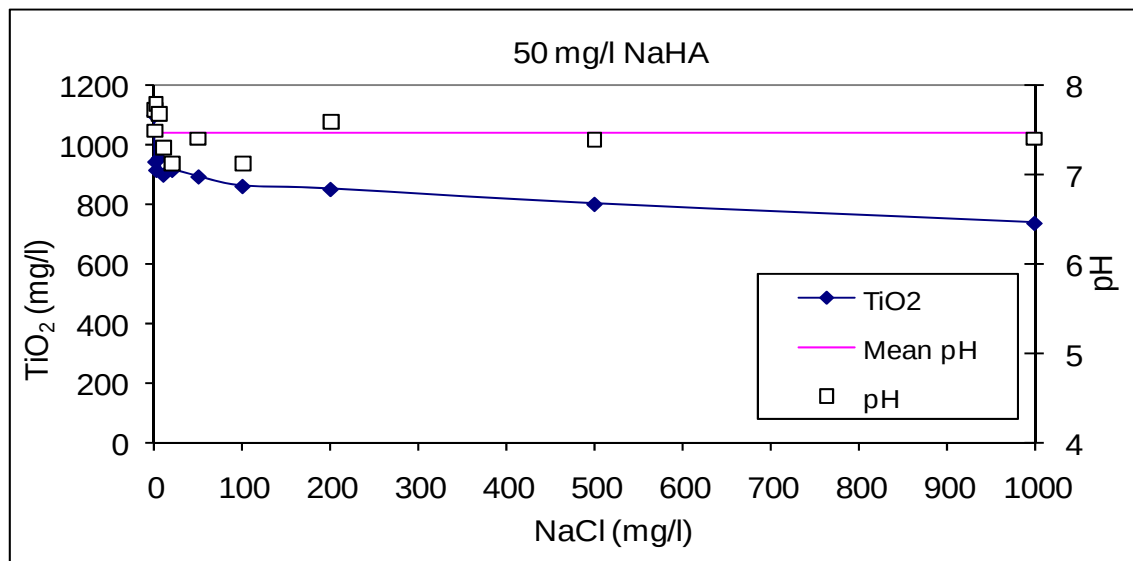


Figure 11. Effect of NaCl concentration on supernatant concentration of TiO₂ 10 cm below suspension surface after 1 hour sedimentation at a NaHA concentration of 50 mg/l as well as pH determined in suspensions

When Figures 10 and 11 are compared it can be clearly seen that TiO_2 flocculation due to salt addition is more pronounced with the lower NaHA concentration (20 mg/l) than with the higher one. Again it can be observed that pH is higher with the higher NaHA concentration. The increased pH leads to a larger negative surface charge which antagonizes electrical double layer compression.

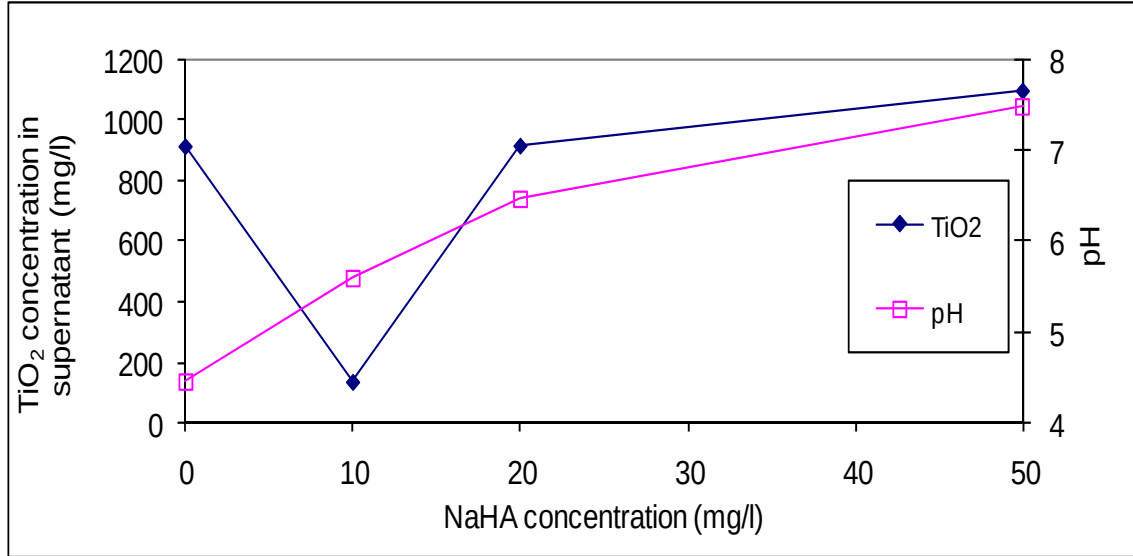


Figure 12. Effect of NaHA concentration on supernatant concentration of TiO_2 , 10 cm below liquid surface after 1 hour sedimentation in the absence of NaCl

Figure 12 summarizes the flocculation experiments without NaCl addition. It shows that NaHA addition increases pH. As discussed above, the TiO_2 concentration in supernatant is very low when pH is close to PZC. It can be concluded that TiO_2 particles in suspensions prepared with 50 and 20 mg/l NaHA are predominantly negatively charged due to the pH values above PZC which is considered to be around 5.8. The surface charge of TiO_2 particles in suspensions that do not contain NaHA and exhibiting pH values around 5.0 (which is well below the assumed PZC) can be looked at as predominantly positive. Moreover, it can also be stated that TiO_2 surfaces that are in suspensions with an NaHA concentration of 50 mg/l are more negatively charged when compared to those that are in suspensions of 20 mg/l NaHA due to increasing pH with increasing NaHA addition.

Table 4. Mean TiO_2 concentrations in supernatant obtained from gravimetric analysis 10 cm below suspension after 1 hour sedimentation and mean pH values of suspensions prepared with different HA concentrations and containing either NaCl or NaHCO_3 (data for suspensions with NaHCO_3 adopted from [39]).

NaHA concentration	Mean TiO_2 concentration in suspensions with NaCl (mg/l)	Mean TiO_2 concentration in suspensions with NaHCO_3 (mg/l)	Mean pH for suspensions with NaCl	Mean pH for suspensions with NaHCO_3
0	783 $\pm$ 265	321 $\pm$ 379	4.7	7.0
10	52 $\pm$ 33	659 $\pm$ 250	5.8	7.3
20	765 $\pm$ 225	847 $\pm$ 106	6.4	8
50	898 $\pm$ 92	788 $\pm$ 142	7.5	8

The experimental procedure for the model wastewaters was also utilized by Sohmen [39]. The only difference between Sohmen's and this thesis's data collection was the salt. Instead of NaCl investigated in this thesis, Sohmen utilized NaHCO_3 . In table 4, results of TiO_2 flocculation investigations of both studies using the pipette method are compared. As the same patterns of salt concentrations (0, 1, 2, 5, 10, 20, 50, 100, 200, 500, and 1000 mg/l) at four different NaHA concentrations (0, 10, 20, 50 mg/l) were used, for each set of experiments with one NaHA concentration, average TiO_2 concentrations in the supernatants after 1 hour sedimentation were calculated. When results obtained with two different salts are considered it can be concluded that for NaHA concentration of 0 mg/l, the average TiO_2 concentration in supernatants containing NaCl is higher than in those with NaHCO_3 . The reason might be the pH value in the NaCl suspensions which are well below PZC. This results in a higher (positive) surface charge when compared to suspensions with NaHCO_3 which exhibited pH values close to the PZC for these suspensions. Additionally, variance of pH was larger in suspensions containing different concentrations of NaHCO_3 in comparison to the NaCl suspension. When the suspensions with 10 mg/l NaHA are taken into account it can be deduced that

due to a pH close to PZC in suspensions with NaCl addition (which does not act as a pH buffer), the TiO_2 concentration in supernatants was much lower when compared with TiO_2 concentrations for suspensions containing NaHCO_3 . For an NaHA concentration of 20 mg/l, the higher TiO_2 concentration in supernatant of suspensions prepared with NaHCO_3 might be due to higher pH compared with suspensions prepared with NaCl. Finally for an NaHA concentration of 50 mg/l the NaHCO_3 suspensions with higher pH values exhibited a lower TiO_2 concentration in supernatant when compared to those with NaCl. This might be explained by a slightly larger compression of electric double layer by NaHCO_3 at similar mass concentrations, although the NaCl containing suspensions represent higher salt concentrations on a molar basis.

5.2.2 Influence of NaCl Concentration on Adsorption of Humic Acid Sodium Salt to Photocatalyst

For the analysis of adsorption characteristics for each sample the difference between the theoretical TOC concentration that should be found (Table 5) (if TiO_2 was not added) and the actual TOC values found in the samples prepared for the irradiation experiments prior to irradiation (after removing the TiO_2 particles with centrifugation) is assumed to be adsorbed on TiO_2 . In Figure 13, Figure 14 and Figure 15, the amount of NaHA adsorption to TiO_2 particles versus the NaCl concentration is displayed for each initial NaHA concentration.

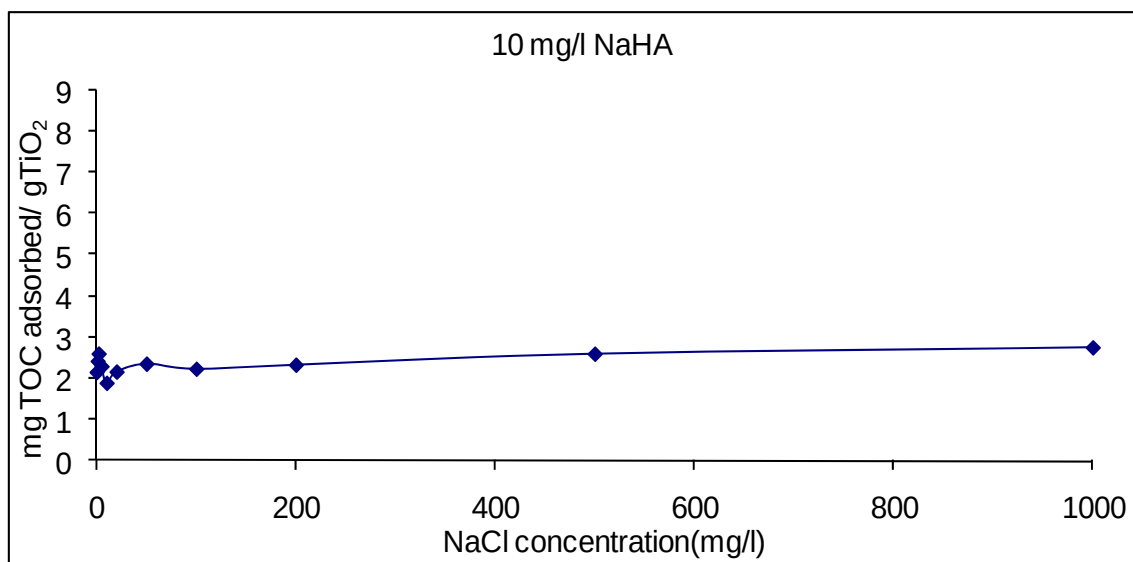


Figure 13. Mass of TOC adsorbed per gram TiO₂ at different NaCl concentrations for an initial NaHA concentration of 10 mg/l.

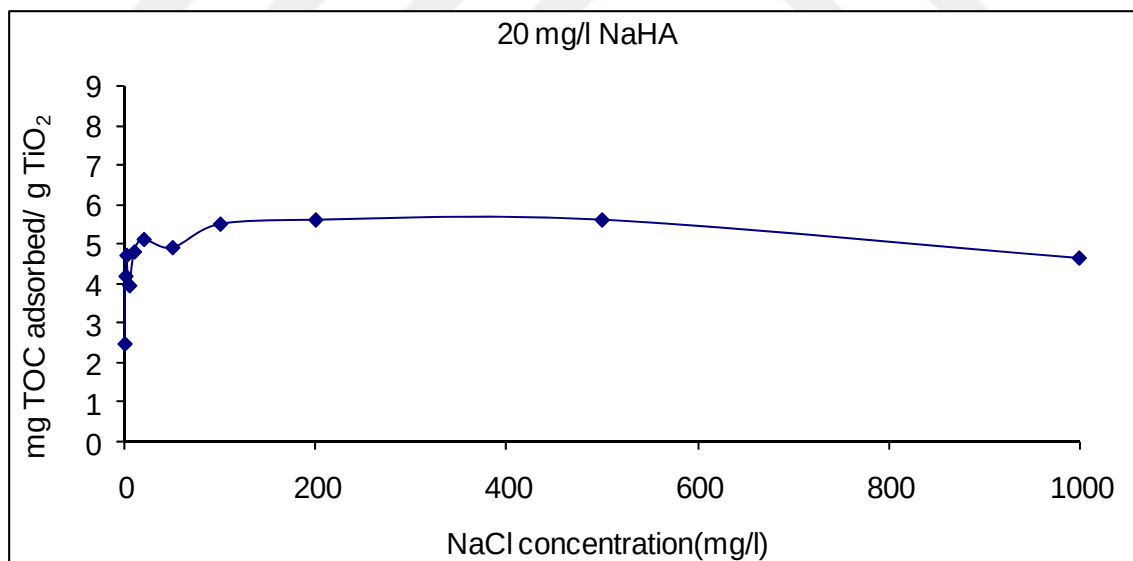


Figure 14. Mass of TOC adsorbed per gram TiO₂ at different NaCl concentrations for an initial NaHA concentration of 20 mg/l

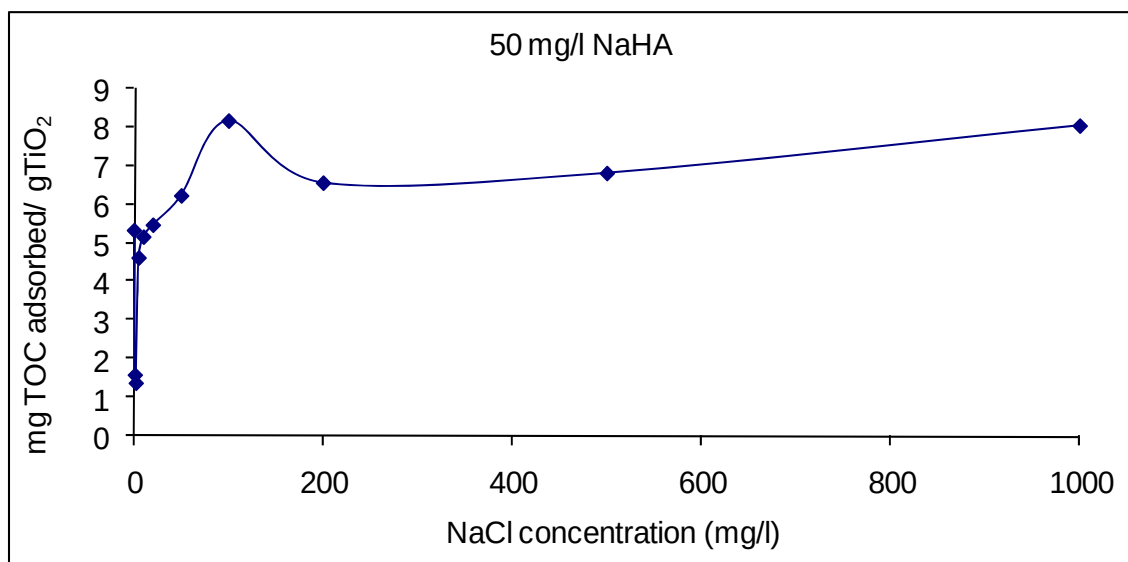


Figure 15. Mass of TOC adsorbed per gram TiO₂ at different NaCl concentrations for an initial NaHA concentration of 50 mg/l.

When the graphs regarding the adsorption characteristics of varying initial NaHA concentrations at different NaCl concentrations are examined it can be concluded that there is an increasing pattern of NaHA adsorption with increasing concentrations of NaCl for NaHA concentrations of 20 and 50 mg/l. By some researchers it was reported that with the addition of salts the adsorption of HA is decreasing in a low salt concentration range as it would be expected with respect to competition for finding binding sites. However, when the concentration range of NaCl is at a level of 10^{-2} molar (585 mg NaCl/l) the opposite effect (increase of NaHA adsorption due to decrease of repulsion between different segments of HA with increasing ionic strength) was observed [29]. This phenomenon might be the reason behind the differences in NaHA solid phase concentrations for low and high salt concentration ranges. However, the increase of adsorption with increasing NaCl concentrations was also observed for lower NaCl concentrations (≥ 20 mg/l) than reported in [29]. This might be caused by different tertiary structures of humic acids investigated in this thesis and in [29].

The TOC concentrations obtained for different NaHA concentrations in the absence of TiO_2 are given in Table 5 and Figure 16. They can be used for calibration in order to express TOC results after addition of TiO_2 as NaHA concentration.

Table 5. TOC equivalents of NaHA additions in NaHA solutions in the absence of TiO_2

NaHA (mg/l)	TOC (mg/l)
10	2.8
20	5.6
50	14.0

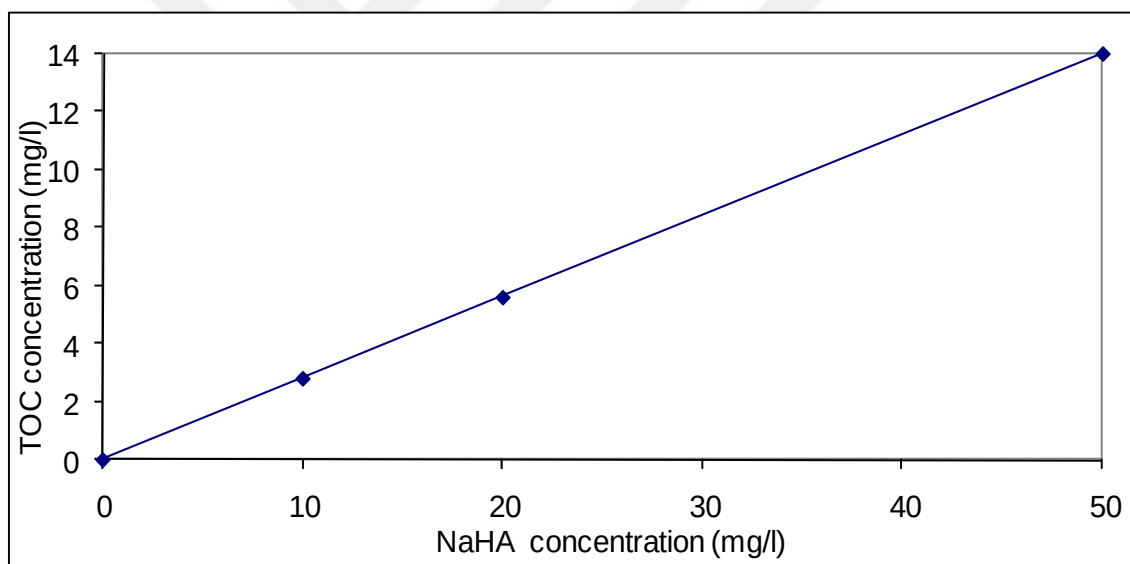


Figure 16. TOC versus NaHA concentration in NaHA solutions in the absence of TiO_2

Mean adsorption values and their standard deviations for the suspensions can be found in Table 6 and the percentages of TOC adsorbed to TiO_2 that was introduced into the suspensions are presented in Figure 17.

Table 6. Mean NaHA adsorption and standard deviation for different NaHA addition to suspensions, means were calculated for suspensions with all investigated NaCl concentrations.

NaHA concentration before TiO ₂ addition (mg/l)	Mean adsorption of NaHA to TiO ₂ (mg/g)	Standard deviation of NaHA solid phase Concentration (mg/g)
10	2.33	0.25
20	4.67	0.92
50	5.40	2.24

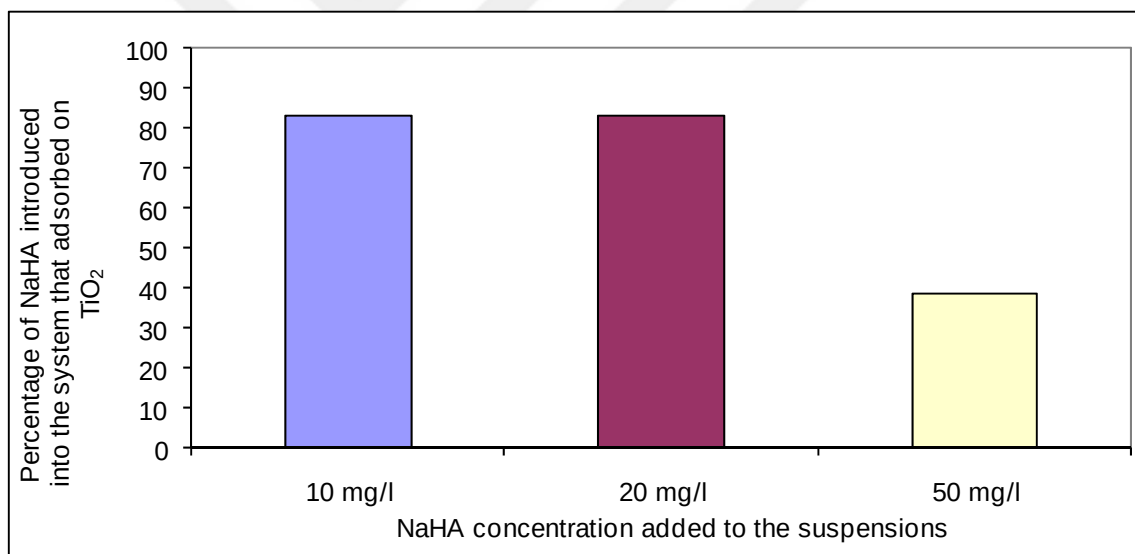


Figure 17. The percentage of NaHA adsorbed on TiO₂ (100 % was the amount of NaHA introduced to the suspensions) with varying NaHA concentrations.

From the mean adsorption values it can be concluded that the amount of TOC adsorbed per gram of TiO₂ increases with increasing initial NaHA concentration (Table 6). When the percentage of NaHA adsorbed is considered, the values obtained for 10 and 20 mg/l of initial NaHA concentrations are comparable. However, the percentage value referring to an initial NaHA concentration of 50 mg/l is lower due to the larger amount of NaHA molecules offered to a constant TiO₂ surface (if flocculation effects are not considered).

As already mentioned, the suspensions prepared with 50 mg/l NaHA had the highest negative charge on the TiO_2 particle surface. This might be an additional reason why negatively charged HA anions were adsorbed less on TiO_2 (on a percentage base) compared to the other two suspension sets with 20 and 10 mg/l NaHA addition. The ability of negatively charged HA to adsorb to negatively charged TiO_2 in suspensions at high pH values is claimed to be due to the coexistence of both positively and negatively charged sites of TiO_2 over a wide pH range. It is also asserted that in alkaline media the adsorption of HA can occur by specific (non-coulombic) interactions between HA functional groups at their surface sites. Presence of simple inorganic ions including Na^+ and Cl^- enhances this process [29].

Finally it is worth to note that the obstruction of photocatalytic oxidation due to high initial HA adsorption is reported in literature. The reason is claimed to be due to lower mass transfer between TiO_2 surface and bulk solution due to agglomeration of HA on TiO_2 surface that blocks the desorption and adsorption of molecules. In other words, with high initial adsorption of HA, desorption of photodegraded organics from TiO_2 surface and adsorption of organics to be photodegraded are inhibited by the HA agglomerated on TiO_2 surface. Thus, higher initial adsorption of HA may actually hamper its photocatalytic efficiency [29].

5.2.3 Irradiation Experiments

For the calculation of rate constants for photodegradation in different suspensions the following concentration profiles gathered were used. Unfortunately, total irradiation periods applied to the different suspensions were different (6 hours and 24 to 26 hours) in the different photocatalytic oxidation experiments. While the experiments of the 10 mg/l NaHA series were limited to 6 hours, some experiments of the 20 and 50 mg/l NaHA series extended to more than 24 hours.

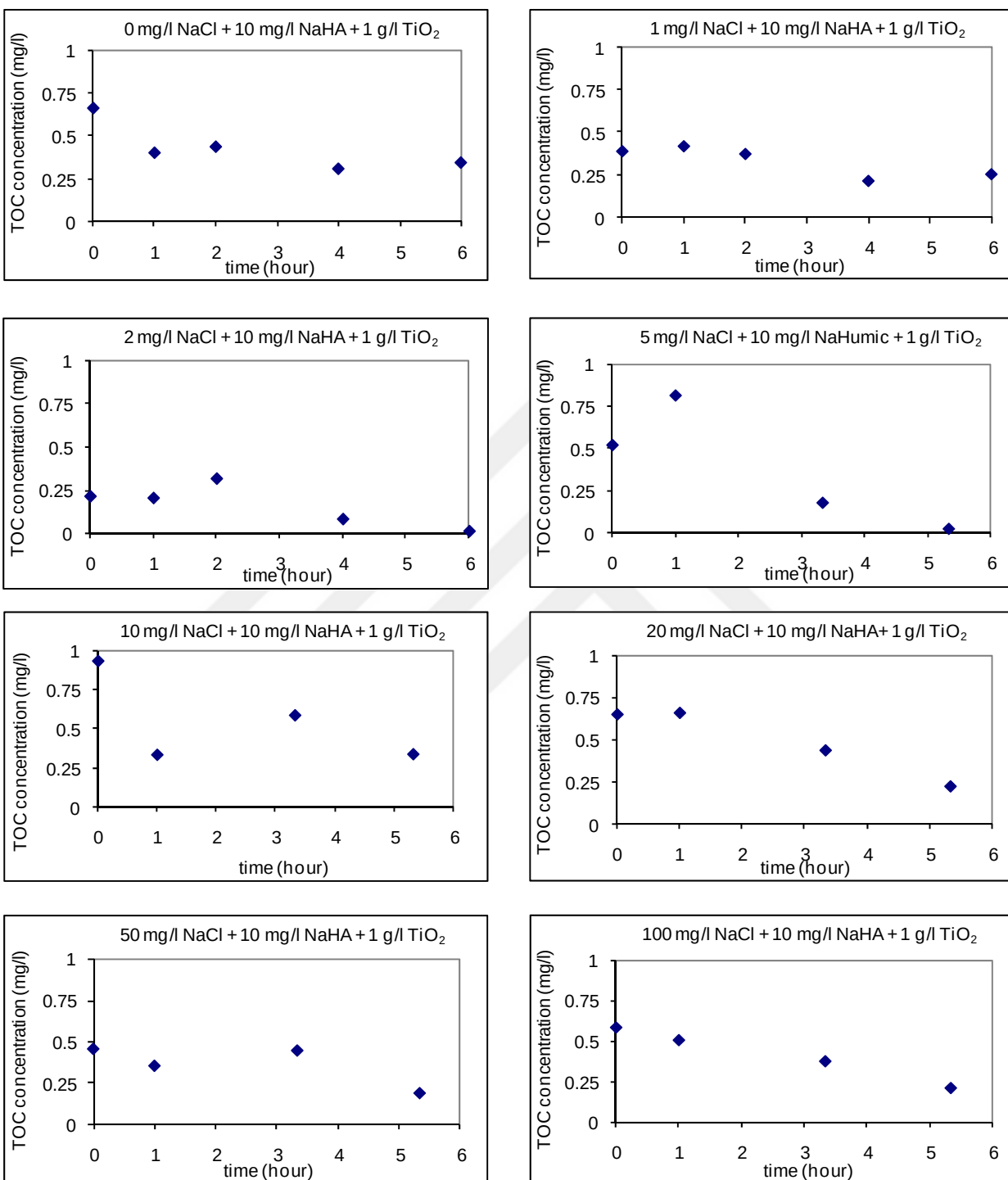


Figure 18. TOC concentrations in supernatants of 1 g/l TiO_2 suspensions as a function of irradiation time containing 10 mg/l NaHA and different NaCl concentrations

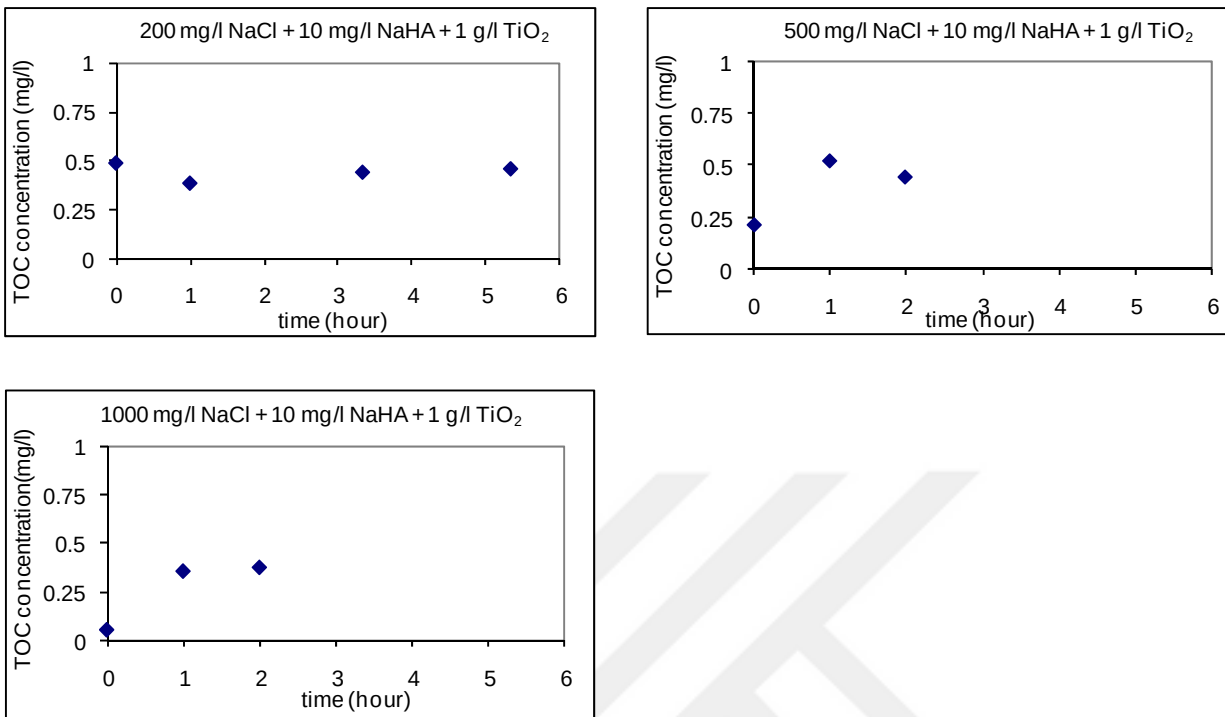


Figure 18. Continued

TOC data displayed in Figure 18 are assumed to be below the limit of quantification of the analytical TOC procedure (about 0.5 mg TOC/l). This explains high data variation in many graphs and does not allow for proper estimation of influence of NaCl concentrations on rate constants of photocatalytic oxidation at this low initial NaHA concentration.

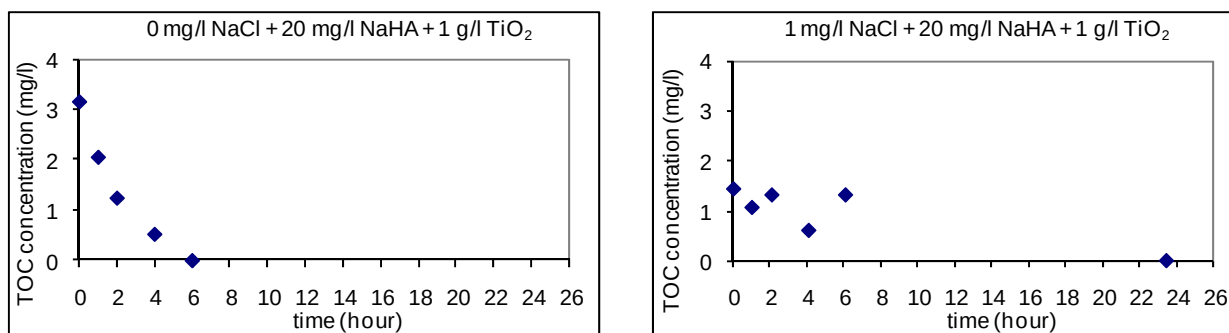


Figure 19. TOC concentrations in supernatants of 1 g/l TiO_2 suspensions containing 20 mg/l NaHA and different NaCl concentrations as a function of irradiation time

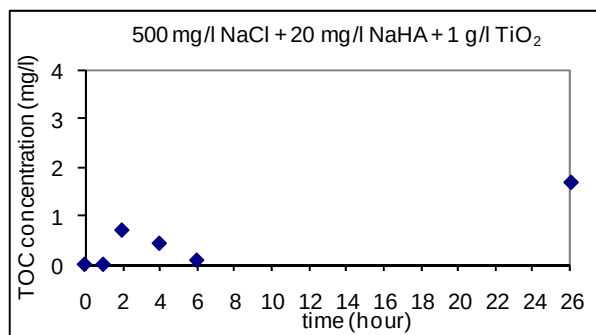
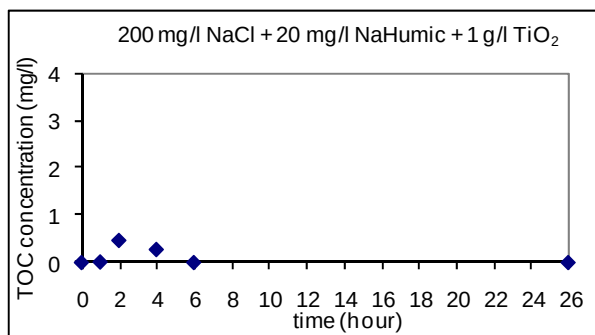
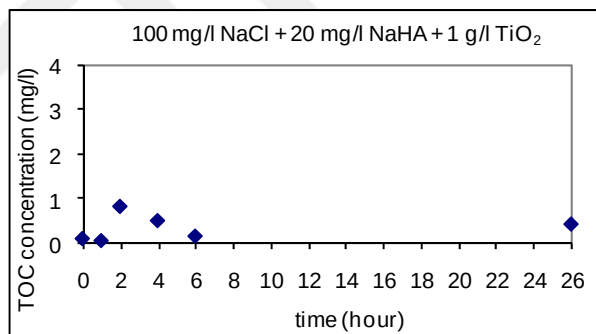
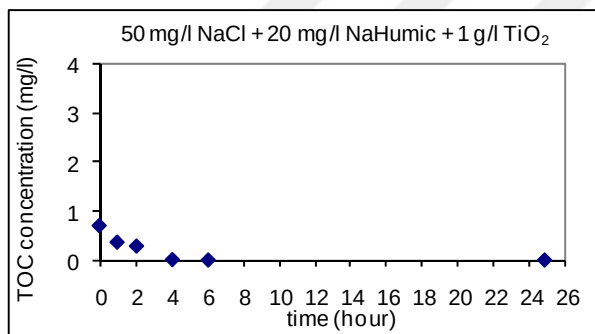
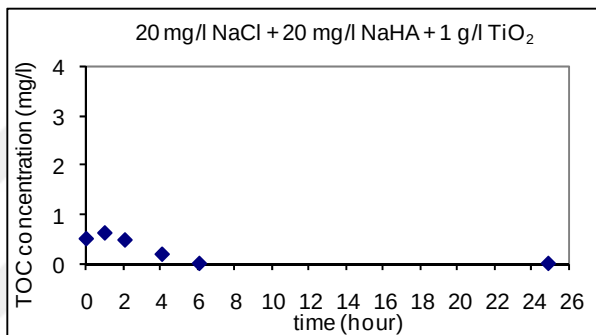
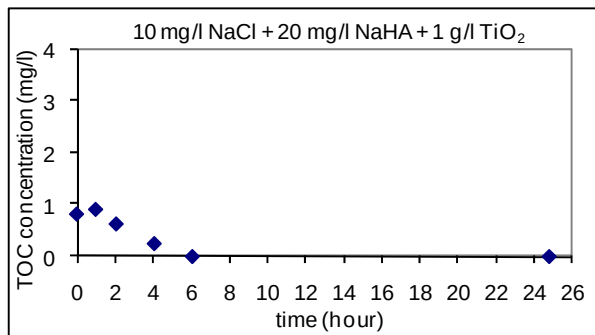
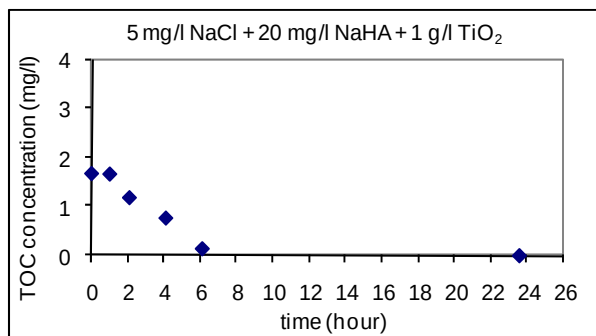
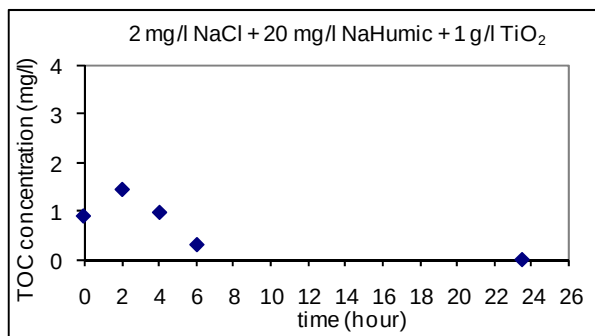


Figure 19. Continued

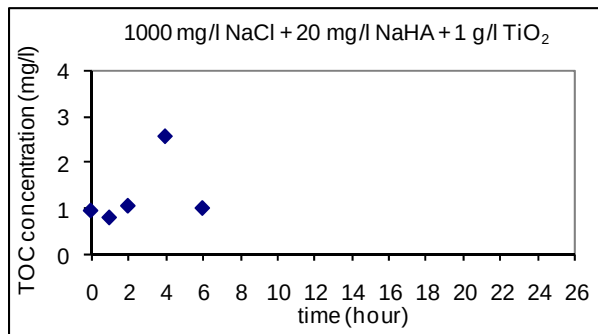


Figure 19. Continued

Also the addition of NaHA in a concentration of 20 mg/l (Figure 19) resulted in very low TOC concentrations around 1 mg/l in the liquid phase. This is obviously due to NaHA adsorption to the photocatalyst as discussed in chapter 5.2.2. In some experiments (2, 100, 200, 500 and especially 1000 mg NaCl/l) even a TOC increase in the liquid phase during irradiation was observed. It cannot be deduced with certainty from the results whether this is due to data variation because of analytical errors or to desorption of more polar NaHA oxidation products which are less adsorbable to TiO_2 and which have been generated during irradiation.

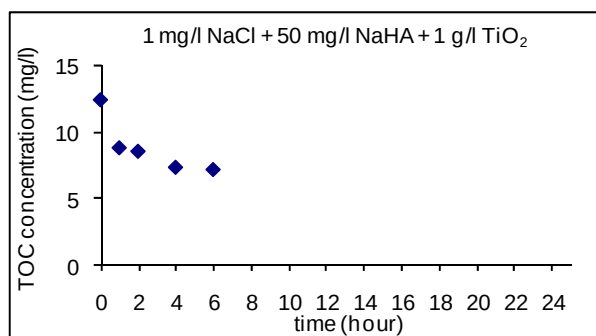
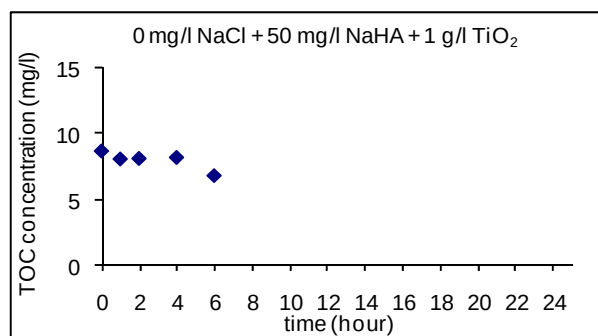


Figure 20. TOC concentrations in supernatants of 1 g/l TiO_2 suspensions containing 50 mg/l NaHA and different NaCl concentrations as a function of irradiation time

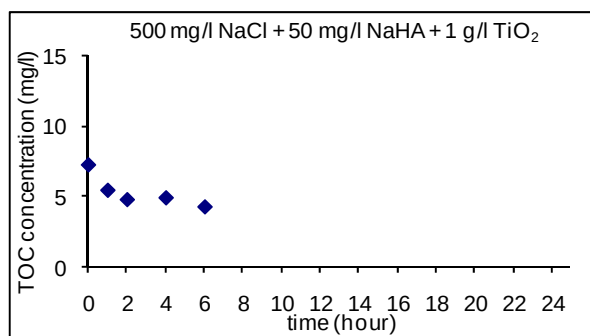
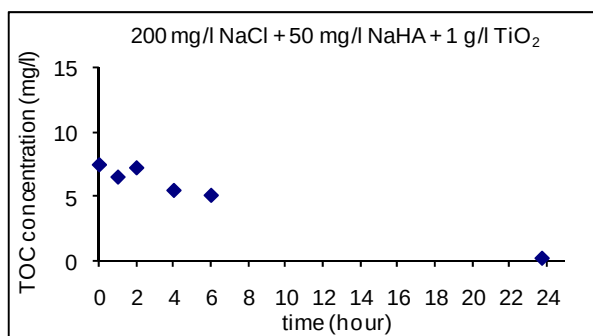
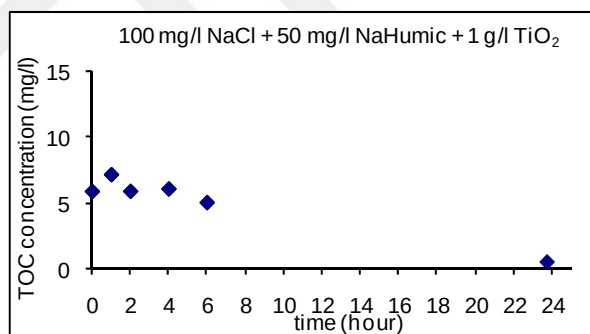
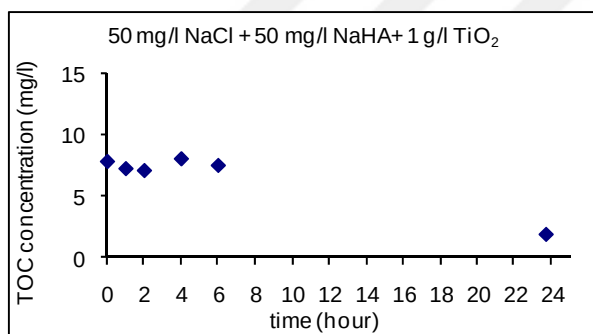
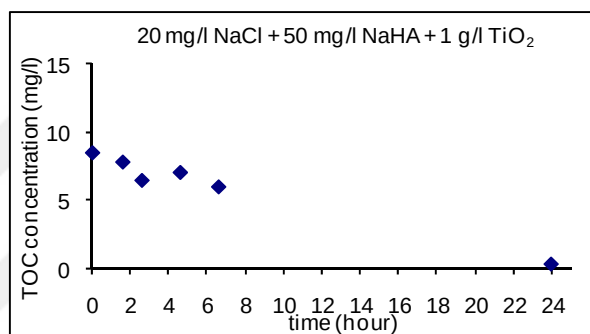
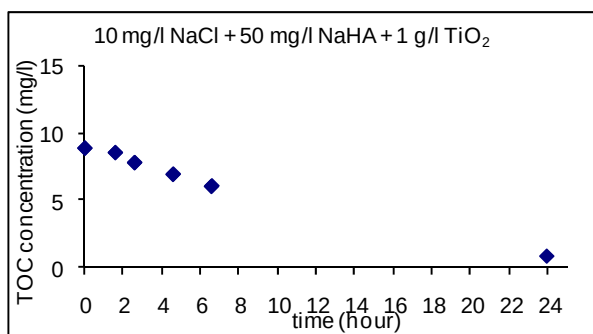
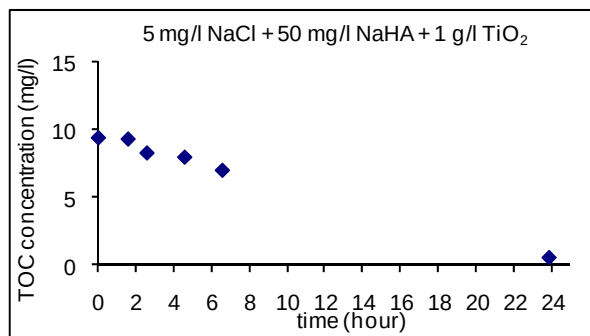
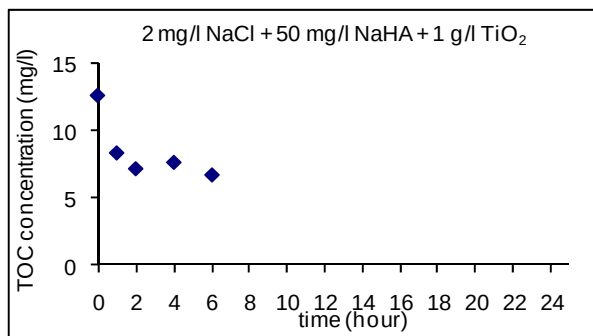


Figure 20. Continued

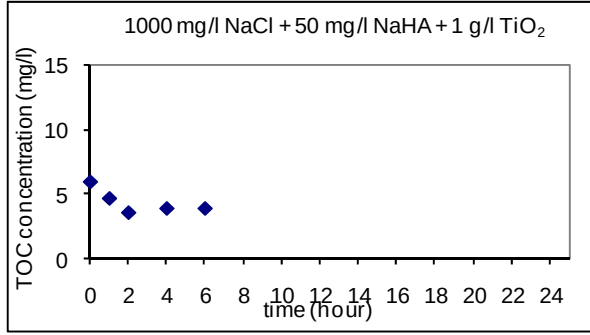


Figure 20. Continued

The data obtained during experiments with added NaHA concentrations of 50 mg/l (Figure 20) are much more certain because of more reliable TOC analyses in the range above 5 mg TOC/l. Decreasing dissolved TOC concentration at irradiation time 0 with increasing NaCl concentration can be explained by increasing NaHA adsorption to TiO₂ as discussed in chapter 5.2.2.

In other studies, it has been shown that photocatalytic oxidation of organic wastewater constituents, including humic acid, obeys pseudo-first order reaction kinetics in low concentration range (Eq. 19) [40,41,42]. This could also be found in some experiments within this thesis.

$$\frac{dc_{\text{TOC}}}{dt} = -k_{\text{TOC}} \cdot c_{\text{TOC}} \quad (19)$$

k_{TOC} = Product of actual rate constant and adsorption constant

c_{TOC} = Concentration of organics

Thus for the determination of photocatalytic rate constants, data regarding the concentration profile of humic acid versus irradiation time was collected (Figure 21) and another graph was derived from these data with the natural logarithm of concentration values calculated versus time (Figure 22) and the slope of this new graph, which is equal

to the rate constant, was determined. The figures regarding the rate constant calculations for the other suspensions can be found in the appendix II.

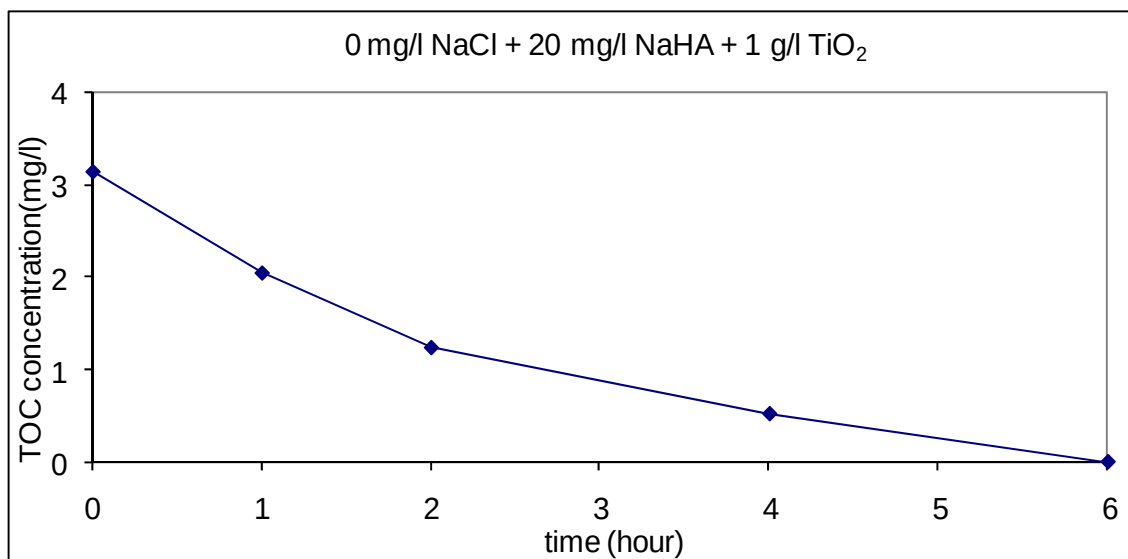


Figure 21. TOC versus time graph for the suspension without NaCl, containing 20 mg/l NaHA and 1 g/l TiO₂

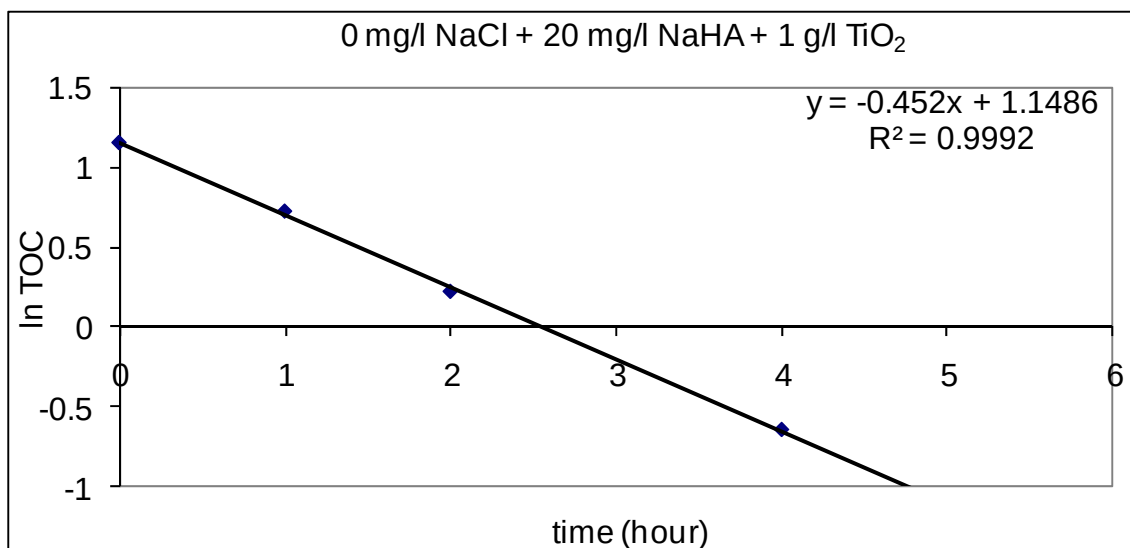


Figure 22. Natural logarithm of TOC versus time graph for the suspension without NaCl, containing 20 mg/l NaHA and 1 g/l TiO₂

Unfortunately, the recorded kinetics were not following apparent 1st order kinetics in many cases. Also an initial lag phase was visible in some experiments with a NaHA concentration of 50 mg/l (Figure 23). In the initial phase (first day of irradiation) moderate decrease of TOC was observed. During the following night no samples could be taken due to laboratory safety regulations, and the 24 hour sample showed a very low TOC. This indicates that the lag phase may have lasted for a time which could not be determined and proper kinetics could not be recorded. Therefore, the determined rate constants cannot be looked as very precise.

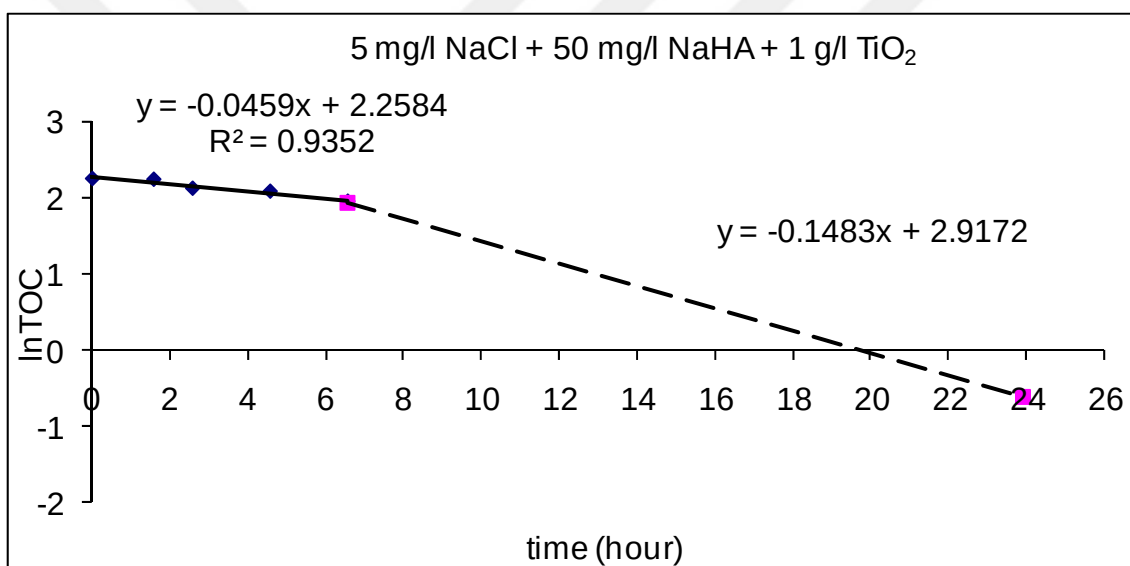


Figure 23. Natural logarithm of TOC versus time graph for the suspension with 5 mg/l NaCl, 50 mg/l NaHA and 1 g/l TiO₂ concentration for the initial (First 6 hours) and final period (between 6 and 24 hours).

Also, in previous studies, global evolution of the degradation of HA showed two distinct domains [27, 43, 44]. In the first domain (at the initial phase of photocatalysis) TOC concentrations decreased slowly, while in the second domain pseudo-first order mineralization kinetics were observed. The reason behind the slow decrease of TOC in domain one is probably due to photodepolymerization of adsorbed HA on TiO₂ surface without substantial mineralization [44]. This phenomenon seems to be the case for most of the samples with an initial 50 mg/l NaHA concentration. As it can be deduced from

Figure 23 for the experiments with 50 mg/l NaHA and 5 mg/l NaCl, the rate constant is found as 0.0459 h^{-1} when the first six hours of irradiation are considered. However, when only the period between 6 and 24 hours is considered for the rate constant calculations the result is 0.1483 h^{-1} . This behavior of rate constant is in accordance with the characteristics of two distinct domains present in degradation of NaHA stated by other authors. Therefore, distinct rate constants have been calculated for all experiments for the first 6 hours and –if possible – for the phase between 6 and 24 hours irradiation as well as for the entire irradiation period. Additionally, percent TOC removal after about 24 hours irradiation (100 % = initial dissolved TOC concentration after TiO_2 addition) were calculated when data available. All these data are presented in Table 7 to Table 9 for the different added NaHA concentrations. This behavior with two kinetic phases was found for all the experiments with an initial NaHA concentration of 50 mg/l which were performed with durations of around 24 hours.

Table 7. Kinetic data of suspensions with an initial NaHA concentration of 10 mg/l obtained after irradiation experiments; - indicates a positive slope and the rate constants are looked at as “0” in these cases; n.d. could not be determined

NaHA concentration (mg/l)	NaCl concentration (mg/l)	k_{TOC} initial (hour^{-1})	k_{TOC} total (hour^{-1})	k_{TOC} 6-24 hours (hour^{-1})	% removal in 24 hours
10	0	0.0962	n.d.	n.d.	n.d.
10	1	0.1033	n.d.	n.d.	n.d.
10	2	0.4847	n.d.	n.d.	n.d.
10	5	0.6085	n.d.	n.d.	n.d.
10	10	0.1109	n.d.	n.d.	n.d.
10	20	0.2052	n.d.	n.d.	n.d.
10	50	0.1288	n.d.	n.d.	n.d.
10	100	0.1893	n.d.	n.d.	n.d.
10	200	-	n.d.	n.d.	n.d.
10	500	-	n.d.	n.d.	n.d.
10	1000	-	n.d.	n.d.	n.d.

Table 8. Kinetic data of suspensions with an initial NaHA concentration of 20 mg/l obtained after irradiation experiments; - indicates a positive slope and the rate constants are looked at as “0” in these cases; n.d. could not be determined

NaHA concentration (mg/l)	NaCl concentration (mg/l)	k _{TOC} initial (hour ⁻¹)	k _{TOC} total (hour ⁻¹)	k _{TOC} 6-24 hours (hour ⁻¹)	% removal in 24 hours
20	0	0.452	n.d.	n.d.	n.d.
20	1	0.0416	0.0416	-	100
20	2	0.2732	0.2732	-	100
20	5	0.3934	0.3934	-	100
20	10	0.3147	0.3147	-	100
20	20	0.2677	0.2677	-	100
20	50	1.0357	1.0357	-	100
20	100	-	-	-	-
20	200	-	-	-	100
20	500	-	-	-	-
20	1000	-	n.d.	n.d.	n.d.

Table 9. Kinetic data of suspensions with an initial NaHA concentration of 50 mg/l obtained after irradiation experiments; - indicates a positive slope and the rate constants are looked at as “0” in these cases; n.d. could not be determined

NaHA concentration (mg/l)	NaCl concentration (mg/l)	k _{TOC} initial (hour ⁻¹)	k _{TOC} total (hour ⁻¹)	k _{TOC} 6-24 hours (hour ⁻¹)	% removal in 24 hours
50	0	0.0332	n.d.	n.d.	n.d.
50	1	0.0785	n.d.	n.d.	n.d.
50	2	0.0791	n.d.	n.d.	n.d.
50	5	0.0459	0.1259	0.1483	94.3
50	10	0.0605	0.1057	0.1181	91.2
50	20	0.0478	0.1525	0.1816	97.0
50	50	-	0.0619	0.0784	76.2
50	100	0.0342	0.1101	0.1273	91.0
50	200	0.0649	0.1648	0.1918	97.7
50	500	0.0709	n.d.	n.d.	n.d.
50	1000	0.0610	n.d.	n.d.	n.d.

The derived kinetic data given in Tables 7 to 9 were used to visualize eventual effects of NaCl concentration or TiO₂ flocculation on photocatalytic oxidation kinetics discussed in the next chapter.

5.2.4 Relation between Agglomeration of TiO_2 particles and Photocatalytic Degradation Rates

For clarifying a possible relation between the agglomeration of TiO_2 particles and the photocatalytic rate of humic acid degradation, graphs of rate constants over the concentrations of TiO_2 in supernatants of the respective suspensions which were determined by gravimetric analysis (pipette method) were drawn (Figure 24 a, Figure 25 a and Figure 26 a) and for the inquiry of the relation between the NaCl concentration and the photocatalytic rate of humic acid degradation, graphs were drawn with the amount of NaCl present in different suspensions and with rate constants that belong to those combinations (Figure 24 b, Figure 25 b and Figure 26 b).

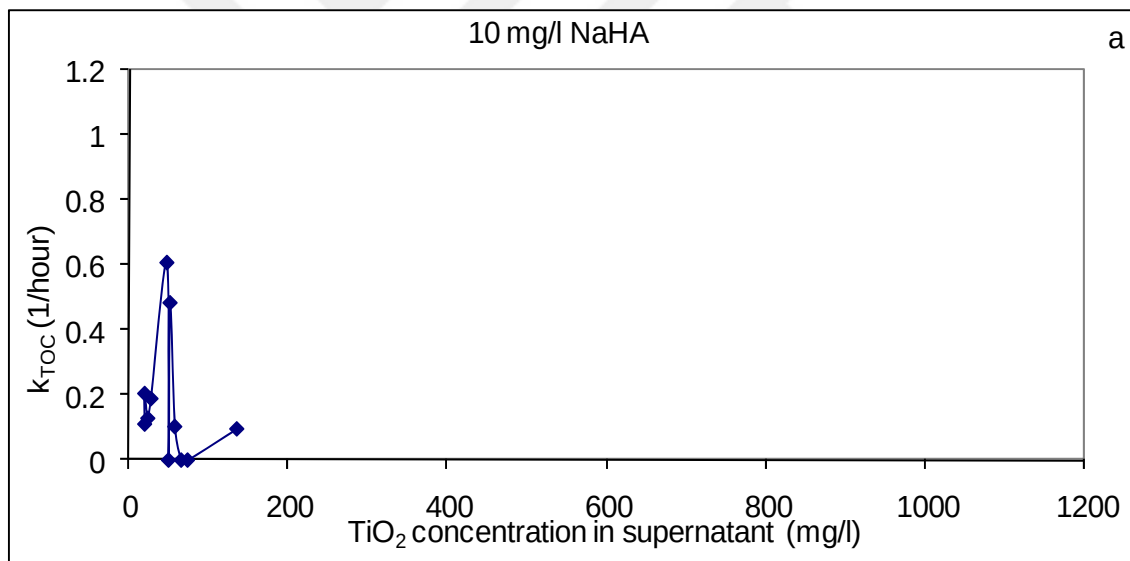


Figure 24. Rate of photocatalytic degradation (for the total (6 hours) irradiation period) for NaHA concentration of 10 mg/l versus (a) TiO_2 concentration in supernatants after 1 hour of sedimentation (b) and NaCl concentration in the liquid phase

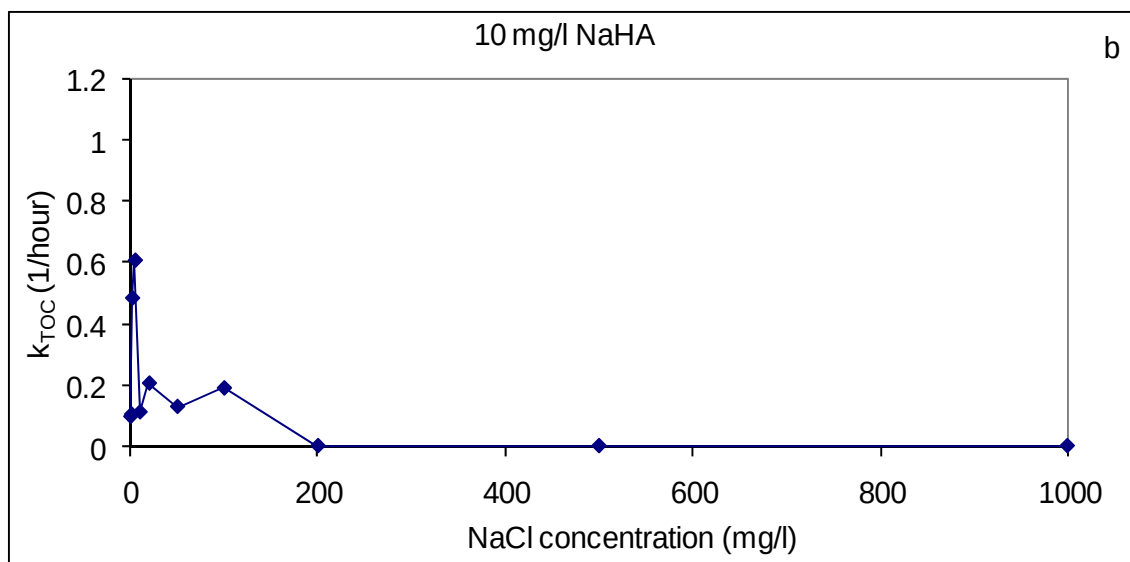


Figure 24. Continued

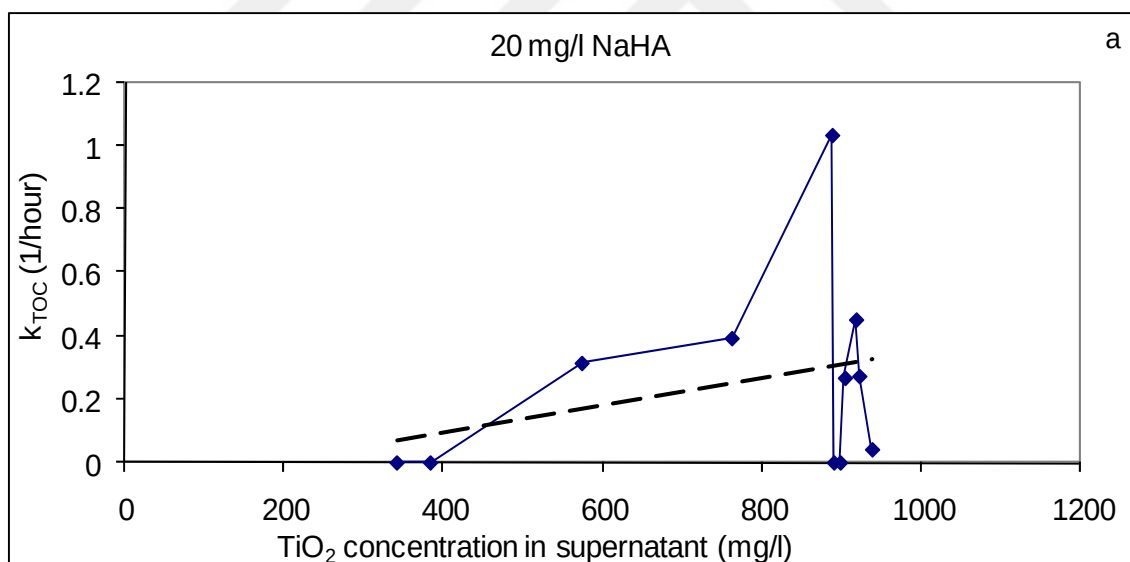


Figure 25. Rate of photocatalytic degradation (for the initial (6 hours) irradiation period) for NaHA concentration of 20 mg/l versus (a) TiO₂ concentration in supernatants after 1 hour of sedimentation (b) and NaCl concentration in the liquid phase

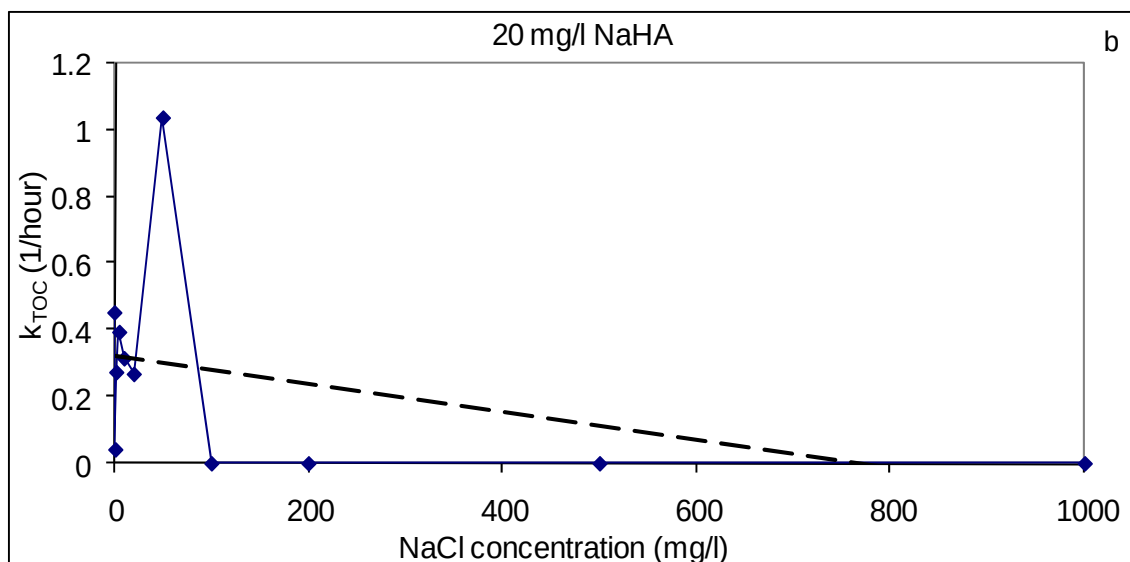


Figure 25. Continued

As discussed in chapter 5.2.3, rate constants determined for the experiments with 10 and 20 mg/l NaHA were not very reliable due to low TOC concentrations in the liquid phase. This is reflected by the highly varying rate constants shown in Figure 24 and Figure 25. With some uncertainty the following trend can be seen for 20 g/l NaHA: The lower the flocculation of the photocatalyst, the higher the rate constants (Figure 25 a) which is referring to the (very uncertain) dependence of rate constants on NaCl concentration (Figure25 b).

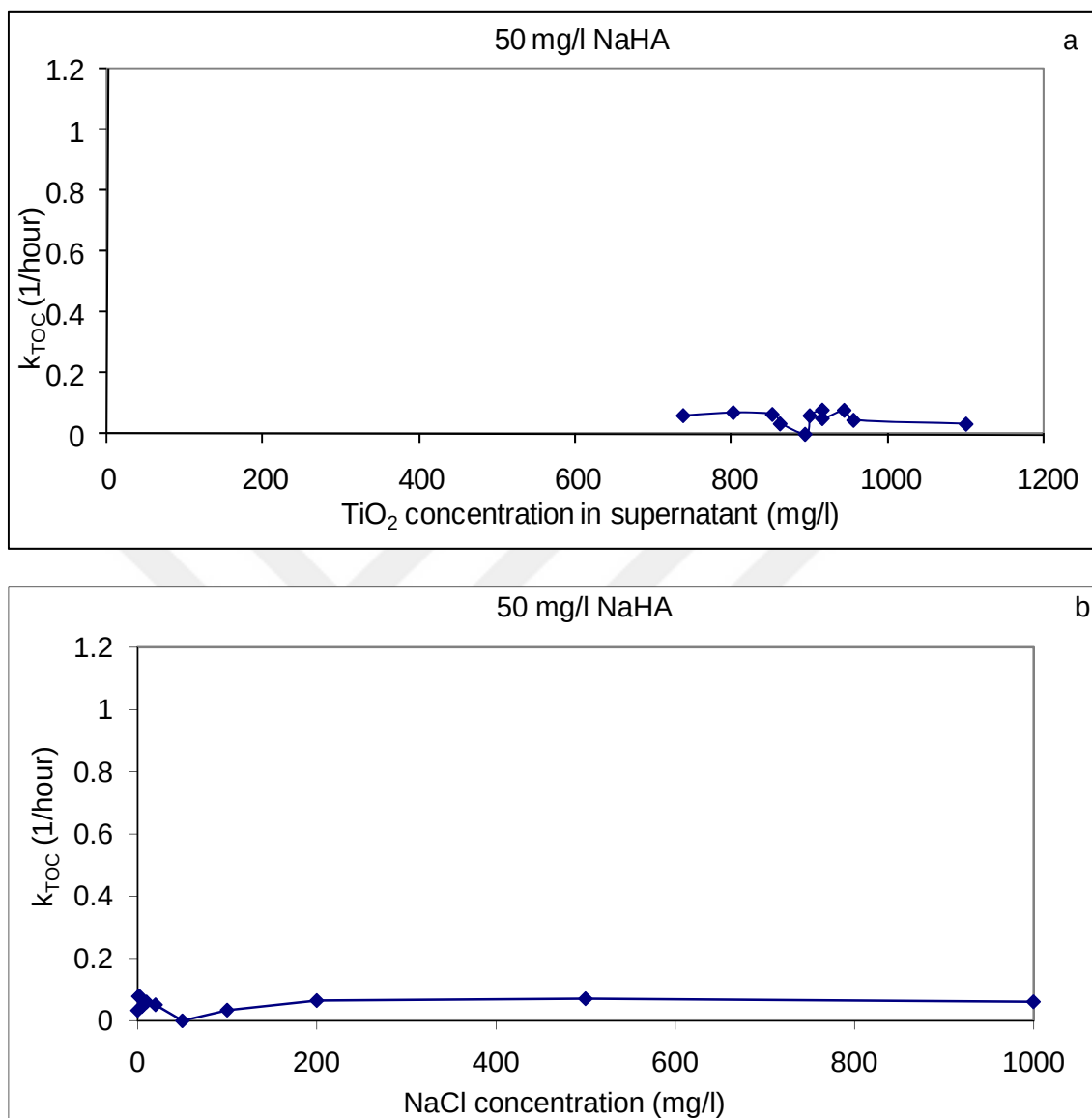


Figure 26. Rate of photocatalytic degradation (for the initial (6 hours) irradiation period) for NaHA concentration of 50 mg/l versus (a) TiO_2 concentration in supernatants after 1 hour of sedimentation (b) and NaCl concentration in the liquid phase

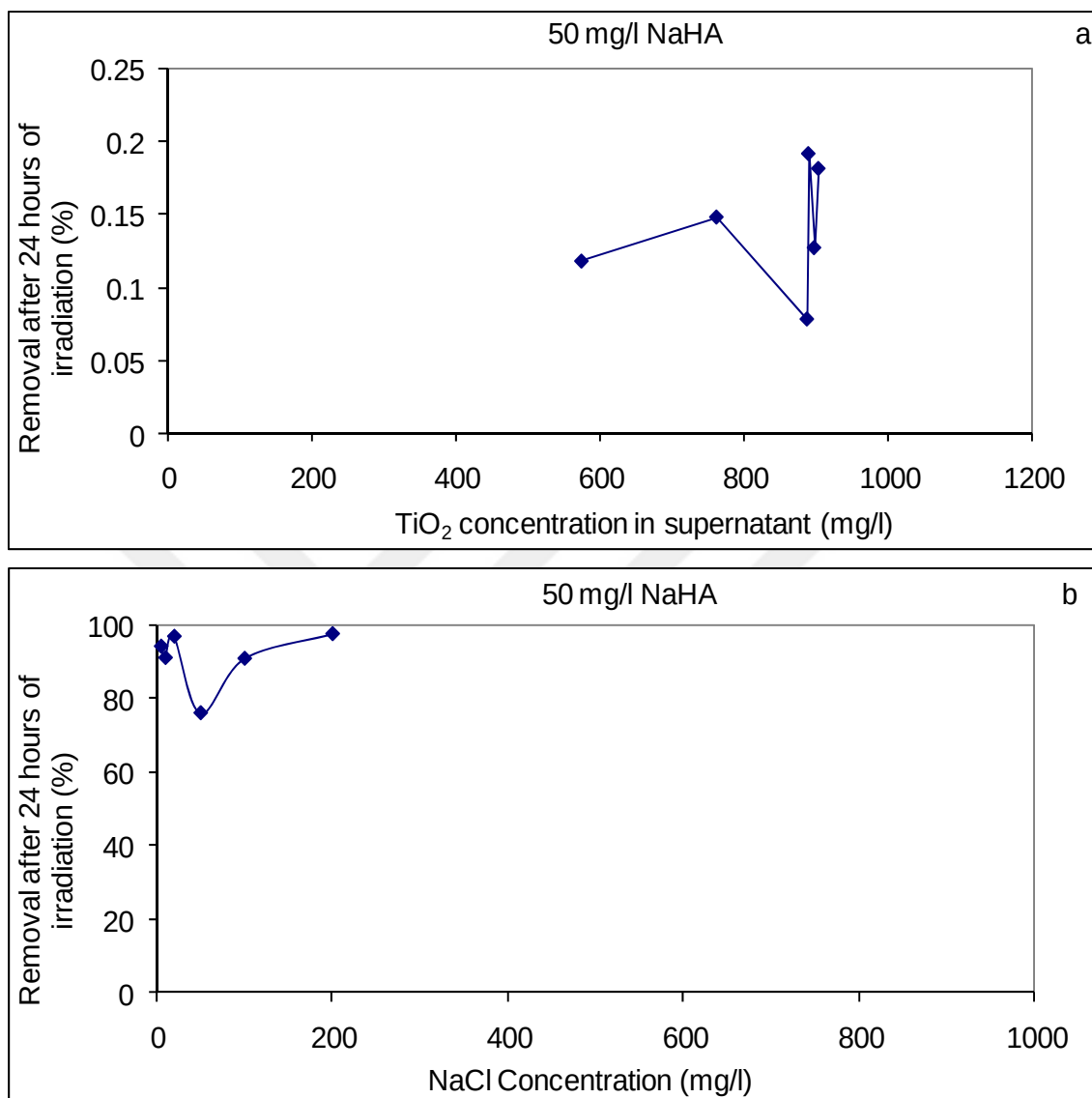


Figure 27. Percent removal of TOC (in 24 hours) introduced for NaHA concentration of 50 mg/l versus (a) TiO_2 concentration in supernatants after 1 hour of sedimentation (b) and NaCl concentration in the liquid phase

The rate constants for the 50 mg/l NaHA experiments seem to be more reliable because of higher TOC concentrations in liquid phase. But a clear dependence of rate constants was neither detectable on TiO_2 flocculation (Figure 26 a) nor on NaCl concentration in liquid phase (Figure 26 b). A similar conclusion can be drawn when TOC removals after about 24 hours are plotted vs. flocculation data (Figure 27 a) or NaCl concentration in liquid phase (Figure 27 b).

As opposed to the other two, the plot for an initial NaHA concentration of 50 mg/l has a different, fairly uniform pattern through different concentrations of NaCl (Figure 26 and Figure 27).

It can be concluded from the Figure 24 to Figure 27, that no distinct correlation between TiO_2 flocculation and rate of constants could be found. As already stated, at an NaHA concentration of 10 mg/l the resulting pH was very close to PZC resulting in agglomeration of TiO_2 particles (Figure 9) when compared to suspensions with other NaHA concentrations (Figure 8, Figure 10, Figure 11). However, when the rate constants of the 10 mg/l NaHA suspensions are compared to the suspensions with other NaHA concentrations which exhibited less TiO_2 flocculation according to gravimetric analysis, it can be roughly concluded that they are comparable to those of the suspensions with 20 mg/l NaHA, but higher than those with 50 mg/l NaHA. This situation might be an indication that there is no direct correlation between the particle size of TiO_2 aggregates and its rate constants. However, it should also be noted that the pH of the suspensions with different NaHA concentrations are different and low pH is beneficial for the photocatalytical oxidation of humic acids [43]. Thus, the reason behind high degradation rates for 10 mg/l NaHA (if substantial at all with respect to problems with analysis of low TOC concentrations) might be that the pH values for suspensions with 10 mg/l NaHA were the lowest among all NaHA concentrations tested in the irradiation experiments. This influence of pH might have compensated the negative effects of particle size. Therefore, comparison of degradation rates obtained from different suspensions with different pH might be misleading for evaluating the influence of particle size on degradation rate.

From the data collected regarding the effect of NaCl concentration on photocatalytic oxidation of NaHA, it can also be stated that there is no markedly specific pattern. For the suspensions with 10 and 20 mg/l NaHA containing NaCl above 200 mg/l the observed degradation rate was zero. This might be referred to the scavenging characteristics of Cl^- . Furthermore, the increasing agglomeration of TiO_2 particles with increasing salt content might contribute to decreasing photocatalytic oxidation rates.

Overall it can be said that there is a complex interrelationship between pH (affected by NaHA concentration) and NaCl concentration at one hand and particle flocculation as well as photocatalytic oxidation kinetics on the other hand. Understanding these relationships would require many more experiments than conducted in this thesis with a limited time frame.

5.3 Experiments with Real Biologically Pre-Treated Greywater

5.3.1 Characteristics of Biologically Pre-Treated Greywater

As already stated a sample of separately collected and biologically pre-treated (through constructed wetland) greywater was taken for analysis and for irradiation experiments. The analyses of this sample were made in duplicate. Results of these are given in Table 10.

Table 10. Constituents of biologically pre-treated greywater; - below detection limit

Constituent	Concentration in Sample A (mg/l)	Concentration in Sample B (mg/l)
Na⁺	123	122
K⁺	6.48	6.48
Mg²⁺	10.5	10.8
Ca²⁺	94.3	93.5
Cl⁻	79	79
NO₂⁻	-	-
NO₃⁻	18	18
PO₄³⁻ by IC	6	6
PO₄³⁻ by cuvette tests	7.4	7.3
TOC	5.50	5.27
Alkalinity (as CaCO₃)	380	390
Conductivity (μS/cm)	1042	1044

As shown in Table 10, biologically treated greywater contains considerable concentrations of salts which originate from different household chemicals. Nitrate can be looked at as the oxidation product of ammonia. The determined chloride concentration is equivalent to about 130 mg NaCl/l. Thus, real greywater was included in the NaCl range investigated with the model wastewaters. The determined alkalinity shows,

however, that the NaCl containing model wastewaters may be far away from the real sample with respect to alkalinity, as they did not contain any HCO_3^- or CO_3^{2-} .

5.3.2 Photocatalyst Flocculation in Greywater

From the gravimetric analysis of TiO_2 in biologically pre-treated greywater samples by the pipet method, a very intense flocculation was observed leading to a very low photocatalyst concentration in the supernatants after 1 hour sedimentation (Table 11).

Table 11. Results from gravimetric analysis of TiO_2 in biologically pre-treated greywater after 1 hour sedimentation 10 cm below suspension surface (see Table 9)

Concentration of TiO_2 in supernatant (mg/l)	pH
54	7.66

The mean TOC value of the greywater samples was 5.4 mg/l with a standard deviation of 0.16 mg/l (see Table 10). Assumed that all TOC in the greywater sample was presented by humic acid (which is not true), this TOC value is approximately comparable with the TOC value of the 20 mg/l NaHA aqueous solution (5.5 mg/l). Moreover, from the analysis of the samples (Table 10) it was found that the Cl^- concentration is (79 mg/l) was equivalent to a NaCl concentration of 130 mg/l. Thus, findings obtained from gravimetric analysis of real greywater can be compared with the model wastewater at a NaCl concentration of 130 mg/l and a NaHA concentration of 20 mg/l. The data derived from gravimetric sedimentation analysis were integrated in the graph of the respective model wastewater (Figure 28).

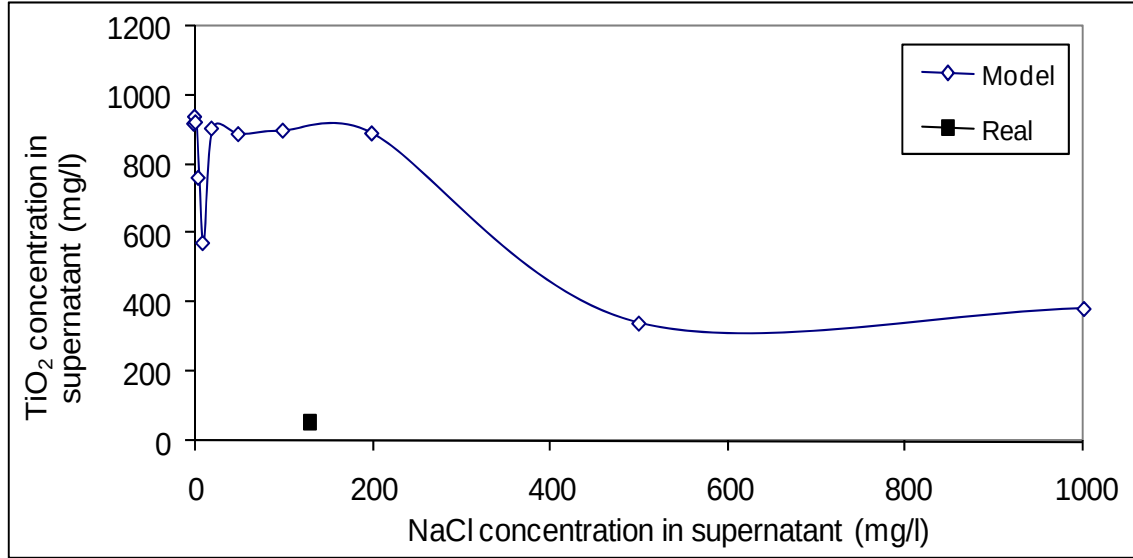


Figure 28. Comparison of gravimetric analysis of real and model (20 mg/l NaHA) biologically pretreated greywater

As it can be deduced from Figure 28, the TiO₂ concentration in the supernatant after 1 hour sedimentation obtained from gravimetric analysis of a TiO₂ suspensions prepared with real biologically pre-treated greywater is much lower than the models investigated. The reason behind this difference is considered to be the difference in the ionic strength. The ionic strength (I) of samples can be calculated by means of equation 20 [45].

$$I = \sum C_i \cdot z_i^2 \quad (20)$$

C_i = Concentration of ion i

z_i = Charge number of ion i

The results of the calculations (Table 12) will represent an ionic strength of the greywater which is lower than the true ionic strength as not all salts present in the greywater sample were analyzed. This calculated (underestimated) ionic strength is compared to the ionic strength of a model wastewater (containing 130 mg/l NaCl and 20 mg/l NaHA) including the sodium cation of NaHA, however, without consideration of the effect of humic acid

anion for the ionic strength in Table 12. Obviously, the ionic strength of the biologically treated greywater is one order of magnitude higher than the ionic strength of the model wastewaters referring to a similar NaCl and TOC concentration. However, the conductivity of the greywater was only about 3 times higher than the conductivity interpolated for a model wastewater with 130 mg/l NaCl (Table 12).

Table 12. Ionic strength and conductivity of real and model biologically pre-treated greywater.

Sample	Ionic Strength (mmol/l)	Conductivity (μS/cm)
Biologically pre-treated greywater	min. 9.62	1042
Model biologically pretreated greywater	1.11	277.5*

* Derived from interpolation of 100 and 200 mg/l NaCl.

As already stated in section 2.2.5 particle size of TiO_2 is dependent on ionic strength of the suspension. Thus, it is plausible that due to higher ionic strength of biologically pre-treated greywater compared to the model, agglomeration of particles is also higher which leads to lower TiO_2 supernatant concentration found in gravimetric analysis.

The conductivity of the suspension with 20 mg NaHA/l and the highest NaCl concentration was 1959 μ S/cm (Appendix I). However, the TiO_2 flocculation in this suspension was lower when compared to that of real biologically pre-treated greywater which has a conductivity of 1042 μ S/cm (Figure 28). The reason behind the higher TiO_2 supernatant concentration at a higher conductivity may be divalent (Ca^{2+} , Mg^{2+} ; compare Table 10) or perhaps trivalent cations present in real biologically pre-treated greywater as opposed to models prepared with monovalent cations. The conductivity data do not reflect this difference.

5.3.3 Irradiation Experiments

Irradiation experiments with real biologically treated greywater are displaced in duplicate and results can be found in Figure 29 and Figure 30.

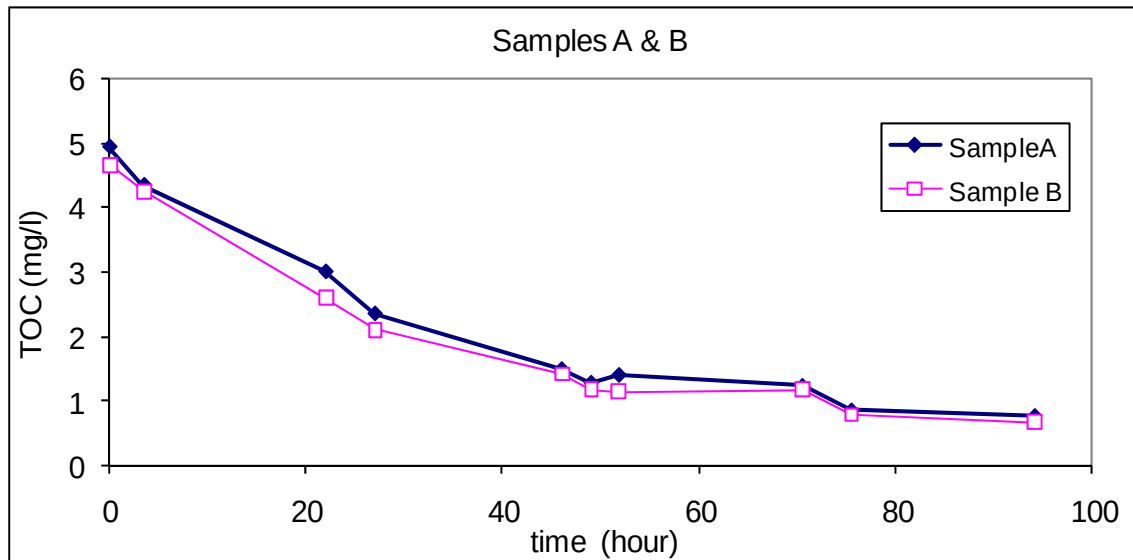


Figure 29. TOC versus time graph for biologically pre-treated greywater sample A and B

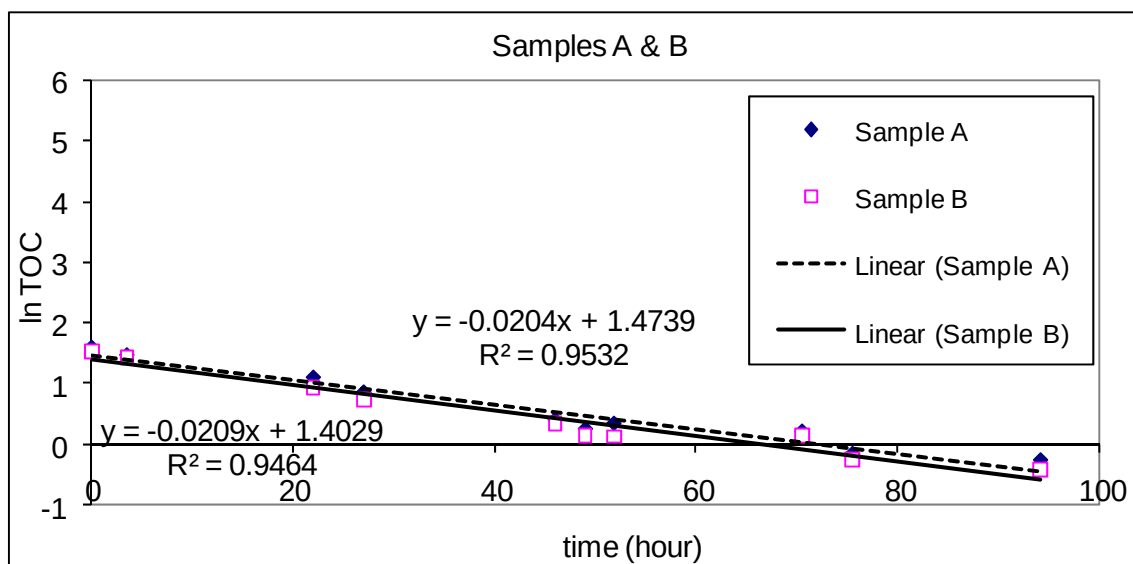


Figure 30. Natural logarithm of TOC versus time graph for biologically pre-treated greywater sample A and B

The pairs of graphs in Figure 29 and Figure 30 show that the degradation experiments with real greywater were well reproducible. When the coefficients of determination (R^2) in Figure 30 are considered, it can be deduced that the photooxidation of biologically pre-treated greywater properly obeys pseudo first order kinetics which was also the case for some of the investigated model wastewaters. However, for the real greywater more time was necessary to achieve an extent of mineralization comparable to that observed with the model wastewaters.

Table 13. Degradation rate and adsorption values for biologically pre-treated greywater samples

Sample	Photocatalytic Degradation Rate (h^{-1})	Average Adsorption per gram of TiO_2 (mg/g)
Biologically pre-treated greywater	0.0207	0.59
Model wastewater (50 mg NaHA/l, 200 mg NaCl/l)	0.165	6.82

With biologically pre-treated greywater the average TOC concentration after addition of TiO_2 was 4.8 mg/l, indicating that only around 5.5 % of TOC were adsorbed to the TiO_2 surface. Therefore, among the investigated model wastewaters the suspensions that contain 50 mg/l NaHA are the ones most close to mimicking the adsorption characteristics of biologically pre-treated greywater on TiO_2 on percentage adsorption base. However, in that case even more than 30% of TOC were adsorbed (Figure 17). While the mean rate constant for an NaHA concentration of 50 mg/l was considered to be 0.053 h^{-1} , the average degradation rate constant found for real biologically pre-treated greywater was equal to 0.0207 h^{-1} (Table 13). When a degradation period is of 24 hours is selected instead of the initial period, the rate constant for the suspension with 50 mg/l NaHA were much higher: 0.1918 h^{-1} for a model wastewater containing 50 mg/l NaHA and 200 mg/l NaCl (Table 9). The reason behind the differences in degradation rates between the real and model might be one or a combination of the following: 1st the

presence of a mixture of anions which adsorb to TiO_2 particle surface and compete with organics for binding site, 2nd the larger TiO_2 particle size in real greywater leading to impaired UV absorbance, 3rd scavenging effects of the mixture of anions present in real biologically pre-treated greywater, 4th the pH of real biologically pre-treated greywater which was higher compared to the model mimicking it, 5th additional organics that are present in biologically pre-treated greywater being different from humic acid.

The lag phase which was present in degradation kinetics of some suspensions with an initial NaHA concentration of 50 mg/l was not observed for the real biologically pre-treated greywater. The reason is probably the constituents of the real biologically pre-treated greywater different from those of the model mimicking it. In addition to humic acid, fulvic acid and polysaccharides are known to be the constituent of biologically pre-treated greywater [7]. Thus, adsorption and photodegradation of the organics (within the initial phase) that are present in real biologically pre-treated greywater other than humic acid may have prevented the occurrence of the lag phase.

When the adsorption of organics from biologically pre-treated greywater (Table 13), which was calculated from the difference between the TOC values of the biologically pre-treated greywater before and after TiO_2 addition (without irradiation), is compared to adsorption from model wastewaters, it can be concluded that the TOC adsorption from the real greywater is much lower. The possible reasons can be the competitive adsorption between the mixture of inorganic anions present in biologically pre-treated greywater and the organics, the pH of the aqueous media which was higher in greywater indicating the presence of a more negative surface charge on TiO_2 particles hindering the adsorption of negatively charged organics and the presence of organics other than NaHA in real biologically pretreated greywater that do probably not adsorb to TiO_2 .

Considering all the comparisons between model and real biologically pre-treated greywater it can be concluded that the selection of the organic model compound was improper. Future studies should use an organic dissolved in model wastewaters which will not dissociate.

6. Conclusion

1st In model wastewaters containing humic acid sodium salt, flocculation as a consequence of double layer compression was observed at NaCl concentrations $\geq$ 500 mg/l.

2nd The flocculation was affected by the concentration of NaHA itself which is a buffering substance influencing the pH of the aqueous phase. This led to adjustment of pH to the point of zero charge (PZC) of TiO₂ suspended in model wastewaters with a NaHA concentration of 10 mg/l with the consequence of instability of TiO₂ suspensions and massive flocculation.

3rd Unfortunately, for recording photocatalytic oxidation kinetics with this very low NaHA concentrations (10 mg/l), the TOC analysis was too insensitive, which was also the case for 20 mg/l NaHA solutions. An NaHA concentration of 50 mg/l was sufficiently high to record kinetics. There was some evidence that the kinetics exhibit two phases: a slow initial phase and a subsequent faster one. This is according to literature data about photocatalytic oxidation of humic acids.

4th Contrasting to expected competition of chloride and humic acid anions for binding sites on the photocatalyst surface, the addition of NaCl in concentrations above 10 mg/l led to increasing adsorption of the humic acid sodium salt to TiO₂. This phenomenon is explained in the literature by effects of inorganic salts on the tertiary structure of humic acids.

5th Real biologically treated greywater could not be properly modeled by simple NaCl/NaHA mixtures in deionized water with respect to photocatalytic oxidation. Obviously, due to organics which are known to be present in biologically treated greywater additional to humic acids, no biphasic photocatalytic oxidation kinetics could be observed for the real wastewater. Moreover, the photocatalytic mineralization of organics in biologically treated greywater was markedly slower than in model wastewater containing 50 mg/l NaHA irrespective of the NaCl concentration.

6th Also the high extent of TiO₂ flocculation in biologically treated greywater could not be modeled even by high NaCl dosages to model wastewater containing NaHA.

7th The interactions of very different effects like that of pH on flocculation when the PZC is adjusted, OH radical scavenging properties of inorganic species and the enhancement of NaHA adsorption to TiO₂ by NaCl are extremely complex. Therefore, even the selection of a simple model wastewater with the two constituents NaHA and NaCl did not lead to unequivocal conclusions about the influence of NaCl on the impairment of photocatalytic efficiency by flocculation. For classifying this, a model organic is recommended which does not dissociate in water (as humic acid does) and thus does not influence flocculation phenomena which are caused by pH alterations.

8th In order to minimize area consumption for solar photocatalytic oxidation of biologically treated greywater, suitable measures have to be taken to overcome the low efficiency for this type of wastewater. As flocculation of photocatalyst in biologically pretreated greywater was large, massive increase of photocatalyst concentration might be a way for compensation. The photocatalyst losses during photocatalyst separation are considered to be low. With respect to TiO₂ sedimentation the photocatalyst flocculation is advantageous.

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Appendices

Appendix I

Results of Gravimetric Analysis of Suspensions without NaHA

Suspensions	Mass Retained on Membrane After Gravimetric Analyses (mg)	pH	Conductivity ($\mu\text{S}/\text{cm}$)
0 mg/l NaCl + 0 mg/l NaHA + 1 g/l TiO_2	45.8	4.45	10
1 mg/l NaCl + 0 mg/l NaHA + 1 g/l TiO_2	45.3	4.42	13
2 mg/l NaCl + 0 mg/l NaHA + 1 g/l TiO_2	45.5	4.71	14
5 mg/l NaCl + 0 mg/l NaHA + 1 g/l TiO_2	45.2	4.68	20
10 mg/l NaCl + 0 mg/l NaHA + 1 g/l TiO_2	45.1	4.66	28
20 mg/l NaCl + 0 mg/l NaHA + 1 g/l TiO_2	45.3	4.65	56
50 mg/l NaCl + 0 mg/l NaHA + 1 g/l TiO_2	44.9	4.68	115
100 mg/l NaCl + 0 mg/l NaHA + 1 g/l TiO_2	43.5	4.83	216
200 mg/l NaCl + 0 mg/l NaHA + 1 g/l TiO_2	43.7	4.85	456
500 mg/l NaCl + 0 mg/l NaHA + 1 g/l TiO_2	20.4	4.91	1010
1000 mg/l NaCl + 0 mg/l NaHA + 1 g/l TiO_2	6	4.98	1928

Results of Gravimetric Analysis of Suspensions with 10 mg/l NaHA concentration

Suspensions	Mass Retained on Membrane After Gravimetric Analyses (mg)	pH	Conductivity ($\mu\text{S}/\text{cm}$)
0 mg/l NaCl + 10 mg/l NaHA + 1 g/l TiO_2	6.8	5.60	22
1 mg/l NaCl + 10 mg/l NaHA + 1 g/l TiO_2	2.9	5.93	8
2 mg/l NaCl + 10 mg/l NaHA + 1 g/l TiO_2	2.6	5.98	9
5 mg/l NaCl + 10 mg/l NaHA + 1 g/l TiO_2	2.4	6.04	16
10 mg/l NaCl + 10 mg/l NaHA + 1 g/l TiO_2	1	5.76	32
20 mg/l NaCl + 10 mg/l NaHA + 1 g/l TiO_2	1	5.80	48
50 mg/l NaCl + 10 mg/l NaHA + 1 g/l TiO_2	1.2	5.83	110
100 mg/l NaCl + 10 mg/l NaHA + 1 g/l TiO_2	1.4	5.67	221
200 mg/l NaCl + 10 mg/l NaHA + 1 g/l TiO_2	2.5	5.68	425
500 mg/l NaCl + 10 mg/l NaHA + 1 g/l TiO_2	3.3	5.65	1010
1000 mg/l NaCl + 10 mg/l NaHA + 1 g/l TiO_2	3.7	5.63	1928

Results of Gravimetric Analysis of Suspensions with 20 mg/l NaHA concentration

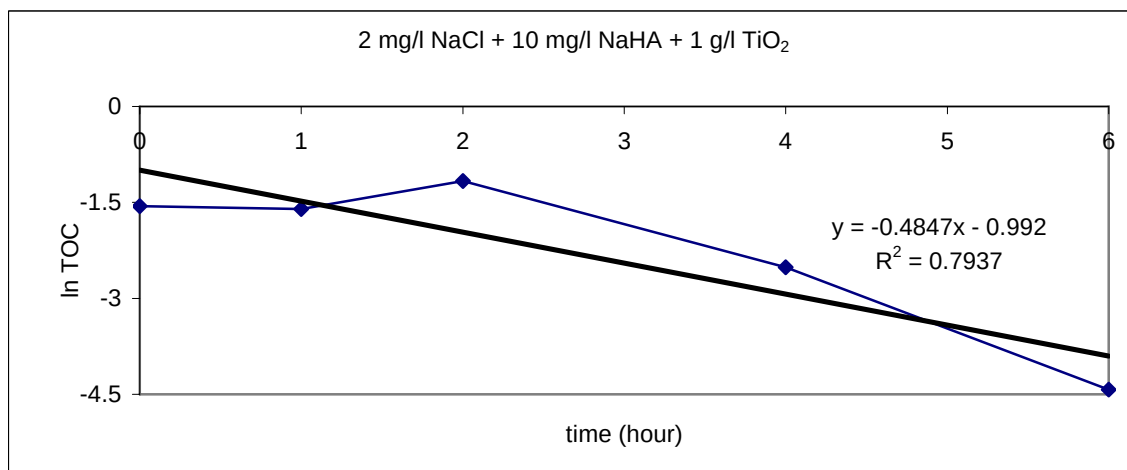
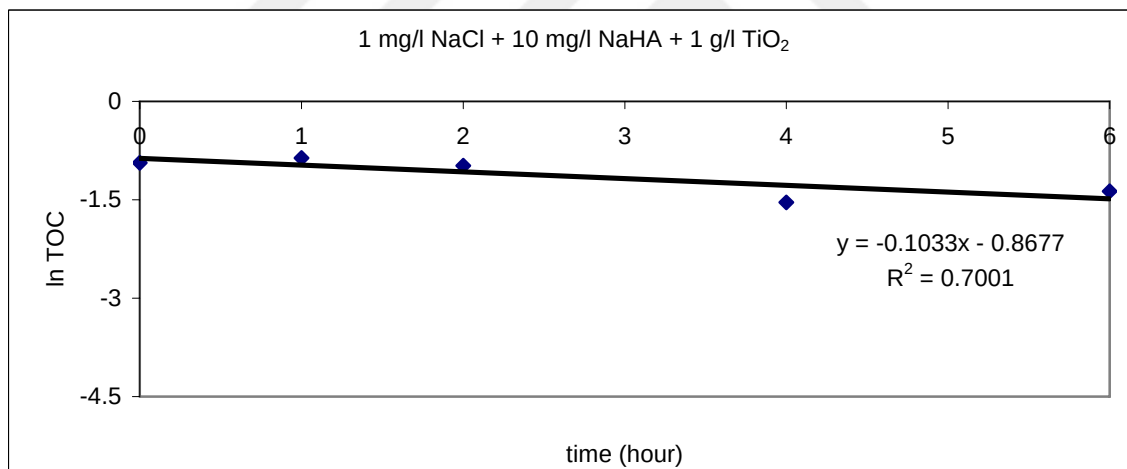
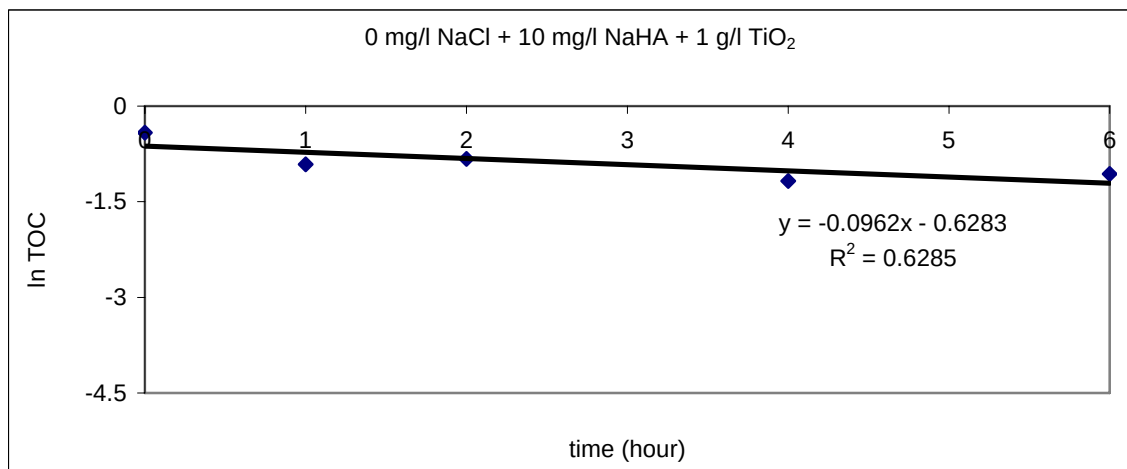
Suspensions	Mass Retained on Membrane After Gravimetric Analyses (mg)	pH	Conductivity ($\mu\text{S}/\text{cm}$)
0 mg/l NaCl + 20 mg/l NaHA + 1 g/l TiO_2	45.9	6.47	16
1 mg/l NaCl + 20 mg/l NaHA + 1 g/l TiO_2	46.9	6.35	19.7
2 mg/l NaCl + 20 mg/l NaHA + 1 g/l TiO_2	46.1	6.29	20.5
5 mg/l NaCl + 20 mg/l NaHA + 1 g/l TiO_2	38.1	6.17	19.7
10 mg/l NaCl + 20 mg/l NaHA + 1 g/l TiO_2	28.7	6.49	44.6
20 mg/l NaCl + 20 mg/l NaHA + 1 g/l TiO_2	45.2	6.40	50.6
50 mg/l NaCl + 20 mg/l NaHA + 1 g/l TiO_2	44.4	5.83	110
100 mg/l NaCl + 20 mg/l NaHA + 1 g/l TiO_2	44.9	5.67	221
200 mg/l NaCl + 20 mg/l NaHA + 1 g/l TiO_2	44.5	5.68	425
500 mg/l NaCl + 20 mg/l NaHA + 1 g/l TiO_2	17.1	5.65	1010
1000 mg/l NaCl + 20 mg/l NaHA + 1 g/l TiO_2	19.2	5.63	1928

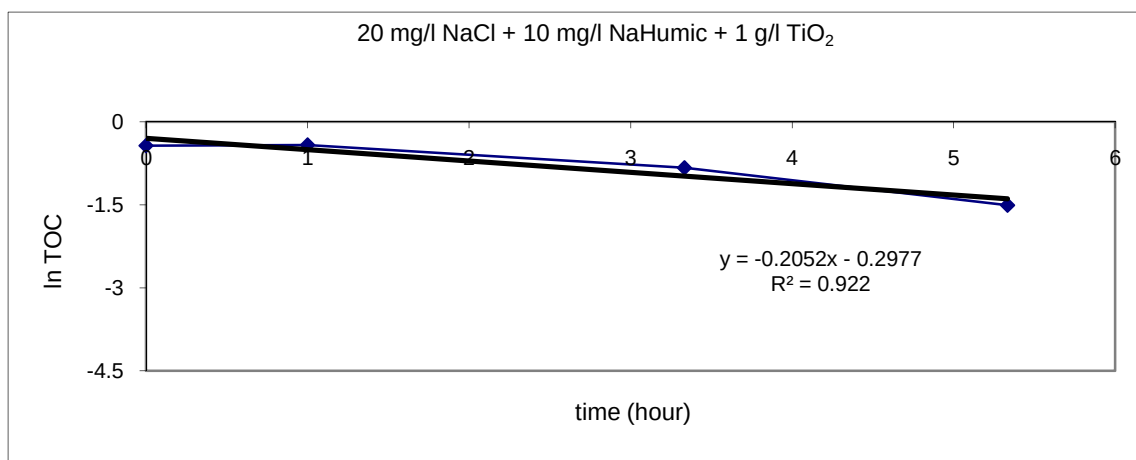
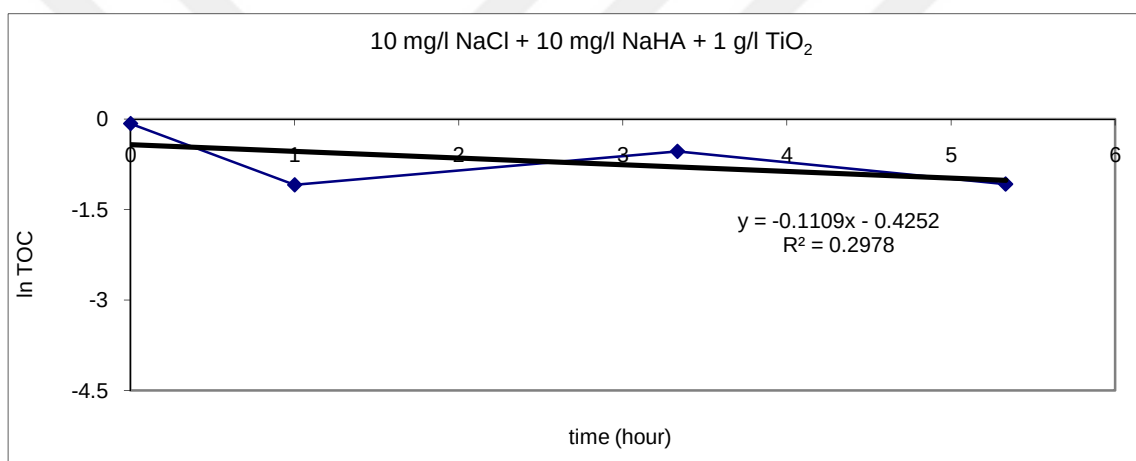
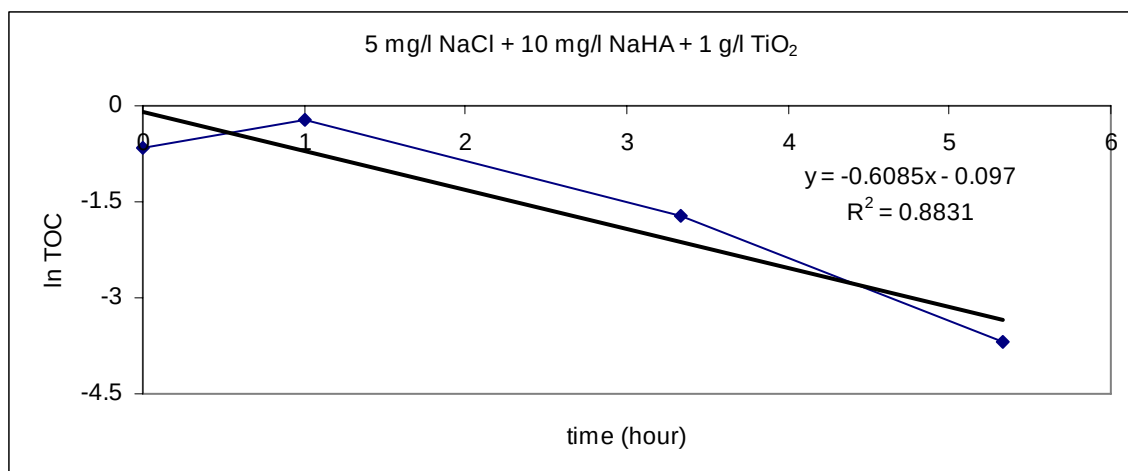
Results of Gravimetric Analysis of Suspensions with 50 mg/l NaHA concentration

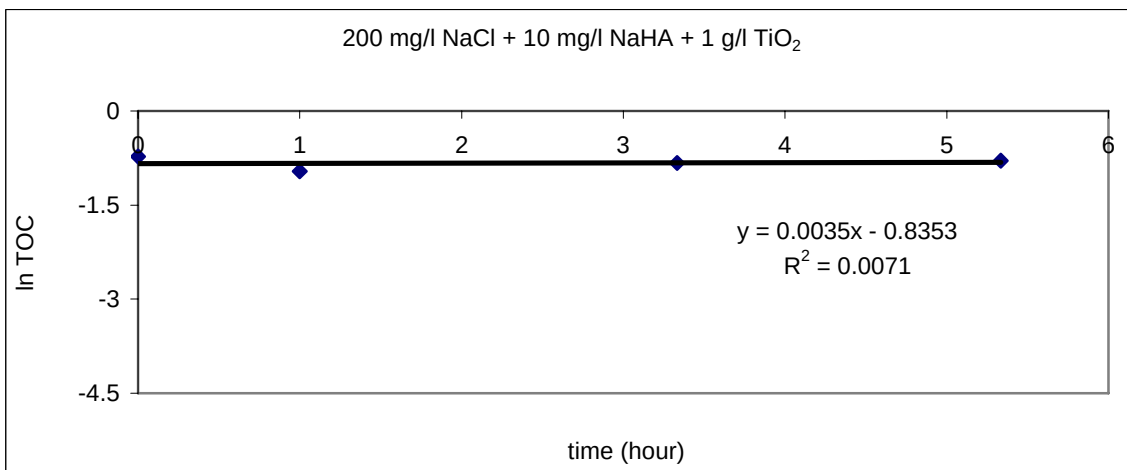
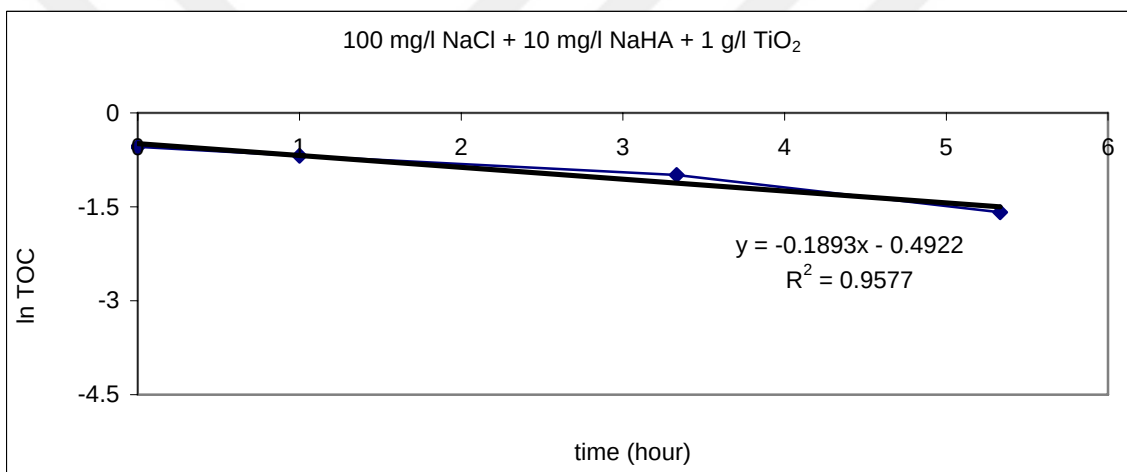
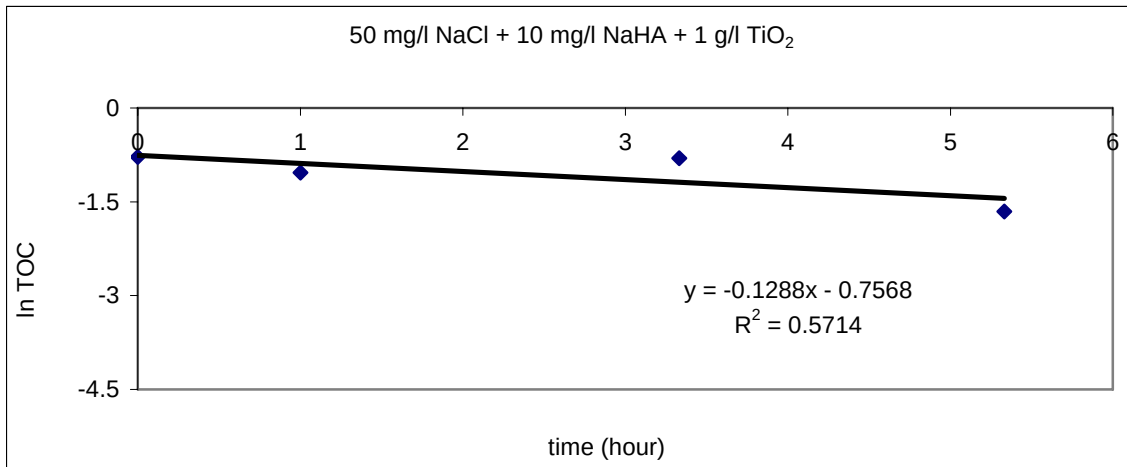
Suspensions	Mass Retained on Membrane After Gravimetric Analyses (mg)	pH	Conductivity ($\mu\text{S}/\text{cm}$)
0 mg/l NaCl + 50 mg/l NaHA + 1 g/l TiO_2	55	7.50	18.5
1 mg/l NaCl + 50 mg/l NaHA + 1 g/l TiO_2	47.2	7.73	21
2 mg/l NaCl + 50 mg/l NaHA + 1 g/l TiO_2	45.8	7.80	21.6
5 mg/l NaCl + 50 mg/l NaHA + 1 g/l TiO_2	47.8	7.69	46.6
10 mg/l NaCl + 50 mg/l NaHA + 1 g/l TiO_2	45	7.31	40.6
20 mg/l NaCl + 50 mg/l NaHA + 1 g/l TiO_2	45.8	7.13	63.7
50 mg/l NaCl + 50 mg/l NaHA + 1 g/l TiO_2	44.4	5.83	123.6
100 mg/l NaCl + 50 mg/l NaHA + 1 g/l TiO_2	44.9	5.67	221
200 mg/l NaCl + 50 mg/l NaHA + 1 g/l TiO_2	44.5	5.68	530
500 mg/l NaCl + 50 mg/l NaHA + 1 g/l TiO_2	17.1	5.65	1015
1000 mg/l NaCl + 50 mg/l NaHA + 1 g/l TiO_2	19.2	5.63	1968

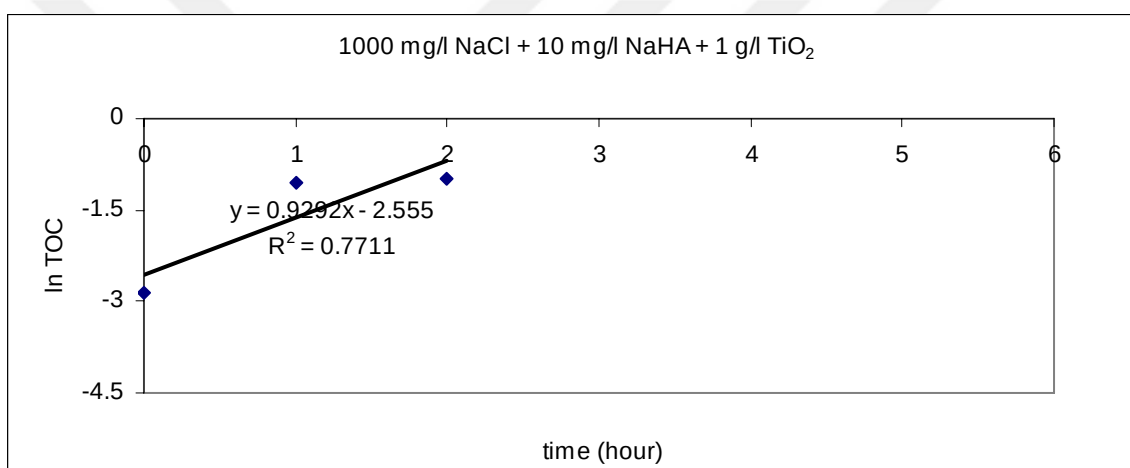
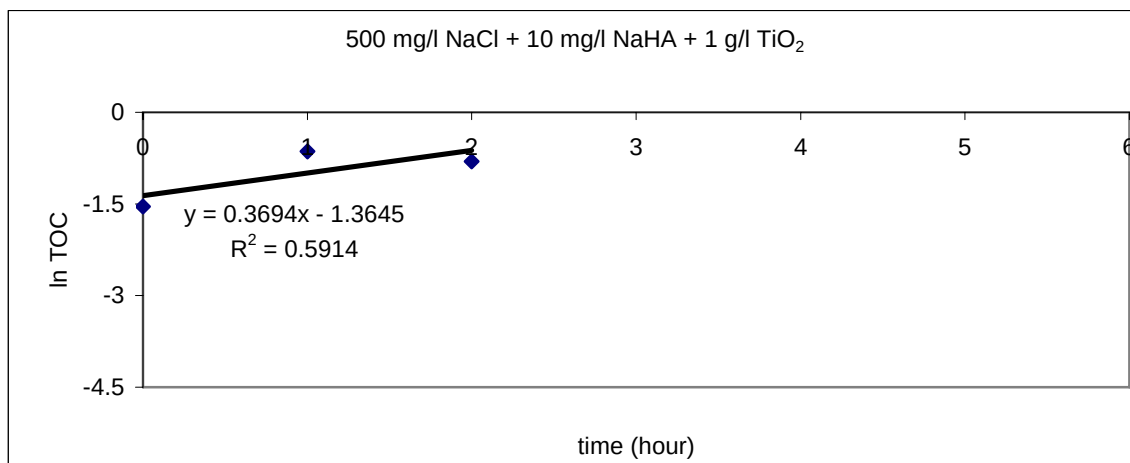
Appendix II

Results of Degradation Rate Determination of Suspensions with 10mg/l NaHA concentration

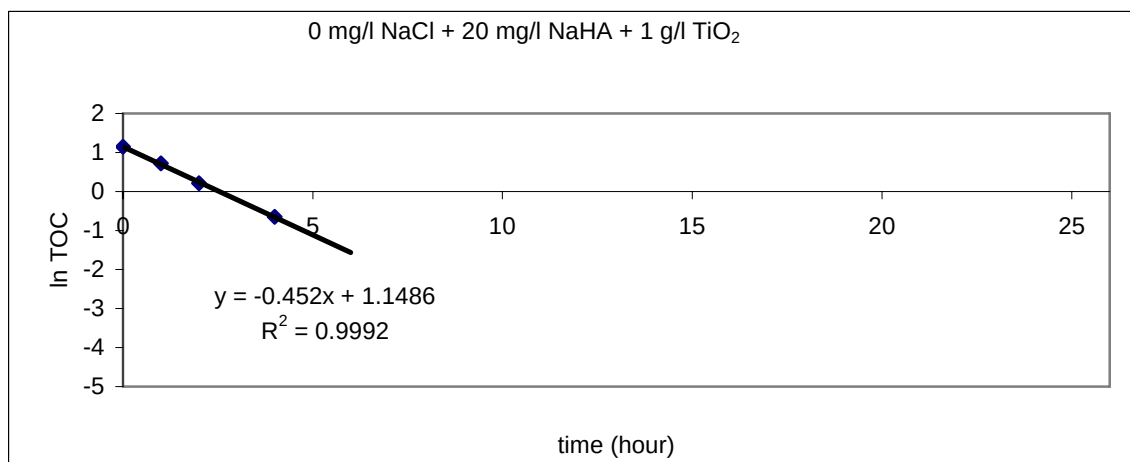


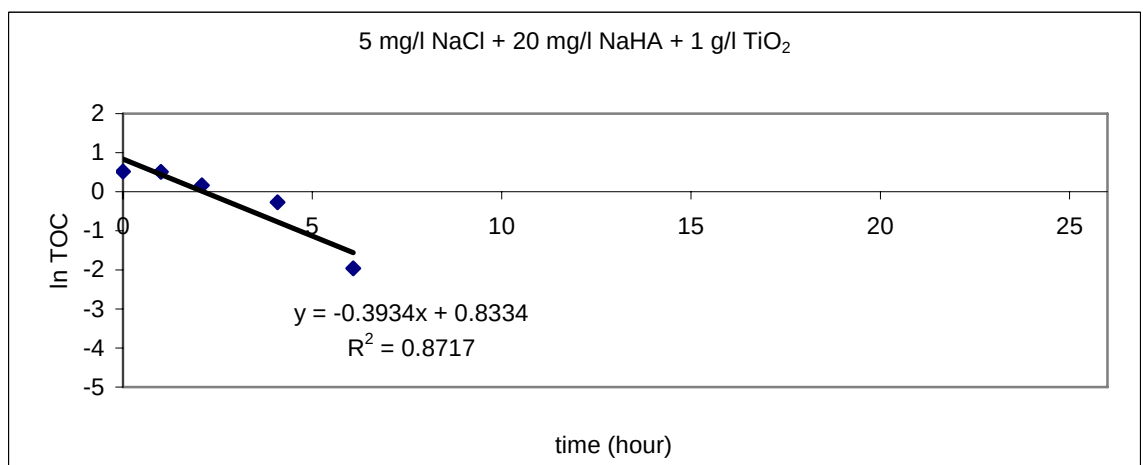
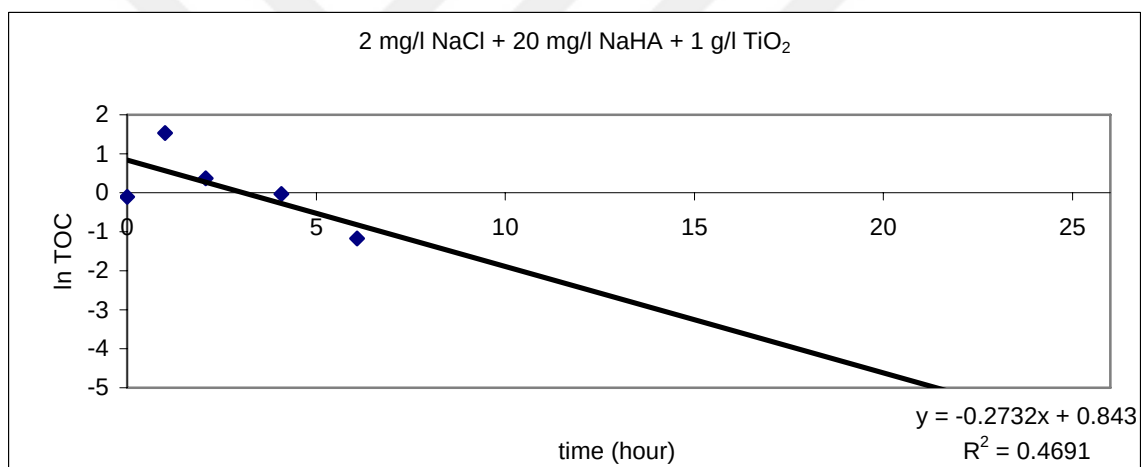
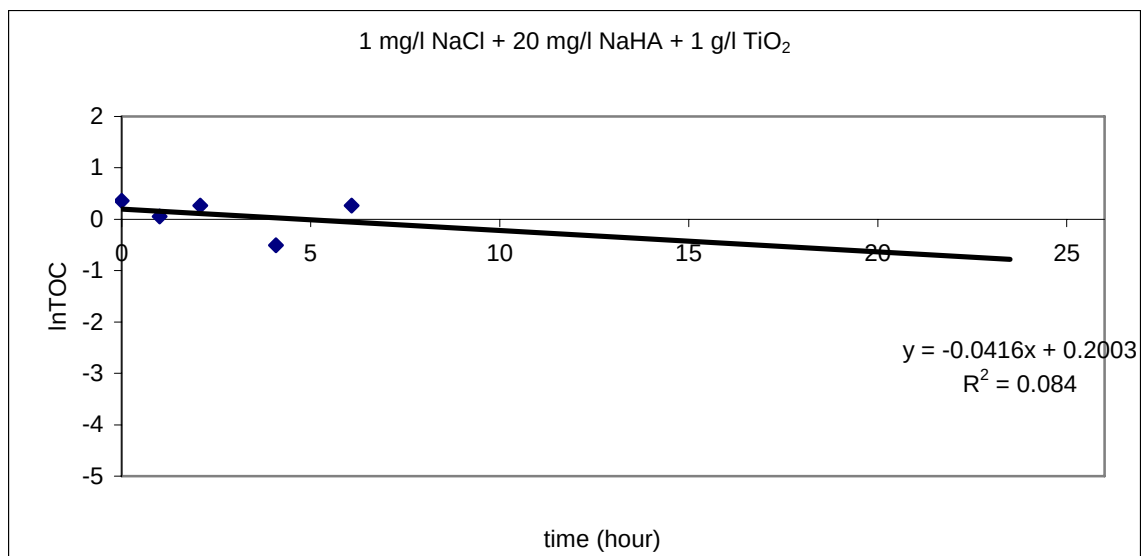


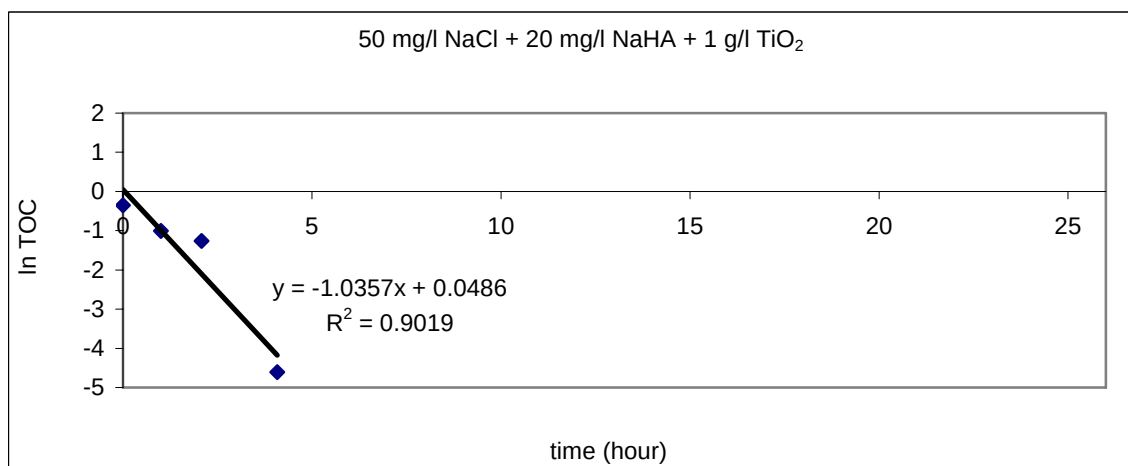
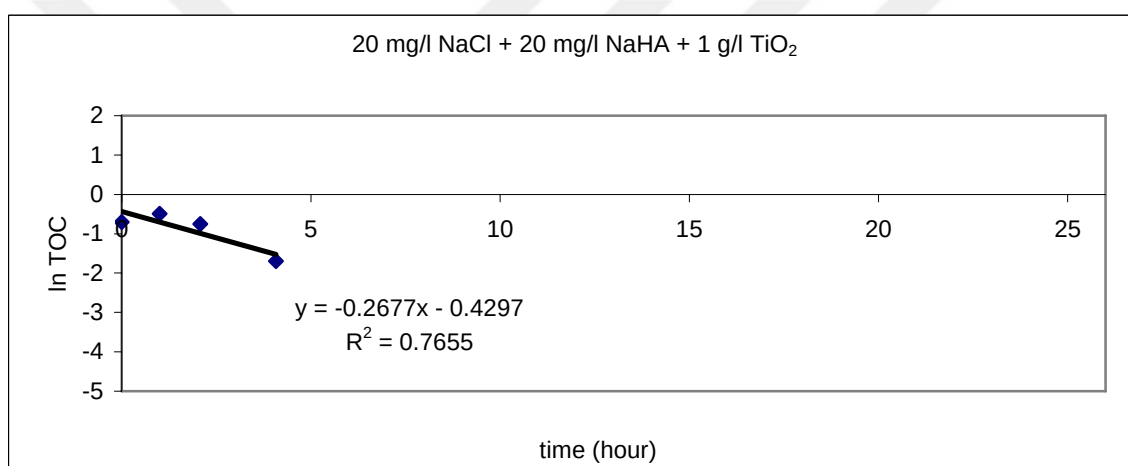
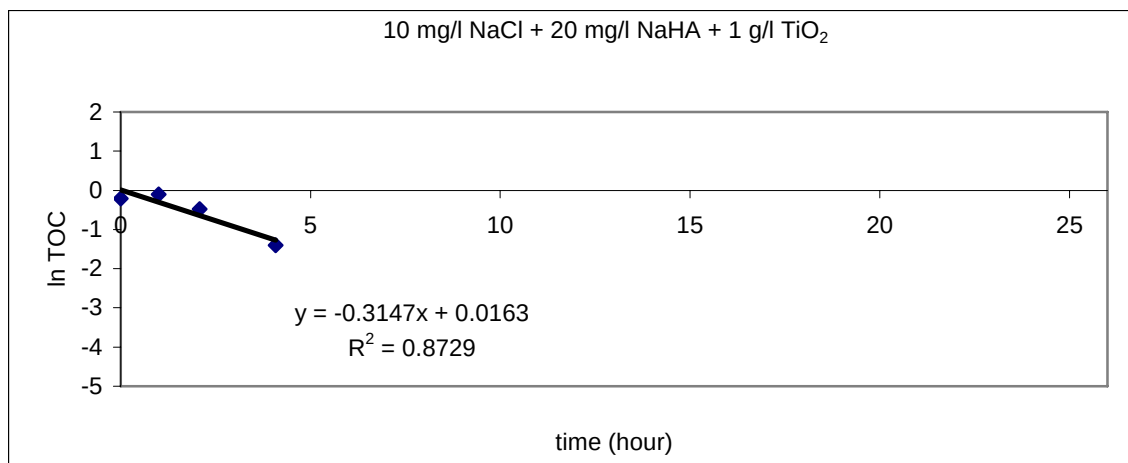


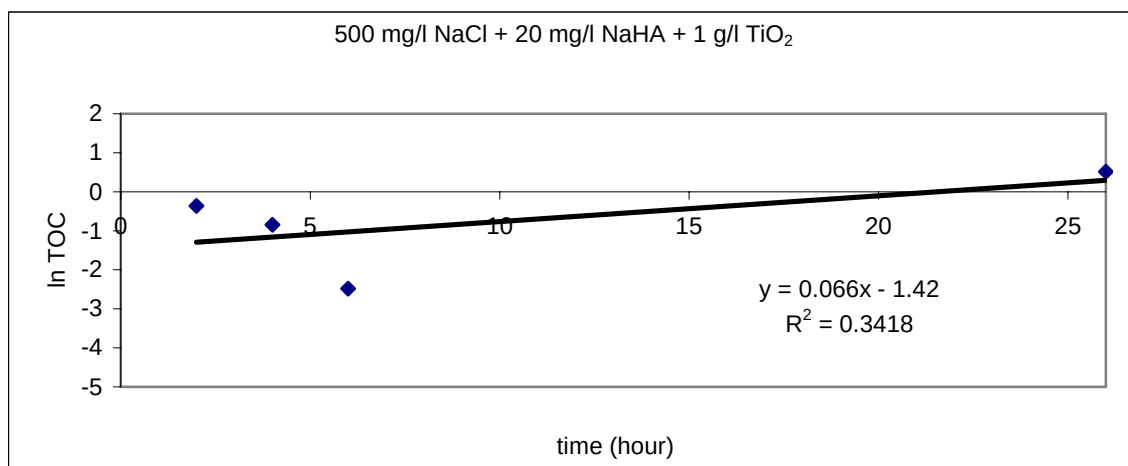
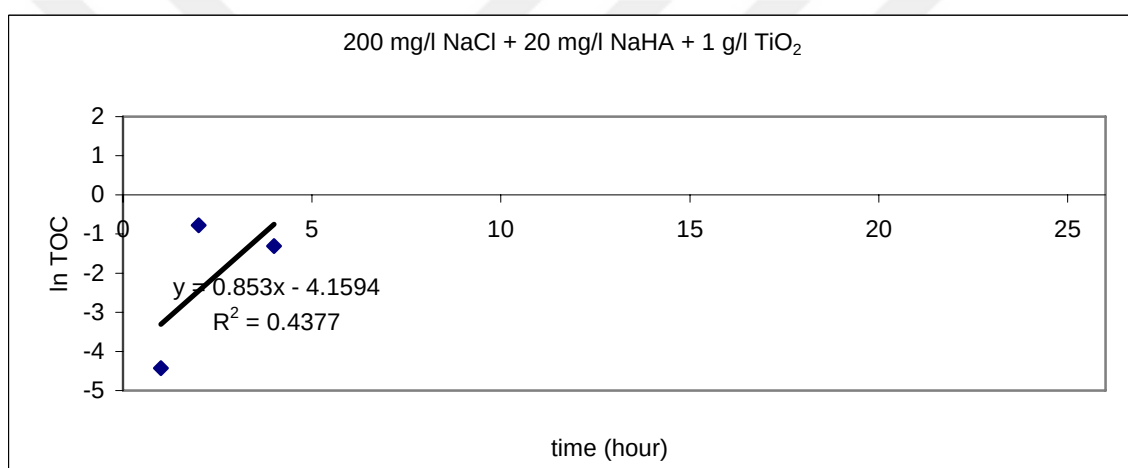
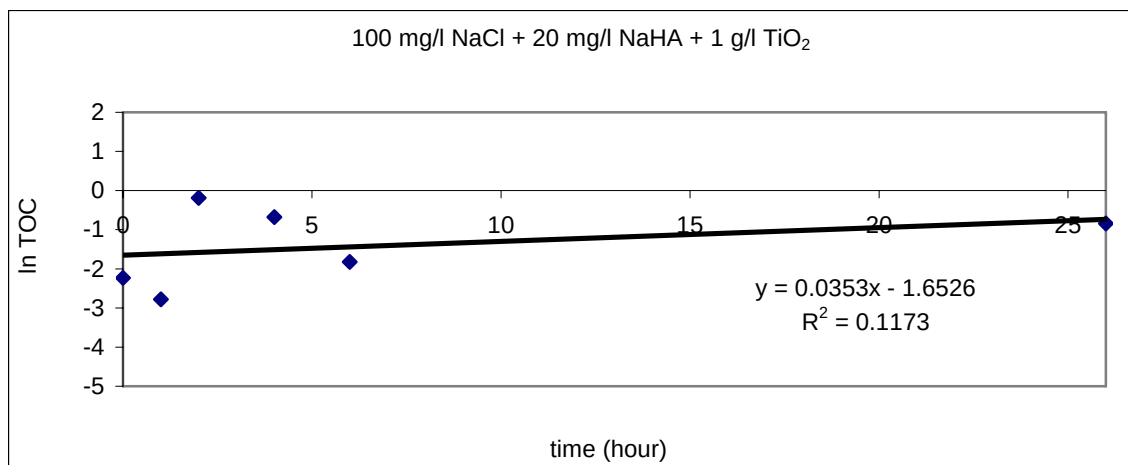


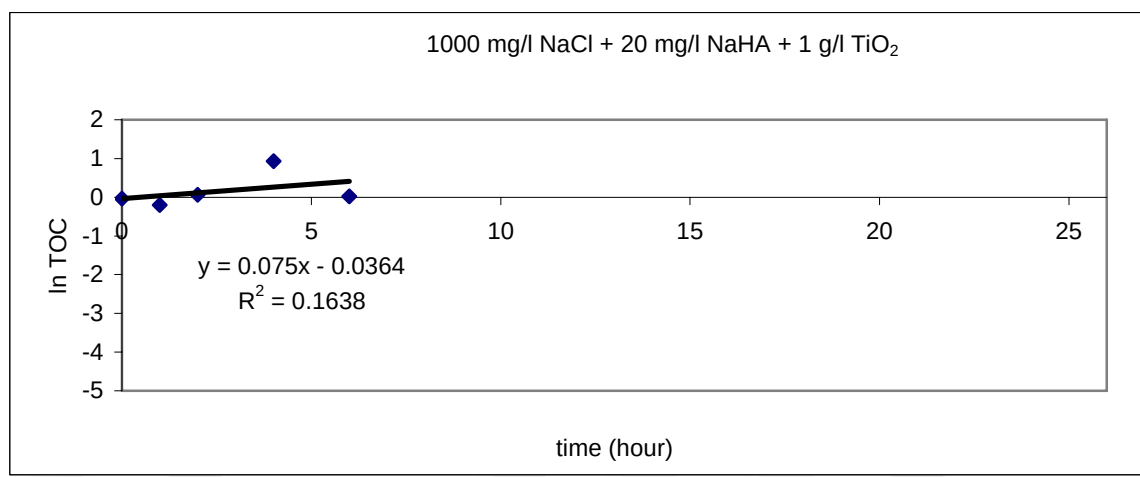
Results of Degradation Rate Determination of Suspensions with 20mg/l NaHA concentration











Results of Degradation Rate Determination of Suspensions with 50mg/l NaHA concentration

