

Palacky University Olomouc  
Faculty of Science  
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Bachelor thesis

DEGRADATION OF IBUPROFEN  
USING NZVI

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Supervisor: RNDr. Eva Otyepková, Ph.D.

Olomouc 2015

I hereby declare that this bachelor thesis has been composed by myself autonomously under the supervision of RNDr. Eva Otyepková, Ph.D. All of the literary sources used in this work are listed in the references section.

In Olomouc .....

.....

Lucie Skácelová

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Abstract: The aim of this thesis is to determine the rate of degradation of ibuprofen using various concentrations of stabilized nZVI particles, which are used for *in situ* groundwater remediation. The percentage decrease of the initial amount of ibuprofen in solution and the reaction rate constant,  $k_{obs}$ , were chosen as efficiency criteria for the degradation analysis. A spectrophotometric method was utilized for the assessment of the ibuprofen concentration in solution.

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Abstrakt:	<p>Cílem této práce je stanovení míry odbourání ibuprofenu pomocí různě koncentrovaných, stabilizovaných nZVI částic, které se využívají v <i>in situ</i> sanaci podzemních vod. Jako kritéria účinnosti degradační analýzy byly vybrány procentuální úbytek počátečního množství ibuprofenu v roztoku a rychlostní konstanta reakce <math>k_{obs}</math>. Spektrofotometrická metoda byla použita pro určení koncentrace ibuprofenu v roztoku.</p>
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# 1. Introduction

nZVI (Nanosized Zero-Valent Iron,  $\text{Fe}^0$ ) has first been tested for contaminated water remediation by Dr. Wei-xian Zhang at the Institute of Sustainable Nanotechnology at Lehigh University, Bethlehem. Due to its ability to degrade many environmental contaminants, such as poly-chlorinated biphenyls, and its use in contaminant remediation in ground waters, the methods using nZVI have undergone substantial development over the past few years. However, not many studies focus on the question of toxicity of these particles and their impact on the environment.

In order to lower the cost of the nanoparticles and eliminate other limitations of the current synthesis methods, a research into green production of nZVI has been launched. For such an approach, the scientists utilised extracts of natural products, such as green tea, and discovered that the compounds present in them react with iron (III) to form iron(0) nanoparticles and also that this synthetic method uses a less toxic reducing reagent than the methods employed prior to this revelation.

( $\text{Fe}^0$ ) acts as an extremely strong reduction agent. The nZVI particles are prone to instability in other than reduction environments. Several methods are used to prevent nZVI particles from oxidising, such as storing the particles in inert atmosphere or keeping them in a suspension. Water and oxygen are just two examples of the reagents that cause rapid oxidation of  $\text{Fe}^0$  to  $\text{Fe}^{2+}$ . Another common practice is coating the particles with different surface modifiers to help control their reactivity and mobility. When used in water treatment, the nZVI is formed into permeable reactive barriers (PRBs) which work as a filter for toxic substances such as heavy metals or various pharmaceuticals.

One of the pharmaceuticals that can be found in water and is classified as a contaminant is ibuprofen. Ibuprofen is a non-steroidal anti-inflammatory drug (NSAID), available without prescription since 1984, used for relieving pain, lessening fever and reducing inflammation. It has been discovered by the Boots Company in the UK and patented in 1961. It is known by many different trademark names across the world, the name *ibalgin* being used in the Czech Republic.

The aim of this thesis is to determine the appropriate method of measurement of ibuprofen and assess the degree of degradation of ibuprofen by nZVI.



## **2. THEORETICAL PART**

## 2.1. Nanotechnology and nanomaterials

Nanotechnology is a relatively new but a highly popular field of study pertaining to materials within the size range of 1-100 nm.<sup>1</sup> During his lecture titled “There is plenty of room at the bottom” at CalTech in 1959 Richard Feynman entertained the notion of operating on an atomic scale, but it was not until the development of the Scanning Tunneling Microscope (STM) in 1981 and the subsequent discovery of fullerene in 1985, that this area of study began its plummeting rise in the scientific world. Since then, numerous discoveries have taken place, such as that of carbon nanotubes in 1991 or graphene in 2004.<sup>2,3,4,5</sup>

There are many various definitions of the word nanomaterials; however, most of them seem to agree on the fact that nanomaterials can be defined as having at least one of their dimensions in the size range 1-100nm.<sup>1</sup> The nanomaterials can therefore be separated into several groups according to the number of dimensions in this range. The 0D (dimensional) nanomaterials, with all of their dimensions in the mentioned size range, are most commonly nanoparticles or quantum dots. The 1D nanomaterials, with one dimension outside the nanoscale, include nanotubes, nanorods and nanowires. The 2D nanomaterials, with two dimensions outside the nanoscale, take on planar shape such as for example nanofilms or nanolayers. Lastly the 3D nanomaterials are defined as having all three dimensions outside the nanoscale but at the same time possessing nanocrystalline structures or other nanosized features.<sup>6</sup>

Nanomaterials all possess several unique electrical, optical and mechanical properties, which greatly differ from those of their microscale counterparts.<sup>1</sup> These make them invaluable in their application to other fields of study.

Magnetic nanoparticles can be used for targeted drug delivery with the help of a magnetic field gradient.<sup>7</sup> This method is highly desirable as it can potentially aid in the treatment of tumours.

Due to their high reactivity, some nanoparticles are used in reactions as catalysts. An example of this is the Fischer-Tropsch reaction: the conversion of synthesis gas, a mixture of CO and H<sub>2</sub>, to hydrocarbons by passing the gas over a catalyst at high temperature and pressure. The catalyst, typically a group VII metal, is used for the creation of carbon-carbon bonds. Recent studies have shown the iron nanoparticles based catalyst to have a catalytic activity six times that of a conventional material.<sup>7</sup>

The great surface area of nanomaterials is also critical for their use in ground and waste water treatment and soil sanitation. Due to their high reactivity and ability to adsorb certain materials, specific nanomaterials, such as iron nanoparticles, are applied in the process of degradation of pollutants.<sup>1,7</sup>

Although the study of nanomaterials is a relatively new field and therefore the use of synthetic nanomaterials is only dated back a few decades, there are instances through history when nanomaterials were used unknowingly. The Lycurgus glass cup, now a part of the exhibition in the British Museum, dates back to 4<sup>th</sup> century Rome and is famous for the changing of its original colour red, to the colour green depending on light intensity. The cup has undergone an extensive scientific analysis and it was determined that its unique optical properties can be attributed to the presence of golden nanoparticles which developed in the glass during the melting process.<sup>8</sup>

Nanomaterials can be separated into two categories according to their origin. The anthropogenic nanomaterials, also called man-made, are further categorized as engineered, for example metallic nanoparticles or oxides, and incidental which are by-products of human activities, such as burning of fossil fuels. The other main category covers nanomaterials occurring naturally – in organisms or as a result of natural events such as dust storms, volcanic eruptions and forest fires.<sup>6</sup>

### **2.1.1. nZVI**

The abbreviation nZVI stands for nano-sized zero valent iron particles, which are a miniaturization of microscopic Fe<sup>0</sup> particles. Their size varies from 1 to 100 nanometres; as is defined by the inclusion of the term “nano”. The main advantage of the nano-sized particles is their increased reactivity and tendency to adsorb.<sup>7</sup>

The nZVI particles, in particular, have great reduction properties and are therefore used in water and soil treatment for the reduction of undesirable substances to their less environmentally dangerous oxidation states. Since being first tested for water remediation by Wang and Zhang at Lehigh University, USA, the nZVI particles have been proven to degrade/remove a wide range of pollutants, including  $\beta$ -lactam, azo dyes or chlorinated pesticides.<sup>9,10</sup>

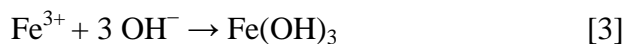
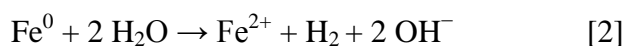
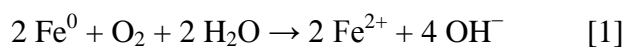
### 2.1.1.1. Properties

While not possessing any significant optical properties, the iron nanoparticles have magnetic properties and are able to reach the state of superparamagnetism. However, their most important characteristic is their high reactivity which stems from their great surface area (surface to volume ratio). Their extreme reactivity with oxidising agents, oxygen in particular, causes a spontaneous ignition of the nanoparticles. Several procedures are employed to ensure the stability of the pyrophoric nanoparticles, the most feasible of which is the submersion of the nanoparticles in a liquid or solid dispersant, such as ethanol, in order to prevent the access of oxygen. A controlled pre-oxidisation of the nanoparticles, resulting in the formation of a layer of a passivating oxide, is also utilized.<sup>7</sup>

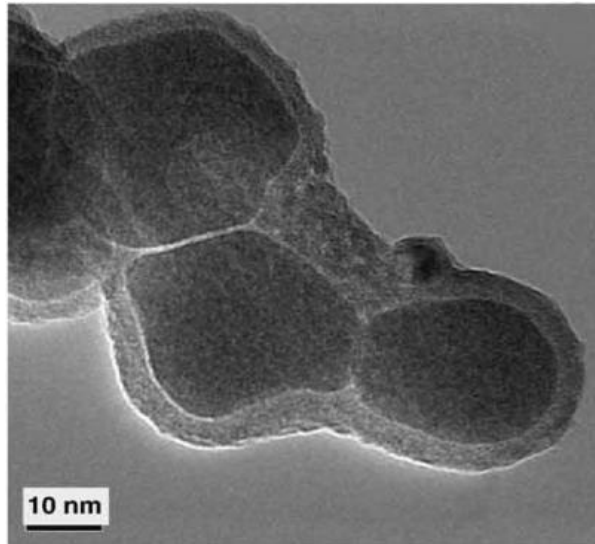
Due to their magnetic properties, iron nanoparticles have a strong tendency to agglomerate to micron size particles in solutions and adhere to soil surfaces.<sup>11,12</sup> This results in decreased reactivity and mobility and therefore a decrease in the efficiency of the degradation of water pollutants. In order to prevent particle agglomeration various coatings and polymers have been used to stabilize the nZVI.<sup>13,14</sup>

### 2.1.1.2. Core-shell structure

The nZVI particles have a core-shell structure formed by the reaction of Fe<sup>0</sup> with oxygen (equation [1]) or water (equation [2]) and the subsequent production of Fe<sup>2+</sup> ions. Fe<sup>2+</sup> can be further oxidised to Fe<sup>3+</sup>, which then reacts either with OH<sup>-</sup> to form a hydroxide (equation [3]) or with water to form an oxyhydroxide (equation [4]). The iron(III) hydroxide can dehydrate to form the oxyhydroxide.<sup>15</sup>



The oxyhydroxide is the main component of the outer shell of the nZVI particles. The core, consisting mainly of Fe<sup>0</sup>, provides the reducing power and the shell provides sites for chemical complex formation.<sup>13,15</sup>

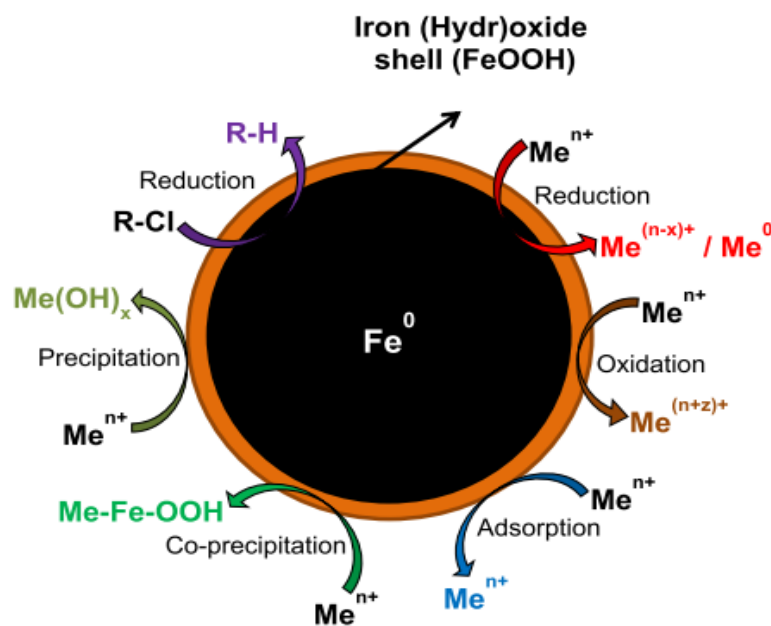


**Figure 1:** TEM image of a nanoparticle agglomerate showing core-shell structure <sup>16</sup>

The outer layer is typically 2-4 nm thick. Due to the tendency of the nZVI to agglomerate, the particles form a chain-like structure with a continuous oxide shell, as seen in Figure 1. The individual  $\text{Fe}^0$  cores are separated by a thin (1nm) oxide layer.<sup>16</sup>

### 2.1.1.3. Reaction mechanism

Depending on the type of substance in contact with the nZVI, different reaction mechanisms take place. A schematic representation of the degradation pathways of organic and inorganic contaminants can be seen in Figure 2.<sup>13</sup>



**Figure 2:** Core-shell structure of nZVI, illustrating the mechanisms for removal of metals and chlorinated compounds <sup>13</sup>

One of the most researched topics in this area of study is the degradation of chlorinated compounds, which can be achieved through at least two reactive pathways. The first is hydrogenolysis, the replacement of a chlorine atom by a hydrogen atom as shown in equation [5]<sup>17</sup>. The second is the more complex reductive elimination (dihaloelimination), during which the chlorinated compound releases chlorine atoms without the addition of hydrogen.<sup>13</sup>



Heavy metals are non-biodegradable, toxic and in some cases carcinogenic contaminants that tend to accumulate in organisms. The removal of heavy metals includes specific mechanisms that depend on the standard reduction potential of the metal contaminant.<sup>9,13</sup>

The interaction mechanisms can be classified as follows (Figure 2):

1. Reduction – Cr, As, Cu, U, Pb, Ni, Se, Co, Pd, Pt, Hg, Ag.
2. Adsorption – As, Ba, Cd, Co, Cr, Pb, Ni, Se, U, Zn,
3. Oxidation – As, Pb, Se, U
4. Co-precipitation – As, Cr, Ni, S.
5. Precipitation – Co, Cu, Cd, Pb, Zn

There is a wide range of both organic and inorganic contaminants that can be degraded by the nZVI, including for example perchlorates, nitrates, azo dyes or phenols (Figure 4). However, there is not much information on their reactivity with pharmaceutical pollutants, such as ibuprofen.<sup>18</sup>

#### **2.1.1.4. Synthesis of NZVI**

In general the many methods of the synthesis of iron nanoparticles can be divided into two groups: top-down methods and bottom-up methods. Depending on the type of synthesis the nanoparticles vary in size, surface area, structural configuration, shape, reactivity and ability to agglomerate.

## *Top-down*

The top-down methods are based on the process of decomposition of macromolecular materials, either mechanically or chemically, in order to obtain iron nanoparticles.

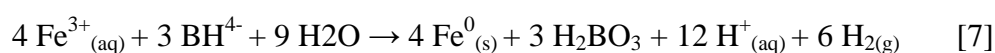
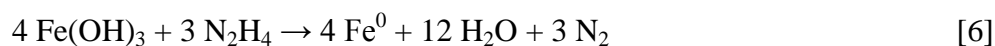
An example of a chemical method is the decomposition of iron pentacarbonyl. The method itself is a simple process, only demanding the presence of the iron pentacarbonyl, energy (heat or sonication), an appropriate surfactant/solvent system, and a means to remove the only byproduct, carbon monoxide. However, there are factors affecting the decomposition in such a way that complicates the growth of nanoparticles of controlled size and shape.<sup>7</sup>

Other ways to produce iron nanoparticles are for example by vacuum sputtering, reduction of hematite and goethite particles using hydrogen gas at high temperatures, electrodeposition of ferrous salts and lastly by high energy milling. While milling is economically advantageous, the nanoparticles produced greatly vary in size and shape.<sup>7,15</sup>

## *Bottom-up*

The bottom-up methods focus on the “growth” of nanoparticles through chemical synthesis or self-assembling. An example of a bottom-up method is the reduction of iron salts and oxides.<sup>7,18,19</sup>

The reduction of aqueous ferric (Fe(III)) or ferrous (Fe(II)) salts can be done using a wide variety of reducing agents such as hydrazine in basic media (equation [6]<sup>20</sup>), lithium borohydride or the most commonly utilized sodium borohydride (equation [7]).<sup>7,19,21</sup> The method using sodium borohydride, in literature often abbreviated as Fe(B) or Fe<sup>BH</sup>, produces nZVI in the particle size range of 10-100nm.<sup>13</sup>



The process is a relatively simple one, however, there are certain disadvantages to this method, such as the production of flammable hydrogen gas and the toxicity of the sodium borohydride.<sup>19</sup>

The iron oxides need stronger encouragement for their reduction; therefore, iron oxide nanoparticles are generally used. The process usually starts with the precipitation of

iron needles and their subsequent dehydration to iron oxide (hematite,  $\alpha\text{-Fe}_2\text{O}_3$ ), which is then reduced by hydrogen gas.<sup>7</sup>

### *Green nZVI*

Considering the use of iron nanoparticles for water remediation and the toxicity of the most commonly used reducing agent, sodium borohydride, for their synthesis, studies of possible “greener” synthesis methods, utilizing extracts from natural products as reducing agents, have been conducted. The antioxidant capacity of extracts from different types of leaves, such as apple, pine, green tea etc., was measured and the extracts were used for the synthesis of zero-valent iron nanoparticles. Among others, black tea leaves, grape marc and vine leaves were used for the reduction of Fe (III) ions in an aqueous solution. The produced nZVI particles were then successfully used in the process of degradation of ibuprofen.<sup>18,19</sup>

Even though a more comprehensive study is in order; the method already presents significant advantages, as it uses non-toxic natural products (some considered waste material). In addition, the polyphenols present in the extracts decrease agglomeration of the nanoparticles and increase reactivity.<sup>18</sup>

### *Commercial nZVI*

There are several companies focusing on the production and use of the iron nanoparticles and therefore there exist several brand names for certain types of nZVI, which are specific to one company and a synthesis method.

For example, the reactive nanoscale iron particles (RNIP), originating from Toda Kogyo Corp. The RNIP are produced by reducing goethite and hematite particles using hydrogen gas at high temperature, which results in nZVI with a 40-70 nm particle diameter.<sup>13</sup>

The nanoparticles used in this thesis, NANOFER, were synthesised from nanosized ferrihydrite and were acquired from the Czech company NANO IRON.<sup>22</sup> The company offers stable or pyrophoric nZVI powder and several types of aqueous dispersions of the nZVI particles all with the average particle size of 50 nm.<sup>23</sup>



### 2.1.1.5. Use of nZVI for groundwater treatment

Over 40% of the world's population do not have access to clean water, one of the most basic necessities required for sustaining life. In the past years the situation has become more and more severe, as industrial and urban activities have led to increasing concentrations of a wide range of pollutants in groundwater and wastewater.<sup>9</sup> Until the early 90s, the main approach to decreasing groundwater contamination was pump-and-treat, however, this type of *ex situ* treatment is very expensive and time consuming.<sup>22</sup>

#### *Permeable reactive barriers (PRBs)*

In 1994 the first *in situ* method, a direct injection of the particles into groundwater, introduced the use of granular zero valent iron (ZVI) in permeable reactive barriers (PRBs). PRBs are essentially engineered iron walls positioned in the groundwater flow in such a way, so that the contaminants can be adsorbed, precipitated or transformed in contact with the ZVI surface.<sup>15,24</sup> The basic schematic of a PRB is shown in Figure 3. The PRB technology offers the possibility of *in situ* plume capture and treatment, simultaneous treatment of multiple types of contaminants and low maintenance costs.<sup>25</sup> ZVI PRBs have been proved to remediate groundwater contaminated with a wide variety of pollutants such as heavy metals, chlorinated hydrocarbons, nitrates and others.<sup>9,22</sup>

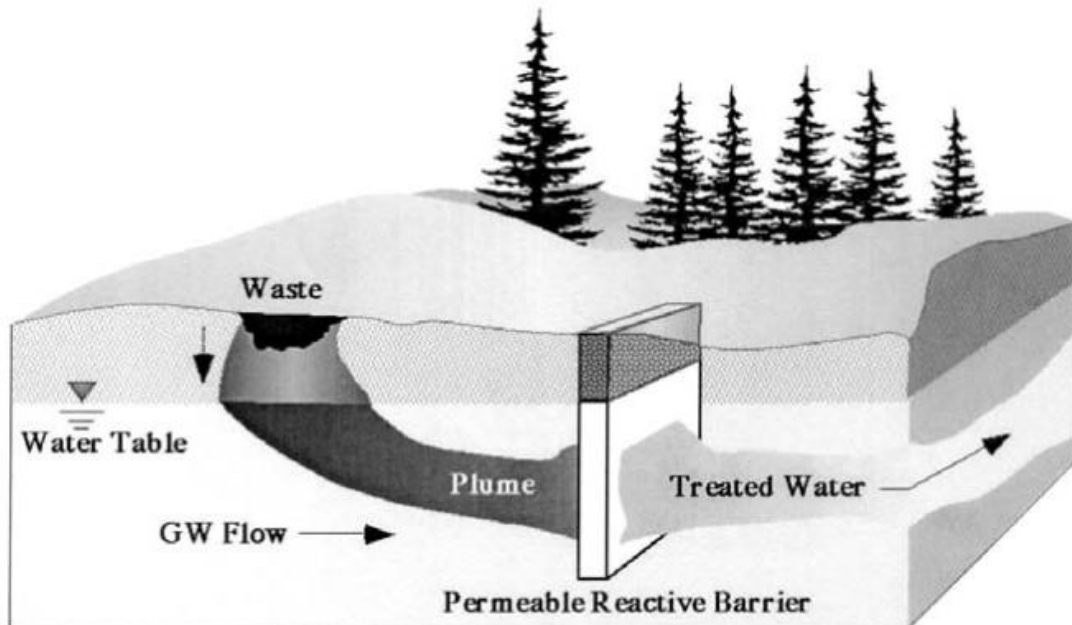


Figure 3: Typical configuration of a PRB <sup>17</sup>

After the development of nZVI, the possibility of the use of nZVI particles in groundwater treatment has been investigated, with focus on their reactivity, mobility in porous media, reactive longevity and toxicity.<sup>10</sup> The nanoscale zero valent iron particles are significantly more reactive than the ZVIs, due to their larger surface area. The ability of the nZVI particles to degrade contaminants has been investigated and the results can be seen in Table 1. The nZVI is the most commonly utilized nanomaterial for soil and groundwater treatment, as its ability to migrate allows active remediation of the source of the contamination.<sup>22</sup> The nZVI can be used instead of the ZVI, or in other cases, the nZVI process can complement established PRBs.<sup>15</sup>

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Chlorinated methanes	Trihalomethanes
Chlorinated benzenes	Chlorinated ethenes
Pesticides	Other polychlorinated hydrocarbons
DDT	PCBs
Lindane	Dioxins
Organic dyes	Other organic contaminants
Orange II	NDMA
Acid Orange	TNT
Acid Red	Inorganic anions
Heavy metal ions	Dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ )
Mercury ( $\text{Hg}^{2+}$ )	Arsenic ( $\text{AsO}_4^{3-}$ )
Nickel ( $\text{Ni}^{2+}$ )	Perchlorate ( $\text{ClO}_4^-$ )
Silver ( $\text{Ag}^+$ )	Nitrate ( $\text{NO}_3^-$ )
Cadmium ( $\text{Cd}^{2+}$ )	

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**Table 1:** Table of common environmental pollutants that can be transformed by nZVI<sup>12</sup>

### *Field applications*

So far, only a small number of pilot tests and site remediation have been conducted in Europe. The remediation efforts focus mainly on groundwater and the degradation of chlorinated hydrocarbons, using the standard nZVI (RNIP, NANOFE, Fe(B)). On the other hand tests performed in the USA focused both on groundwater and soil remediation while using modified nanoparticles, such as the ENZVI, in addition to the standard nZVI.<sup>22</sup>

There are several sites in the Czech Republic, for example Uherský Brod or Spolchemie, where pilot tests have been carried out to assess the quantity of nZVI needed to fully remediate the area. The subsequent full-scale applications in Hořice and Písečná

have yielded positive results with the reductions of up to 80% of the contaminant concentration.<sup>22</sup>

### **2.1.1.6. Stabilization**

As mentioned before, the nZVI particles have an extremely high tendency to aggregate in aqueous media, which significantly limits their mobility and decreases the reactive surface area. To improve the particle mobility, and subsequently their colloidal stability, different methods of surface property modification are employed. However, this presents the challenge of maintaining the material's reactive performance.<sup>10</sup>

In general, there are three approaches to overcoming the attractive forces between the nanoparticles and thus improving the nZVI stability: electrostatic and steric stabilization and the combination of the two.<sup>21</sup>

Electrostatic stabilization is based on surface modification of the particles by adsorption of charged molecules in order to increase the electrostatic repulsive forces between the particles.<sup>21</sup>

Steric stabilization focuses on the use of surfactants and long polymer chains, which are adsorbed onto the nZVI and create artificial hindrances between the particles. However, this method presents a certain disadvantage as a rapid desorption of the surfactant follows immediately after the injection of the nanoparticles into groundwater.<sup>10</sup>

A method utilizing anionic polyelectrolyte coatings acts as an alternative to the methods mentioned above. The particle surface is modified by physisorption of charged macromolecules, which provides the nanoparticles with electro-steric repulsive forces. There is a wide range of polymers suitable to be used as coatings, including cheap, non-toxic, water-soluble and biodegradable options such as carboxymethyl cellulose or guar gum.<sup>10,26</sup>

### ***Emulsification (ENZVI)***

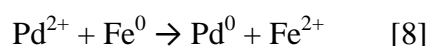
The use of emulsions in the stabilization of nZVI has been recently introduced by the Kennedy Space Center (NASA) and the University of Central Florida. The method prevents unwanted interaction by encapsulating the nZVI particles in biodegradable oil and a surfactant, which form an oil-liquid membrane. This protective hydrophobic membrane prevents the corrosive reaction of the nanoparticles with water. The high viscosity of the emulsion presents a problem for the practical application of this method, as elevated

injection pressures are needed. The issue is partially solved by replacing the viscous vegetable oil with oleic acid.<sup>13,10</sup>

### **2.1.1.7. Bimetallic particles**

In order to increase the reactivity of the nZVI, a thin layer of transitional (noble) metals, specifically Pt, Pd, Ag, Ni and Cu, is deposited onto the surface of the nanoparticles. The noble metal promotes Fe oxidation and catalyses electron transfer. The combination of the nZVI and a noble metal is classified as a bimetallic nanomaterial. The bimetallic nanoparticles are proven to be cost-effective, provide good corrosion stability, increase the speed of the contaminant degradation in comparison with bare nZVI particles and reduce the formation of toxic by-products.<sup>9,10,13,15,24</sup>

The bimetallic nanoparticles are synthesised by soaking freshly prepared nZVI particles in a solution of the noble metal salt. In the case of the Pd/Fe particles the nZVI are soaked in a solution of 1% palladium acetate ( $[\text{Pd}(\text{C}_2\text{H}_3\text{O}_2)_2]_3$ ) in ethanol. The palladium ions react with the surface of the nZVI as shown in equation [8].<sup>15,12</sup>



The palladium/iron nanoparticles are generally used more readily than the other bimetallic nanoparticles as they show high effectiveness in the removal of chlorinated hydrocarbons and polychlorinated biphenyls.<sup>9,10,27</sup>

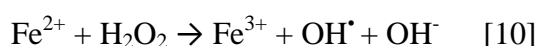
### **2.1.1.8. Immobilization of nZVI onto solid supports**

Researchers from the Helmholtz Centre for Environmental Research in Germany developed a method for anchoring nZVI particles onto activated carbon supports. Immobilizing the nZVI in such way provides easier manipulation in addition to maintaining the excellent reduction ability of the nZVI. The iron nanoparticles supported on a wide range of porous materials, such as resin, zeolite, silica or kaolinite, have been utilized to remove a selection of contaminants with varying success. For example the nZVI nanoparticles supported on bentonite removed nearly 100% of the initial concentration of Cr(VI) after only 20 minutes.<sup>9,10,28</sup>

### 2.1.1.9. Toxicity of nZVI

Considering the many recent developments in nanotechnology and the subsequent application of nanomaterials, the study of the toxicity of the nanomaterials is rapidly becoming a priority. From the few studies that have been conducted came the conclusion, that the toxic effects of nanoparticles are caused by their chemical nature and their physicochemical interactions at the nanoparticle/cell interface, rather than their size, which is similar to that of biological compounds.<sup>19,29</sup>

It has been discovered, that reactive oxygen species (ROS) are formed as a result of the oxidation (corrosion) of nZVI particles (equations [9] and [10]). The reactive oxygen species cause oxidative stress, which can lead to the damage of the cell membrane and cell death.<sup>19,22,29</sup>



There are several studies investigating the effect of nZVI particles on bacteria, specifically *Escherichia coli*, *Pseudomonas fluorescens* and *Bacillus subtilis*. The study focusing on the *Escherichia coli* explored the varying toxicity of magnetite ( $\text{Fe}_3\text{O}_4$ ), maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) and nZVI, with the researchers concluding the nZVI particles to be the most toxic. In addition, the nZVI have been proven to negatively affect earthworms and zooplankton.<sup>19,29</sup>

The mammalian brain is one of the organs at risk from damage caused by the nZVI particles, as it is sensitive to oxidative stress. When inhaled or ingested, nanoparticles can move across biological barriers to various organs and tissues.<sup>14</sup>

A series of experiments determined that partially or completely oxidized nZVI particles show decreased toxicity towards mammalian cells. Surface modifications, such as coating the nanoparticles in polystyrene sulfonate or polyaspartate, also significantly reduce their toxicity.<sup>14,24</sup>

## 2.2. Ibuprofen

Ibuprofen is one of the most commonly utilized drugs in the world. It is classified as a non-steroidal anti-inflammatory drug (NSAID) with antipyretic (lowering fever) and analgesic (pain-relieving) properties.<sup>30</sup> The drug, commercially available in the form of tablets, gel pellets and syrups, is specifically used for the treatment of fever, migraine, muscle aches, arthritis and tooth aches. On the market it is known under various names, depending on the country, for example Brufen, Nurofen or Ibalgin. Due to ibuprofen being the third most popular drug worldwide and its relatively high therapeutic dosage (600-1200 mg/day), several kilotons are globally produced every year.<sup>31,32,33,34</sup>

### 2.2.1. History

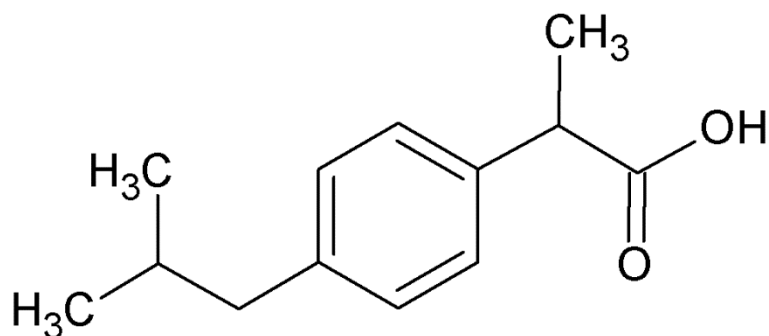
Ibuprofen was first discovered by Dr Steward Adams, working as a pharmacologist for the Boots Pure Drug Company in the UK. He was a part of the research group that focused on finding a new treatment for rheumatoid arthritis, a drug that was not a corticosteroid. In 1961, after years of experimentation, Dr Adams applied for a patent for “Anti-Inflammatory Agents” together with his colleague Dr Nicholson. The patent covered a broad spectrum of compounds, one of which was ibuprofen. Ibuprofen has been approved as a prescription drug in 1967 in the UK and 1974 in the USA. It has been available “over-the-counter” since 1984.<sup>35,36</sup>

### 2.2.2. Properties

#### *Physical and chemical properties*

The word ibuprofen has been derived from the systematic name of the drug: 2-(4-isobutylphenyl) propanoic acid.<sup>35</sup> Ibuprofen is a white crystalline powder with the molecular formula  $C_{13}H_{18}O_2$  and the molecular weight of 206.28 g/mol. The structure of ibuprofen can be seen in Figure 4.

It is soluble in most organic solvents and highly soluble in the eight primary alcohols (methanol through 1-octanol). The reported solubility of ibuprofen in water is 21 mg/l at 25°C.<sup>34,37,38,39</sup>



**Figure 4:** Structure of Ibuprofen <sup>33</sup>

### *Pharmacological properties*

The effect of ibuprofen on the human body is the suppression of the prostaglandin synthesis by inhibiting the enzyme cyclo-oxygenase. Cyclo-oxygenase catalyzes the production of prostaglandin from arachidonic acid, which is formed by the hydrolysis of eicosanoids using fosfolipase A2.

Combining ibuprofen with acetylsalicylic acid (aspirin) causes a reduction in the therapeutic effect and an increase in adverse side-effects, especially in the gastrointestinal area. <sup>35,36,40,41</sup>

### **2.2.3. Pharmaceutical pollutants**

With the increasing use and production of pharmaceuticals in the recent years, the leaking of the residues of pharmaceutical contaminants into the aquatic environment is becoming a common occurrence. While there is no legislation concerning the regulation of pharmaceutical effluents and the concentrations found in waters are seemingly too low to have an impact on the environment, some of the pollutants do negatively affect the aquatic environment. There is a possibility of the pharmaceuticals being introduced into the food-chain or drinking water and being ingested by humans. <sup>42,43</sup>

The wastewater treatment plants (WWTP) do not possess the technology to completely remove the pollutants; therefore concentrations in the range of ng/l to low µg/l can be found in the WWTP effluents. The main sources of the pharmaceutical residues are considered to be the pharmaceutical industry, sewage treatment plants, productions sites, hospitals, excretion or direct disposal of the unwanted products in the toilet or sink. <sup>18,43,44,45,46</sup>

Up to 80% of the therapeutic dose of ibuprofen is excreted, either in the pure form or in the form of its metabolites hydroxyl ibuprofen and carboxyl ibuprofen. As a result, the reported concentrations of ibuprofen in WWTP effluents were 500 ng/l in Canada and up to 10µg/l in Europe. Even concentrations as small as ng/l were proven to have genotoxic effects on fish.<sup>30,32,43</sup>

Considering the impact of ibuprofen on the aquatic environment, there are many methods devised for its degradation, such as TiO<sub>2</sub> photocatalysis, sonolysis, Fenton oxidation, γ-radiation and possibly the use of nZVI. So far, there is only one available publication on the topic of the degradation of ibuprofen using nZVI, however the researcher's experiment yielded positive results.<sup>18,31,47</sup>

## **2.2.4. Toxicity of ibuprofen**

Due to the relatively high concentrations of ibuprofen found in the aquatic environment, several studies on the toxicological impact of the drug on the aquatic organisms have been conducted. As can be expected, the levels of ibuprofen in waters are high enough to negatively affect simpler organisms such as the cladocerans (*Daphnia magna*) or the cnidarians (*Hydra attenuata*). However, they are also high enough to accumulate in mussels, after only a few days of flowing through, and affect more complex organisms, such as fish.<sup>48,49,50</sup>

High concentrations of ibuprofen in water are cytotoxic to fish cells of the rainbow trout. Even concentrations as low as 300 ng/l, which are below the predicted no-effect concentrations for other organisms, proved to be genotoxic to Tilapia fish.<sup>51,52</sup>

The widespread occurrence of ibuprofen in waters is becoming a concern, as the current studies of the toxicology of ibuprofen clearly show its adverse impact on the aquatic environment.<sup>49</sup>



## **3. EXPERIMENTAL PART**

## 3.1. Materials

### 3.1.1. Chemicals

The following chemicals were used during the experiment:

- Ibuprofen powder, (RS)-2-(4-(2-methylpropyl)phenyl)propanoic acid, Fluka Analytical
- ethyl alcohol for UV spectroscopy, CH<sub>3</sub>CH<sub>2</sub>OH, 99,8 %, Lach-Ner
- Iron nanoparticles, NANO FER star, batch number 197, NANO IRON s.r.o. (RCPTM)

### 3.1.2. Equipment

The glassware was supplied by the department of Physical Chemistry. The solids were weighed on a AND HM-120 digital analytical balance. The samples were stirred using an IKA MS 3 basic shaker, then transferred, using a BIOHIT pipette and a B Braun plastic syringe, through a micro filter (0.45 µm porosity, 25 mm diameter) into a fused quartz cuvette. The samples were measured using a Specord S600 spectrometer by the AnalytikJena company.

## 3.2. Experiment

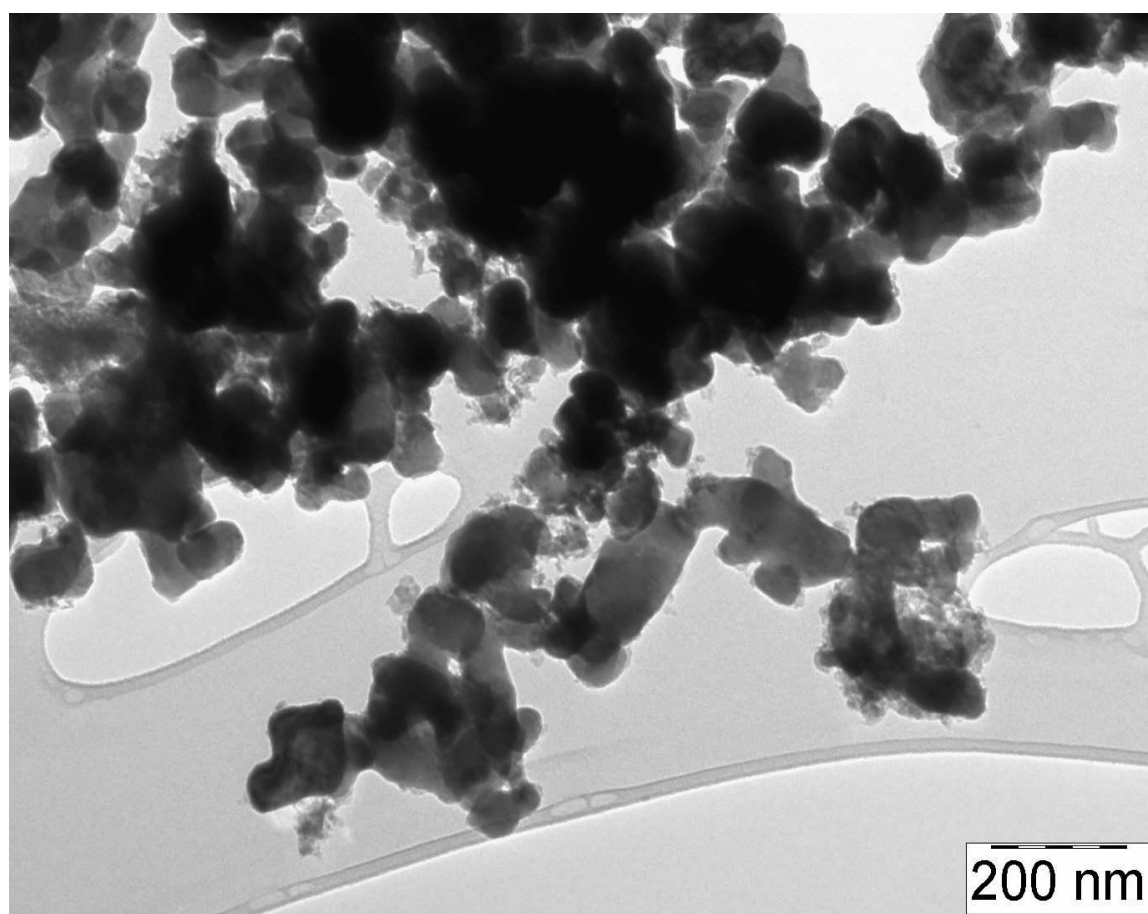
### 3.2.1. Solutions

The ibuprofen stock solution ( $c \sim 0.5 \text{ g.l}^{-1}$ ) was prepared by dissolving the appropriate amount of the ibuprofen powder in a mix of ethanol and distilled water (2:3). An ultrasound bath was used to ensure complete dissolution of the powder.

### 3.2.2. NZVI

The experiment was conducted using a sample of nZVI provided by the Regional Centre of Advanced Technologies and Materials (RCPTM) and originally purchased from a company called NANO IRON s.r.o. The sample was called NF STAR, batch number 197. The characteristics and the transmission electron microscope (TEM) image seen in Figure 5 were provided by RCPTM.

Name:	NF STAR 197
Name in this thesis:	NS197
Surface area:	$\approx 12.6 \text{ m}^2 \cdot \text{g}^{-1}$
Oxidation layer thickness:	$\approx 4 \text{ nm}$
Composition:	97% $\text{Fe}^0$ , 3% $\text{Fe}_3\text{O}_4$
Characteristics:	Surface stabilized, transportable, air-stable, reactive



**Figure 5:** TEM image of NS197

### **3.2.3. Method of determination of the concentration of ibuprofen**

The first method to be investigated was one used for quantitative analysis of ibuprofen in pharmaceuticals and human control serum. The method is based on the reaction of the colouring agent, 1-nitroso-2-naphthol, with cobalt(II) ions and the subsequent formation of the tris(1-nitroso-2-naphtholato)cobalt(III) complex, which is

yellow and absorbs at 410 nm. In the presence of ibuprofen the absorption band at 410 nm moves to 375 nm as the cobalt(III) is displaced from the complex and instead forms a new complex with ibuprofen.<sup>53</sup>

The method was sufficient for the determination of the concentration of ibuprofen; however, it was not suitable for measuring the degradation of ibuprofen using nZVI. The spectra showed the ibuprofen absorption maximum at 264 nm, which was used for the development of a second method.

The second method was decidedly simpler than the first as no colouring agent or substances other than ibuprofen, ethanol and distilled water were used. The method focuses solely on the behaviour of the 264 nm absorption peak, as described below.

### **3.2.4. Procedure**

The experiment was performed at room temperature in a 60 ml glass vial. The required amount of the nZVI particles was measured and added into the vial together with 40 ml of the ibuprofen stock solution ( $c \sim 0.5 \text{ g.l}^{-1}$ ). Throughout the whole experiment, the mixture in the vials was stirred using an orbital shaker at 700 rpm.

At the designated times  $t$ , 1 ml of the mixture was transferred from the vial into a plastic syringe, which was used to push the mixture through a micro filter into a quartz cuvette. 1ml of distilled water was added into the cuvette and the solution was shaken to ensure the components were properly mixed.

Before the start of the reaction (at time  $t=0$ ) 1ml of the ibuprofen stock solution was mixed with 1 ml of distilled water in a quartz cuvette and the absorption was measured to determine the absorption band before any degradation had taken place.

The absorption of the samples was measured in the 230-800 nm range, with the absorption maximum at 264 nm. The data was then used for the determination of the degradation of ibuprofen using nZVI.

### 3.3. Kinetics

The degradation of ibuprofen by nZVI nanoparticles can be described using pseudo-first order kinetics. The efficiency criterion of the experiment is the reaction rate constant, which can be calculated as follows:<sup>54,55</sup>

$$\frac{dc}{dt} = -k_{obs} \cdot c \quad [11]$$

The equation [11] can be adjusted into the form of equation [12], where  $c$  is the actual concentration of ibuprofen ( $\text{mg.l}^{-1}$ ) in time  $t$  (h),  $c_0$  is the initial concentration of ibuprofen ( $\text{mg.l}^{-1}$ ) and  $k_{obs}$  represents the degradation reaction rate constant ( $\text{h}^{-1}$ ).<sup>56,57</sup>

$$\ln c = \ln c_0 - k_{obs} \cdot t \quad [12]$$

The value of the reaction rate constant  $k_{obs}$  can be obtained from the regression equation of the graph showing the dependence of  $\ln c$  on time.

When trying to determine the kinetics of different types of nZVI it is generally more advantageous to utilize the surface area normalized rate constant  $k_{SA}$  ( $\text{h}^{-1} \cdot \text{m}^{-2} \cdot \text{l}$ ), which considers the surface area concentration of the nZVI,  $\rho_a$ , as can be seen in equation [13] and, after mathematical adjustment, equation [14].<sup>56</sup>

$$\frac{dc}{dt} = -k_{SA} \cdot \rho_a \cdot c \quad [13]$$

$$\ln c = \ln c_0 - k_{SA} \cdot \rho_a \cdot t \quad [14]$$

The surface area concentration can be calculated using the specific surface area,  $a_s$  ( $\text{m}^2 \cdot \text{g}^{-1}$ ), and mass concentration of the metal,  $\rho_m$  ( $\text{g.l}^{-1}$ ), following equation [15]. The specific surface area of the metal is experimentally determined through BET analysis.<sup>56</sup>

$$\rho_a = a_s \cdot \rho_m \quad [15]$$

However, as only one type of nZVI particles was used in this experiment, the value of the specific surface area of the metals,  $a_s$ , is constant. With an increasing value of the mass concentration of the metal,  $\rho_m$ , the reaction rate constant,  $k_{obs}$ , also increases. Therefore, the value of the surface area normalized reaction rate constant,  $k_{SA}$ , does not significantly differ for the various mass concentrations of the nZVI.

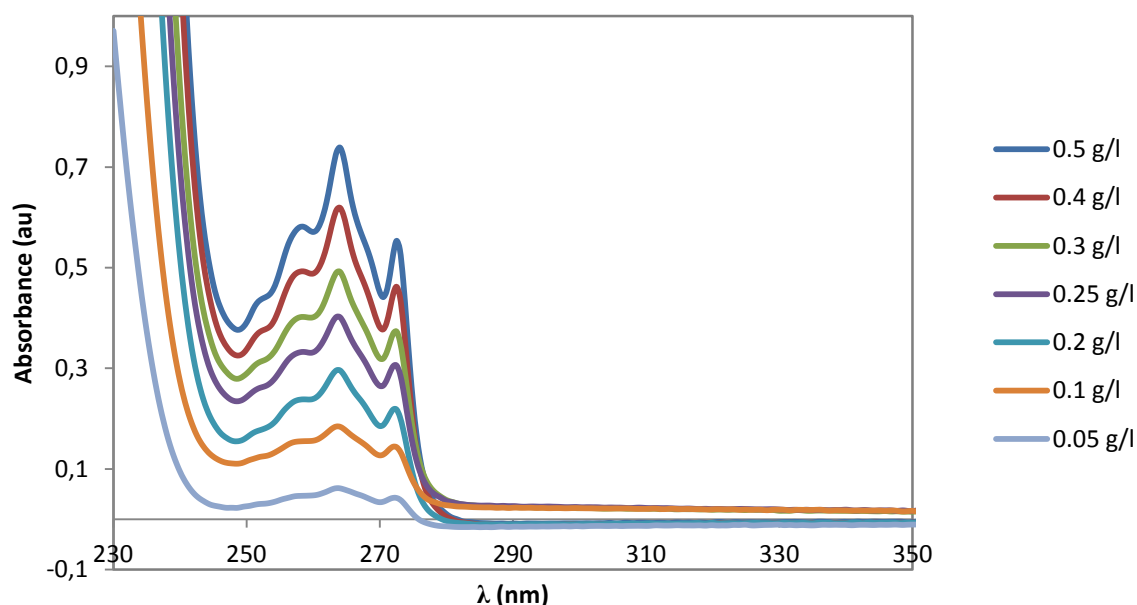
As such, the  $k_{SA}$  cannot be successfully used as an efficiency criterion. Instead,  $k_{obs}$  is used to prove the expected trend – an increase in degradation with increased mass concentration of the nZVI.

## 4. Results and discussion

### 4.1. Ibuprofen spectra

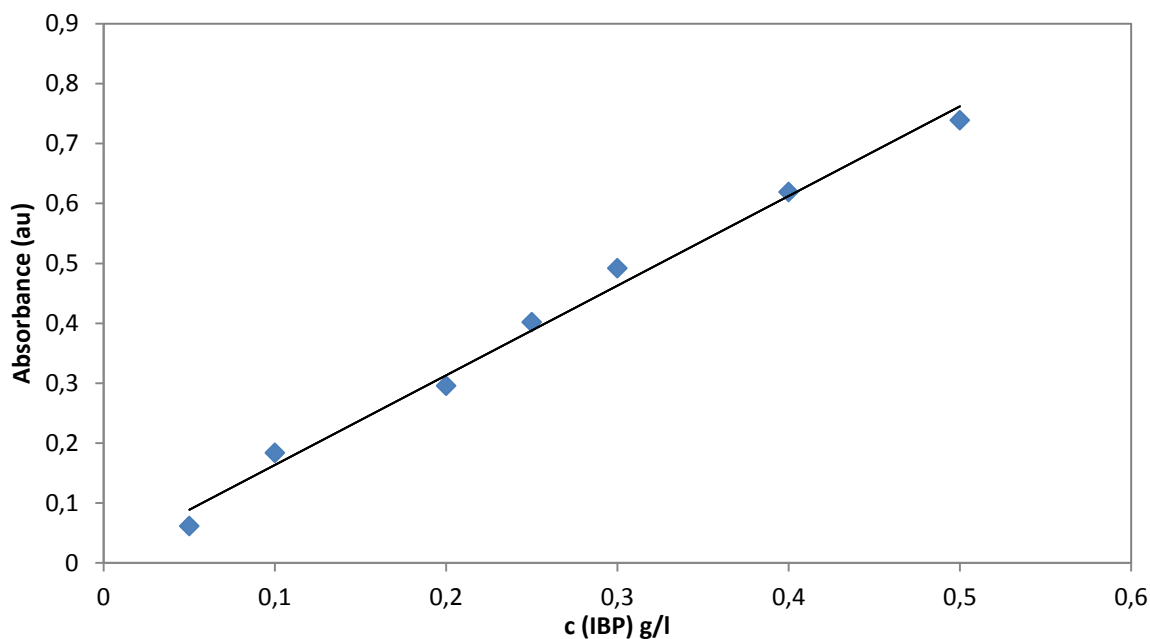
The experimental part of this thesis focused on the determination of the degradation of ibuprofen using different concentrations of nZVI. Several solutions of ibuprofen with varying concentrations were measured in an effort to create a calibration range for the experiment.

As mentioned in section 3.2.3., the absorption peak of ibuprofen was observed during the experiment. Figure 6 shows the change of the absorption spectra with decreasing concentrations of ibuprofen.



**Figure 6:** Absorption spectra for different concentrations of ibuprofen

Ibuprofen has two absorption maxima - at 264 and 272 nm.<sup>38</sup> The absorbance value chosen to be observed was 264 nm, as the absorption peak is more prominent. The absorbance value at 264 nm increases with increasing concentration of ibuprofen, as can be seen in Figure 7.



**Figure 7:** Calibration graph – the relationship between the absorbance at 264 nm and the concentration of ibuprofen; a linear regression line is fitted through the graph points,  $R^2 = 0.9911$

## 4.2. The comparison of nZVI concentrations

In the experiment, six different concentrations (12.5; 25.0; 37.5; 50.0; 62.5 and 75.0 g.l<sup>-1</sup>) of the same type of nZVI (NS197) were used to degrade ibuprofen. These mass concentrations were chosen based on the ratio of ibuprofen to nZVI used in an experiment describing the manufacture and use of green nZVI particles for the degradation of ibuprofen.<sup>18</sup>

The ibuprofen solution used for the actual reaction with nZVI particles was the 0.5 g.l<sup>-1</sup> stock solution, however, the initial measured concentration of ibuprofen (t=0) was 0.25 g.l<sup>-1</sup> (see section 3.2.4.).

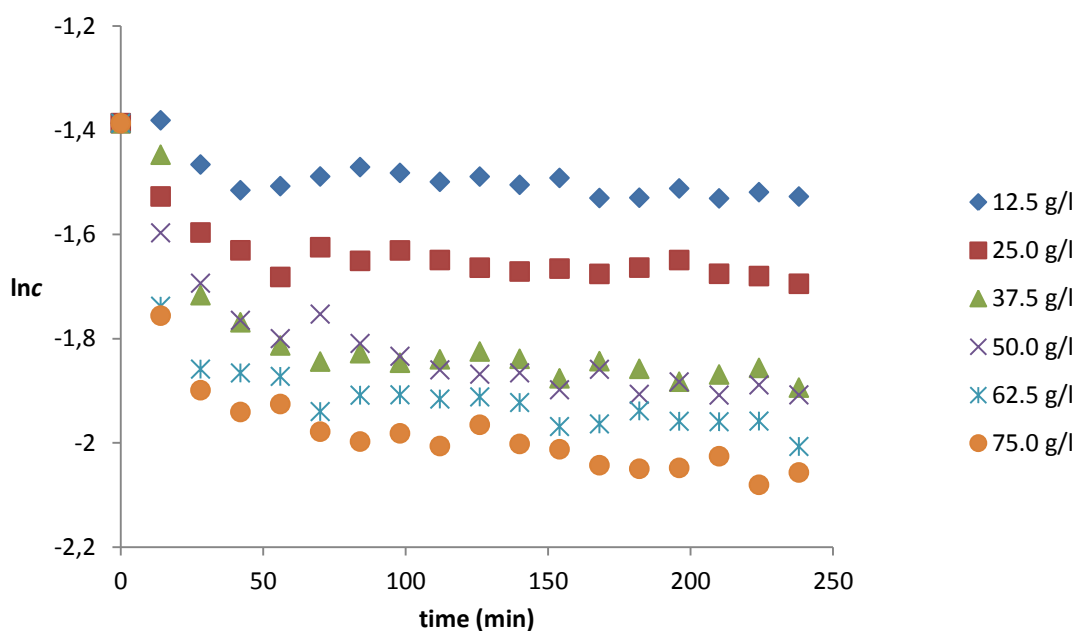
The aforementioned concentrations of nZVI were compared using the percentage decrease of the initial amount of ibuprofen in solution and the reaction rate constant,  $k_{obs}$ . In addition, the surface area normalized reaction rate constant,  $k_{SA}$ , was calculated.

All of the measurements were repeated several times in order to ensure of their reliability.



### 4.2.1. Initial measurement

Initially, the experiment was done in a time period of 4 hours. However, when the obtained data was analyzed, it was discovered, that ibuprofen is not degraded in a linear fashion. Figure 8 shows the dependence of the concentration of ibuprofen ( $\ln c$ ) on time and Table 2 summarises the data acquired from the graph.



**Figure 8:** Dependence of ibuprofen concentration on time for various nZVI concentrations

As the chosen efficiency criterion,  $k_{obs}$ , is obtained from the regression equation, the data shown in Table 2 were clearly not suitable for the evaluation.

Mass concentration of nZVI [g/l]	Regression equation	$R^2$
12,5	$y = -0,0004x - 1,4385$	0,5583
25,0	$y = -0,0007x - 1,5536$	0,4791
37,5	$y = -0,0014x - 1,6274$	0,5169
50,0	$y = -0,0014x - 1,6327$	0,6531
62,5	$y = -0,0013x - 1,7361$	0,4736
75,0	$y = -0,0015x - 1,7708$	0,5113

**Table 2:** Data relating to Figure 8

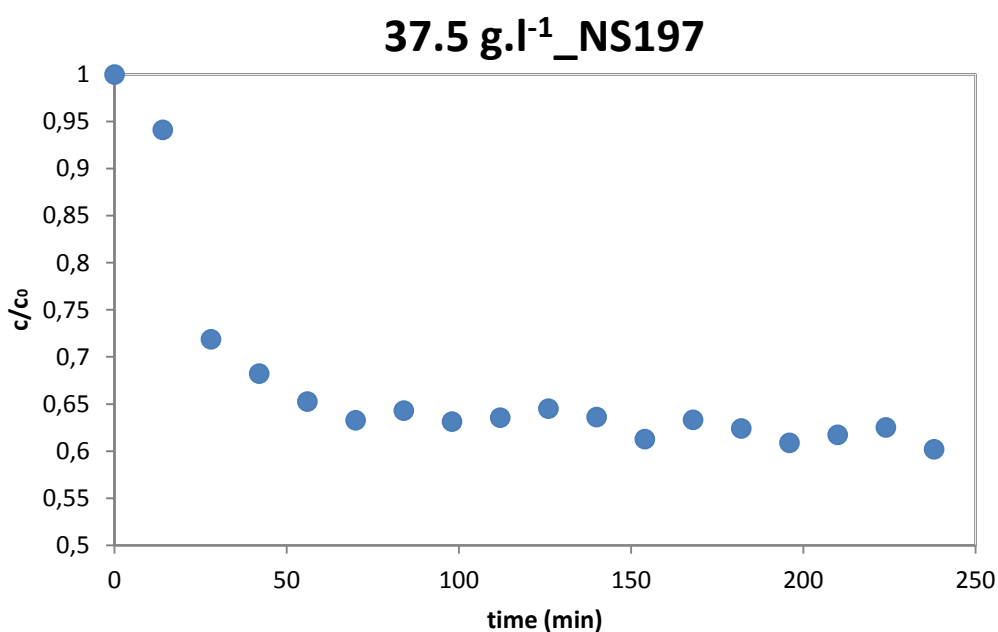
Furthermore, the summary of the percentage degradation of ibuprofen in Table 3 shows that the majority of the degradation occurred during the first 70 minutes with only minimal differences in the 70 to 140 min and 140 to 210 min time periods.

Concentration of NS197 [g/l]	time (min)			
	0	70	140	210
	% degradation of ibuprofen			
12,5	0,00	9,73	11,16	13,44
25,0	0,00	21,19	24,78	25,10
37,5	0,00	36,72	36,38	38,26
50,0	0,00	30,68	38,07	40,66
62,5	0,00	42,51	41,50	43,61
75,0	0,00	44,68	45,97	47,23

**Table 3:** Summary of the percentage degradation of ibuprofen at different times of the analysis

#### 4.2.2. Shortened kinetics

The results clearly show that a significant portion of the initial amount of ibuprofen is degraded during the first hour of the experiment, as seen in Table 3 and Figure 9. Therefore, the degradation rate measurement was repeated with a shorter sampling time interval and the duration of ~ 60 minutes.

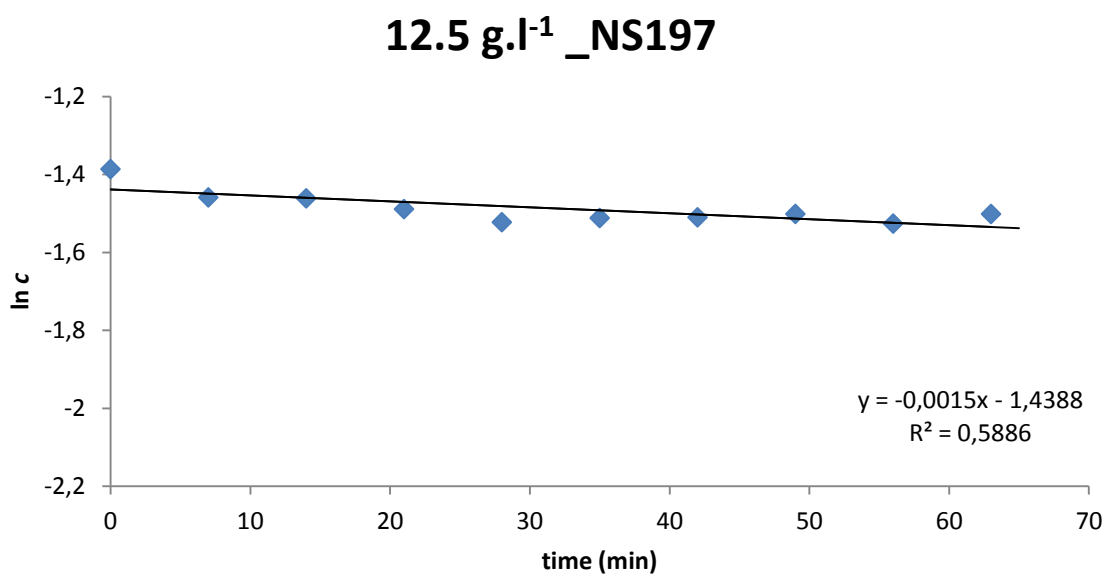


**Figure 9:** The degradation of ibuprofen ( $c/c_0$ ) with time

The kinetic parameters obtained from the shortened analysis are summarised in Table 4. The values of  $k_{obs}$  were acquired from the regression equations of the data representing the relationship between the concentration of ibuprofen ( $\ln c$ ) and time (min) for all the measured nZVI concentrations. Figures 10 to 15 show the graphs representing the aforementioned relationships.

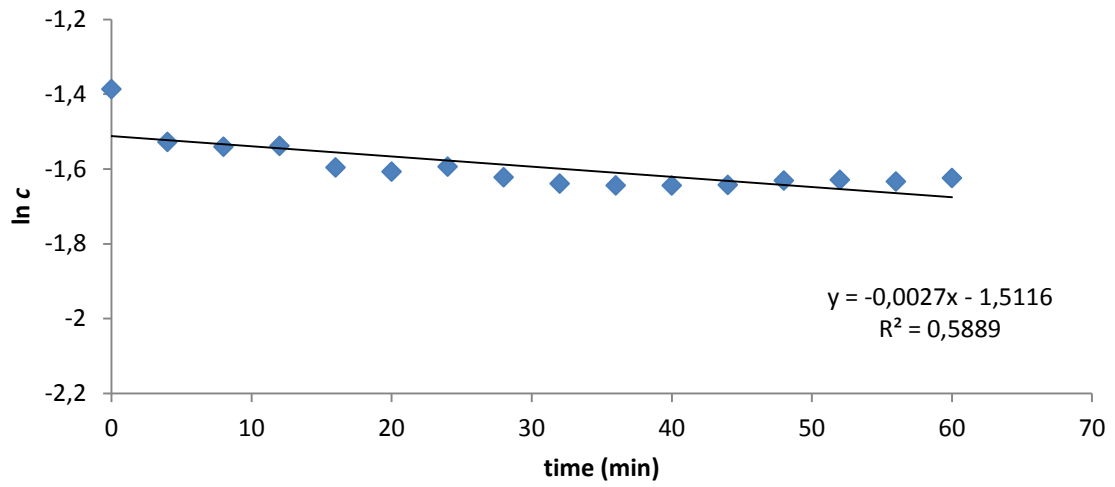
$mFe$ [g]	$\rho_m$ [g.l <sup>-1</sup> ]	BET [m <sup>2</sup> .g <sup>-1</sup> ]	$k_{obs}$ [h <sup>-1</sup> ]	$\bar{k}_{obs}$ [h <sup>-1</sup> ]	$\rho_a$ [m <sup>2</sup> .l <sup>-1</sup> ]	$k_{SA}$ [h <sup>-1</sup> .m <sup>-2</sup> .l]	$\bar{k}_{SA}$ [h <sup>-1</sup> .m <sup>-2</sup> .l]
0,5	12,5	12,6	0,0015	0,0017 ± 0,0003	157,5	9,52·10 <sup>-6</sup>	10,79·10 <sup>-6</sup> ± 1,80·10 <sup>-6</sup>
			0,0019			12,06·10 <sup>-6</sup>	
1,0	25,0	12,6	0,0034	0,0031 ± 0,0005	315,0	10,79·10 <sup>-6</sup>	9,68·10 <sup>-6</sup> ± 1,57·10 <sup>-6</sup>
			0,0027			8,57·10 <sup>-6</sup>	
1,5	37,5	12,6	0,0045	0,0039 ± 0,0009	472,5	9,52·10 <sup>-6</sup>	8,15·10 <sup>-6</sup> ± 1,95·10 <sup>-6</sup>
			0,0032			6,77·10 <sup>-6</sup>	
2,0	50,0	12,6	0,0050	0,0052 ± 0,0002	360,0	7,94·10 <sup>-6</sup>	8,17·10 <sup>-6</sup> ± 0,34·10 <sup>-6</sup>
			0,0053			8,41·10 <sup>-6</sup>	
2,5	62,5	12,6	0,0067	0,0069 ± 0,0003	787,5	8,51·10 <sup>-6</sup>	8,76·10 <sup>-6</sup> ± 0,36·10 <sup>-6</sup>
			0,0071			9,02·10 <sup>-6</sup>	
3,0	75,0	12,6	0,0093	0,0079 ± 0,0020	945,0	9,84·10 <sup>-6</sup>	8,36·10 <sup>-6</sup> ± 2,10·10 <sup>-6</sup>
			0,0065			6,88·10 <sup>-6</sup>	

**Table 4:** Table of kinetic parameters



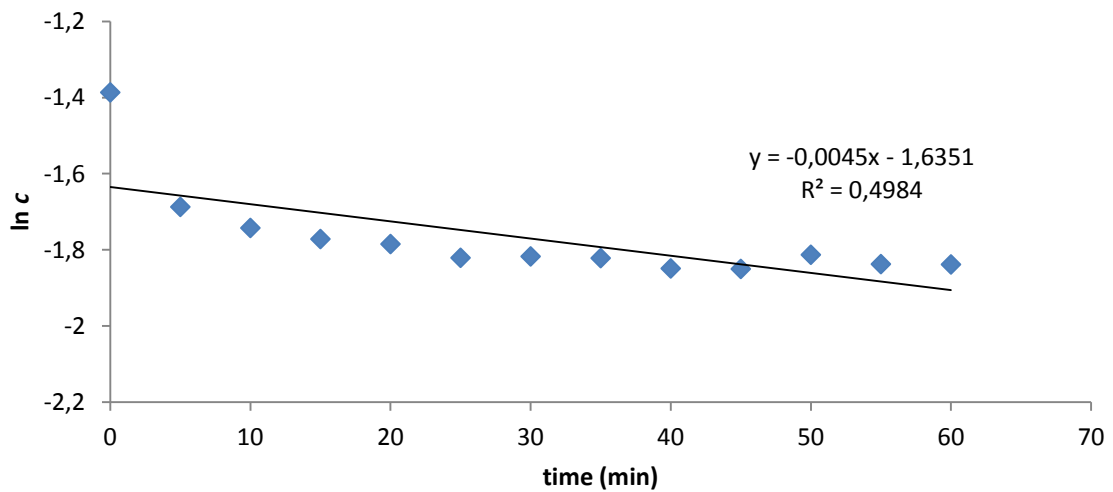
**Figure 10:** The dependence of  $\ln c$  on reaction time;  $c_0(\text{IBP}) = 0.25 \text{ g.l}^{-1}$ ;  $\rho_m(\text{nZVI}) = 12.5 \text{ g.l}^{-1}$

### 25.0 g.l<sup>-1</sup> \_NS197



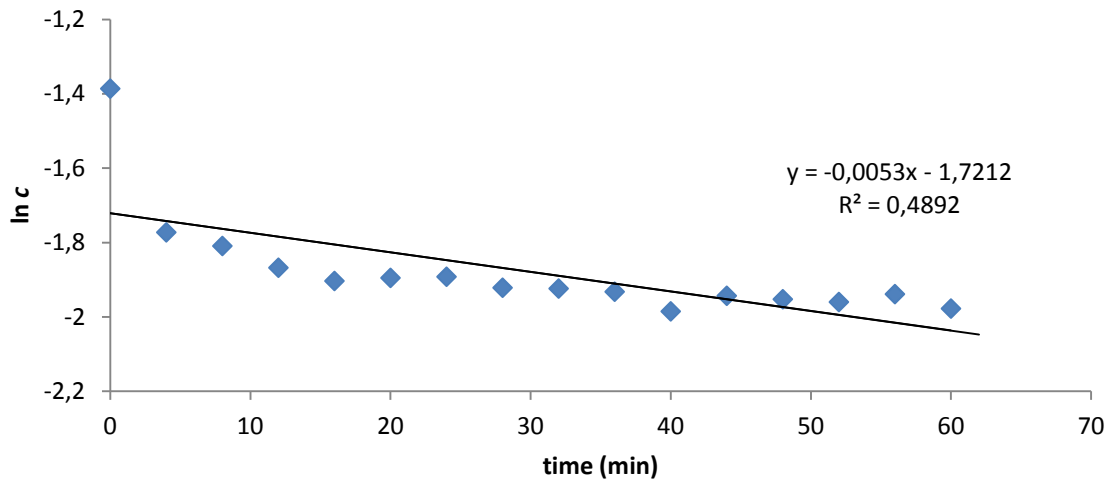
**Figure 11:** The dependence of  $\ln c$  on reaction time;  $c_0(\text{IBP}) = 0.25 \text{ g.l}^{-1}$ ;  $\rho_m(\text{nZVI}) = 25.0 \text{ g.l}^{-1}$

### 37.5 g.l<sup>-1</sup> \_NS197



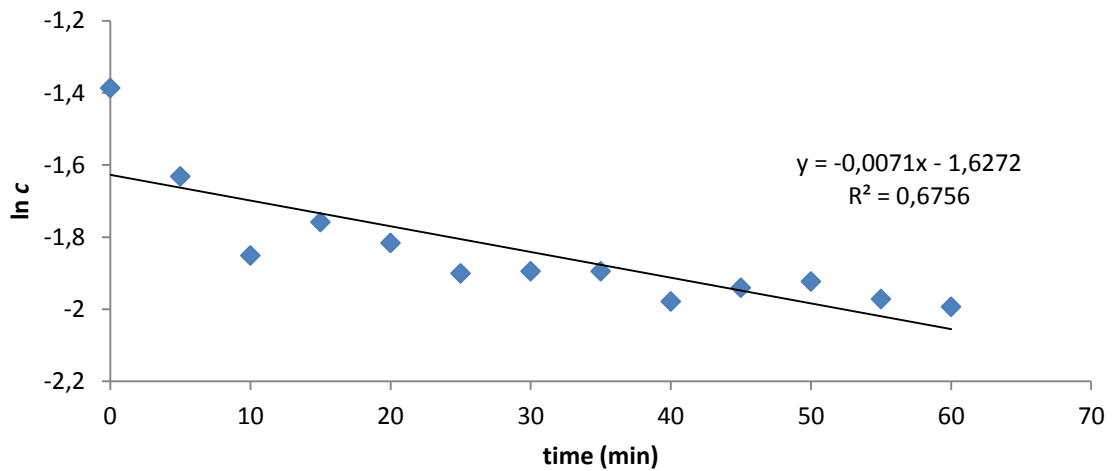
**Figure 12:** The dependence of  $\ln c$  on reaction time;  $c_0(\text{IBP}) = 0.25 \text{ g.l}^{-1}$ ;  $\rho_m(\text{nZVI}) = 37.5 \text{ g.l}^{-1}$

### 50.0 g.l<sup>-1</sup> \_NS197



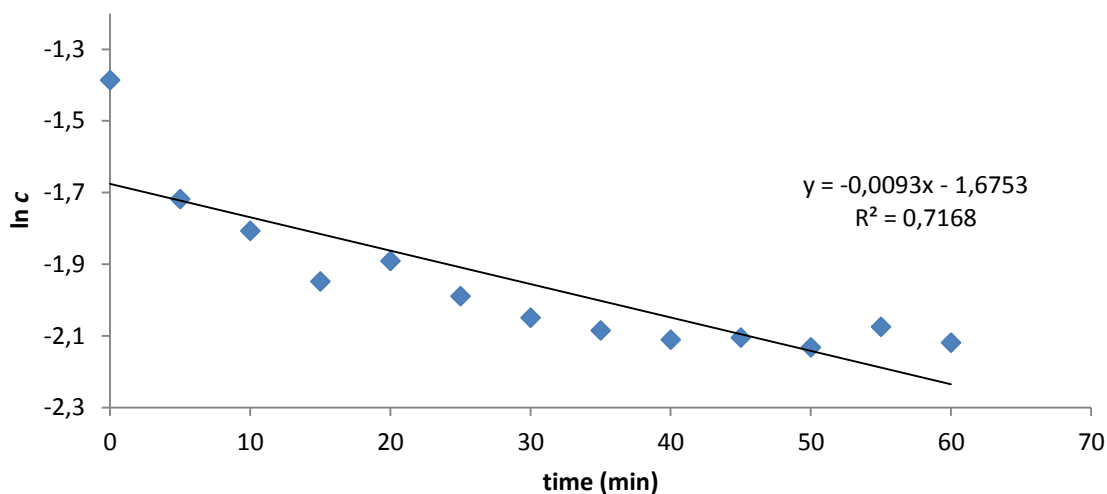
**Figure 13:** The dependence of  $\ln c$  on reaction time;  $c_0(\text{IBP}) = 0.25 \text{ g.l}^{-1}$ ;  $\rho_m(\text{nZVI}) = 50.0 \text{ g.l}^{-1}$

### 62.5 g.l<sup>-1</sup> \_NS197



**Figure 14:** The dependence of  $\ln c$  on reaction time;  $c_0(\text{IBP}) = 0.25 \text{ g.l}^{-1}$ ;  $\rho_m(\text{nZVI}) = 62.5 \text{ g.l}^{-1}$

## 75.0 g.l<sup>-1</sup> \_NS197

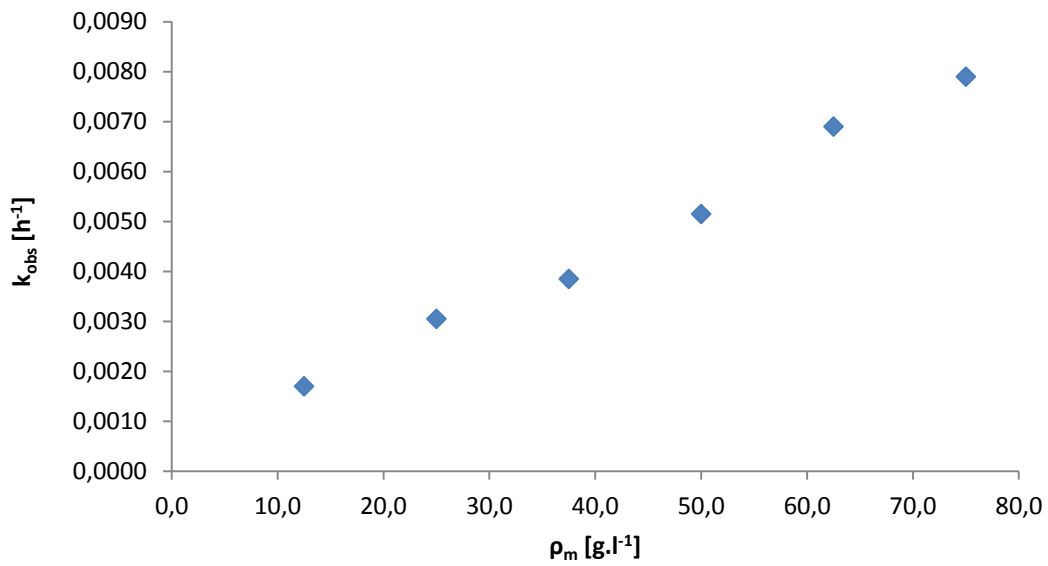


**Figure 15:** The dependence of  $\ln c$  on reaction time;  $c_0(\text{IBP}) = 0.25 \text{ g.l}^{-1}$ ;  $\rho_m(\text{nZVI}) = 75.0 \text{ g.l}^{-1}$

Table 5 summarizes the percentage degradation of ibuprofen over one hour. While the lower concentrations of nZVI do not show a significant change in the degradation percentage at the selected times (other than the 0 to 20 min difference), the higher concentrations exhibit a more gradual degradation, illustrated especially by the difference in percentage degradation in the 20 to 40 minute time period.

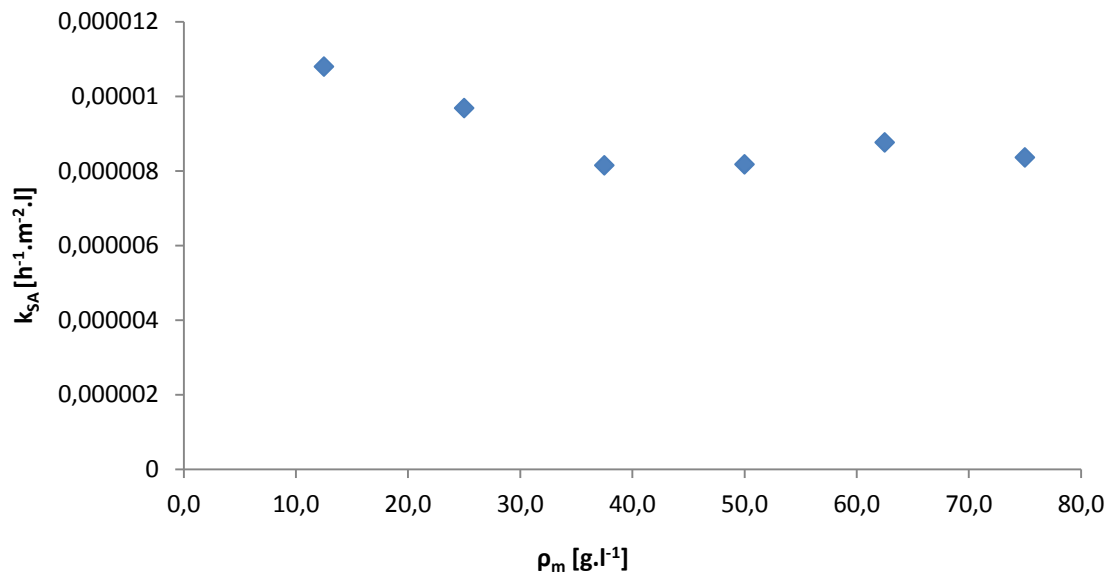
Concentration of NS197 [g/l]	time (min)			
	0	20	40	60
	% degradation of ibuprofen			
12,5	0,00	9,75	11,63	10,88
25,0	0,00	19,80	22,72	21,15
37,5	0,00	32,85	37,02	36,35
50,0	0,00	39,89	45,06	44,65
62,5	0,00	34,93	44,67	45,48
75,0	0,00	39,63	51,54	51,94

**Table 5:** Summary of percentage degradation of ibuprofen over 1 hour



**Figure 16:** Comparison of  $k_{obs}$  for the different mass concentrations of nZVI

As predicted in section 3.3., the value of the reaction rate constant  $k_{obs}$  increases with increasing mass concentration of the nZVI particles (Figure 16). Therefore, increasingly faster degradation of ibuprofen occurs with a higher the nZVI : ibuprofen ratio.



**Figure 17:** Comparison of  $k_{SA}$  for the different mass concentrations of nZVI

The surface area normalized reaction rate constant,  $k_{SA}$ , was calculated for the NS197 nZVI using the experimentally acquired kinetic parameters (see Table 4). The results for the various mass concentrations of nZVI ranged from  $8.15 \times 10^{-6}$  to  $10.79 \times 10^{-6}$ , as can be seen in Figure 17.



## 5. Summary

This thesis focuses on the comparison of the efficiency of different concentrations of stabilized nZVI particles (12.5; 25.0; 37.5; 50.0; 62.5 and 75.0 g.l<sup>-1</sup>) in the process of degradation of ibuprofen, one of the most common pharmaceutical pollutants.

Stabilized nZVI particles, with a 4 nm thick oxidation layer, were used in the experiment. The high concentrations of nZVI used, are related to the tested concentration of ibuprofen (0.5 g.l<sup>-1</sup>), which is significantly higher than the concentrations found in groundwater (see section 2.2.3.).

The concentrations of the nZVI were compared using the percentage decrease of the initial amount of ibuprofen in solution and the reaction rate constant,  $k_{obs}$ . In addition, the surface area normalized reaction rate constant,  $k_{SA}$ , was calculated.

An increase in the degradation of ibuprofen with increasing concentration of nZVI was observed. However, the first hour of the analysis seems to be the most significant part as the degradation rate considerably lowers after one hour. Therefore, this thesis further focuses on the behaviour of the ibuprofen solution during the first hour of the experiment.

While a longer reaction period would, in theory, be required for the complete removal of ibuprofen from the solution, the highest concentration of the nZVI particles (75.0 g.l<sup>-1</sup>) removed up to 50% of the initial amount of ibuprofen. Therefore, it can be said that nZVI particles can be used for at least a partial degradation of ibuprofen.

## 6. Závěr

Tato práce se zaměřuje na porovnání účinnosti různých koncentrací stabilizovaných nZVI částic (12.5; 25.0; 37.5; 50.0; 62.5 a 75.0 g.l<sup>-1</sup>), pro proces odbourání ibuprofenu, který patří mezi nejběžnější farmaceutické polutanty.

Pro tento experiment byly použity stabilizované nZVI částice s tloušťkou oxidické vrstvy 4 nm. Vysoké koncentrace nZVI jsou v souladu s testovanou koncentrací ibuprofenu (0.5 g.l<sup>-1</sup>), která je mnohem vyšší než naměřená koncentrace v podzemních vodách. (viz sekce 2.2.3.)

Koncentrace nZVI byly porovnány pomocí procentuálního úbytku počátečního množství ibuprofenu v roztoku a rychlostní konstanty reakce  $k_{obs}$ . Navíc byla vypočítána normalizovaná rychlostní konstanta plochy povrchu  $k_{SA}$ .

V neposlední řadě byl pozorován vzrůst odbourání ibuprofenu v závislosti na zvyšující se koncentrací nZVI. První hodina analýzy se prokázala být nejvýznamnější, jelikož poté se rychlost reakce výrazně snížila. Z tohoto důvodu se tato práce dále zabývá chováním roztoku ibuprofenu právě v této první hodině experimentu.

I když pro úplné odstranění ibuprofenu z roztoku by byl teoreticky třeba delší reakční čas, nejvyšší použitá koncentrace nZVI částic (75.0 g.l<sup>-1</sup>) odbourala až 50% původního množství ibuprofenu. Proto lze říct, že nZVI částice, alespoň částečně, degradují ibuprofen.

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